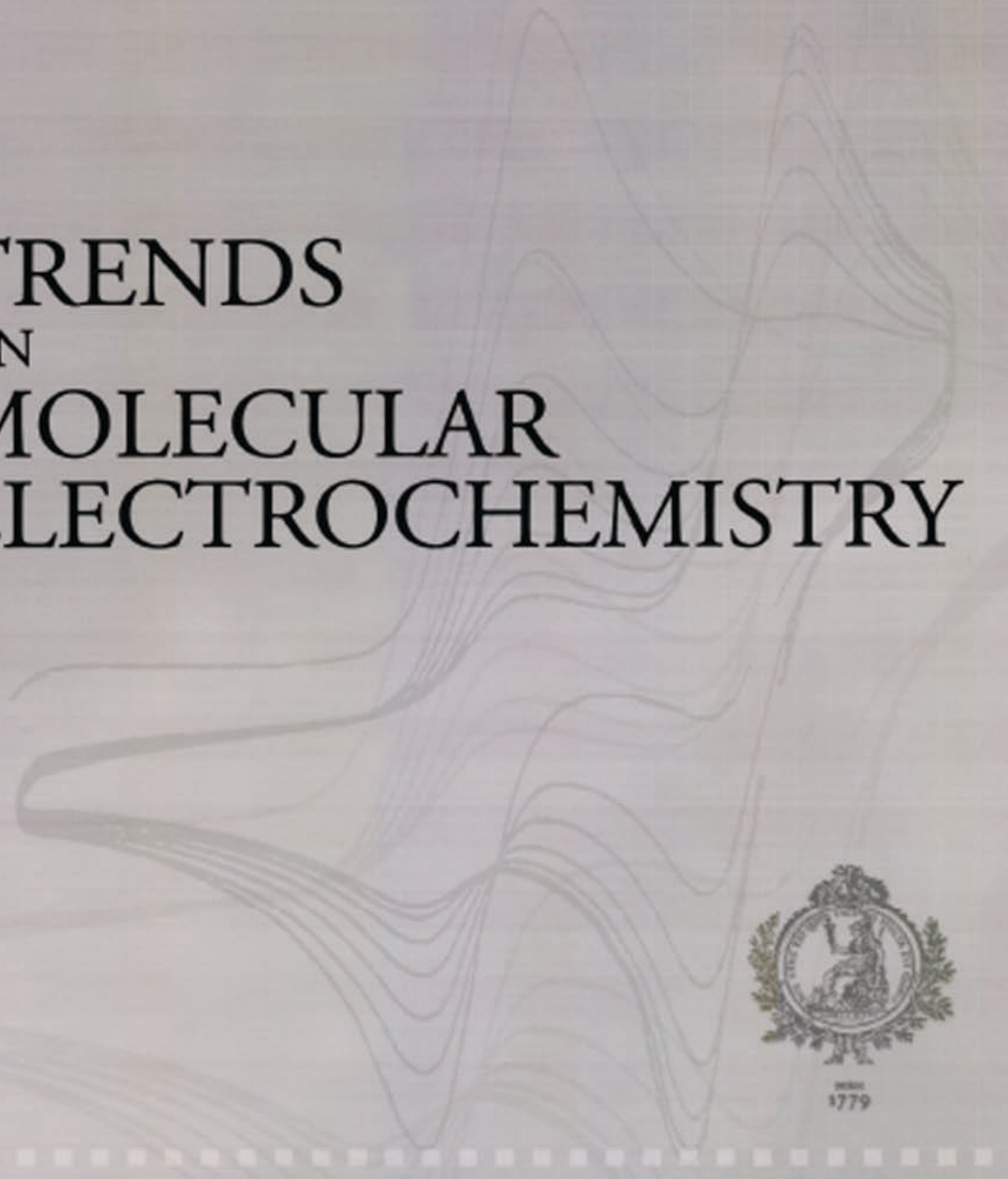


TRENDS IN MOLECULAR ELECTROCHEMISTRY

1779

Edited by
Armando J. L. Pombeiro
and Christian Amatore

CRC Press
Taylor & Francis Group

FONTIS MEDIA

TRENDS IN MOLECULAR ELECTROCHEMISTRY

TRENDS IN MOLECULAR ELECTROCHEMISTRY

Edited by
Armando J.L. Pombeiro

Co-Editor
Christian Amatore

1779

FONTIS MEDIA

CRC Press
Taylor & Francis Group
Boca Raton London New York

CRC Press is an imprint of the
Taylor & Francis Group, an informa business

First published 2004 by Marcel Dekker, Inc.

Published 2018 by CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

© 2004 by Taylor & Francis Group, LLC
CRC Press is an imprint of Taylor & Francis Group, an Informa business

No claim to original U.S. Government works

ISBN-13: 978-0-8247-5352-8 (hbk)

This book contains information obtained from authentic and highly regarded sources. Reasonable efforts have been made to publish reliable data and information, but the author and publisher cannot assume responsibility for the validity of all materials or the consequences of their use. The authors and publishers have attempted to trace the copyright holders of all material reproduced in this publication and apologize to copyright holders if permission to publish in this form has not been obtained. If any copyright material has not been acknowledged please write and let us know so we may rectify in any future reprint.

Except as permitted under U.S. Copyright Law, no part of this book may be reprinted, reproduced, transmitted, or utilized in any form by any electronic, mechanical, or other means, now known or hereafter invented, including photocopying, microfilming, and recording, or in any information storage or retrieval system, without written permission from the publishers.

For permission to photocopy or use material electronically from this work, please access www. copyright.com (http://www.copyright.com/) or contact the Copyright Clearance Center, Inc. (CCC), 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400. CCC is a not-for-profit organization that provides licenses and registration for a variety of users. For organizations that have been granted a photocopy license by the CCC, a separate system of payment has been arranged.

Trademark Notice: Product or corporate names may be trademarks or registered trademarks, and are used only for identification and explanation without intent to infringe.

Visit the Taylor & Francis Web site at
http://www.taylorandfrancis.com

and the CRC Press Web site at
http://www.crcpress.com

Library of Congress Cataloging-in-Publication Data
A catalog record for this book is available from the Library of Congress.

FONTISMEDIA S.A.
FontisMedia S.A.
Avenue Vinet 19
CH-1004 Lausanne, Switzerland

Contents

REDOX AND OTHER MOLECULAR PROPERTIES

MOLECULAR ELECTROACTIVATION AND ELECTROCATALYSIS

BIOELECTROCHEMISTRY

SUPRAMOLECULAR ELECTROCHEMISTRY

SPECTROELECTROCHEMISTRY

UNCONVENTIONAL ELECTROCHEMISTRY

CHAPTER 13

CHAPTER 14

CHAPTER 15

Introduction

Chemists increasingly apply electrochemical methods to the investigation of their systems, in particular towards a better understanding of molecular properties, the exploration of chemical reactions involving electron-transfer (ET), the initiation of further reactions by ET, the kinetic measurements and the establishment of the reaction mechanisms, as well as the synthesis (electrosynthesis) of desired products.

This book highlights the state-of-the-art in the application of electrochemistry, by taking an interdisciplinary approach to the study of both static and dynamic molecular properties, mainly of coordination compounds, but including inorganic, bioinorganic and organometallic complexes. Supramolecular systems and metalloenzymes are also covered. The principles and approaches are often also valid for organic systems which are illustrated in various contexts.

This book is addressed to those chemists interested on the application of electrochemical techniques to their systems, as well as to electrochemists who have had their attention drawn to chemical problems. This work is therefore of certain value for experienced scientists as well as for relative newcomers. Addressed to senior researchers, it is also of interest to postgraduates and, in some aspects, to advanced undergraduates.

To some extent, it updates the previous book entitled "Molecular Electrochemistry of Inorganic, Bioinorganic and Organometallic Compounds" (NATO ASI Series C385, Kluwer, Dordrecht, 1993), edited by one of us (AJLP), that appeared approximately 12 years ago following a NATO Advanced Research Workshop (ARW) on that field in Sintra, Portugal, in 1992. This pioneering conference, also organized by one of us, was followed, since 1998, by other regular meetings (1998, 2000, 20002), held in Siena, Italy (organized by Prof. P. Zanello), on the same overall field, which also comprised educational purposes.

There is undoubtedly a rapidly increasing interest on the field and on its expansion through the use of modern concepts and unconventional approaches, which in our view justified the preparation of this new volume which provides an updated overview of the field about one decade after the publication of the above NATO ARW book.

The contents of this new book were recently presented at a symposium on "New Trends in Molecular Electrochemistry", organized by the Academy of Sciences of Lisbon within its "Frontiers of Knowledge" series, held at its premises.

The book deals, in an interdisciplinary approach, with the developments achieved in areas such as:

(i) Redox and other molecular properties (electronic, optical and magnetic properties; electrochemical properties – structure relationships; metal-metal interactions; mixed valence compounds, etc.).
(ii) Molecular electroactivation and electrocatalysis (reactions induced by ET).
(iii) Bioelectrochemistry (metalloenzymes).
(iv) Supramolecular electrochemistry (supramolecular architectures, metallodendrimers and molecular devices)
(v) Spectroelectrochemistry.
(vi) Unconventional electrochemistry (ultrafast electrochemical techniques, new types of supporting electrolytes, electrochemistry without added electrolyte, ET through the liquid-liquid interface).

Therefore it covers both static and dynamic aspects, the former dealing mainly with structures and their relationships with particular properties and the latter concerning reactivity, kinetics and mechanisms of a wide variety of systems mainly within the broad filed of "inorganic" coordination chemistry (including also organometallic, supramolecular, bioinorganic and metalloenzyme chemistries) and, in a number of cases, also with illustrations in organic chemistry.

We acknowledge the authors of the various chapters for having accepted our invitation and for their so valuable and high quality contributions, as well as Dr. Fred Fenter (FontisMedia) for his continuous encouragement and highly professional assistance in the publication of the book. Thanks are also due to the Academy of Sciences of Lisbon, in particular to its Presidents, Prof. J.M. Toscano Rico and Prof. J.V. de Pina Martins (of the Classes of Sciences and Letters, respectively, who have been swapping the Presidency and Vice-Presidency along the last years) and Treasurers, Prof. F.R. Dias Agudo (also coordinator and representative of the international affairs board) and, recently, Prof. A. Torres Pereira, and to the President of the High Studies Institute (Prof. M. Jacinto Nunes), for approving and kindly supporting the initiative.

Armando J.L. Pombeiro
The Editor

Christian Amatore
The Co-Editor

Preface

This volume is the first of the resumed "Frontiers of Knowledge" series, initiated to mark the bicentennial anniversary of the foundation (on December 24th, 1779, by Queen Maria I) of the Academy of Sciences of Lisbon. For the presentation and discussion of the contents of the book, still in preparation, a symposium on "New Trends in Molecular Electrochemistry" was held, within that series, at the Academy (September 16-20th, 2003), together with the XII Meeting of the Portuguese Electrochemical Society covering all fields of Electrochemistry.

The "Frontiers of Knowledge" series first appeared in the late 70s within the activity of the High Studies Institute (Instituto de Altos Estudos) of the Academy, at the suggestion of General Luís Maria da Câmara Pina, its Treasurer at that time, and was expanded also under the initiative of other members of the Academy, namely Professors José Pinto Peixoto (President), Fernando Dias Agudo (Teasurer), Manuel Jacinto Nunes (President), José Tiago de Oliveira (Secretary), João Fraústo da Silva, R.J.P. Williams, António Xavier and Armando J.L. Pombeiro. The decision to resume this series was recently taken by the Administrative Council of the Academy: Professors José Manuel Toscano Rico (President), José Vitorino de Pina Martins (Vice-President), Fernando R. Dias Agudo (Treasurer), Armando J.L. Pombeiro (Secretary-General) and João Bigotte Chorão (Vice-Secretary-General). The series includes such representative titles as: "New Trends in Bioionorganic Chemistry" (1979); "New Trends in the Chemistry of Nitrogen Fixation" (1982); "Some Recent Advances in Statistics" (1983); "Advances in Geophysics", Vol. II, "Theory of Climate" (1983); "Estudos de Álgebra, Geometria e Análise" (1978). Usually both national and international editions were published, the latter by Academic Press, and the publications were based on the corresponding symposia held at the Academy to discuss the state-of-the-art in those fields.

Other representative symposia and publications, within the bicentenary celebration programme, include the following subjects: (i) History and Development of Science in Portugal: "A Actividade Pedagógica da Academia das Ciências de Lisboa nos séculos XVIII e XIX" (1981); "The History and Development of Science in Portugal" (up to the 19th century, 2 vols., 1986;

20th century, 3 vols., 1992); "Colóquio sobre Termodinâmica e Reactividade de Sistemas Moleculares" (1994). (ii) Humanism in Portugal: "Erasmo na Academia das Ciências" (1987); "Humanism in Portugal 1500-1600" (1988). (iii) Problems of Modern Society (drug abuse, tobacco addiction, alcoholism, traffic accidents, euthanasia, peace, etc.): "Colóquio sobre a Problemática da Droga em Portugal" (1988); "Colóquio sobre a Problemática do Tabagismo em Portugal (1988); "Colóquio sobre a Problemática do Alcolismo em Portugal" (1989); "Colóquio sobre a Eutanásia" (1993); "A Bioética e o Futuro" (1995); and "Colóquio sobre Portugal e a Paz" (1989).

Other major publications of the Academy include:

(i) Facsimiles of manuscripts and of old books (limited editions) such as the "Livro das Armadas" (The book of the Armadas, from 1497 to 1563) (1979), "Atlas" (the collection of the Viscount of Santarém), the "Atlas de Lázaro Luís" (1563) (1990), the "Crónica dos Reis de Espanha" (Chronicles of the Kings of Spain, 13th and 14th centuries) (in preparation), the "Livro de Horas" (Prayer Book) of the Countess of Bretiandos (XVI ? century) (in preparation), "Colóquios dos Simples e Drogas e Cousas Medicinais da India" by Garcia d'Orta (1563) (1963), "Obras de Pedro Nunes" (16th century, the complete re-edition and translation, with recently found new data, is now under way), "Os Lusíadas" by Luís de Camões (fac-simile of the 1st editions, 1572) (1980), "Dicionário da Língua Portuguesa" of the Academy (vol. I, 1793) (1993) and "A Santa Casa da Misericórdia de Lisboa" by Victor Ribeiro (1902) (1998). Critical editions of old books: "Crónicas dos Reis de Portugal e Sumários de Suas Vidas" by Gaspar Correia (1996), "Gramática da Linguagem Portuguesa" by Fernão de Oliveira (1536) (2000), and " A Arte da Grammatica da Lingua Portugueza" by António José dos Reis Lobato (1770-1869, various editions) (2000).

(ii) The "Memórias", regular proceedings currently in two series (Sciences and Letters, until now with 39 and 32 volumes); some of the volumes concern symposia held at the Academy: "Paleoambientes do Jurássico Superior em Portugal" (vol. 37, 1998), "Últimos Neandertais em Portugal" (vol. 38, 2000) and "Geoquímica e Petrogénese de Rochas Granitóides" (vol. 39, 2001). The "Memórias Económicas" (5 volumes, 1789-1815) and the "Memórias Económicas Inéditas" (1987) concerning the period 1780-1808.

(iii) The "Dicionário da Língua Portuguesa Contemporânea" (Dictionary of the Contemporary Portuguese Language), recently published (2001) within the activities of the Instituto de Lexicologia e Lexicografia da Língua Portuguesa (Institute of Lexicology and Lexicography of the Portuguese Language) of the Academy; other dictionaries are currently in preparation.

(iv) Catalogues: "Catálogo dos Manuscritos" (Série Vermelha, 2 volumes) (1976, 1978); "Livros Quinhentistas Espanhóis da Biblioteca da Academia das Ciências de Lisboa" (1989); "Livros Quinhentistas Portugueses da Biblioteca da Academia das Ciências de Lisboa" (1990); "Livros Quatrocentistas da Biblioteca da Academia das Ciências de Lisboa" (1992); "O Material Didáctico dos séculos XVIII e XIX do Museu Maynense da Academia das Ciências de Lisboa", Rómulo de Carvalho (1993); and "O Material Etnográfico do Museu Maynense da Academia das Ciências de Lisboa", Rómulo de Carvalho (2000). The preparation of a data base with the old books of the Library of the Academy is underway.

(v) Other books with scientific, historical, literary or political interest: "Reconhecimento científico de Angola" (1979); "Portugaliae Monumenta Histórica" (Nova Série, vol. II/1 e vol. II/2 æ Livro de Linhagens do Conde D. Pedro) (1980); "Bibliografia mais relevante sobre Botânica pura e aplicada referente aos países de expressão portuguesa" (1982); "D. João Carlos de Bragança, 2º Duque de Lafões, fundador da Academia das Ciências de Lisboa" (1987); "Estudos sobre a projecção de Camões em Culturas e Literaturas estrangeiras", vol. III (1984); "Colóquio de Estudos Camilianos" (1993); "Descriptive List of the State Papers of Portugal 1661-1780 in the Public Record Office London" (1983).

Apart from the editorial activity and the organization of symposia, the Academia, guided by its original motto "Nisi utile est quod facimus stulta est Gloria" (unless what we do is useful, our fame is foolish), also promotes analyses and discussions of problems of national relevance (Portuguese language, ethics in science, etc.). In the past, it was (i) from the "Instituto Vacínico" (Vaccinic Institute), an initiative of the Academy, that the Council for Public Health emerged, (ii) from the Geological Commission of the Academy that the Geological Services of Portugal were created (only recently they left the Academy premises which however still house the Geological Museum) and (iii) from the Higher Course of Arts (organized by the Academy) that the Faculty of Letters of Lisbon emerged. After this Faculty has left the Academy premises, the freed space was temporarily occupied by the Biblioteca Popular (Popular Library) but is now being renovated for conference, library and museum rooms of the Academy.

The Academy also houses, apart from a museum, one of the four most valuable libraries in the country, with over one million items and which includes the former library of the Convent of Jesus, a magnificent 16th-17th century building which was donated by Queen Maria II, in 1838, to the Academy for its premises. The peripheral legacy libraries (Júlio M. Fogaça and Vasco Magalhães Vilhena) have recently been installed herein.

The museum has several sections, namely Natural History, Physics and Etnography (Indian culture from the Amazonas). It is under reorganization, but the Maynense Gallery, with a valuable collection of scientific instruments, has already been opened.

The Academy awards prizes for outstanding contributions to both sciences and humanities.

Moreover, the Academy also promotes international scientific and cultural relationships and exchanges with other countries. It is the Portuguese representative organization to the International Council of Science (ICSU), former International Council of Scientific Unions, since the foundation of this Council in 1931, and it is one of the Portuguese members of the European Science Foundation, and a member of the Union Académique Internationale (UAI), of ALLEA (All European Academies) and of the recently created European Academies' Science Advisory Council (EASAC).

The preparation of this book and the organization of a symposium on Molecular Electrochemistry are an expression of this internationally oriented policy of the Academy, applied in this case towards the development of this promising scientific field.

For further information, see: (a) Peixoto, J.P.; Pombeiro, A.J.L. "The Academy of Sciences of Lisbon", in "International Encyclopedia of Learned Societies and Academies", Kiger, J.C. (ed.), Greenwood Press, Westport, 1993, pp. 237-241. (b) "The Academy of Sciences of Lisbon", Academia das Ciências de Lisboa, 1994 (booklet). (c) "Comemorações do II Centenário da Academia das Ciências de Lisboa", Academia das Ciências de Lisboa, 1995. (d) Iria, A. "A Fundação da Academia das Ciências de Lisboa" in "História e Desenvolvimento da Ciência em Portugal", vol. II, Academia das Ciências de Lisboa (1986). (e) Dias Agudo, F.R. "Contribuição da Academia das Ciências de Lisboa para o Desenvolvimento da Ciência", ibid. (f) Peixoto, J.P. "A Revolução Cultural e Científica dos Séculos XVII e XVIII e a Génese das Academias", ibid. (g) Baião, A. "A Infância da Academia (1788-1794)" (1934). (h) Ayres, C. "Para a História da Academia das Sciências de Lisboa", Academia das Ciências de Lisboa, Separata do Boletim da Segunda Classe, vol. XII (1927). (i) "III Jubileu da Academia das Ciências de Lisboa" (1931).

M. Toscano Rico, President of the Academy
F. Dias Agudo, Coordinator of International Affairs of the Academy
Armando J.L. Pombeiro, The Editor, Secretary General of the Academy

Part 1

Redox and Other Molecular Properties

Chapter 1

Homoleptic, Mononuclear Transition Metal Complexes of 1,2-Dithiolenes: Updating their Electrochemical-to-Structural Properties

Piero Zanello and Emanuela Grigiotti

Dipartimento di Chimica dell'Università di Siena, Via Aldo Moro, 53100 Siena, Italy

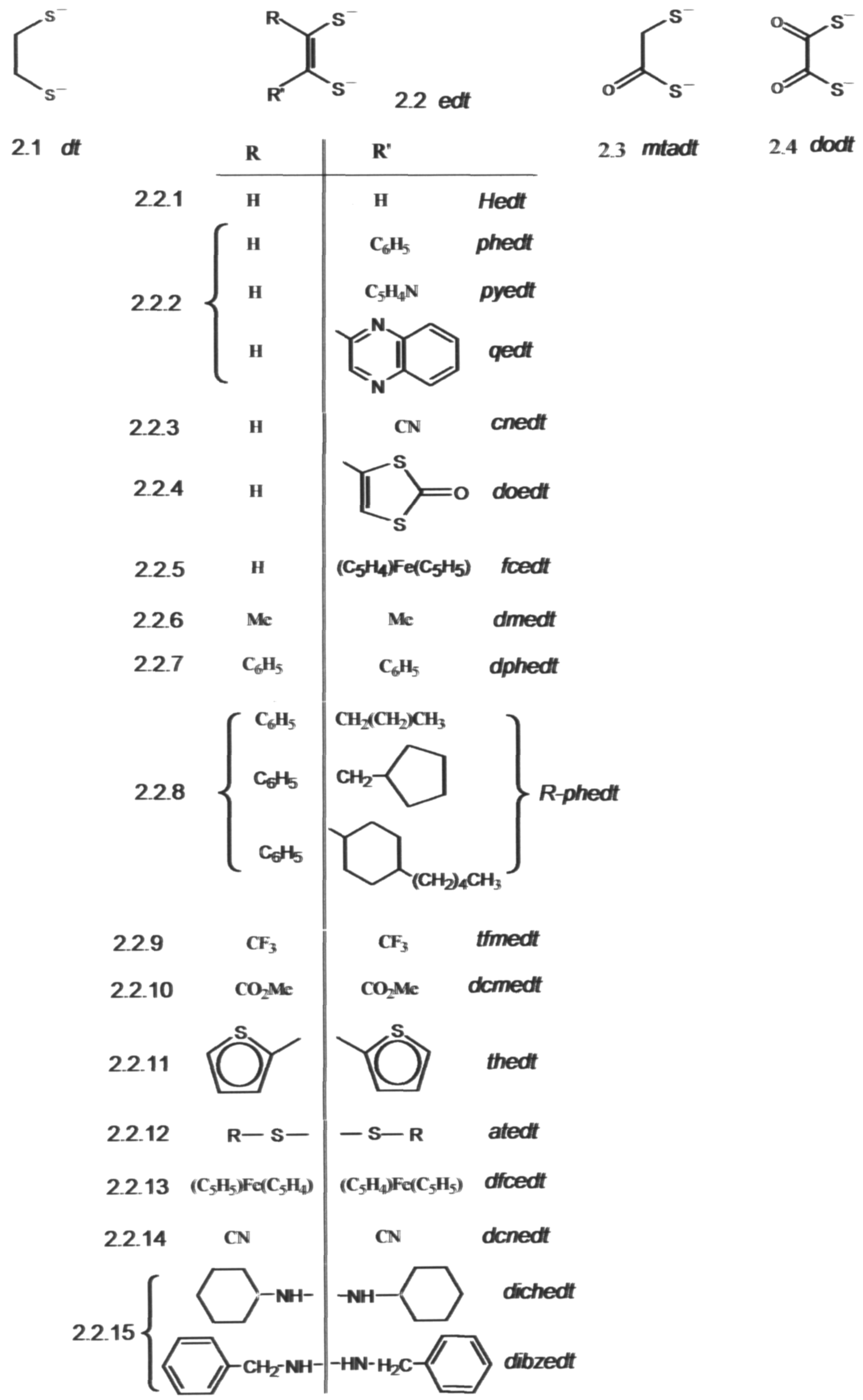
1 INTRODUCTION

Metal complexes of 1,2-dithiolenes appeared in literature about seventy years ago as analytical reagents [1]. The subsequent elucidation of their molecular and electronic structure at first and then either their relationships with some enzyme-mimicking activity, or the continuous discovery of their novel applications in material science (related to their uncommon conducting, magnetic, non-linear optic, sensing and dyeing properties) made them one of the most promising and persisting topic in inorganic chemistry. This is reflected on the numerous review papers from time to time devoted to the different aspects of their chemistry [2]. The 1968 McCleverty's pioneering work [2b] focussed on the structural and redox properties of such compounds, both the aspects being crucial to most innovative applications. The present review wishes to update just such a matter.

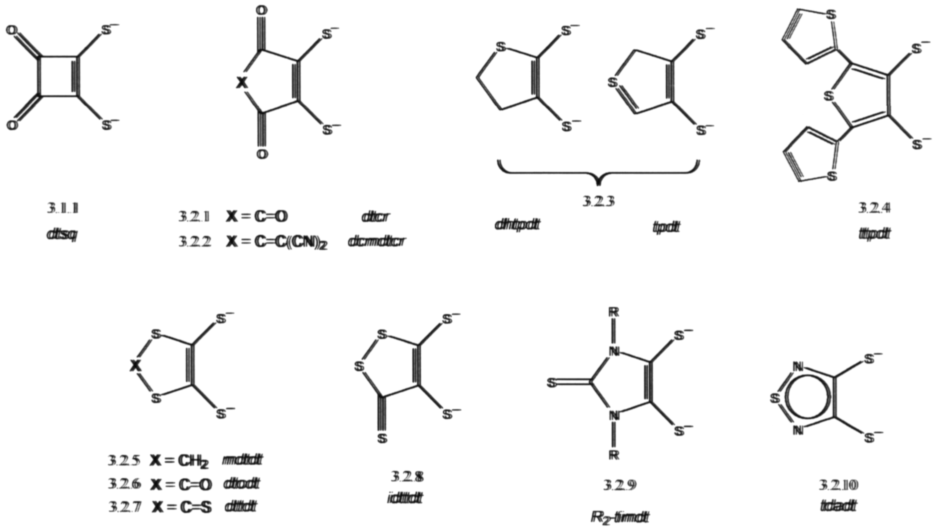
The different subclasses of ligands used in metal complexes discussed here are illustrated in Schemes 1-4. They have been subdivided depending upon if the 1,2-dithiolate substituents give rise to lateral ring(s), as well as on the type of lateral ring(s).

Since, from the structural viewpoint, we wish to give evidence only to the most significant reorganizations following electron transfer processes, for sake of simplicity bond lengths will be approximated to the hundredth of Å (neglecting any esd value).

It must be preliminarily taken into account that transition metal complexes with *dithiolene* ligands constitute an intriguing class of complexes as far as their


2.1 dt
2.2 edt
2.3 mtadt
2.4 dodt
R
R'
2.2.1 H H Hedt
2.2.2 H C6H5 phedt
H C5H4N pyedt
H qedt
2.2.3 H CN cnedt
2.2.4 H doedt
2.2.5 H (C5H4)Fe(C5H5) fcedt
2.2.6 Me Me dmedt
2.2.7 C6H5 C6H5 dphedt
2.2.8 C6H5 CH2(CH2)CH3
C6H5 CH2
C6H5 (CH2)4CH3
R-phedt
2.2.9 CF3 CF3 tfmedt
2.2.10 CO2Me CO2Me dcmedt
2.2.11 thedt
2.2.12 R— S— —S— R atedt
2.2.13 (C5H5)Fe(C5H4) (C5H4)Fe(C5H5) dfcedt
2.2.14 CN CN dcnedt
2.2.15 –NH– –NH– dichedt
–CH2-NH– –HN-H2C– dibzedt

Scheme 1



3.1.1 *dtsq*

3.2.1 **X = C=O** *dtcr*
3.2.2 **X = C=C(CN)$_2$** *dcmdtcr*

3.2.3 *dhtpdt* *tpdt*

3.2.4 *ttpdt*

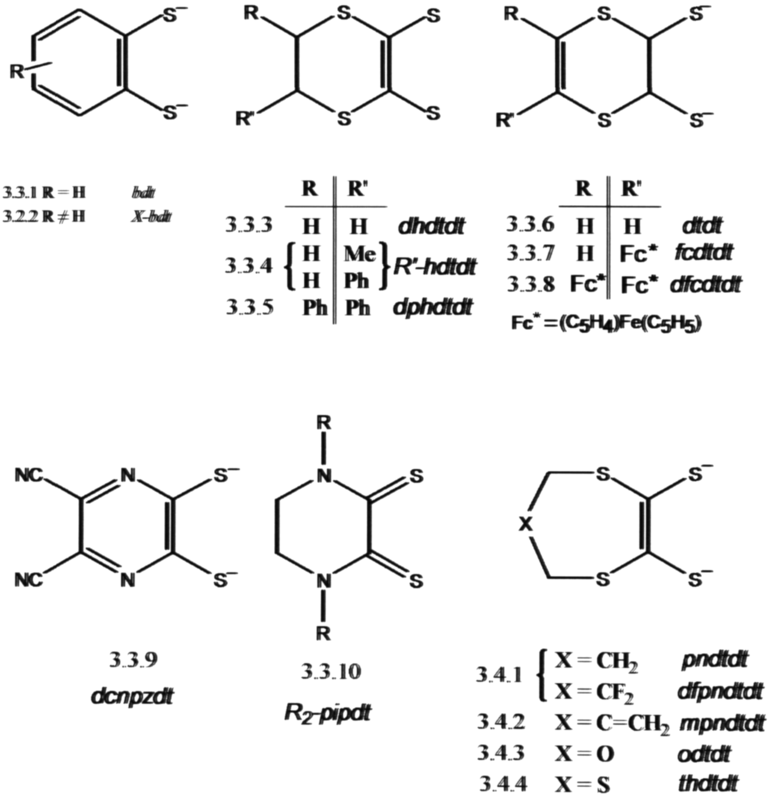
3.2.5 **X = CH$_2$** *mdtdt*
3.2.6 **X = C=O** *dtodt*
3.2.7 **X = C=S** *dttdt*

3.2.8 *idttdt*

3.2.9 *R$_2$-timdt*

3.2.10 *tdadt*

Scheme 2



3.3.1 **R = H** *bdt*
3.2.2 **R ≠ H** *X-bdt*

	R	R''	
3.3.3	H	H	*dhdtdt*
3.3.4	H	Me	*R'-hdtdt*
	H	Ph	
3.3.5	Ph	Ph	*dphdtdt*

	R	R''	
3.3.6	H	H	*dtdt*
3.3.7	H	Fc*	*fcdtdt*
3.3.8	Fc*	Fc*	*dfcdtdt*

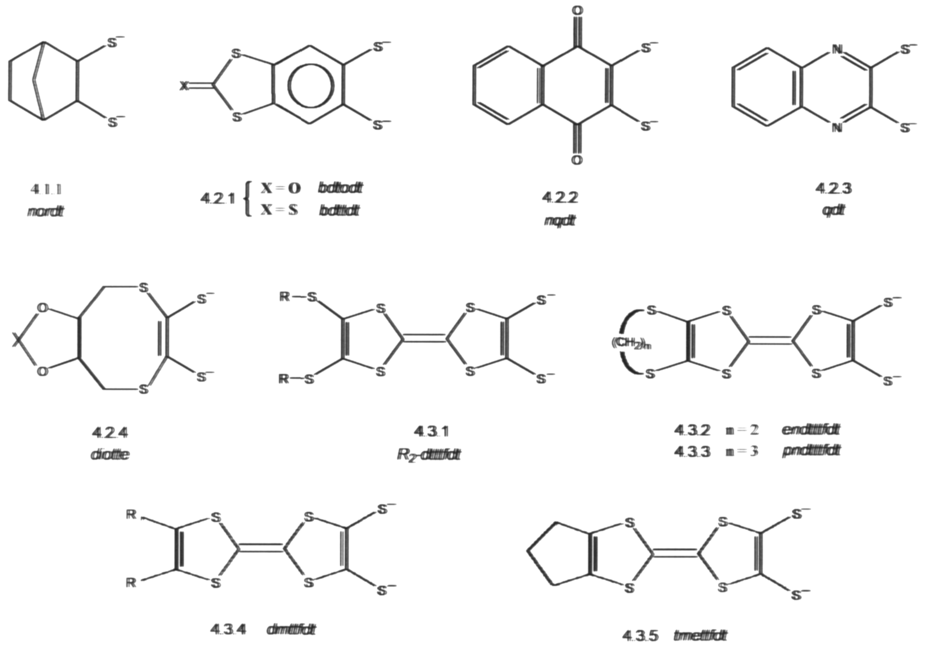
Fc* = (C$_5$H$_4$)Fe(C$_5$H$_5$)

3.3.9 *dcnpzdt*

3.3.10 *R$_2$-pipdt*

3.4.1 X = CH$_2$ *pndtdt*
X = CF$_2$ *dfpndtdt*
3.4.2 X = C=CH$_2$ *mpndtdt*
3.4.3 X = O *odtdt*
3.4.4 X = S *thdtdt*

Scheme 3



Scheme 4

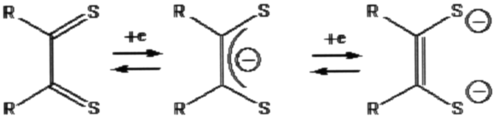
electrochemical behaviour is concerned. In fact, considering that such ligands are able to shuttle reversibly the sequence *1,2-dithione/1,2-dithione monoanion/ene-1,2-dithiolate* illustrated in Scheme 5, their metal complexes should display a notably extended redox activity.

For instance, the most common homoleptic bis-dithiolene metal complexes $[M^{II}(S_2C_2R_2)_2]^{n-}$ (M = Ni, Pd, Pt) should potentially display the redox sequence illustrated in Scheme 6.

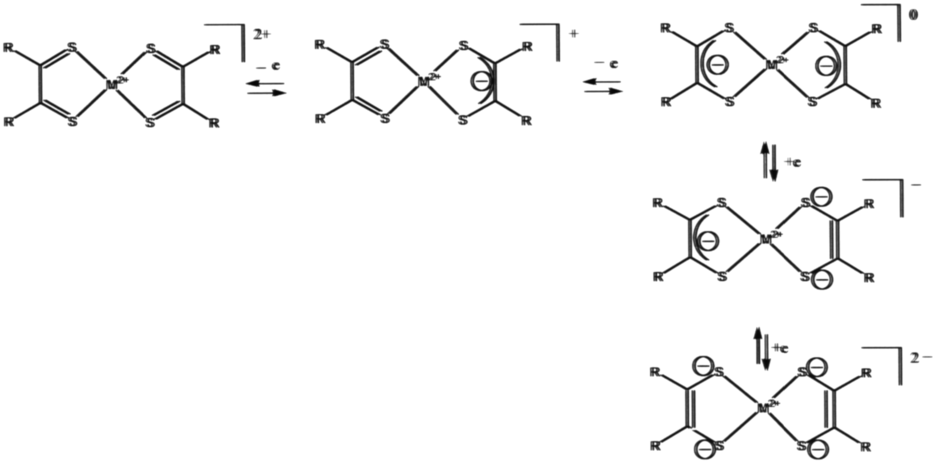
Obviously, the different steps can proceed at different or at coincident potential values depending upon the extent of intramolecular communication existing inside the molecule.

In reality, this has to be considered as a simplified sequence, in that it assumes that the central metal ion maintains its oxidation state unchanged, but the concomitant occurrence of metal centred redox processes cannot be disregarded, and out the subsequent occurrence of internal metal-to-ligand electron transfer reorganization can not be ruled out.

In fact, in those cases in which metal-based and ligand-based frontier orbitals are comparable in energy, the ligands under subject are defined as redox "non-innocent" [3].



Scheme 5



Scheme 6

2 1,2-DITHIOLATES NOT FORMING LATERAL RINGS

2.1 dt Complexes

In literature, metal complexes of the 1,2-ethanedithiolate dianion $[SCH_2CH_2S]^{2-}$ (here abbreviated as *dt*) and those of (unsubstituted) 1,2-ethenedithiolate dianion $[SCH{=}CHS]^{2-}$ (hereinafter abbreviated as *Hedt*) are commonly undifferentiated, at least as far as their nomenclature is concerned, both being often designated as “edt” complexes.

2.1.1 Bis(dt) complexes

The crystal structures of a number of homoleptic bis-dithiolenes of general formula $[M^{II}(dt)_2]^{2-}$ (M = Cr, Mn, Co, Ni, Zn, Pd, Cd) are available [4]. Excluding $[Ni(dt)_2]^{2-}$ [4d], the electrochemical behaviour of these complexes has not been reported, even if the molecular structure of the redox couple $[Co(dt)_2]^{2-/-}$ is known, Table 1 [4c].

Table 1. Selected structural parameters (average bond distances, Å; dihedral angles, °) in the redox couple $[Co(dt)_2]^{2-/-}$

Complex	Co-S	S-C	C-C	α^a	Cation
$[Co(dt)_2]^{2-}$	2.28	1.80	1.40	88.5	$[NMe_4]^+$
$[Co(dt)_2]^-$	2.17	1.79	1.33	6.8	$[NMe_4]^+$

[a] Dihedral angle between the two CoS_2 planes

It is not only interesting to note that the dianion has a tetrahedral geometry, whereas the monoanion assumes a (nearly) square-planar geometry, but also the significant variation of the Co-S distance, which allows one to assume a mainly metal-centred electron transfer.

$[Ni(dt)_2]^{2-}$ in MeCN solution gives rise to a quasireversible one-electron oxidation ($E^{\circ\prime} = -0.68$ V, *vs.* SCE), which is accompanied by relatively fast decomposition of the electrogenerated monoanion [4d].

The vanadyl and thiovanadyl complexes $[V^{IV}E(dt)_2]^{2-}$ (E = O, S) have been structurally characterised [5]. They possess a square-pyramidal geometry, with the chalcogenyl atom apically coordinated and the metal ion placed out (towards the apex) of the thiolene-sulfur basal plane. From the electrochemical viewpoint, these V(IV) complexes in MeCN solution only put in evidence irreversible electron-transfer processes [5b].

Brief electrochemical data have been also reported for the square pyramidal Re(V) and Tc(V) complexes $[ME(dt)_2]^-$ (E = O, S) [6a,b]. In MeCN solution, metal-centered reductions occur at very negative potential values ($E^{\circ\prime}_{-/2-}$: ReO, < -2.1 V; ReS $= -1.83$ V; TcO $= -1.86$ V, *vs.* SCE), whereas no ligand-centred reversible electron transfer process seem to be present [6a,c].

In conclusion, the absence of reversible electron transfer processes in the actual complexes is likely due to the absence of the carbon/carbon unsaturation in the dithiolene backbone. In fact, just the π-delocalization along the whole molecular frame arising from unsaturation commonly triggers electron mobility. In this light, the partial chemical reversibility of the one-electron oxidation of $[Ni(dt)_2]^{2-}$ can be attributed to the instability of the electrogenerated Ni(III) monoanion $[Ni(dt)_2]^-$.

2.1.2 Tris(dt) complexes

The solid-state structures of the tris-chelates $[M(dt)_3]^{n-}$ (M = Ti(IV), n = 2; M = Nb(V), Ta(V), n = 1) are known [4b,c,7]. As exemplified in Figure 1, which

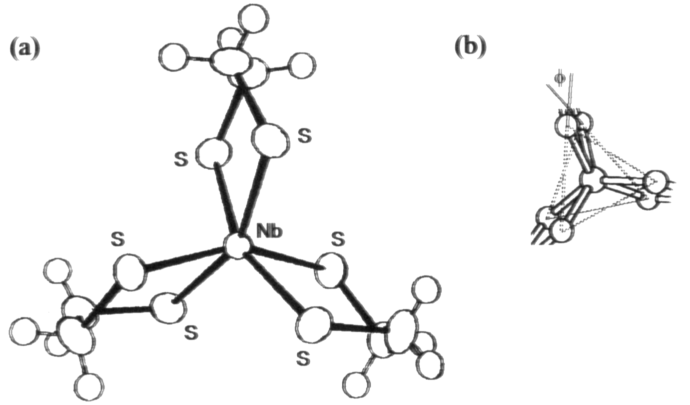


Figure 1. (a) X-Ray structure of $[Nb(dt)_3]^-$ ($[NEt_4]^+$ cation). Average Nb-S distance = 2.43 Å. Twist angle (ϕ) between the equilateral triangles formed by the three upper and the three lower sulfur atoms = about 30°. (b) Meaning of "twist" angle.

refers to $[Nb(dt)_3]^-$ [7], they possess a geometry, which, based on the value of the twist angle ϕ, is intermediate beween trigonal-prismatic and octahedral (trigonal prism: ϕ = 0; octahedron: ϕ = 60°).

Further supporting the redox inactivity of the saturated dt ligand, dmso solutions of $[M(dt)_3]^-$ (M = Nb, Ta) only display a metal-centred, quasireversible, one-electron reduction (Nb: $E^{\circ\prime}_{-/2-} = -1.20$ V; Ta: $E^{\circ\prime}_{-/2-} = -1.56$ V, *vs.* SCE) [7].

2.2 edt Complexes

2.2.1 Hedt Complexes (Better known as "edt")

2.2.1.1 Bis(Hedt) complexes

The square planar geometry of the monoanion $[Ni(Hedt)_2]^-$ is shown in Figure 2 [8].

In dmso solution it undergoes reversibly either a one-electron oxidation or a one-electron reduction, Table 2 [2b, 9].

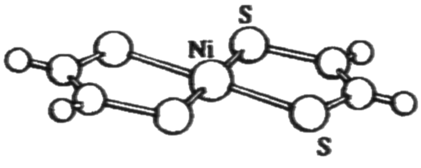


Figure 2. X-Ray structure of $[Ni(Hedt)_2]^-$ ($[Fe(C_5Me_5)_2]^+$ cation). Bond lengths: Ni-S = 2.14 Å; S-C = 1.71 Å; C=C = 1.32 Å.

The neutral complex $[Ni(Hedt)_2]$ maintains the square-planar geometry of the monoanion, with a slight decrease of the Ni-S and S-C distances (by about 0.04 Å and 0.02 Å, respectively) and a slight increase of the C=C distance (by about 0.04 Å) [10].

Such structural change does not allow the precise determination of the oxidation state of the central Ni atom inside the redox couple $[Ni(Hedt)_2]^{-/0}$. In spite of the Ni(III)/Ni(IV) assignment [8], we note that $[Pd(Hedt)_2]^-$, which is difficulty assignable as Pd(III) compound, displays a similar electrochemical behaviour, Table 2 [2b]. Hence, it cannot be ruled out that the $[Ni(Hedt)_2]^{-/0}$ complexes might be seen as oxidation products of the Ni(II) precursor $[Ni^{II}(Hedt)_2]^{2-}$, with the extra electrons stepwise removed from the dithiolene ligands. The same likely holds for the other $[M(Hedt)_2]^-$ complexes listed in Table 2. In this connection, in agreement with the easy oxidation exhibited by $[Pd(Hedt)_2]^-$, the crystal structure of the neutral $[Pd(Hedt)_2]$ has been reported [11]. As expected, the $PdS_4C_4H_4$ frame is planar, but in the solid state the neutral complex looks like a dimer because of the presence of a direct intermolecular metal-metal bond (2.79 Å).

Table 2. Formal electrode potentials (V, *vs.* SCE) for the redox changes exhibited by a few $[M(Hedt)_2]^{n-}$ complexes

M	$E^{o'}_{-/2-}$	$E^{o'}_{-/0}$	Solvent	Reference
Ni	–0.84	+0.16	dmso	2b,9
	–0.97	+0.07	dmf	2b
Pd	–0.64	-	dmso	2b,9
	–0.77	+0.11	dmf	2b
Co	–0.93	-	dmso	2b,9
Cu	–0.74	-	dmso	2b,9

Figure 3 illustrates the square-pyramidal structure of the oxo-Mo(IV) dianion $[MoO(Hedt)_2]^{2-}$ [12].

In MeCN solution it undergoes a reversible one-electron oxidation (E°' = –0.61 V, *vs.* SCE), followed by a further irreversible oxidation [12]. The crystal structure of the corresponding monoanion has been solved [12]. It maintains the square pyramidal geometry of the parent dianion with the following structural variations: (a) the average Mo-S distance shortens by about 0.02 Å; (b) the Mo=O distance shortens by about 0.06 Å; (c) both the S-C and C=C distances

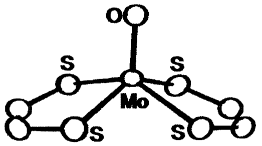


Figure 3. X-Ray structure of $[MoO(Hedt)_2]^{2-}$ ($[NEt_4]^+$ cation). Average bond lengths: Mo-S = 2.40 Å; Mo-O = 1.74 Å; S-C = 1.75 Å; C=C = 1.33 Å.

shorten by about 0.02 Å. Because of the significant variation of the Mo=O distance, it has been assumed that the one-electron removal is due to the $Mo^{IV}O$/$Mo^{V}O$ oxidation.

2.2.1.2 *Tris(Hedt) complexes*

To the best of our knowledge, the only crystallographically characterized tris(Hedt) metal complex still remains $[Mo(Hedt)_3]$, whose structural and voltammetric data have been already reported [2b].

2.2.2 *phedt, pyedt, qedt* Complexes

2.2.2.1 *Bis(phedt), bis(X-pyedt) (X = 2, 3, 4), and bis(qedt) complexes*

Like $[MoO(Hedt)_2]^{2-}$, the square pyramidal $[MoO(phedt)_2]^{2-}$ undergoes a reversible one-electron oxidation, which has been assigned to the $Mo^{IV}O$/$Mo^{V}O$ process [13]. Analogous assignment has been made to the one-electron oxidation exhibited by the pyridin-2-yl, -3-yl, 4-yl $[MoO(X\text{-}pyedt)_2]^{2-}$ and quinoxalin-2-yl $[MoO(qedt)_2]^{2-}$ dianions [13]. The pertinent redox potentials are compiled in Table 3.

Table 3. Formal electrode potentials (V, *vs.* SCE) for the one-electron oxidation of $[MoO(phedt)_2]^{2-}$, $[MoO(X\text{-}pyedt)_2]^{2-}$ and $[MoO(qedt)_2]^{2-}$ complexes in dmf solution

Complex	$E^{\circ\prime}_{2-/-}$
$[MoO(phedt)_2]^{2-}$	−0.48
$[MoO(2\text{-}pyedt)_2]^{2-}$	−0.42
$[MoO(3\text{-}pyedt)_2]^{2-}$	−0.38
$[MoO(4\text{-}pyedt)_2]^{2-}$	−0.35
$[MoO(qedt)_2]^{2-}$	−0.28

As seen, the different pendant groups of the dithiolene units exert appreciable inductive effects, the phedt ligand favouring the one-electron removal with respect to pyedt and qedt, respectively.

2.2.3 cnedt Complexes

2.2.3.1 Bis(cnedt) complexes

The square planar dianion $[Ni(cnedt)_2]^{2-}$ exhibits in MeCN solution a first, reversible one-electron oxidation ($E^{\circ\prime} = -0.31$ V, *vs.* SCE), followed by a further irreversible process ($E_p = +0.65$ V) [14]. As a consequence of the one-electron removal, the corresponding monoanion maintains the square planar geometry, the Ni-S and S-C distances shorten by 0.04 Å and 0.02 Å, respectively, whereas the other bond lengths remain unaltered [14]. Thus, in spite of theoretical calculation on the HOMO composition of $[Ni(cnedt)_2]^{2-}$, which suggests thai it is essentially contributed by the ligand [14], it seems almost certain that the appreciable variation of the Ni-S distance implies that the HOMO level is contributed also by the metal.

2.2.4 doedt Complexes

2.2.4.1 Bis(doedt) complexes

Nothing is known about the redox properties of the (almost) square planar complex $[Ni(doedt)_2]^-$ [15].

2.2.5 fcedt Complexes

2.2.5.1 Bis(fcedt) complexes

It has been briefly reported that $[Ni(fcedt)_2]$ undergoes two separate, ligand-centred, reversible processes ($[Ni(fcedt)_2]^{0/-}$: $E^{\circ\prime} = +0.51$ V; $[Ni(fcedt)_2]^{-/2-}$: $E^{\circ\prime} = -0.20$ V, *vs.* SCE) and a single two-electron oxidation ($[Ni(fcedt)_2]^{0/2+}$: $E^{\circ\prime} = +0.76$ V) which has been attributed to the two non-communicating ferrocenyl subunits [16]. In reality, such an interpretation would deserve revision in favour of two separate ferrocene-centred oxidations, also in the light of the behaviour of the related tetraferrocenyl complex which will be discussed below (see Section 2.2.13).

2.2.6 dmedt Complexes

2.2.6.1 Bis(dmedt) complexes

The electrochemical behaviour of the dianions $[M(dmedt)_2]^{2-}$ (M = Ni, Pd, Pt) has been reviewed [2b]. As a typical example, Figure 4 shows the voltammetric response of the square planar $[Ni(dmedt)_2]^{2-}$ [17].

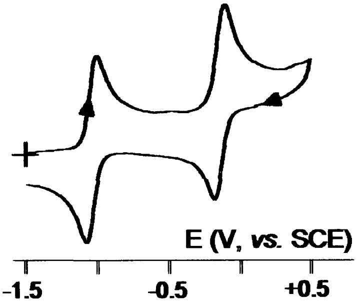


Figure 4. Cyclic voltammogram recorded at a platinum electrode in MeCN solution of $[Ni(dmedt)_2]^{2-}$. Scan rate 0.1 V s^{-1}.

It undergoes two separate one-electron oxidations with features of chemical reversibility ($E^{\circ\prime}_{2-/-} = -1.05$ V; $E^{\circ\prime}_{-/0} = -0.15$ V, *vs.* SCE). As a matter of fact, all the members of the reversible sequence 2−/−/0 have been structurally characterized, Table 4 [17].

Table 4. Selected bond distances (average values, Å) in the redox sequence $[Ni(dmedt)_2]^{2-/-/0}$

Complex	Ni-S	S-C	C=C	$C-C_{(Me)}$	Cation
$[Ni(dmedt)_2]^{2-}$	2.18	1.76	1.34	1.51	$[NEt_4]^+$
$[Ni(dmedt)_2]^{-}$	2.14	1.74	1.34	1.51	$[NEt_4]^+$
$[Ni(dmedt)_2]^{0}$	2.13	1.71	1.36	1.51	-

On passing gradually from the neutral 1,2-dithionate to the dianionic 1,2-dithiolate, the Ni-S and C-S distances progressively increase, whereas the C=C distance slightly decreases. The minor but significant variation of the Ni-S distance with the electron addition/removal processes suggests that the redox processes are centered on molecular orbitals significantly contributed not only by the dithiolene ligand but also by the metal.

As far as the oxo-dianions $[MO(dmedt)_2]^{2-}$ (M = Mo, W) are concerned, they also undergo two reversible one-electron oxidations according to the sequence $[MoO(dmedt)_2]^{2-/-/0}$ [18]. The crystal structures of two of the three-membered series are available, namely $[MoO(dmedt)_2]^{2-/-}$ [18a] (also available is the crystal structure of $[WO(dmedt)_2]^{2-}$ [18b]). Apart from their usual square-pyramidal geometry, the structural consequences of the one-electron removal are reported in Table 5, together with the formal electrode potentials of the electron transfer sequences [18].

Table 5. Formal electrode potentials (V, *vs.* SCE) for the redox sequence $[MO(dmedt)_2]^{2-/-/0}$ (MeCN solution) and selected interatomic distances (Å) in the couple $[MO(dmedt)_2]^{2-/-}$

Complex	$E^{\circ\prime}_{2-/-}$	$E^{\circ\prime}_{-/0}$	M-S	C-S	C=C	M-O	Cation
$[MoO(dmedt)_2]^-$	-	-	2.37	1.75	1.33	1.68	$[NEt_4]^+$
$[MoO(dmedt)_2]^{2-}$	−0.62	+0.14	2.39	1.78	1.33	1.71	$[NEt_4]^+$
$[WO(dmedt)_2]^{2-}$	−0.91	−0.05	2.38	1.79	1.33	1.74	$[NEt_4]^+$

Based on the variation of the Mo=O length, the overall reversible sequence has been assigned as: $M^{IV}O/M^{V}O/M^{VI}O$ (M = Mo, W) [18], even if the participation of the ligand to the electron transfer series cannot be ruled out.

2.2.6.2 *Tris(dmedt) complexes*

The trigonal prismatic derivatives $[M(dmedt)_3]$ (Mo, W) undergo reversibly the sequence $[M(dmedt)_3]^{0/-/2-}$ (M = Mo: $E^{\circ\prime}_{0/-} = -0.34$ V; $E^{\circ\prime}_{-/2-} = -0.86$ V. M = W: $E^{\circ\prime}_{0/-} = -0.36$ V; $E^{\circ\prime}_{-/2-} = -0.92$ V; MeCN solution, V *vs.* SCE) [19, 18a]. Stated that all the members of the two families $[M(dmedt)_3]^{0/-/2-}$ (M = Mo, W) are isostructural, the most significant structural changes accompanying the redox sequences are compiled in Table 6 [18a, 19].

Table 6. Selected bond distances (Å) and twist angles (°) in the three-membered series $[M(dmedt)_3]^{0/-/2-}$ (M = Mo, W)

Complex	M-S	S-C	C=C	ϕ	Cation
$[Mo(dmedt)_3]^0$	2.36	1.71	1.36	3.5	-
$[Mo(dmedt)_3]^-$	2.37	1.72	1.35	1.6	$[NEt_4]^+$
$[Mo(dmedt)_3]^{2-}$	2.40	1.75	1.33	2.6	$[NEt_4]^+$
$[W(dmedt)_3]^-$	2.38	1.73	1.36	2.8	$[NEt_4]^+$
$[W(dmedt)_3]^{2-}$	2.39	1.76	1.33	2.4	$[NEt_4]^+$

The slight variations of both the metal-to-ligand and the intraligand distances support that the electrons are transferred from orbitals contributed from either the metal or the ligand.

2.2.7 dphedt Complexes

2.2.7.1 Bis(dphedt) complexes

Metal complexes of 1,2-diphenylethene-1,2-dithiolate are long known and widely investigated either from the structural or redox viewpoints [2b]. Our discussion will be hence limited to updating previous data.

As illustrated in Figure 5, the square planar complex [Ni(dphedt)$_2$] undergoes two chemically reversible one-electron reductions and a partially chemically reversible one-electron oxidation [20a].

The same behaviour is exhibited by both [Pd(dphedt)$_2$] and [Pt(dphedt)$_2$], Table 7.

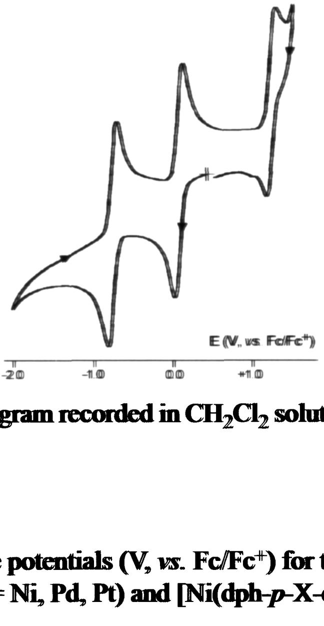


Figure 5. Cyclic voltammogram recorded in CH_2Cl_2 solution of [Ni(dphedt)$_2$]. Scan rate 0.2 V s^{-1}.

Table 7. Formal electrode potentials (V, *vs.* Fc/Fc$^+$) for the redox processes exhibited by [M(dphedt)$_2$] (M = Ni, Pd, Pt) and [Ni(dph-*p*-X-edt)$_2$] in CH_2Cl_2 solution

Complex	$E^{\circ\prime}_{0/+}$ ^{a}	$E^{\circ\prime}_{0/-}$	$E^{\circ\prime}_{-/2-}$	Reference
[Ni(dphedt)$_2$]	+1.15	+0.02	–0.80	20a
	-	+0.01	–0.81	20b
	-	–0.04	–0.87	20c
[Ni(dph-*p*-Br-edt)$_2$]	-	+0.07	–0.74	20c
[Ni(dph-*p*-F-edt)$_2$]	-	+0.03	–0.79	20c
[Ni(dph-*p*-Me-edt)$_2$]	-	–0.10	–0.92	20c
[Ni(dph-*p*-OMe-edt)$_2$]	-	–0.11	–0.93	20c
[Pd(dphedt)$_2$]	+1.17	+0.02	–0.61	20a
[Pt(dphedt)$_2$]	+1.20	–0.06	–0.80	20a

^{a} Partial chemical reversibility

The monoanions $[M(dphedt)_2]^-$ (M = Ni [21], Pt [22]) have been structurally characterised. Concerned with the Ni monoanion, the most significant variations in bond lengths with respect to the neutral species are summarized in Table 8 (together with those of a few asymetrically substituted complexes which will be discussed in the next Section 2.2.8.1).

Once again, both the metal and the dithiolene ligands look like involved in the electron transfer process.

A series of para-phenyl substituted Ni complexes have been also prepared and their electrochemical behaviour studied, Table 7. The inductive effects exerted by the para-substituents strictly obey the Hammett equation [20c].

Like the related $[MoO(Hedt)_2]^{2-}$ (and at variance with the dmedt analogues), the square pyramidal dianions $[WE(dphedt)_2]^{2-}$ (E = O, S) only exhibit a chemically reversible one-electron oxidation to the corresponding monoanions $[WE(dphedt)_2]^-$ (E = O, S: $E°' = -0.62$ V, *vs.* SCE; MeCN solution [18b]). No crystallographic data are available for the likely isostructural monoanions. A second irreversible oxidation is present for E = O (MeCN: $E_p = -0.21$ V).

Table 8. Selected bond distances (average values, Å) in the redox couple $[Ni(dphedt)_2]^{0/-}$, together with those of the asymmetrically substituted $[Ni(R\text{-}phedt)_2]^0$

Complex	M-S	S-C	C=C	Cation	Reference
$[Ni(dphedt)_2]^0$	2.10	1.71	1.37	-	2b
	2.12	1.70	1.41	-	23
$[Ni(dphedt)_2]^-$	2.14	1.75	1.34	$[NBu_4]^+$	21a
	2.14	1.77	1.34	$[NEt_4]^+$	21b
$[Pt(dphedt)_2]^-$	2.26	1.73	1.38	$[NBu_4]^+$	22
$[Ni(Bu\text{-}phedt)_2]^0$	2.12	1.71	1.36	-	20b
$[Ni(C_5H_9CH_2\text{-}phedt)_2]^0$	2.12	1.71	1.37	-	20b

2.2.7.2 Tris(dphedt) complexes

Structural data for the neutral complexes $[M(dphedt)_3]$ (M = V, Re) have been reviewed, together with the electron transfer ability of the series M = V, Mo, W, Re [2b]. They usually display the sequence $[M(dphedt)_3]^{3-/2-/-/0}$. In particular, $[W(dphedt)_3]$ exhibits in dmf solution two reversible one-electron reductions ($E^{°'}_{0/-} = -0.54$ V; $E^{°'}_{-/2-} = -1.13$ V, *vs.* SCE) [2b]. Both the neutral derivative and its monoanion possess a trigonal prismatic geometry, and the passage from [W(dphedt)$_3$]$^-$ to [W(dphedt)$_3$]^0 involves an increase of the W-S, S-C, and C=C distances (by 0.03 Å, 0.05 Å, and 0.02 Å, respectively) [18b]. It seems evident that also in this case either the metal or the ligand is involved in the electron transfer process.

2.2.8 R-phedt Complexes

2.2.8.1 Bis(R-phedt) complexes

A series of asymmetrically substituted Ni(II)-dithiolenes bearing a phenyl group and either a butyl, or a cyclopentylmethyl, or a 4-pentylcyclohexyl group have been characterised [20b]. The crystal structures of the complexes [Ni(Bu-phedt)$_2$] and [Ni(C$_5$H$_9$CH$_2$-phedt)$_2$] have been solved and the pertinent data are collected in Table 8.

As a consequence of the electron-donating effect of the alkyl substituent, the present complexes in CH$_2$Cl$_2$ solution undergo reversibly the 2–/–/0 sequence at slightly more negative potential values than [Ni(dphedt)$_2$] (R = Bu: $E^{\circ\prime}_{0/-}$ = –0.13 V, $E^{\circ\prime}_{-/2-}$ = –0.96 V; R = CH$_2$C$_5$H$_9$: $E^{\circ\prime}_{0/-}$ = –0.13 V, $E^{\circ\prime}_{-/2-}$ = –0.97 V; R = C$_5$H$_{11}$C$_6$H$_{10}$: $E^{\circ\prime}_{0/-}$ = –0.14 V, $E^{\circ\prime}_{-/2-}$ = –0.98 V; V, *vs.* Fc/Fc$^+$).

2.2.9 tfmedt Complexes (better known as "tdf")

2.2.9.1 Bis(tfmedt) complexes

Among complexes [M(tfmedt)$_2$]$^{n-}$, the Ni, Pd, Pt derivatives usually exhibit the reversible sequence 2–/–/0, the Cu, Co, Fe complexes only undergo the 2–/– process, and the Au complex is stable only as monoanion [2b].

Wishing to point out the structural variations following the electron transfer processes, we dwell upon the square planar couple [Ni(tfmedt)$_2$]$^{0/-}$, a few selected structural parameters of which are collected in Table 9.

Table 9. Selected bond distances (average values, Å) in the couple [Ni(tfmedt)$_2$]$^{0/-}$

Complex	Ni-S	S-C	C=C	C-C$_{(CF3)}$	Cation	Reference
[Ni(tfmedt)$_2$]^0	2.12	1.71	1.38	1.48	-	25
[Ni(tfmedt)$_2$]$^-$	2.14	1.70	1.40	1.47	[C$_7$H$_7$]$^+$	24a
	2.13	1.72	1.36	1.50	[PTZ]$^{+\,a}$	24b
	2.14	1.73	1.35	1.51	[Fe(C$_5$Me$_5$)$_2$]$^+$	24c

[a] PTZ = phenothiazine

The slight structural variations occurring at the ligand frame suggest that the electron transfer involves orbitals which are substantially contributed by the ligand. Further support to such a proposal comes from the electrochemical finding, that in MeCN solution the ligand-centred reversible reductions $[Ni(tfmedt)_2]^{0/-/2-}$ are followed by a further reversible one-electron step at very negative potential values (E°' = –2.34 V, *vs.* SCE), which proved to generate the Ni(I) trianion $[Ni(tfmedt)_2]^{3-}$ [26].

It has been briefly reported that the square-pyramidal [27] dianion $[MoO(tfmedt)_2]^{2-}$ undergoes in MeCN solution the (common) sequence $[MoO(tfmedt)_2]^{2-/-/0}$ [12], but no structural data are available for any of the oxidised members of the family. The crystal structure of $[WO(tfmedt)_2]^{2-}$ is also known [27].

2.2.9.2 Tris(tfmedt)complexes

The trigonal prismatic dianions $[M(tfmedt)_3]^{2-}$ (M = Mo, W) undergo, in MeCN solution, two reversible one-electron oxidations [2b].

The crystal structures of all the members of the redox family $[Mo(tfmedt)_3]^{2-/-/0}$ are available and selected structural parameters are reported in Table 10 [27, 28].

Table 10. Selected bond distances (average values, Å) in the redox family $[Mo(tfmedt)_3]^{2-/-/0}$

Complex	M-S	S-C	C=C	Cation	Reference
$[Mo(tfmedt)_3]^0$	2.35	1.70	1.36	-	27
$[Mo(tfmedt)_3]^-$	2.37	1.72	1.37	$[Fe(C_5Me_5)_2]^+$	28
$[Mo(tfmedt)_3]^{2-}$	2.37	1.74	1.33	$[NEt_4]^+$	27
	2.38	1.74	1.36	$Fe(C_5Me_5)_2]^+$	28
$[W(tfmedt)_3]^{2-}$	2.37	1.74	1.34	$[NEt_4]^+$	27

Once again, the (slight) variation of the interatomic distances with the overall charge appears like extended along the whole metallacycle fragments. Infact, the most significant structural differences inside the three members reside in the extent of trigonal prismatic geometry. The neutral complex adopts a perfect trigonal prismatic structure; the monoanion also possesses a nearly perfect trigonal prismatic structure; the dianion is significantly distorted ($\phi \approx 16°$) [27, 28].

2.2.10 dcmedt Complexes

2.2.10.1 Bis(dcmedt)complexes

The crystal structures of the square planar anions $[Ni(dcmedt)_2]^-$ and $[Ni(dcmedt)_2]^{2-}$ are known [29], even if the pertinent electrochemical data are not available. Passing from the dianion to the monoanion, The Ni-S and S-C distances undergo a slight decrease (by 0.04 Å and 0.02 Å, respectively), whereas the C=C and the peripheral C=O distances remain substantially unaltered [29b]. These data suggest that the extra electron is removed from a molecular orbital contributed by both the metal and the ligand.

The square-pyramidal dianion $[MoO(dcmedt)_2]^{2-}$ undergoes in MeCN solution a reversible one-electron oxidation ($E^{o'} = -0.03$ V, *vs.* Ag/AgCl), followed by a further irreversible oxidation ($E_p = +0.82$ V) [30a]. Nothing is known about the redox activity of the square-pyramidal monoanion $[TcO(dcmedt)_2]^-$ [30b].

2.2.10.2 Tris(dcmedt)complexes

The (slightly) distorted trigonal prismatic geometry of the dianion $[Mo(dcmedt)_3]^{2-}$ is shown in Figure 6, together with its cyclic voltammetric profile in CH_2Cl_2 solution [30a,c].

It undergoes two reversible one-electron oxidations ($E^{o'}_{2-/-} = +0.02$ V; $E^{o'}_{-/0} = +0.42$ V, *vs.* SCE), which support the stability of the corresponding monoanion and neutral derivatives [30a,c].

Even if not strictly pertinent to the present review, we would mention that crystal the structure and electrochemistry of the spectacular hexanuclear complex $[Pd(dcmedt)_2]_6$ are available [31].

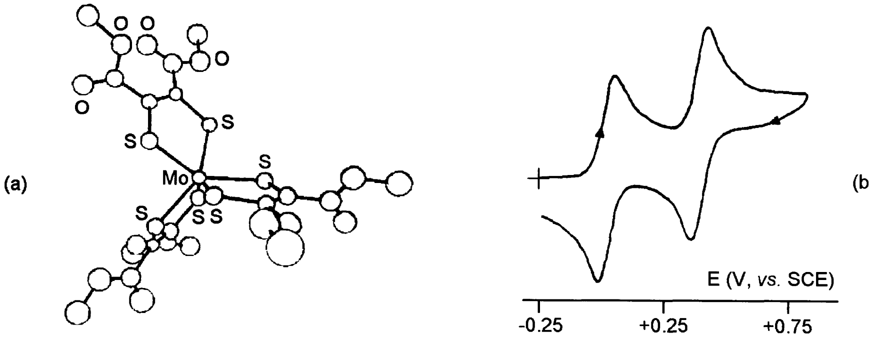


Figure 6. (a) X-Ray structure of $[Mo(dcmedt)_3]^{2-}$. Average interatomic distances: Mo-S = 2.39 Å; C-S = 1.74 Å; C=C = 1.35 Å; $C\text{-}C_{(COOMe)}$ = 1.49 Å. Twist angle $\phi \approx 15°$. (b) Cyclic voltammetric behaviour of the dianion in CH_2Cl_2 solution.

2.2.11 thedt Complexes

2.2.11.1 Bis(thedt) complexes

[Ni(thedt)$_2$] gives rises in CH$_2$Cl$_2$ solution to two one-electron reductions ($E^{\circ\prime}_{0/-}$ = +0.13 V; $E^{\circ\prime}_{-/2-}$ = −0.66 V, *vs.* SSCE) and a one-electron oxidation ($E^{\circ\prime}_{0/+}$ = +1.08 V), all having features of chemical reversibility [32].

2.2.12 atedt Complexes

2.2.12.1 Bis(atedt) complexes

A few $[Ni(atedt)_2]^{n-}$ complexes can display up to three reversible one-electron processes, which have been assigned to the sequence $[Ni(atedt)_2]^{+/0/-/2-}$. Nevertheless, since the cyclic voltammogram of [Ni(C$_{11}$H$_{23}$-tedt)$_2$] [34a] could be better interpreted as due to the sequence $[Ni(C_{11}H_{23}\text{-tedt})_2]^{2+/+/0/-}$ and in view of important discrepancies with the electrochemistry of $[Ni(CH_3\text{-tedt})_2]^-$ [33b], we prefer to set the redox sequences exhibited by $[M(atedt)_2]^{n-}$ (M = Ni, Pd, Pt) within the series $[Ni(atedt)_2]^{2+/+/0/-/2-}$, Table 11.

Table 11. Formal electrode potentials (V, *vs.* SCE) for the redox processes exhibited by $[M(atedt)_2]^{n-}$ complexes

M	alkyl group	$E^{\circ\prime}_{2+/+}$	$E^{\circ\prime}_{+/0}$	$E^{\circ\prime}_{0/-}$	$E^{\circ\prime}_{-/2-}$	Solvent	Reference
Ni	CH_3	-	+0.78	−0.09	-	CH_2Cl_2	33a
	CH_3	-	-	+0.05	−0.72	dmf	33b
	C_4H_9	+1.12	+0.77	−0.08	-	CH_2Cl_2	34a
	C_6H_{13}	+1.11	+0.76	−0.08	-	CH_2Cl_2	34a
	$C_{11}H_{23}$	+1.12	+0.76	−0.11	-	CH_2Cl_2	34a
Pd	CH_3	-	-	+0.13	−0.50	dmf	33b
Pt	CH_3	-	-	+0.14	−0.64	dmf	33b

2.2.13 dfcedt Complexes

2.2.13.1 Bis(dfcedt) complexes

As illustrated in Figure 7, the tetraferrocenyl-substituted dithiolate [Ni(dfcedt)$_2$] [35] undergoes in CH$_2$Cl$_2$ solution, four separate one-electron oxidations ($E^{\circ\prime}_{0/+}$ = −0.02 V; $E^{\circ\prime}_{+/2+}$ = +0.15 V; $E^{\circ\prime}_{2+/3+}$ = +0.28 V; $E^{\circ\prime}_{3+/4+}$ = +0.49 V, *vs.* Fc/Fc$^+$), which are attributed to the gradual oxidation of the four ferrocenyl subunits, and two one-electron reductions ($E^{\circ\prime}_{0/-}$ = −0.67 V; $E^{\circ\prime}_{-/2-}$ = −1.43 V) centred on the Ni-dithiolene core [36].

The result is significant in that proves that the central NiS_4C_4 group does not create a barrier to the mutual electronic interaction among the four ferrocene subunits.

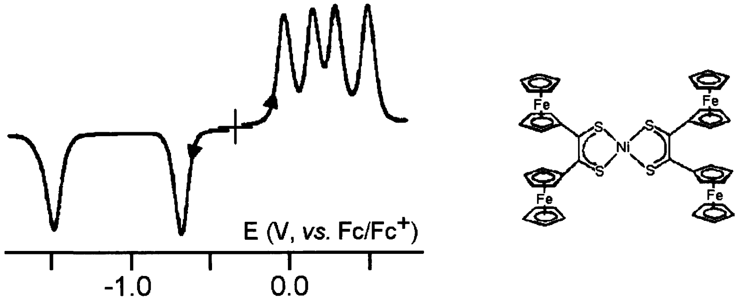


Figure 7. Differential pulse voltammogram recorded in CH_2Cl_2 solution of [Ni(dfcedt)$_2$]. Anodic scan: [NBu$_4$][B(C$_6$F$_5$)$_4$] supporting electrolyte; cathodic scan: [NBu$_4$][PF$_6$] supporting electrolyte.

2.2.14 dcnedt Complexes (better known as "mnt")

2.2.14.1 Bis(dcnedt) complexes

The square planar complexes [M(dcnedt)$_2$]$^{n-}$ (M = Ni, Cu, Pd, Pt, Au) undergo partially or completely the electron transfer sequence [M(dcnedt)$_2$]$^{2-/-/0}$, Table 12.

As a consequence of the reversibility of these processes, the crystal structures of different [M(dcnedt)$_2$]$^{2-/-}$ couples are available. In particular, a lot of structural data exist for [Ni(dcnedt)$_2$]$^{2-/-}$ as a function of the nature of the counter-cations. Figure 8 just exemplifies that in both oxidation states the square planar geometry

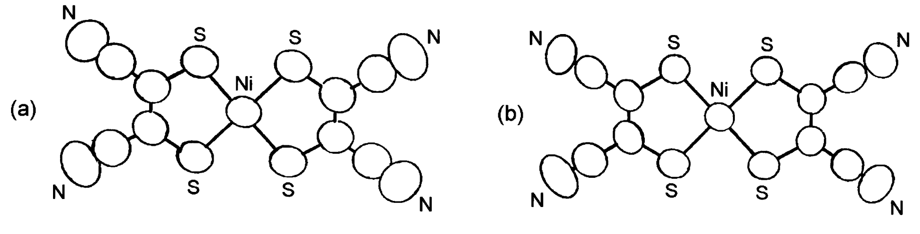


Figure 8. X-Ray structures of: (a) [Ni(dcnedt)$_2$]$^{2-}$; (b) [Ni(dcnedt)$_2$]$^{-}$.

Table 12. Formal electrode potentials (V, *vs.* SCE) for the redox processes exhibited by $[M(dcnedt)_2]^{2-}$.

M	$E^{\circ\prime}_{0/-}$	$E^{\circ\prime}_{-/2-}$	$E^{\circ\prime}_{2-/3-}$	Solvent	Reference
Ni	+1.02	+0.23	−1.68	MeCN	2b, 26
	-	+0.49	-	MeCN	37a
	+1.04[a]	+0.09	-	MeCN	37b
	-	+0.23	−1.74	dme[b]	26
	-	+0.21	-	dmf	2b
	-	+0.12	-	CH_2Cl_2	2b
Pd	-	+0.46	-	MeCN	2b
	+0.70	+0.26	-	MeCN	37b
	-	+0.44	−1.90	MeCN	37c
	+1.16	-	-	CH_2Cl_2	37c
Pt	-	+0.21	-	MeCN	2b
	+0.94	+0.06	-	MeCN	37b
	+1.07	+0.22	−2.41	MeCN	37c
Cu	-	+0.34	-	MeCN	2b
	+1.18[a]	+0.19	−0.85	MeCN	37b
Au	-	−0.42	-	MeCN	2b
	+1.10	−0.93	-	CH_2Cl_2	37d

[a] Peak-potential value for irreversible processes; [b] 1,2-dimethoxyethane

is maintained [38f] and Table 13 summarizes how some interatomic distances vary with the electron addition/removal.

As in most previous cases, the variations of the bond lengths are minimal and extended along the whole molecular frame, thus once again supporting the substantially ligand centred nature of the electron transfer. Also in this case, such an assumption is supported by the electrochemical detection of the $[Ni(dcnedt)_2]^{2-/3-}$ reduction step and the concomitant EPR characterization of the trianion as a Ni(I) species [40].

Crystallographic data for the square planar couples $[Pd(dcnedt)_2]^{2-/-}$ and $[Pt(dcnedt)_2]^{2-/-}$ are reported in Table 14.

Also in this case, the M(II)/M(I) process $[M(dcnedt)_2]^{2-/3-}$ occurs at very negative potential values [40b].

In agreement with the preferred square planar coordination of Cu(III) ion, the geometry of the monoanion $[Cu(dcnedt)_2]^-$ is square planar [2b]. The easy access

Table 13. Selected bond distances (average values; Å) in the redox couple $[\mathrm{Ni(dcnedt)_2}]^{2-/-}$.

Complex	Ni-S	S-C	C=C	C-C$_{(\mathrm{CN})}$	C≡N	Cation	Ref.
$[\mathrm{Ni(dcnedt)_2}]^{2-}$	2.16	1.75	1.30	1.43	1.13	$[\mathrm{NMe_4}]^{+}$	38a
	2.17	1.75	1.33	1.41	1.13	$[\mathrm{NMe_4}]^{+}$	38b
	2.18	1.73	1.38	1.42	1.14	$[\mathrm{TMPD}]^{+}$ [a]	38c
	2.17	1.74	1.35	1.44	1.14	$[\mathrm{KOS}]^{+}$ [b]	38d
	2.18	1.73	1.39	1.44	1.13	$[\mathrm{Ag(PPh_3)_2}]^{+}$	38e
	2.17	1.73	1.36	1.43	1.14	$[\mathrm{NBu_4}]^{+}$	38f
	2.17	1.73	1.36	1.43	1.14	$[\mathrm{NMP}]^{+}$ [c]	38g
	2.17	1.74	1.37	1.43	1.13	$[\mathrm{MV}]^{2+}$ [d]	38h
	2.18	1.73	1.38	1.43	1.14	$[\mathrm{A}]^{2+}$ [e]	38i
	2.19	1.71	1.36	1.50	1.12	$[\mathrm{DPD\text{-}Me}]^{2+}$ [f]	38l
	2.17	1.74	1.36	1.43	1.15	$[\mathrm{N\text{-}MeA}]^{+}$ [g]	38m
$[\mathrm{Ni(dcnedt)_2}]^{-}$	2.15	1.71	1.36	1.43	1.14	$[\mathrm{PMePh_3}]^{+}$	39a
	2.15	1.72	1.37	1.43	1.13	$[\mathrm{NEt_4}]^{+}$	38f
	2.15	1.72	1.37	1.43	1.14	$[\mathrm{C_7H_7}]^{+}$	39b
	2.15	1.71	1.31	1.43	1.15	$[\mathrm{TMPD}]^{+}$ [a]	39c
	2.14	1.72	1.34	1.44	1.12	$[\mathrm{NMe_3Ph}]^{+}$	39d
	2.15	1.72	1.37	1.44	1.13	$[\mathrm{TTM\text{-}TTF}]^{+}$ [h]	39e
	2.15	1.70	1.40	1.43	1.12	$[\mathrm{Fc}^{\#}]^{+}$ [i]	39f
	2.14	1.71	1.37	1.42	1.15	$[\mathrm{Fc}^{\dagger}]^{+}$ [l]	39g
	2.14	1.71	1.37	1.44	1.14	$[\mathrm{Fc}^{\ddagger}]^{+}$ [m]	39g
	2.15	1.71	1.40	1.40	1.17	$[\mathrm{Etpy}]^{+}$	39h
	2.15	1.71	1.39	1.44	1.13	$[\mathrm{(DT\text{-}TTF)_2}]^{+}$ [n]	39i
	2.15	1.71	1.34	1.45	1.14	$[\mathrm{Na(15\text{-}crown\text{-}5)}]^{+}$	39l
	2.15	1.71	1.37	1.43	1.14	$[\mathrm{NO_2ql}]^{+}$ [o]	39m
	2.15	1.71	1.36	1.43	1.14	$[\mathrm{C_{13}H_{13}\text{-}N_2O_2}]^{+}$ [p]	39n
	2.14	1.70	1.38	1.46	1.11	$[\mathrm{BrFBzPy}]^{+}$ [q]	39o
	2.15	1.71	1.36	1.44	1.14	$[\mathrm{FbzPy}]^{+}$ [r]	39p
	2.14	1.72	1.36	1.43	1.14	$[\mathrm{AMPY}]^{+}$ [s]	39q
	2.13	1.71	1.35	1.43	1.15	$[\mathrm{FbzPyNH_2}]^{+}$ [t]	39r

[a] TMPD = N,N,N',N'-tetramethyl-*p*-phenylendiamine; [b] KOS = 1-ethyl-4-carbomethoxypyridine; [c] NMP = N-methylphenazine; [d] MV = methyl viologen = 1,1'-dimethyl-4,4'-bipyridine; [e] A = trans-4,4'-(1,2-ethendiyl)bis[1-(3-cyano-propyl)pyridine]-dibromide; [f] DPD-Me = trans-4,4-azobis(1-methyl-pyridine); [g] *N*-MeA = *N*-methylacridine; [h] TTM-TTF = tetra(methylthio) tetrathiafulvalene; [i] Fc# = 1,1'-bis[2-(4-methylthio)phenylethenyl]ferrocene; [l] Fc† = 2,2', 3,3', 4,4', 5,5'-octamethyl-1,1'-bis(methylthio) ferrocene; [m] [Fc‡] = 2,2', 3,3', 4,4', 5,5'-octamethyl-1,1'-bis(*tert*-butylthio)ferrocene; [n] DT-TTF = dithiopheno-tetrathiafulvalene; [o] $\mathrm{NO_2ql}$ = 1-(4-nitrobenzyl)quinoline; [p] $\mathrm{C_{13}H_{13}\text{-}N_2O_2}$ = 2-methyl-1-(4-nitrobenzyl)pyridine; [q] BrFBzPy = 1-(4'-bromo-2'-fluorobenzyl)pyridine; [r] FBzPy=1-(4'-fluorobenzyl)pyridine; [s] AMPY=4-aminopyridine; [t] $\mathrm{FbzPyNH_2}$ = [1-(4'-fluorobenzyl)-4-aminopyridine]

Table 14. Selected bond distances (average values; Å) in the redox couples $[M(dcnedt)_2]^{2-/-}$ (M = Pd, Pt)

Complex	M-S	S-C	C=C	$C-C_{(CN)}$	C≡N	Cation	Ref.
$[Pd(dcnedt)_2]^{2-}$	2.30	1.73	1.38	1.43	1.14	$[MV]^{2+}$[a]	41a
	2.29	1.72	1.39	1.45	1.14	$[ITTF]^{+}$[b]	41b
	2.30	1.74	1.34	1.44	1.14	$[Pt(CNMe)_4]^{2+}$	41c
$[Pd(dcnedt)_2]^{-}$	2.26	1.71	1.34	1.46	1.10	$[(Perylene)_2]^{+}$	42a
	2.29	1.73	1.39	1.45	1.14	$[K]^{+}$	42b
	2.28	1.71	1.40	1.43	1.13	$[NH_4]^{+}$	42b
$[Pt(dcnedt)_2]^{2-}$	2.28	1.72	1.36	1.40	1.16	$[NBu_4]^{+}$	43a
	2.28	1.71	1.42	1.43	1.15	$[PhCNSSN]^{+}$[c]	43b
	2.30	1.73	1.36	1.44	1.15	$[Pt(Me_2pipdt)_2]^{2+}$[d]	43c
	2.31	1.75	1.35	1.41	1.14	$[Pt(CNMe)_4]^{2+}$	41c
	2.29	*e*	*e*	*e*	*e*	$[Pt(NH_2Oc)_4]^{2+}$[f]	43d
$[Pt(dcnedt)_2]^{-}$	2.26	1.70	1.39	1.43	1.14	$[Rb]^{+}$	44a
	2.27	1.70	1.39	1.42	1.14	$[H_3O]^{+}$	44b
	2.27	1.71	1.38	1.43	1.15	$[NEt_4]^{+}$	44b
	2.26	1.71	1.39	1.42	1.16	$[(p\text{-}ClC_6H_4CNSSN)_2Cl]^{+}$[g]	43a
	2.27	1.71	1.37	1.43	1.13	$[TTM\text{-}TTF]^{+}$[h]	39e
	2.26	1.70	1.38	1.42	1.15	$[Fc‡]^{+}$[i]	39h
	2.27	1.72	1.37	1.43	1.14	$[(DT\text{-}TTF)_2]^{+}$[j]	391
	2.26	*e*	1.36	*e*	1.13	$[Pt(NH_2Oc)_4]^{2+}$[f]	44c

[a] MV=methylviologen=1,1'-dimethyl-4,4'-bipyridine; [b] ITTF=4-iodo-tetrathioful-valene; [c] PhCNSSN = 4-Phenyl-1,2-dithia-3,5-diazole; [d] $[Pt(Me_2pipdt)_2]^{2+}$ = N,N'-dimethyl-piperazine-2,3-dithione-Pt(II); [e] not reported; [f] $[Pt(NH_2Oc)_4]^{2+}$ = octylamine-Pt(IV); [g] $(p\text{-}ClC_6H_4CNSSN)_2Cl$ = bis(4-(4-chlorophenyl)- 1,2-dithia-3,5-diazole; [h] TTM-TTF = tetra(methylthio)tetrathiafulvalene; [i] [Fc‡] = 2,2', 3,3', 4,4', 5,5'-octamethyl-1,1'-bis(*tert*-butylthio)ferrocene; [j] DT-TTF = dithiopheno-tetrathiafulvalene;

to $[Cu(dcnedt)_2]^{2-}$ allowed its isolation and crystallographic characterisation, Table 15.

The significant elongation of the Cu-S bond upon one-electron reduction seems to support its Cu(III)/Cu(II) nature. Further support arises from the fact that, in some cases, the dianion $[Cu(dcnedt)_2]^{2-}$ displays a tetrahedrally distorted geometry. In this connection, Table 15 also reports the interatomic distances of the tetrahedral dianion $[Zn(dcnedt)_2]^{2-}$.

Table 15. Selected bond distances (average values; Å) and dihedral angles (°) in the redox couple $[Cu(dcnedt)_2]^{2-/-}$ and $[Zn(dcnedt)_2]^{2-}$

Complex	M-S	S-C	C=C	$C\text{-}C_{(CN)}$	C≡N	α	Cation	Ref.
$[Cu(dcnedt)_2]^-$	2.17	1.72	1.31	1.43	1.14	-	$[NBu_4]^+$	45
$[Cu(dcnedt)_2]^{2-}$	2.27	1.73	1.36	1.43	1.14	-	$[NEt_4]^+$	46a
	2.28	1.73	1.36	1.43	1.14	-	$[NBu_4]^+$	46b
	2.25	1.73	1.36	1.43	1.13	47.4	$[MB]^{+a}$	46c
	2.28	1.74	1.34	1.44	1.13	-	$[NMP]^{+b}$	46d
	2.26	1.74	1.34	1.45	1.13	41.1	$[NMe_4]^+$	46e
	2.27	1.73	1.36	1.42	1.15	-	$[Fe(C_5Me_5)_2]^+$	46f
$[Zn(dcnedt)_2]^{2-}$	2.33	1.74	1.36	1.43	1.14	83.9	$[AsPh_4]^+$	47a
	2.33	1.73	1.38	1.43	1.14	81.8	$[MV]^{2+c}$	47b
	2.32	1.73	1.36	1.42	1.15	90	$[N\text{-}MeA]^{+d}$	38m

[a] MB = methylene blue = 3,9-bis(dimethylamino)phenazothione; [b] NMP = N-methyl-phenazine; [c] MV = methyl viologen = 1,1'-dimethyl-4,4'-bipyridine; [d] *N*-MeA = *N*-methylacridine

As far as the gold complex is concerned, the only structural data are concerned with the square planar Au(III) monoanion $[Au(dcnedt)_2]^-$ [37d, 39i, 42a, 48].

The square planar Co(II) dianion $[Co(dcnedt)_2]^{2-}$ undergoes in thf solution either a reversible one-electron reduction ($E^{\circ\prime}_{2-/3-} = -1.83$ V, *vs.* SCE), or a one-electron oxidation ($E^{\circ\prime}_{2-/-} = -0.02$ V), which is followed by slow dimerisation to $[Co(dcnedt)_2]_2{}^{2-}$ [49]. In agreement with the slowness of the dimerization reaction and the electrochemical reversibility of the $[Co(dcnedt)_2]^{2-/-}$ process, the isolated monoanion maintains a square planar geometry [39h]. The interatomic distances for the couple $[Co(dcnedt)_2]^{2-/-}$ are compiled in Table 16, and, also in this case, they support the substantial ligand-centered nature of the unpaired electron.

Concerned with the electrochemical behaviour of $[Zn(dcnedt)_2]^{2-}$, it has been briefly reported that in MeCN solution it undergoes an (obviously ligand-centred) irreversible oxidation ($E_{p(2-/-)} = +1.00$ V, *vs.* SCE) [47a, 38i].

The dianions $[MoO(dcnedt)_2]^{2-}$ [12, 51] and $[WO(dcnedt)_2]^{2-}$ [52] exhibit the square pyramidal geometry typical of $[MO(dithiolene)_2]^{n-}$. $[MoO(dcnedt)_2]^{2-}$ undergoes a one-electron oxidation, which displays features of chemical reversibility in the cyclic voltammetric time scale ($E^{\circ\prime}_{2-/-} = +0.35$ V, *vs.* SCE, in CH_2Cl_2 solution [53a]; $E^{\circ\prime}_{2-/-} = +0.40$ V, *vs.* SCE, in MeCN solution [53b]). Macroelectrolysis tests prove however that the electrogenerated monoanion slowly disproportionates to $[Mo(dcnedt)_3]^{2-}$ (see below) [53b].

Table 16. Selected bond distances (average values; Å) in the redox couple $[Co(dcnedt)_2]^{2-/-}$

Complex	Co-S	S-C	C=C	$C\text{-}C_{(CN)}$	C≡N	Cation	Reference
$[Co(dcnedt)_2]^{2-}$	2.16	1.72	1.34	1.40	1.15	$[NBu_4]^+$	50a
	2.16	1.72	1.37	1.44	1.13	$[BQ]^{2+}$ [a]	50b
	2.25	1.73	1.36	1.43	1.13	$[Cu(tim)]^{2+}$ [b]	50c
	2.19	1.73	1.37	1.42	1.14	$[Ni(tim)]^{2+}$ [b]	50c
$[Co(dcnedt)_2]^-$	2.19	1.71	1.36	1.43	1.14	$[Fc^\dagger]^+$ [c]	39h
	2.18	1.72	1.34	1.43	1.14	$[Fc^\ddagger]^+$ [d]	39h

[a] [BQ] = 6,7,8,9-tetrahydrodipyrido[1,4]diazocene; [b] tim = 2,3,9,10-tetramethyl-1,4,8,1-tetraaza-cyclo-tetradeca-1,3,8,10-tetraene; [c] Fc† = 2,2', 3,3', 4,4', 5,5'-octamethyl-1,1'-bis(methylthio)-ferrocene; [d] [Fc‡] = 2,2', 3,3', 4,4', 5,5'-octamethyl-1,1'-bis(*tert*-butylthio)ferrocene

Finally, the (likely square pyramidal) anions $[MO(dcnedt)_2]^-$ (M = Tc, Re), in MeCN solution display a reversible one-electron reduction (M = Tc: $E^{\circ\prime}_{-/2-}$ = –0.64 V; M = Re: $E^{\circ\prime}_{-/2-}$ = –1.05 V, *vs.* SCE), and a reversible one-electron oxidation (M = Tc: $E^{\circ\prime}_{-/0}$ = +1.73 V; M = Re: $E^{\circ\prime}_{-/0}$ = +1.76 V) [6a], whereas $[VO(dcnedt)_2]^{2-}$ only exhibits, in CH_2Cl_2 solution, a reversible one-electron oxidation ($E^{\circ\prime}_{2-/-}$ = +0.40 V, *vs.* SCE) [53a] .

2.2.14.2 Tris(dcnedt) complexes

The redox ability of the tris-chelates $[M(dcnedt)_3]^{n-}$ (M = V, Cr, Fe, Co, Mo, W, Re) is long known [2b, 54]. From the structural viewpoint, they usually display geometrical arrangements ranging from octahedral (M = Fe [55a]) to distorted trigonal prismatic (M = V, Mo, W [55 b,c]). For example, $[Cr(dcnedt)_3]^{3-}$ undergoes two reversible one-electron oxidations (MeCN:

Table 17. Selected bond distances (average values; Å) in the redox couples $[Cr(dcnedt)_3]^{3-/2-}$ and $[Ru(dcnedt)_3]^{3-/2-}$

Complex	M-S	S-C	C=C	$C\text{-}C_{(CN)}$	C≡N	ϕ	Cation
$[Cr(dcnedt)_3]^{3-}$	2.39	1.73	1.35	1.43	1.14	*a*	$[PPh_4]^+$
$[Cr(dcnedt)_3]^{2-}$	2.34	1.73	1.33	1.45	1.13	*a*	$[PPh_4]^+$
$[Ru(dcnedt)_3]^{3-}$	2.35	1.71	1.39	1.43	1.13	50.2	$[NEt_4]^+$
$[Ru(dcnedt)_3]^{2-}$	2.34	1.72	1.36	1.43	1.13	47.1	$[AsPh_4]^+$

[a] Not reported

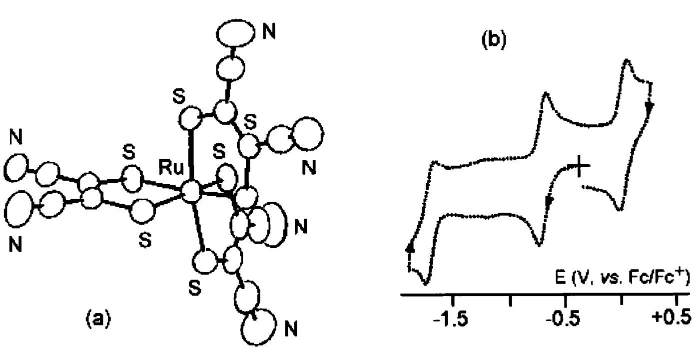


Figure 9. (a) X-Ray structure and (b) cyclic voltammogram (glassy carbon electrode; CH_2Cl_2 solution; scan rate 0.1 Vs^{-1}) of $[Ru(dcnedt)_3]^{2-}$ ($[AsPh_4]^+$ cation).

$E^{\circ\prime}_{3-/2-} = +0.16$ V; $E^{\circ\prime}_{2-/-} = +0.76$ V, *vs.* SCE) [2b], and the crystal structures of the redox couple $[Cr(dcnedt)_3]^{3-/2-}$ are available, Table 17 [56].

Both the complexes are described as octahedral. The significant variations of the Cr-S distance in this case seem to support a chromium centered [Cr(IV)/Cr(V)] process.

In this connection, however, complex $[Ru(dcnedt)_3]^{2-}$ probably better accounts for either the redox and structural properties of this class of compounds. In fact, as shown in Figure 9, it undergoes in CH_2Cl_2 solution two one-electron reductions ($E^{\circ\prime}_{2-/3-} = -0.70$ V; $E^{\circ\prime}_{3-/4-} = -1.71$ V, *vs.* Fc/Fc^+) and a one-electron oxidation ($E^{\circ\prime}_{2-/-} = +0.03$ V), all displaying features of chemical reversibility in the cyclic voltammetric time scale [57].

In the longer times of exhaustive electrolysis, only the trianion proved to be quite stable. The crystallographic data of the couple $[Ru(dcnedt)_3]^{3-/2-}$ are compiled in Table 17 [57]. The variations in the interatomic distances are minimal. The most significant structural change probably resides in the twist angle between the two S3 triangles. In fact it passes from 50.2° in the trianion to 47.1° in the dianion. Taking into account that for a perfect octahedron $\phi = 60°$, whereas for a perfect trigonal prism $\phi = 0°$, it ensues that the electron removal causes the molecular frame to pass from an (almost perfect) octahedron to a trigonally distorted octahedron.

2.2.15 dichedt, dibzedt Complexes

2.2.15.1 Bis(dichedt) and bis(dibzedt) complexes

The square planar complexes $[Pd(dichedt)_2]$ and $[Cu(dibzedt)_2]^{2+}$ have been crystallographically characterised [58], but no electrochemical data are available.

2.3 mtadt Complexes

2.3.1 Bis(mtadt) complexes

In MeCN solution, the square pyramidal monoanion $[TcO(mtadt)_2]^-$ [59] exhibits a reversible one-electron reduction ($E^{\circ\prime}_{-/2-} = -1.35$ V, *vs.* SCE) [6a]. The isoelectronic $[ReO(mtadt)_2]^-$ is harder to reduce ($E^{\circ\prime}_{-/2-} = -1.84$ V), but, as a consequence, easier to oxidise ($E^{\circ\prime}_{-/0} = +1.23$ V) [6a].

2.4 dodt Complexes

2.4.1 Bis(dodt) complexes

The dithioxalato ligand dodt constitutes a special case of dithiolene ligand, in that in its bis- or tris-chelates the α-diketone group can simultaneously coordinate more than one metal ion [60a]. Even in $[K_2Ni(dodt)_2]$, the dianion $[Ni(dodt)_2]^{2-}$ strongly interacts with the K^+ ion *via* the dioxo group such to form a true adduct (K-O = 2.77 Å) [60a].

Structural data exist for complexes $[M(dodt)_2]^{n-}$ (M = Ni, Pd: n = 2, square planar [60a,b]; M = Pt: n = 3, square planar [60b]; M = Zn, n = 2, tetrahedral [60c]).

It has been recently mentioned that the Ni and Pd dianions (unexpectedly) do not show reversible redox processes [60a]. In contrast, the dianion $[Cu(dodt)_2]^{2-}$ undergoes in CH_2Cl_2 solution a one-electron oxidation ($E^{\circ\prime}_{2-/-} = +0.13$ V, *vs.* SCE) [60d]. Even if such a process is accompanied by slow chemical complications (at slow scan rate the i_{pc}/i_{pa} ratio is significantly lower than 1), fast precipitation of $[Cu(dodt)_2]^-$ blocks such decomposition. In fact, the crystal structure of the redox couple $[Cu(dodt)_2]^{2-/-}$ is known [60d,e]. Both the complexes have a square planar geometry; the passage from the dianion to the monoanion causes a significant shortening of the Cu-S bond length (by 0.09 Å), whereas the intraligand distances undergo minor variations (of the order of 0.02 Å). These results support the formal assignment as $[Cu^{II}(dodt)_2]^{2-}$ and $[Cu^{III}(dodt)_2]^-$, respectively.

As far as the square pyramidal oxoanions are concerned, the crystal structures of $[MoO(dodt)_2]^{2-}$ [60f] and $[ReO(dodt)_2]^-$ [60g] are available. The monoanions $[MO(dodt)_2]^-$ (M = Tc, Re) exhibit in MeCN solution two reversible one-electron reductions (Tc: $E^{\circ\prime}_{-/2-} = -0.75$ V, $E^{\circ\prime}_{2-/3-} = -1.56$ V; Re: $E^{\circ\prime}_{-/2-} = -0.94$ V, $E^{\circ\prime}_{2-/3-} = -1.35$ V, *vs.* SCE) and two reversible one-electron oxidations (Tc: $E^{\circ\prime}_{-/0} = +1.91$ V, $E^{\circ\prime}_{0/+} = +2.28$ V; Re: $E^{\circ\prime}_{-/0} = +1.64$ V, $E^{\circ\prime}_{0/+} = +2.17$) [6a].

2.4.2 Tris(dodt) complexes

As far as we know, the distorted octahedral geometry of the trianion $[Co(dodt)_3]^{3-}$ is available [60h], but nothing is known about its redox activity.

3.0 1,2-DITHIOLATES FORMING LATERAL SINGLE RINGS

3.1 1,2-Dithiolates forming lateral four-membered rings

3.1.1 dtsq Complexes

3.1.1.1 Bis(dtsq) complexes

The square planar geometry of the dianion $[Ni(dtsq)_2]^{2-}$ in $[K_2Ni(dtsq)_2]$ is crystallographically ascertained [61a,b]. As it happens in $[K_2Ni(dodt)_2]$, the two oxo groups of each ligand coordinate one K^+ counterion (K-O = 2.91 Å). As exemplified in Figure 10, complexes $[M(dtsq)_2]^{2-}$ (M = Pt [61c], Pd [61d,e], Cu [61f]) possess a square planar geometry.

The Pt dianion exhibits a partially chemically reversible one-electron oxidation ($E^{o'}_{2-/-}$ = +0.58 V, *vs.* Ag/AgCl) [61b,c], whereas $[Au(dtsq)_2]^-$ exhibits a partially chemically reversible one-electron reduction [61b].

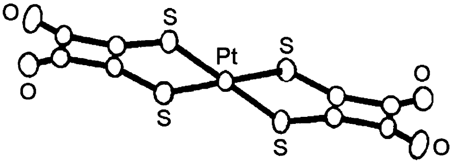


Figure 10. X-Ray structure of $[Pt(dtsq)_2]^{2-}$ ($[BEDT-TTF]^+$ cation).

3.2 1,2-Dithiolates forming lateral five-membered rings

3.2.1 dtcr Complexes

3.2.1.1 Bis(dtcr) complexes

We are not aware of crystal structures of bis(dtcr) metal complexes. $[Pt(dtcr)_2]^{2-}$ undergoes two one-electron reductions and a one-electron oxida-

Table 18. Formal electrode potentials (V, *vs.* SCE) for the redox processes exhibited by complexes $[M(dtcr)_2]^{2-}$ in MeCN solution

M	$E^{o'}_{2-/-}$	$E^{o'}_{2-/3-}$	$E^{o'}_{3-/4-}$
Ni	+0.47	−1.26	−1.44
Pd	+0.66	−1.26	−1.5[a]
Pt	+0.40	−1.30	−1.50

[a] Peak-potential for irreversible processes

tion, all exhibiting features of chemical reversibility in the cyclic voltammetric time scale [62a]. Similar behaviour is exhibited by the analogues $[Ni(dtcr)_2]^{2-}$ and $[Pd(dtcr)_2]^{2-}$. The relative formal electrode potentials are summarized in Table 18 [62a].

EPR spectroscopy supports the substantial ligand centred nature of the $[M(dtcr)_2]^{2-/-}$ process [62a].

3.2.1.2 Tris(dtcr) complexes

A few $[M(dtcr)_3]^{3-}$ trianions (M = Cr, Fe, Co) have been characterised. $[Co(dtcr)_3]^{3-}$ displays a (almost perfect) octahedral geometry [62b].

All these complexes display in MeCN solution a reversible one-electron oxidation (M = Cr: $E^{\circ\prime}_{3-/2-}$ = +0.47 V; M = Fe: $E^{\circ\prime}_{3-/2-}$ = +0.15 V; M = Co: $E^{\circ\prime}_{3-/2-}$ = +0.48 V, *vs.* SCE) and a one-electron reduction, which possesses features of chemical reversibility only in the case of the Fe(III) complex ($E^{\circ\prime}_{3-/4-}$ = −0.59 V) [62b].

3.2.2 dcmdtcr Complexes

3.2.2.1 Bis(dcmdtcr) complexes

Figure 11 shows the crystal structure of the dianion $[Pd(dcmdtcr)_2]^{2-}$ present in the adduct $[NBu_4]_2[Pd(dcmdtcr)_2]\cdot I_2$ [62a].

The PdS_4 core is planar, but the ligands are slightly inclined (about 4°) with respect to the central plane.

$[Cu(dcmdtcr)_2]^{2-}$ exhibits a tetrahedrally distorted geometry (dihedral angle 36.8°) [63].

Like the dianions $[M(dtcr)_2]^{2-}$, complexes $[M(dcmdtcr)_2]^{2-}$ (M = Ni, Pd, Pt) exhibit two reversible one-electron reductions and a one-electron oxidation, Table 19 [62a].

It is interesting to note that, with respect to the related $[M(dtcr)_2]^{2-}$ derivatives, the cyano-substituted complexes are more difficult to oxidize by about 0.2 V, but

Table 19. Formal electrode potentials (V, *vs.* SCE) for the redox processes exhibited by complexes $[M(dcmdtcr)_2]^{2-}$ in MeCN solution

M	$E^{\circ\prime}_{2-/-}$	$E^{\circ\prime}_{2-/3-}$	$E^{\circ\prime}_{3-/4-}$
Ni	+0.66[a]	−0.70	−0.94
Pd	+0.74[a]	−0.66	−0.85
Pt	+0.58[a]	−0.69	−0.94

[a] Peak-potential for oxidation processes affected by electrode adsorption

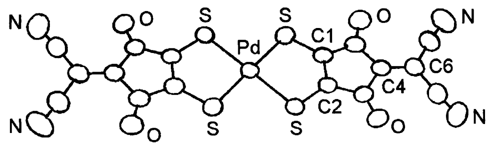


Figure 11. X-Ray structure of $[Pd(dcmdtcr)_2]^{2-}$ ($[NBu_4]^+$ cation). Average bond distances: Pd-S = 2.30 Å; S-C = 1.70 Å; C1-C2 = 1.38 Å; $C\text{-}C_{(ring)}$ = 1.47 Å; C=O = 1.22 Å; C4-C6 = 1.35 Å; $C\text{-}C_{(CN)}$ = 1.43 Å.

notably easier to reduce by about 0.5 V. Also in this case, EPR spectroscopy confirms the substantial ligand centered nature of the $[M(dcmdtcr)_2]^{2-/-}$ process [62a].

3.2.2.2 Tris(dcmdtcr) complexes

Like the trianions $[M(dtcr)_3]^{3-}$ (M = Cr, Fe, Co), the corresponding complexes $[M(dcmdtcr)_3]^{3-}$ (M = Cr, Fe, Co) have been characterised [62b]. $[Fe(dcmdtcr)_3]^{3-}$ displays either a reversible one-electron oxidation or a reversible one-electron reduction, both the processes being anodically shifted by about 0.3 V with respect to $[Fe(dtcr)_3]^{3-}$ ($E^{\circ\prime}_{3-/2-}$ = +0.30 V; $E^{\circ\prime}_{3-/4-}$ = −0.31 V, *vs.* SCE) [62b]. A similar shift in redox potentials occurs for the oxidation $[M(dcmdtcr)_3]^{3-/2-}$ (M = Cr, Co) [62b].

3.2.3 dhtpdt, tpdt Complexes

3.2.3.1 Bis(dhtpdt) and bis(tpdt) complexes

The unsaturated square planar monoanion $[Au(tpdt)_2]^-$ and its isomer $[Au(\alpha\text{-}tpdt)_2]^-$ undergo in CH_2Cl_2 solution a reversible one-electron reduction (E°'= −0.90 V and −1.16 V, *vs.* Ag/AgCl, respectively) and a one-electron oxidation affected by electrode adsorption (E°' = +0.75 V and +0.46 V, respectively) [64].

In contrast, the (almost) planar saturated monoanion $[Au(dhtpdt)_2]^-$ only displays in CH_2Cl_2 solution the one-electron oxidation process affected by electrode adsorption ($E^{\circ\prime}_{-/0}$ = +0.20 V, *vs.* Ag/AgCl) [64].

3.2.4 ttpdt Complexes

3.2.4.1 Bis(ttpdt) complexes

The square planar dianion $[Ni(ttpdt)_2]^{2-}$ [65] undergoes at first, chemically reversible, dithiolene-based, one electron oxidation ($E^{\circ\prime}_{2-/-}$ = −0.13 V, *vs.* Ag/AgCl), followed by a second irreversible process ($E_{p\ -/0}$ = +0.46 V). A reduction process is also present at negative potential values which is centred on the terthiophene ligand [65].

A roughly similar behaviour is displayed by $[Pd(ttpdt)_2]^{2-}$ and $[Au(ttpdt)_2]^-$ [65].

3.2.5 mdtdt Complexes (better known as "mdt")

3.2.5.1 Bis(mdtdt) complexes

The monoanion $[Ni(mdtdt)_2]^-$ possesses a tetrahedrally distorted planar geometry (dihedral angle, 14.77°) [66]. In nitrobenzene solution it exhibits a chemically reversible one-electron reduction ($E^{\circ\prime}_{-/2-}$ = −0.55 V, *vs.* SCE) and a chemically reversible one-electron oxidation ($E^{\circ\prime}_{-/0}$ = +0.08 V). A further oxidation process (E_p = +0.74 V) is affected by electrode adsorption phenomena [66].

3.2.6 dtodt Complexes (better known as "dmid")

3.2.6.1 Bis(dtodt) complexes

The tetrahedrally distorted $[Ni(dtodt)_2]^{2-}$ [67a] undergoes a chemically reversible oxidation to $[Ni(dtodt)_2]^-$ ($E^{\circ\prime}_{2-/-}$ = −0.33 V, in MeCN; [67b]; $E^{\circ\prime}_{2-/-}$ = −0.25 V, in dmf [67c,d]; V, *vs.* SCE). The monoanion is less distorted from the planar geometry than the dianion [67b,e], but, as usual, the variations of the interatomic distances along the whole molecular frame are minimal, Table 20.

Supported also by EPR spectroscopic data, it follows that the electron removal is substantially centred on the dithiolene ligand [67e].

$[Pd(dtodt)_2]^{2-}$ undergoes a reversible one-electron oxidation ($E^{\circ\prime}_{2-/-}$ = −0.03 V, *vs.* SCE) [67b].

Table 20. Selected bond distances (average values; Å) and dihedral angles (°) in the couple $[Ni(dtodt)_2]^{2-/-}$.

Complex	Ni-S	S-C	C=C	$C\text{-}S_{(\text{outer ring})}$	C=O	α	Cation	Ref.
$[Ni(dtodt)_2]^{2-}$	2.19	1.73	1.34	1.76	1.21	17.4	$[NEt_4]^+$	67a
$[Ni(dtodt)_2]^-$	2.16	1.72	1.34	1.75	1.23	≈2	$[NBu_4]^+$	67b
	2.15	1.72	1.35	1.74	1.20	10.7	$[AsPh_4]^+$	67e
	2.14	1.71	1.31	1.73	1.21	-	$[Fe(C_5Me_5)_2]^+$	67f
	2.16	1.72	1.36	1.74	1.21	-	$[Mn(C_5Me_5)_2]^+$	67g

3.2.6.2 Tris(dtodt) complexes

$[W(dtodt)_3]^{2-}$ possesses a trigonally distorted octahedral geometry [68]. Like the Mo analogue, it undergoes two reversible one-electron oxidations, Table 21 [68].

Table 21. Formal electrode potentials (V, *vs.* Ag/AgCl) for the redox processes exhibited by complexes $[M(dtodt)_3]^{2-}$ in CH_2Cl_2 solution

M	$E^{o\prime}_{2-/-}$	$E^{o\prime}_{-/0}$	$E^{o\prime}_{2-/3-}$
Mo	−0.02	+0.33	−1.44
W	−0.07	+0.27	-

3.2.7 dttdt Complexes (better known as "dmit")

3.2.7.1 Bis(dttdt) complexes

Dttdt metal complexes appeared in literature in the mid 1970's and they still constitute the most studied class of metallo-dithiolenes [2i,n].

The crystal structure of the Fe(III) anion $[Fe(dttdt)_2]^-$ shows that it is dimerised, thus giving rise to monoanion units that are not perfectly planar [69]. It is, however, thought that in strong coordinating solvents (such as dmf, dmso, py) dimerisation might be prevented. As a matter of fact, in dmf solution, the monoanion exhibits a reversible one-electron reduction (E°' = −0.43 V, *vs.* SCE), and an oxidation process affected by adsorption phenomena at the platinum electrode (E_p = +0.14 V). The cathodic process is attributed to the Fe(III)/Fe(II) reduction, whereas the anodic process is attributed to a ligand-centred electron transfer [68].

The dianion $[Co(dttdt)_2]^{2-}$ possesses a tetrahedral geometry; in fact, the two dithiolene ligands around the Co(II) centre form a dihedral angle of 98.1° [70]. The cyclic voltammetric behaviour of the dianion in CH_2Cl_2 solution has been reported, but the interpretation is doubted [70].

Let us now deal with the abundant series of Ni complexes. The monoanion $[Ni(dttdt)_2]^-$ undergoes a chemically reversible one-electron reduction and a one-electron oxidation which is complicated by electrode adsorption phenomena. Table 22 summarizes the formal electrode potentials of such electron transfer processes in different solvents.

The dianion $[Ni(dttdt)_2]^{2-}$ shows the typical planar geometry of this class of complexes [72a], and in agreement with the electrochemical reversibility of the 2−/−/0 changes, the same geometry is maintained by $[Ni(dttdt)_2]^-$ and $[Ni(dttdt)_2]^0$, Table 23.

In confirmation of the extended delocalization of the electron transfers, most distances inside the ligand remain essentially unaltered. Nevertheless, the progressive shortening of the Ni–S bond suggests a significant contribution of the metal *d* orbitals to the frontier orbitals.

At variance with $[Ni(dttdt)_2]^{2-}$ and $[Pt(dttdt)_2]^{2-}$, $[Pd(dttdt)_2]^{2-}$ only exhibits

Table 22. Formal electrode potentials (V, *vs.* SCE) for the redox processes exhibited by $[Ni(dttdt)_2]^{n-}$

$E^{\circ\prime}_{2-/-}$	$E^{\circ\prime}_{-/0}$	Solvent	Reference
–0.23	+0.42	Me_2CO	71°
–0.20	+0.19^a	MeCN	71°
–0.13	+0.22^a	MeCN	71b
–0.17	≈+0.2^a	MeCN	71c
–0.14	+0.18	MeCN	71d
–0.25	-	dmf	71e
–0.18	≈+0.3^a	dmf/MeCN (3:2)	71e

^{a} Affected by electrode adsorption

a single oxidation. Literature reports are not unequivocal, describing such a process either as a two-electron process complicated by electrode adsorption [72c] or as a reversible one-electron process [75, 71e, 73m], Table 24.

The square planar geometry of the monoanion $[Pt(dttdt)_2]^-$ is known [73e].

Like $[Co(dttdt)_2]^{2-}$, the dianion $[Cu(dttdt)_2]^{2-}$ possesses a tetrahedrally distorted geometry (the dihedral angle between the two ligand planes is 57.3°) [76]. In MeCN solution, it displays two close one-electron oxidations affected by electrode adsorption ($E_{p\ 2-/-}$ = +0.02 V; $E_{p\ -/0}$ = +0.08 V, *vs.* SCE) [76]. In view of the preference of Cu(III) ion for planar geometry, it cannot be ruled out that one of the two processes might be metal based.

The square planar monoanion $[Au(dttdt)_2]^-$ [67g, 77a-d] undergoes a one-electron reduction having features of chemical reversibility in the cyclic voltammetric time scale ($E^{\circ\prime}_{-/2-}$ = –0.62 V, dmf solution [77a]; –0.60 V, MeCN solution [77e]; V, *vs.* SCE) and a one-electron oxidation {$E_{p\ -/0}$ = +0.72 V (coupled to electrode adsorption, in dmf solution) [77a]; $E^{\circ\prime}_{-/0}$ = +0.35 V, MeCN solution [77e]}.

Like the dianions $[M(dttdt)_2]^{2-}$ (M = Co, Cu), $[Zn(dttdt)_2]^{2-}$ also has a tetrahedrally distorted geometry (the dihedral angle between the two ligand planes is around 95°) [78].

The square pyramidal dianion $[MoO(dttdt)_2]^{2-}$ [79] exhibits a first, chemically reversible, one-electron oxidation ($E^{\circ\prime}_{2-/-}$ = +0.12 V, *vs.* SCE) followed by a second one-electron oxidation affected by electrode adsorption ($E^{\circ\prime}_{-/0}$ = +0.52 V) [79].

The isostructural monoanion $[ReO(dttdt)_2]^-$ [80], undergoes in CH_2Cl_2 solution a partially chemically reversible one-electron reduction ($E_{p\ -/2-}$ = –1.7 V, *vs.* SCE) and an irreversible one-electron oxidation ($E_{p\ -/0}$ = +0.9 V) [80].

Table 23. Selected bond distances (average values; Å) in the redox family $[Ni(dttdt)_2]^{2-/-/0}$

Complex	Ni-S	S-C[a]	C=C	C-S[b]	S-C[b]	C=S	Cation	Ref.
$[Ni(dttdt)_2]^{2-}$	2.22	1.75	1.39	1.71	1.73	1.68	$[NBu_4]^+$	72a
	2.20	1.73	1.35	1.74	1.72	1.65	$[NBu_4]^+$	72b
	2.19	1.74	1.33	1.74	1.72	1.65	$[NHBu_3]^+$	72c
	2.19	1.74	1.34	1.75	1.72	1.66	$[\text{Oct-py}]^+$[c]	72d
	2.19	1.73	1.35	1.74	1.72	1.65	$[\text{Rb(dchyl-18c6)}]^+$[d]	72e
	2.19	1.73	1.34	1.74	1.73	1.65	$[\text{Cs(dchyl-18c6)}]^+$[d]	72e
$[Ni(dttdt)_2]^-$	2.16	1.72	1.35	1.73	1.73	1.63	$[NBu_4]^+$	73a
	2.16	1.70	1.42	1.70	1.73	1.63	$[\text{DB-TTF}]^+$[e]	73b
	2.16	1.70	1.32	1.76	1.71	1.66	$[\text{BEDT-TTF}]^+$[f]	73c
	2.16	1.72	1.35	1.74	1.74	1.62	$[NEt_4]^+$	73d
	2.16	1.72	1.34	1.75	1.72	1.65	$[NBu_4]^+$	73e
	2.16	1.71	1.36	1.74	1.72	1.65	$[NMe_4]^+$	73f
	2.16	1.71	1.35	1.75	1.73	1.63	$[NPr_4]^+$	73f
	2.16	1.71	1.36	1.74	1.73	1.66	$[Fe(C_5Me_5)_2]^+$	73g
	2.17	1.70	1.38	1.73	1.73	1.63	$[\text{tmiz}]^+$[g]	73h
	2.15	1.71	1.36	1.74	1.72	1.64	$[DIPSPh_4]^+$[h]	73i
	2.16	1.72	1.33	1.74	1.72	1.64	$[Co(C_5H_5)_2]^+$	73l
	2.16	1.71	1.36	1.74	1.73	1.64	$[PPN]^+$[i]	71a
	2.16	1.71	1.36	1.74	1.73	1.64	$[SmeEt_2]^+$	71a
	2.16	1.71	1.35	1.74	1.74	1.62	$[PPN]^+$[i]	73m
	2.16	1.71	1.36	1.73	1.72	1.65	$[EDA]^+$[l]	73n
	2.17	1.72	1.36	1.74	1.73	1.64	$[DMMP]^+$[m]	73o
	2.16	1.71	1.37	1.74	1.72	1.65	$[DMPPEMP]^+$[n]	73o
	2.16	1.73	1.33	1.74	1.73	1.65	$[\text{DPD-Me}]^+$[o]	38l
	2.16	1.72	1.35	1.74	1.73	1.64	$[\text{K(DA-18-crown-6)}]^+$[p]	73p
	2.16	1.71	1.35	1.74	1.73	1.64	$[\text{Rb(DA-18-crown-6)}]^+$[p]	73p
	2.15	1.73	1.35	1.74	1.72	1.65	$[\text{Rb(dchyl-18c6)}]^+$[d]	72e
	2.16	1.71	1.35	1.75	1.73	1.63	$[V]^+$[q]	73q
	2.16	1.71	1.34	1.75	1.72	1.64	$[NBu_4]^+$	73r
	2.16	1.71	1.40	1.73	1.73	1.65	$[Mn(C_5Me_5)_2]^+$	67g
$[Ni(dttdt)_2]^0$	2.15	1.70	1.39	1.73	1.75	1.62	-	74
	2.14	1.70	1.39	1.73	1.74	1.63	-	72c

[a]Inner ring; [b]outer ring; [c]Oct-py = N-octadecylpyridine; [d]dchyl-18c6 = dicyclohexyl-18-crown-6; [e]DB-TTF = dibenzotetrathiafulvalene; [f]BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene; [g] tmiz = 1,2,3-trimethylimidazole; [h]DIPSPh$_4$ = tetraphenyldithiapyranylidene; [i]PPN = bis(triphenylphosphoranylidene); [l] EDA = 2-diethylamino-1,3-dithiolane; [m]DMMP = 4-(dimethylamino)-1-methylpyridine; [n]DMPPEMP = 4-[2-(4-(dimethylamino)phenyl)ethenyl]-1-methylpyridine; [o]DPD-Me = trans-4,4'-azobis(1-methylpyridine); [p]DA-18-crown-6 = 4,13-diaza-18-crown-6; [q]V = 3-[4-(diethyl methylamino)phenyl-1,5-diphenyl-6-oxoverdazole

Table 24. Formal electrode potentials (V, *vs.* SCE) for the redox processes exhibited by $[M(dttdt)_2]^{n-}$ (M = Pd, Pt) in MeCN solution

M	$E^{o\prime}_{2-/-}$	$E^{o\prime}_{-/0}$	Reference
Pd	+0.07[a,b]	-	74b
	+0.05	-	75
	+0.11	-	73m
	−0.09	-	71e
Pt	−0.08	+0.11	75
	−0.27	-	71e

[a] Peak potential value for a two-electron process; [b] affected by electrode adsorption

An even more limited redox aptitude is exhibited by $[VO(dttdt)_2]^{2-}$ (an irreversible oxidation at E_p = +0.19 V, *vs.* SCE, in MeCN solution) [81].

3.2.7.2 Tris(dttdt) complexes

A few tris-chelate complexes $[M(dttdt)_3]^{n-}$ (M = V, Mo, W, Re) have been electrochemically characterised. The V and Re complexes exhibit the whole sequence 3−/2−/−/0, whereas the Mo and W complexes only exhibit the sequence 2−/−/0, Table 25.

As a consequence of the chemical reversibility of the 2−/− electron transfer, the structural data for the (almost) trigonal prismatic redox couples $[W(dttdt)_3]^{2-/-}$ and $[V(dttdt)_3]^{2-/-}$ are available (in the last couple the integral oxidation states could be uncertain), Table 26.

As seen, the structural variations are minimal, thus once again supporting the ligand centred nature of the respective anodic processes.

Table 25. Formal electrode potentials (V, *vs.* SCE) for the redox processes exhibited by $[M(dttdt)_3]^{n-}$ (M = V, Mo, W, Re)

M	$E^{o\prime}_{3-/2-}$	$E^{o\prime}_{2-/-}$	$E^{o\prime}_{-/0}$	Solvent	Reference
V	−0.78	+0.15	+0.65[a]	MeCN	81a
Re	−1.28	−0.63	+0.76[a]	CH_2Cl_2	80
Mo		+0.18	+0.38[a]	dmf	82b
		−0.01	+0.26	CH_2Cl_2	68
W		+0.14	+0.32[a]	dmf	82b

[a] Affected by electrode adsorption

Table 26. Selected bond distances (average values, Å) in the couples $[M(dttdt)_3]^{n-}$.

Complex	M-S	S-C[a]	C=C	C-S[b]	S-C[b]	C=S	Cation	Reference
$[V(dttdt)_3]^-$	2.36	1.70	1.38	1.74	1.73	1.63	[BEDT-TTF]$^{+}$ [c]	81b
$[V(dttdt)_3]^{2-}$	2.38	1.73	1.34	1.75	1.72	1.66	[NMP]$^{+}$ [d]	81a
$[W(dttdt)_3]^-$	2.38	1.71	1.34	1.74	1.72	1.65	$[Fe(C_5Me_5)_2]^+$	82b
$[W(dttdt)_3]^{2-}$	2.39	1.73	1.34	1.73	1.72	1.65	$[NBu_4]^+$	82b
$[Mo(dttdt)_3]^{2-}$	2.40	1.73	1.35	1.72	1.71	1.66	$[NBu_4]^+$	82a,b

[a] Inner ring; [b] outer ring; [c] BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene; [d] NMP = N-methylphenazine

3.2.8 idttdt Complexes (better known as "dmt")

3.2.8.1 Bis(idttdt) complexes

In sharp contrast with the huge number of metal complexes of the dttdt ligand, a limited number of complexes of the isomeric ligand idttdt have been characterised.

A series of dianions $[M(idttdt)_2]^{2-}$ (M = Ni, Pd, Pt, Cu) have been prepared, but the only crystal structure we are aware of is that of the square planar $[Ni(idttdt)_2]^{2-}$ [83a,b].

All these complexes only display the reversible oxidation to the corresponding monoanions, Table 27.

Comparison with the corresponding process for the $[M(dttdt)_2]^{2-}$ analogues shows that the actual complexes are slightly more difficult to oxidize by about 0.2 V.

Table 27. Formal electrode potentials (V, *vs.* SCE) for the one-electron oxidation of $[M(idttdt)_2]^{2-}$ (M = Ni, Pd, Pt, Cu) in MeCN solution

M	$E^{o'}_{2-/-}$	Reference
Ni	−0.07	83a
	+0.20	83c
	+0.06	71d
Pd	+0.18	83a
Pt	−0.08	83a
Cu	+0.09	83a

3.2.8.2 Tris(idttdt) complexes

To the best of our knowledge, the only crystal structure of tris-idttdt complexes is concerned with $[V(idttdt)_3]^{2-}$ [84], which is substantially similar to that of $[V(dttdt)_3]^-$ [81]. No electrochemical data are in this case available.

3.2.9 R_2-timdt complexes

3.2.9.1 Bis(R_2-timdt) complexes

Figure 12 shows the square planar geometry of the neutral $[Ni(Pr^i_2\text{-timdt})_2]$, together with its cyclic voltammetric behaviour [85a,b].

In addition to the reversible sequence 0/–/2– exhibited by most $[Ni(dithiolene)_2]^{n-}$ complexes, it also undergoes a single two-electron oxidation with features of partial chemical reversibility.

It is interesting to note that, as illustrated in Figure 13, the square planar $[Pd(Et_2\text{-timdt})_2]$ [85c] displays that five-membered sequence $[Pd(Et_2\text{-timdt})_2]^{2+}$/

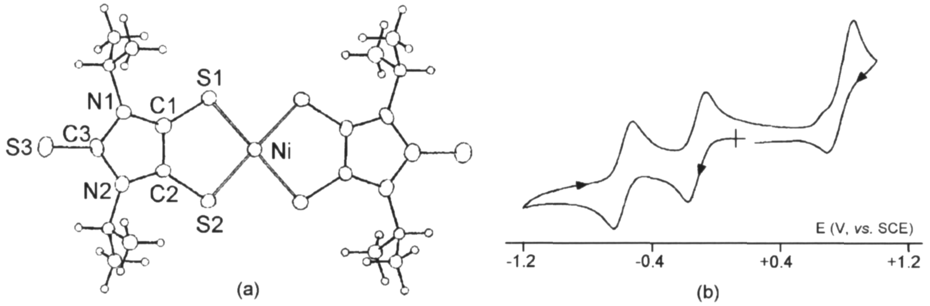


Figure 12. (a) X-Ray structure (a) and cyclic voltammogram (Pt working electrode; CH_2Cl_2 solution; scan rate 0.1 V s^{-1}) (b) of $[Ni^{II}(Pr^i_2\text{-timdt})_2]$.

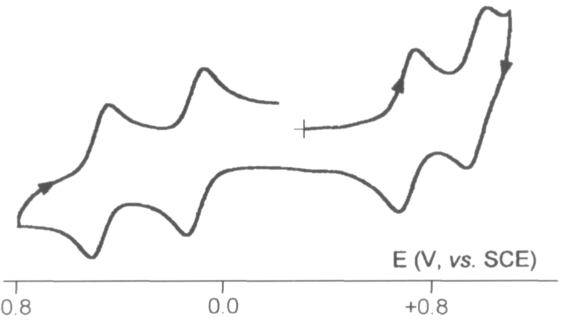


Figure 13. Cyclic voltammogram recorded at a platinum electrode in CH_2Cl_2 solution of $[Pd(Et_2\text{-timdt})_2]$. Scan rate 0.2 V s^{-1}.

Table 28. Formal electrode potentials (V, *vs.* SCE) for the redox processes exhibited by $[M(R_2\text{-timdt})_2]$ (M = Ni, Pd) in CH_2Cl_2 solution

M	R	$E^{\circ\prime}_{2+/+}$	$E^{\circ\prime}_{+/0}$	$E^{\circ\prime}_{0/-}$	$E^{\circ\prime}_{-/2-}$	Reference
Ni	Me	+0.63[a]	+0.63[a]	−0.13	−0.59	85d
	Et	+0.78[a]	+0.78[a]	−0.11	−0.56	85a
		+0.65	+0.65	−0.14	−0.59	85d
	Pr^i	+0.75[a]	+0.75[a]	−0.17	−0.65	85a
	Bu	+0.77[a]	+0.77[a]	−0.12	−0.59	85a
	Ph	+0.73	+0.73	−0.04	−0.53	85d
Pd	Et	+0.72[a]	+0.72[a]	0.00	−0.36	85c
		+0.97	+0.71	−0.12	−0.49	85d
	Ph	+1.00	+0.74	+0.01	−0.38	85d
Pt	Me	+0.91[a]	+0.69	−0.06	−0.43	85d
	Et	+1.03	+0.74	−0.13	−0.59	85d
	Ph	+1.2[b]	+0.74	−0.01	−0.51	85d

[a] Peak potential value for partially chemically reversible processes; [b] overlapped by a further oxidation

$[Pd(Et_2\text{-timdt})_2]^+/[Pd(Et_2\text{-timdt})_2]^0/[Pd(Et_2\text{-timdt})_2]^-/[Pd(Et_2\text{-timdt})_2]^{2-}$ theoretically expected for bis-dithiolenes (see Scheme 6) [85d].

As a matter of fact, concerned with the anodic path, inside the class $[M(R_2\text{-timdt})_2]$ (M = Ni, Pd, Pt), Ni complexes afford a single two electron removal, whereas Pd and Pt complexes give rise two separate one-electron removals. Table 28 compiles the formal electrode potentials for the whole redox changes exhibited by the present derivatives.

In agreement with the electrochemical reversibility of the 0/− reduction, the monoanion $[Ni(Pr^i_2\text{-timdt})_2]^-$ maintains the square planar geometry of the neutral precursor [85e]. The pertinent structural parameters show quite minimal changes in bond lengths (the largest variation, 0.03 Å, is concerned with the C=C bond), which also in this case support the ligand centred nature of the electron transfer process.

3.2.10 tdadt Complexes (better known as "tdas")

3.2.10.1 Bis(tdadt) complexes

The square planar dianion $[Ni(dtadt)_2]^{2-}$ [86a] undergoes in MeCN solution a quasireversible oxidation to the corresponding monoanion $[Ni(dtadt)_2]^-$ $(E^{\circ\prime}_{2-/-}$

= +0.95 V, *vs.* SCE) [86b]. Crystallographic data on the monoanion seem to support a slight departure from planarity because of its tendence to dimerise, but structural data are not accessible [86c]. Crystal data are available for the monoanion $[Fe(dtadt)_2]^-$ [86c], but no electrochemical data are known.

3.3 1,2-Dithiolates forming six-membered lateral rings

3.3.1 bdt Complexes

3.3.1.1 Bis(bdt) complexes

As seen in most of the preceding cases, transition metal bis(bdt) complexes commonly exhibit the 0/–/2– redox processes [2b]. For example, in dmf solution, the formal electrode potential for the couple $[Ni(bdt)_2]^{2-/-}$ is –1.05 V, *vs.* Ag/ $AgClO_4$ [2b]. Both the members of the couple adopt a square planar geometry, and also in this case the pertinent bond lengths show quite minimal variations. In fact, on passing from the dianion to the monoanion, the Ni-S distance shortens by 0.02 Å, the S-C length elongates by 0.02 Å, and the inner ring C=C distance remains unvaried [87]. These data once again suggest that the electron transfer is delocalised along the whole molecular frame.

A square planar geometry is also displayed by $[Au(bdt)_2]^0$ obtained by electrochemical oxidation of the monoanion $[Au(bdt)_2]^-$ [88].

The redox couples of the square pyramidal oxo-complexes $[MO(bdt)_2]^{2-/-}$ (M = Mo, W) have been crystallographically characterised (Mo: $E^{\circ\prime}_{2-/-} = -0.35$ V, *vs.* SCE, in dmf solution [89a]; W: $E^{\circ\prime}_{2-/-} = -0.63$ V, *vs.* SCE, in MeCN solution [18b]). The related structural data are compiled in Table 29.

Once again, the relative increase of the M=O distance upon one-electron reduction with respect to the metal-ligand and intraligand distances is diagnostic of metal-centred processes.

Table 29. Selected bond distances (average values; Å) in the redox couples $[MO(bdt)_2]^{2-/-}$ (M = Mo, W)

Complex	M-S	S-C	C=C[a]	M=O	Cation	Reference
$[MoO(bdt)_2]^{2-}$	2.39	1.77	1.39	1.70	$[NEt_4]^+$	89a
$[MoO(bdt)_2]^-$	2.38	1.76	1.40	1.67	$[PPh_4]^+$	89a
$[WO(bdt)_2]^{2-}$	2.37	1.76	1.38	1.73	$[NEt_4]^+$	89c
$[WO(bdt)_2]^-$	2.37	1.76	1.39	1.69	$[PPh_4]^+$	89c

[a] Inner ring

3.3.1.2 Tris(bdt) complexes

Structural data are available for the (distorted) octahedral anions $[Zr(bdt)_3]^{2-}$ [90a], $[Nb(bdt)_3]^-$ [90b], and $[Ta(bdt)_3]^-$ [90c], and $[Tc(bdt)_3]^-$ [90d]. The electrochemical The electrochemical irreversibility of the 2–/– redox change in these complexes testifies that they are the only stable members of their potential redox families [91].

As far as we know, the only stable redox couples of the $[M(bdt)_3]^{n-}$ complexes are concerned with the M = Mo, W families. The neutral $[Mo(bdt)_3]$ undergoes in CH_2Cl_2 solution two sequential reversible reductions to the corresponding mono- and di-anions, respectively ($E^{\circ\prime}_{0/-} = +0.20$ V; $E^{\circ\prime}_{-/2-} = -0.39$ V, *vs.* SCE) [92a]. Table 30 compares the bond distances in the neutral and monoanion complexes.

With respect to the trigonal prismatic geometry of the neutral complex, the one-electron addition causes a geometrical reorganization intermediate between trigonal prismatic and octahedral.

In turn, the dianion $[W(bdt)_3]^{2-}$ undergoes in MeCN solution two reversible oxidations to the corresponding monoanion and neutral complexes [93c]. The crystallographic data of the couple $[W(bdt)_3]^{2-/-}$ are reported in Table 30.

In both the Mo and W redox couples, the frontier orbitals look like metal and ligand based.

Table 30. Selected bond distances (average values; Å) and twist angles (°) in the redox couples $[M(bdt)_3]^{n-}$ (M = Mo, W)

Complex	M-S	S-C	C=C^a	ϕ	Cation	Reference
$[Mo(bdt)_3]^0$	2.37	1.73	1.41	0	-	92b
$[Mo(bdt)_3]^-$	2.38	1.72	1.38	33.5	$[PPh_4]^+$	92a
$[W(bdt)_3]^-$	2.37	1.71	1.39	33	$[PPh_4]^+$	93a
	2.39	1.78	1.42	*b*	$[NMe_4]^+$	93b
$[W(bdt)_3]^{2-}$	2.39	1.75	1.40	3.5	$[NEt_4]^+$	93c
	2.39	1.72	1.39	*b*	$[AsPh_4]^+$	93d

^{a} Inner ring; ^{b} not reported

3.3.2 X-bdt Complexes

3.3.2.1.1 Bis(4-Me-bdt) Complexes (better known as "tdt")

The electrochemical behaviour of a number of $[M^{II}(4\text{-Me-bdt})_2]^{2-}$ (M = Mn, Fe, Co, Ni, Cu, Zn) complexes has been investigated [94]. But for the Zn(II) complex, all the dianions undergo the chemically reversible oxidation to the corresponding monoanions, Table 31.

Table 31. Formal electrode potentials (V, *vs.* SCE) for the redox processes exhibited by $[M^{II}(4\text{-Me-bdt})_2]^{2-}$

M	$E^{\circ\prime}_{2-/-}$	$E^{\circ\prime}_{-/0}$	Solvent	Reference
Mn	−0.63	+0.22[a]	MeCN	94a
	−0.81	-	dmf	94b,c
	−0.68	-	CH_2Cl_2	94b,c
	−0.67	-	$C_2H_4Cl_2$	94b,c
Fe	−0.83[b]	-	MeCN	94a
Co	−0.73	+0.20	MeCN	94a
Ni	−0.47	+0.44	MeCN	94a
Cu	−0.53	+0.62	MeCN	94a

[a] Peak potential value for irreversible processes; [b] the anion is dimeric

It is interesting to note that, as illustrated in Figure 14, as a consequence of the chemically reversible ($i_{pa}/i_{pc} \approx 1$), but electrochemically quasireversible (ΔE_p = 290 mV, at 0.1 Vs^{-1}), one electron reduction, the square planar monoanion $[Mn(4\text{-Me-bdt})_2]^-$ reorganizes to the tetrahedral dianion $[Mn(4\text{-Me-bdt})_2]^{2-}$ [94b,c].

The pertinent structural data indicate that the dianion/monoanion redox change is characterised by a shortening of the Mn-S distance by 0.14 Å, whereas the S-C and C=C distances do not undergo variations. It seems hence evident that the extra electron is essentially delocalised on the manganese atom.

Structural data are also available for the square planar monoanions $[M(4\text{-Me-bdt})_2]^-$ (M = Co [94d]; M = Cu [94a]; M = Au [94e]) and the tetrahedral dianion $[Cd(4\text{-Me-bdt})_2]^{2-}$ [94f].

The square pyramidal oxo-complex $[MoO(4\text{-Me-bdt})_2]^{2-}$ [89b] undergoes in dmf solution two reversible one-electron oxidations ($E^{\circ\prime}_{2-/-} = -0.46$ V; $E^{\circ\prime}_{-/0} = +0.52$ V, *vs.* SCE) [89b]. For the isostructural monoanions $[MO(4\text{-Me-bdt})_2]^-$

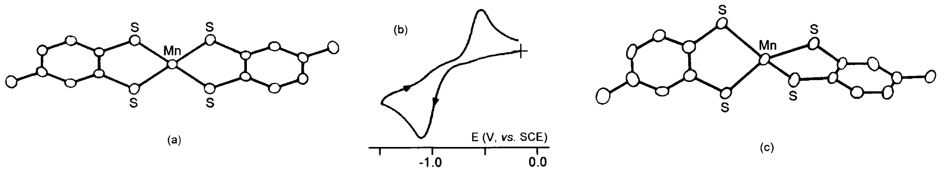


Figure 14. (a) X-Ray structure of $[Mn(4\text{-Me-bdt})_2]^-$ ($[PPh_4]^+$ cation); (b) cyclic voltammogram recorded at a glassy carbon electrode in dmf solution of $[Mn(4\text{-Me-bdt})_2]^-$ (scan rate 0.1 V s^{-1}); (c) X-ray structure of $[Mn(4\text{-Me-bdt})_2]^{2-}$ ($[PPh_4]^+$ cation).

(M = Re, Tc), the 2–/–/0 redox processes occur at notably different potential values (Re: $E^{\circ\prime}_{2-/-} = -2.00$ V, $E^{\circ\prime}_{-/0} = +1.00$ V; Tc: $E^{\circ\prime}_{2-/-} = -1.52$ V, $E^{\circ\prime}_{-/0} = +0.95$ V, *vs.* SCE) [6a].

3.3.2.1.2 Tris(4-Me-bdt) complexes

The electrochemical behaviour of the tris-chelates $[M(4\text{-}Me\text{-}bdt)_3]^{n-}$ (M = V, Mo, W, Re) has been reviewed [2b]. $[Zr(4\text{-}Me\text{-}bdt)_3]^{2-}$ only exhibits an irreversible reduction ($E_p = -1.71$ V, *vs.* Ag/AgClO$_4$) [91].

3.3.2.2.1 Bis(3-SiPh$_3$-bdt) and bis (3-SiPh$_3$-5-Me-bdt) complexes

As expected on the basis of the inductive effects, the square pyramidal dianions $[MoO(3\text{-}SiPh_3\text{-}bdt)_2]^{2-}$ [89b] and $[MoO(3\text{-}SiPh_3\text{-}5\text{-}Me\text{-}bdt)_2]^{2-}$ are slightly more difficult to oxidise than $[MoO(4\text{-}Me\text{-}bdt)_2]^{2-}$ ($E^{\circ\prime}_{2-/-} = -0.41$ V and –0.45 V, respectively; V, *vs.* SCE) [89b].

3.3.2.3.1 Bis(3,5-Bu^t-bdt) complexes

The square planar $[Ni(3,5\text{-}Bu^t\text{-}bdt)_2]^-$ undergoes in thf solution either a one electron oxidation ($E^{\circ\prime}_{-/0} = +0.35$ V, *vs.* NHE) or a one electron reduction ($E^{\circ\prime}_{-/2-} = -0.61$ V), both processes being chemically reversible [95]. As a matter of fact, the square planar three-membered series has been structurally characterised and the pertinent data are compiled in Table 32 [95].

Slight variations along the whole molecular frame occur, suggesting that the frontier orbitals have both metallic and ligand character.

Table 32. Selected bond distances (average values; Å) in the redox family $[Ni(3,5\text{-}But\text{-}bdt)_2]^n$

Complex	Ni-S	S-C	C=C^a	Cation
$Ni(3,5\text{-}Bu^t\text{-}bdt)_2]^{2-}$	2.17	1.76	1.40	$[AsPh_4]^+$
$Ni(3,5\text{-}Bu^t\text{-}bdt)_2]^-$	2.14	1.75	1.41	$[AsPh_4]^+$
$Ni(3,5\text{-}Bu^t\text{-}bdt)_2]^0$	2.13	1.73	1.42	-

^{a} Inner ring

3.3.3 dhdtdt Complexes (better known as "dddt")

3.3.3.1 Bis(dhdtdt) complexes

The square planar monoanion $[Ni(dhdtdt)_2]^-$ in MeCN solution undergoes a chemically reversible one-electron reduction and a one-electron oxidation

Table 33. Formal electrode potentials (V, *vs.* SCE) for the redox processes exhibited by $[M(dhdtdt)_2]^{n-}$ complexes

M	$E^{\circ\prime}_{2-/-}$	$E^{\circ\prime}_{-/0}$	$E^{\circ\prime}_{0/+}$	Solvent	Reference
Ni	-0.85	-0.03^a	-	dmf	33b, 96b
	-0.78	0.00	$+0.80^b$	dmf	96c
	-0.69	$+0.06^a$	-	MeCN	71b
	-0.68	$+0.06^a$	-	MeCN	96d
	-0.59	$+0.17$	-	MeCN	96e
	-0.73	$+0.05$	-	thf	96f
Cu	-0.54	$+0.33^a$	-	dmf	96g
Pd	-0.47	$+0.16$	-	dmf	33b
	-0.43	$+0.14$	-	Me_2CO	71a
Pt	-0.64	-0.02	-	dmf	33b
	-0.74	-0.11	$+0.80^c$	PhCN	96c
Au	-1.32	$+0.41$	$+0.82^c$	CH_2Cl_2	96h

[a] Coupled to chemical reactions; [b] peak-potential value for irreversible processes; [c] coupled to electrode adsorption

Table 34. Selected bond distances (average values; Å) in the square planar redox couple $[Ni(dhdtdt)_2]^{-/0}$

Complex	Ni-S	S-C	C=C^a	C-S^b	S-C^b	C-C^b	Cation	Reference
$[Ni(dhdtdt)_2]^-$	2.15	1.73	1.34	1.77	1.80	1.51	$[NEt_4]^+$	96b
	2.14	1.72	1.34	1.75	1.82	1.28	$[NBu_4]^+$	96h
	2.15	1.72	1.35	1.75	1.78	1.39	$[NMe_4]^+$	97a
$[Ni(dhdtdt)_2]^0$	2.12	1.69	1.37	1.75	1.82	1.47	-	97b

[a] Inner ring; [b] outer ring

Table 35. Selected bond distances (average values; Å) in the square planar redox couples $[M(dhdtdt)_2]^{-/0}$ (M = Pt, Au)

Complex	M-S	S-C^a	C=C^a	C-S^b	S-C^b	C-C^b	Cation	Reference
$[Pt(dhdtdt)_2]^-$	2.27	1.74	1.34	1.77	1.80	1.50	$[NEt_4]^+$	98a
$[Pt(dhdtdt)_2]^0$	2.24	1.70	1.40	1.75	1.83	1.52	-	98b
$[Au(dhdtdt)_2]^-$	2.31	1.76	1.33	1.77	1.78	1.46	$[TTF]^+$	98c
$[Au(dhdtdt)_2]^0$	2.30	1.70	1.38	1.77	1.83	1.39	-	96h

[a] Inner ring; [b] outer ring; [c] TTF = tetrathiofulvalene

coupled to slow degradation of the electrogenerated neutral complex [71b]. Table 33 compiles the relative formal electrode potentials, together with those of the related copper, palladium and platinum complexes.

In spite of the relative instability, the neutral complex $[Ni(dhdtdt)_2]$ has been isolated and crystallographically characterised. Selected interatomic distances relative to the redox couple $[Ni(dhdtdt)_2]^{-/0}$ are reported in Table 34. Once again, they suggest that the extra electron is delocalised along the whole molecular frame.

Surprisingly, to the best of our knowledge, no structural data are available for the stable dianion $[Ni(dhdtdt)_2]^{2-}$.

As far as the monoanion $[Cu(dhdtdt)_2]^-$ is concerned, the central CuS_4 core is planar in $[NMe_3H][Ni(dhdtdt)_2]$ and tetrahedrally distorted (dihedral angle = 29°) in $[NBu_4][Ni(dhdtdt)_2]$ [96g]. This points out the role played by countercations in modifying those crystal packing forces which are crucial to tune conducting properties triggered by stacking effects in metallodithiolenes.

Crystal data for the square planar couples $[Pt(dhdtdt)_2]^-/[Pt(dhdtdt)_2]^0$ and $[Au(dhdtdt)_2]^-/[Au(dhdtdt)_2]^0$ are reported in Table 35.

As usual, significant variations of the bond distances occur both at the metal-sulfur cores and at the ligand itself. Fractionally positive $[Pt(dhdtdt)_2]^{\delta+}$ cations have been also crystallographically characterised. No significant structural variation seems be present with respect to $[Pt(dhdtdt)_2]^0$ [71a,b].

3.3.3.2 Tris(dhdtdt) complexes

The electrochemical behaviour of a number of $[M(dhdtdt)_3]^{n-}$ complexes (M = Ti, V, Mn, Nb, Ta) has been investigated. As shown in Table 36, they can accede the 3–/2–/–/0 redox changes, only part of which are chemically reversible.

The crystal structures of the redox couple $[V(dhdtdt)_3]^{-/0}$, Table 37, indicate minimal variations in bonding distances, but, as previously noted for other

Table 36. Formal electrode potentials (V, *vs.* SCE) for the redox processes exhibited by $[M(dhdtdt)_3]^{n-}$ complexes in dmf solution

Complex	$E^{\circ\prime}_{3-/2-}$	$E^{\circ\prime}_{2-/-}$	$E^{\circ\prime}_{-/0}$	Reference
$[Ti(dhdtdt)_3]^{2-}$	−1.47	+0.03[a]	+0.50[a]	99a
$[V(dhdtdt)_3]^-$	−1.44	−0.51	+0.39	99b
$[Mn(dhdtdt)_3]^{2-}$	−0.62[b]	+0.08[a]	-	99a
$[Nb(dhdtdt)_3]^{2-}$	−1.71	−0.68	+0.48[a]	99b

[a] Peak-potential value for irreversible processes; [b] coupled to slow chemical complications

thris-dithiolenes, the main structural change following the electron transfer is the geometrical reorganization from the (almost) perfect trigonal prism of the monoanion to the octahedrally distorted trigonal prism of the neutral complex.

The crystal structure of the dianion $[Ti(dhdtdt)_3]^{2-}$ is also known [99c].

Table 37. Selected bond distances (average values, Å) and twist angles (°) in the couple $[V(dhdhdt)_3]^{-/0}$

Complex	V-S	S-C^a	C=C^a	C-S^b	S-C^b	C-C^b	ϕ	Cation	Reference
$[V(dhdtdt)_3]^-$	2.34	1.72	1.35	1.76	1.74	1.34	3.7	$[NBu_4]^+$	99a
	2.34	1.72	1.36	1.75	1.78	1.47	5.0	$[TTF]^{+c}$	99b
$[V(dhdtdt)_3]^0$	2.35	1.70	1.38	1.74	1.76	1.28	15.7	-	99b

^{a} Inner ring; ^{b} outer ring; ^{c} TTF = tetrathiofulvalene

3.3.4 R'- hdtdt Complexes

3.3.4.1 Bis(mehdtdt) and bis(phhdtdt) complexes (better known as "medt" and as "phdt", respectively)

As far as we know, the only mehdtdt and phhdtdt metallo-complexes up-to-now structurally and electrochemically studied are the square-planar nickel complexes. The monoanions $[Ni(mehdtdt)_2]^-$ and $[Ni(phhdtdt)_2]^-$ in MeCN solution reversibly undergo either a one-electron reduction or a one-electron oxidation, Table 38.

The crystal structures of the redox couple $[Ni(mehdtdt)_2]^{-/0}$ are available, Table 39.

The most significant structural change looks like centred on the peripheral regions of the ligand.

By way of comparison, Table 39 also reports the structural data of $[Ni(phhdtdt)_2]^0$, and those of the related diphenyl substituted $[Ni(dphdtdt)_2]^-$, which will be discussed in the next Section.

Table 38. Formal electrode potentials (V, *vs.* SCE) for the redox processes exhibited by $[Ni(R'\text{-}hdtdt)_2]^{n-}$ complexes

Complex	$E^{\circ\prime}_{2-/-}$	$E^{\circ\prime}_{-/0}$	Solvent	Reference
$[Ni(mehdtdt)_2]^-$	–0.70	+0.05	MeCN	96d
$[Ni(phhdtdt)_2]^-$	–0.65	+0.06	MeCN	100a
	–0.36	+0.37	MeCN	100b
	–0.71	+0.08	thf	96f

Table 39. Selected bond distances (average values; Å) in the square planar complexes $[Ni(R'\text{-}hdtdt)_2]^{-/0}$ and related complexes

Complex	Ni-S	S-C[a]	C=C[a]	C-S[b]	S-C[b]	C-C[b]	C-C$_{(R')}$	Cation	Reference
$[Ni(mehdtdt)_2]^-$	2.13	1.71	1.32	1.76	1.74	1.24	1.16	$[NBu_4]^+$	98a
$[Ni(mehdtdt)_2]^0$	2.13	1.70	1.40	1.74	1.78	1.32	1.52	-	98b
$[Ni(phhdtdt)_2]^-$	2.13	1.70	1.38	1.74	1.76	1.28	1.51	-	98c
$[Ni(dphdtdt)_2]^-$	2.15	1.75	1.34	1.75	1.86	1.70	1.57	$[PPh_4]^+$	96h

[a] Inner ring; [b] outer ring

3.3.5 dphdtdt Complexes

3.3.5.1 Bis(dphdtdt) complexes

Like the monosubstituted R'-hdtdt complexes, the diphenyl substituted $[Ni(dphdtdt)_2]^-$ exhibits in thf solution either a reversible one-electron reduction ($E^{\circ\prime}_{-/2-} = -0.71$ V, *vs.* SCE) or a reversible one-electron oxidation ($E^{\circ\prime}_{-/0} = +0.09$ V) [96f]. Structural data for the monoanion are reported in Table 39.

3.3.6 dtdt Complexes (better known as "ddt")

3.3.6.1 Bis(dtdt) complexes

Electrochemical data for a few $[M(dtdt)_2]^-$ monoanions (M = Ni, Pd) are available, Table 40.

Like the saturated dhdtdt derivatives, they undergo reversibly the 2–/–/0 redox changes. It is evident that the unsaturation of the peripheral ring makes the –/2– reduction of the nickel complex easier with respect to the saturated analogue.

Based on the crystallographic data for $[Ni(dtdt)_2]^-$ [101b] it seems likely that in the formally represented S–C=C–S fragment of the outer ring, the unsaturation is in reality delocalised over the whole SCCS frame.

Table 40. Formal electrode potentials (V, *vs.* SCE) for the redox processes exhibited by $[M(dtdt)_2]^{n-}$ complexes in MeCN solution and related complexes

Complex	$E^{\circ\prime}_{2-/-}$	$E^{\circ\prime}_{-/0}$	Reference
$[Pd(dtdt)_2]^{n-}$	–0.37	+0.11	101a
$[Ni(dtdt)_2]^{n-}$	–0.51	+0.06	101a
$[Ni(dhdtdt)_2]^{n-}$	–0.69	+0.06[a]	71b

[a] Coupled to chemical reactions

3.3.7 fcdtdt Complexes (better known as "dphdt")

3.3.7.1 Bis(fcdtdt) complexes

Figure 15 shows the structural and electrochemical properties of the NiS_4 square planar monoanion $[Ni(fcdtdt)_2]^-$ [102a].

It undergoes a quasireversible one-electron reduction and a quasireversible one-electron oxidation, both centred on the Ni-dithiolene moiety ($E^{\circ\prime}_{-/2-}$ = −0.95 V, ΔE_p = 190 mV; $E^{\circ\prime}_{-/0}$ = −0.18 V, ΔE_p = 180 mV; V, *vs.* Fc/Fc^+), as well as a single two-electron oxidation (affected by electrode adsorption; $E_{p(0/2+)}$ = +0.48 V), which is centred on the two not-communicating ferrocenyl subunits.

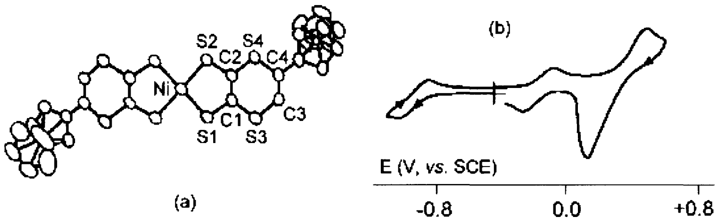


Figure 15. (a) X-Ray structure (average bonding distances: Ni-S = 2.15 Å; S1-C1 = 1.72 Å; C1-C2 = 1.37 Å; C1-S3 = 1.76 Å; S3-C3 = 1.75 Å; S4-C4 = 1.77 Å; C3-C4 = 1.34 Å) and (b) cyclic voltammogram (glassy carbon electrode; thf solution; scan rate 0.05 V s^{-1}) of $[Ni(fcdtdt)_2]^-$ ($[NBu_4]^+$ cation).

3.3.8 dfcdtdt Complexes

3.3.8.1 Bis(dfcdtdt) complexes

The monoanion $[Ni(dfcdtdt)_2]^-$ possesses structural (average bond distances: Ni-S = 2.14 Å; S1-C1 = 1.68 Å; C1-C2 = 1.39 Å; C1-S3 = 1.78 Å; S3-C3 = 1.73 Å; Å; C3-C4 = 1.33 Å) and redox properties (thf solution: $E^{\circ\prime}_{-/2-}$ = −0.98 V, ΔE_p = 170 mV; $E^{\circ\prime}_{-/0}$ = −0.20 V, ΔE_p = 170 mV; $E_{p(0/4+)}$ = +0.54V, *vs.* Fc/Fc^+) rather similar to those of $[Ni(fcdtdt)_2]^-$ [102a,b]. Comparison with the related $[Ni(dfcedt)_2]$ (see Section 2.2.13.1) suggests that the interposition of the dithiin ring between the ferrocenyl subunits and the dithiolate function rises a barrier to the intramolecular communication of the ferrocene groups.

3.3.9 dcnpzdt Complexes

3.3.9.1 Bis(dcnpzdt) complexes

The dianions $[M(dcnpzdt)_2]^{2-}$ (M = Ni, Pd) have been characterised [103]. In MeCN solution, $[Ni(dcnpzdt)_2]^{2-}$ displays two reversible one-electron oxidations ($E^{\circ\prime}_{2-/-}$ = +0.52 V; $E^{\circ\prime}_{-/0}$ = +1.23 V, *vs.* SCE), whereas $[Pd(dcnpzdt)_2]^{2-}$ only exhibits an irreversible oxidation (E_p = +0.77 V). The crystal structure of $[Pd(dcnpzdt)_2]^{n-}$ present in $(TTF)_5[Pd(dcnpzdt)_2]_2$ has been reported [103].

3.3.10 R_2-pipdt Complexes

3.3.10.1 Bis(R_2-pipdt) complexes

A number of square planar $[M(R_2\text{-pipdt})_2]^{2+}$ dications have been characterised (M = Ni, Pd, Pt) [43c, 104a,b]. Figure 16,which refers to $[Pt(Me_2\text{-pipdt})_2]^{2+}$, shows that, as happens for the related R_2-timdt complexes (see Section 3.2.9), the present complexes are able to shuttle reversibly the sequence 2+/+/0/–/2–, Table 41.

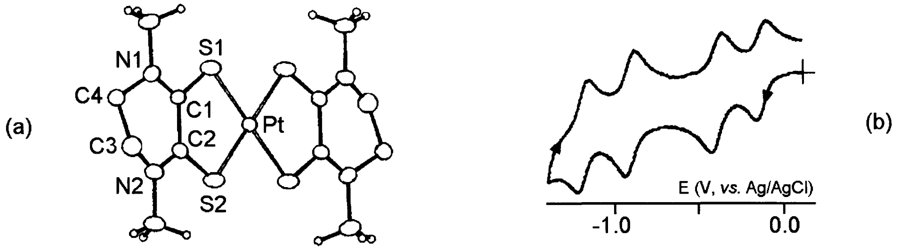


Figure 16. (a) X-Ray structure (average bonding distances: Pt-S = 2.28 Å; S1-C1 = 1.68 Å; C1-C2 = 1.53 Å; C1-N1 = 1.32 Å; N1-C4 = 1.45 Å; C4-C3 = 1.46 Å; N1-$C_{(Me)}$ = 1.45 Å) and (b) cyclic voltammogram (platinum electrode; MeCN solution; scan rate 0.1 V s^{-1}) of $[Pt(Me_2\text{-pipdt})_2]^{2+}$ ($[Pt(dcnedt)_2]^{2-}$ anion).

The fact that the different processes occur at essentially the same potential values, independently from the metal, suggests that the electron transfers are mainly ligand centered. The structural parameters for $[Ni(Me_2\text{-pipdt})_2]^{2+}$ are available [104a].

Table 41. Formal electrode potentials (V, *vs.* Ag/AgCl) for the redox processes exhibited by complexes $[M(Me_2\text{-pipdt})_2]^{2+}$ in MeCN solution [43c]

M	$E^{\circ\prime}_{2+/+}$	$E^{\circ\prime}_{+/0}$	$E^{\circ\prime}_{0/-}$	$E^{\circ\prime}_{-/2-}$
Ni	–0.16	–0.41	–0.96	–1.26
Pd	–0.18	–0.42	–0.87	–1.13
Pt	–0.15	–0.41	–0.92	–1.21

3.4 1,2-Dithiolates forming seven-membered lateral rings

3.4.1 pndtdt (better known as "pddt" or "ddtdt") and dfpndtdt (first named "F_2pdt") Complexes

3.4.1.1 Bis(pndtdt) and bis(dfpndtdt) complexes

Like the related dhdtdt complexes (Section 3.3.3), the monoanions $[M(pndtdt)_2]^-$ (M = Ni, Pt, Cu) and $[Ni(dfpndtdt)_2]^-$ undergo reversibly either the oxidation to the neutral species or the reduction to the corresponding dianions, Table 42.

The electron-withdrawing effect of the fluoride atoms obviously makes the reduction easier and the oxidation more difficult in $[Ni(dfpndtdt)_2]^-$ with respect to $[Ni(pndtdt)_2]^-$.

Crystallographic data for the square planar couple $[Ni(pndtdt)_2]^{-/0}$ are summarized in Table 43.

Once again, the electron transfer looks like delocalised along the whole molecular frame.

The crystal structures of $[Cu(pndtdt)_2]^-$ [105a] and $[Ni(dfpndtdt)_2]^-$ [105b] are also available.

Table 42. Formal electrode potentials (V, *vs.* SCE) for the redox processes exhibited by $[M(pndtdt)_2]^-$ and $[M(dfpndtdt)_2]^-$ complexes

Complex	$E^{\circ\prime}_{2-/-}$	$E^{\circ\prime}_{-/0}$	Solvent	Reference
$[Ni(pndtdt)_2]^-$	−0.71	+0.16	MeCN	71b
	−0.69	+0.17	MeCN	96d
	−0.65	+0.25	dmf	105a
$[Ni(dfpndtdt)_2]^-$	−0.55	+0.30	MeCN	105b
$[Pt(pndtdt)_2]^-$	−0.64	+0.15	MeCN	71b
$[Cu(pndtdt)_2]^-$	−0.61	-	dmf	105a

Table 43. Selected bond distances (average values; Å) in the square planar couple $[Ni(pndtdt)_2]^{-/0}$

Complex	Ni-S	S-C^a	C=C^a	C-S^b	S-C^b	C-C^b	Cation	Reference
$[Ni(pndtdt)_2]^-$	2.15	1.73	1.36	1.76	1.81	1.51	$[NEt_4]^+$	105a
	2.18	1.75	1.33	1.76	1.81	1.52	$[NBu_4]^+$	105c
$[Ni(pndtdt)_2]^0$	2.13	1.71	1.39	1.76	1.81	1.53	-	105d

^{a} Inner ring; ^{b} outer ring

3.4.2 mpndtdt Complexes (better known as "dpdt")

3.4.2.1 Bis(mpndtdt) complexes

A series of square planar monoanions $[M(mpndtdt)_2]^-$ (M = Ni, Au, Cu) have been structurally characterised [106a]. The Ni complex exhibits the usual reversible sequence 2–/–/0, the Cu complex reversibly undergoes the –/2– reduction, and the gold complexes is stable only as monoanion, Table 44.

Table 44. Formal electrode potentials (V, *vs.* SCE) for the redox processes exhibited by $[M(mpndtdt)_2]^-$ complexes in MeCN solution [106a]

Complex	$E^{o\prime}_{2-/-}$	$E^{o\prime}_{-/0}$
$[Ni(mpndtdt)_2]^-$	–0.62	+0.24
$[Cu(mpndtdt)_2]^-$	–0.67	+0.47[a]
$[Au(mpndtdt)_2]^-$	+0.63[a]	+1.28[a]

[a] Peak-potential value for irreversible processes

The neutral complex $[Ni(mpndtdt)_2]$ has been crystallographically solved [106b]. The major variations resulting from the monoanion-to-neutral change lie in the shortening of the Ni-S distance by 0.02 Å and the elongation of the inner ring S-C and C=C distances by 0.03 Å and 0.04 Å, respectively, which support also in this case that the extra electron is removed from a metal-ligand contributed frontier orbital.

3.4.3 odtdt Complexes (better known as "diod")

3.4.3.1 Bis(odtdt) complexes

The square planar monoanions $[M(odtdt)_2]^-$ (M = Ni, Cu) have been structurally characterised [107a,b]. As illustrated in Table 45, the Ni, Cu, Pd,

Table 45. Formal electrode potentials (V, *vs.* SCE) for the redox processes exhibited by $[M(odtdt)_2]^-$ complexes in MeCN solution

Complex	$E^{o\prime}_{2-/-}$	$E^{o\prime}_{-/0}$
$[Ni(odtdt)_2]^-$	–0.65	+0.27
$[Pd(odtdt)_2]^-$	–1.24[a]	+0.26
$[Cu(odtdt)_2]^-$	–1.40[b]	+0.56[a]
$[Au(odtdt)_2]^-$	-	+0.64

[a] Peak-potential value for irreversible processes; [b] coupled to slow chemical reactions

Au monoanions display electrochemical features qualitatively similar to those illustrated in previous complexes forming outer seven-membered rings [107].

3.4.4 thdtdt Complexes (better known as "dtdt" or "ttdt")

3.4.4.1 Bis(thdtdt) complexes

A series of monoanions $[M(thdtdt)_2]^-$ (M = Ni, Pd, Pt, Au, Cu) have been characterised [71a,b, 77e]. As a typical example, Figure 17 shows the structural and electrochemical features of $[Ni(thdtdt)_2]^-$ [71b].

Within the overall molecular chair conformation, the central NiS_4 core is square planar. The monoanion undergoes the reversible reduction to the corresponding dianion, whereas the one-electron oxidation is complicated by electrode adsorption phenomena.

Table 46. Formal electrode potentials (V, *vs.* SCE) for the redox processes exhibited by $[M(thdtdt)_2]^-$ complexes

Complex	$E^{\circ\prime}_{2-/-}$	$E^{\circ\prime}_{-/0}$	Solvent	Reference
$[Ni(thdtdt)_2]^-$	−0.61	+0.27[a]	MeCN	71a
	−0.59	+0.28[a]	MeCN	71b
	−0.59	+0.21	MeCN	77e
	−0.64	+0.23	PhCN	71a
$[Pt(thdtdt)_2]^-$	−0.53	+0.31[a]	MeCN	71a
	−0.59	+0.20	PhCN	71a
$[Cu(thdtdt)_2]^-$	−0.63	+0.45[b]	MeCN	77e
$[Au(pndtdt)_2]^-$	−0.91	+0.46	MeCN	77e

[a] Peak-potential value for processes affected by adsorption; [b] peak-potential value for irreversible processes

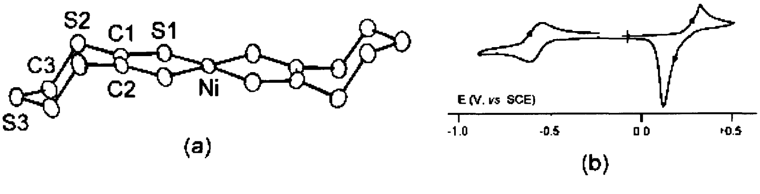


Figure 17. (a) X-Ray structure (average bonding distances: Ni-S = 2.14 Å; S1-C1 = 1.72 Å; C1-C2 = 1.38 Å; C1-S2 = 1.76 Å; S2-C3 = 1.81 Å; C3-S3 = 1.81) and cyclic voltammogram (glassy carbon electrode; MeCN solution; scan rate 0.1 V s^{-1}) (b) of $[Ni(thdtdt)_2]^-$ ($[NBu_4]^+$ cation).

A similar behaviour is displayed by the other metal complexes, Table 46.

The crystal structures of $[Pt(thdtdt)_2]^-$ [71a], $[Cu(thdtdt)_2]^-$ [77e] and $[Au(thdtdt)_2]^-$ [77e] are known.

4 1,2-DITHIOLATES FORMING LATERAL MULTIPLE RINGS

4.1 1,2-Dithiolates forming bicyclic lateral rings

4.1.1 nordt Complexes

4.1.1.1 Bis(nordt) complexes

Figure 18 illustrates the square planar geometry of the NiS_4 core of the dianion $[Ni(nordt)_2]^{2-}$ and its electrochemical behaviour [108].

It reversibly undergoes oxidation to the corresponding monoanion ($E^{o\prime}_{2-/-}$ = −0.76 V, *vs.* SCE). Given the low redox activity of the saturated dithiolene carbon-carbon bond (see Section 2.1.1), it seems plausible to assume that the electron removal involves the Ni(II)/Ni(III) process.

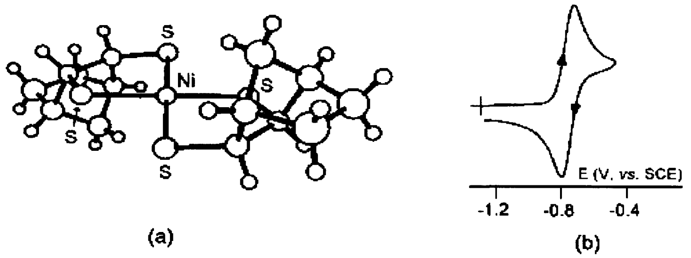


Figure 18. X-Ray structure (a) and cyclic voltammogram (dmf solution) (b) of $[Ni(nordt)_2]^{2-}$ ($[Li]^+$ cation). Selected bond lengths: Ni-S = 2.18 Å; S-C = 1.83 Å; $C\text{-}C_{(inner\ ring)}$ = 1.55 Å.

4.2 1,2-Dithiolates forming lateral fused rings

4.2.1 bdtodt, bdttdt Complexes

4.2.1.1 Bis(bdtodt) and bis(bdttdt) complexes

Brief electrochemical data are available for $[Ni(bdtodt)_2]^-$ and $[Ni(bdttdt)_2]^-$, Table 47, but the pertinent crystallographic data are lacking.

As rather common, the monoanions reversibly reduce to the corresponding dianions, whereas the stability of the neutral congeners is doubted.

Table 47. Formal electrode potentials (V, *vs.* SCE) for the redox processes exhibited by $[Ni(bdtodt)_2]^-$ and $[Ni(bdttdt)_2]^-$

Complex	$E^{o'}_{2-/-}$	$E^{o'}_{-/0}$	Solvent	Reference
$[Ni(bdtodt)_2]^-$	−0.37	+0.32[a]	CH_2Cl_2	109a
	−0.36	0.0[b]	MeCN	109b
$[Ni(bdttdt)_2]^-$	−0.30	+0.26[a]	CH_2Cl_2	109a

[a] Peak-potential value for processes affected by adsorption; [b] peak-potential value for irreversible processes

4.2.2 nqdt Complexes

4.2.2.1 Bis(nqdt) complexes

A structural and electrochemical study on a wide series of $[M(nqdt)_2]^{n-}$ complexes (M = Mn, Fe, Ni, Cu, Zn, Pd, Pt) has been reported [110]. The concomitant presence of the two redox-active quinone and dithiolate centers in the present ligand increases the difficulty to assign the nature of the pertinent redox changes. In fact, most complexes exhibit four redox processes, which, even if not clearly attributed, are thought to be ligand centered, Table 48.

Table 48. Formal electrode potentials (V, *vs.* Ag/AgCl) for the redox processes exhibited by $[M(nqdt)_2]^{n-}$ in MeCN solution

Complex	$E^{o'}_{1st}$	$E^{o'}_{2nd}$	$E^{o'}_{3rd}$	$E^{o'}_{4th}$
$[Mn(nqdt)_2]^{2-}$	−0.28	−0.68	−0.95	−1.47
$[Fe(nqdt)_2]^{2-}$	−0.30	−0.69	-	−1.49
$[Ni(nqdt)_2]^{2-}$	−0.28	−0.65	−0.95	−1.44
$[Cu(nqdt)_2]^-$	−0.29	−0.68	-	−1.47
$[Zn(nqdt)_2]^{2-}$	−0.27	−0.67	−0.94	−1.44
$[Pd(nqdt)_2]^{2-}$	−0.28	−0.54	−1.22	-
$[Pt(nqdt)_2]^{2-}$	−0.29	−0.67	-	−1.41

The structural parameters of the couple $[Ni(nqdt)_2]^{2-/-}$ point out that also in this case the extra electron looks like delocalised on the metal-ligand frame, in that passing from the dianion to the monoanion the Ni-S and C=C distances shorten (by 0.03 Å and 0.02 Å, respectively), whereas the S-C distance remains unvaried. It is however noted that, unexpectedly, the C-O length of the quinoidal function does not change appreciably (from 1.21 Å to 1.22 Å) [110].

X-Ray crystal data are also available for $[Cu(nqdt)_2]^-$ and $[Pd(nqdt)_2]^{2-}$ [110].

4.2.3 qdt Complexes

4.2.3.1 Bis(qdt) complexes

The electrochemical behaviour of the dianions $[M(qdt)_2]^{2-}$ (M = Co, Ni, Cu) shows that they are able to undergo reversibly the oxidation to the corresponding monoanions, Table 49.

The crystallographic data for the square planar redox couple $[Cu(qdt)_2]^{2-/-}$ show that, passing from the dianion to the monoanion, the Cu-S and C=C bond lengths shorten by 0.07 Å and 0.02 Å, respectively, whereas the S-C and C-N distances are substantially unaltered [111c]. The significant shortening of the Cu-S distance upon electron removal suggests that the electron transfer is essentially metal centred (*i.e.* it corresponds to the Cu(II)/Cu(III) process).

The X-ray structure of $[Ni(qdt)_2]^{2-}$ is available [111d].

Table 49. Formal electrode potentials (V, *vs.* SCE) for the redox processes exhibited by $[M(qdt)_2]^{2-}$

Complex	$E^{o'}_{2-/-}$	$E^{o'}_{2-/3-}$	Solvent	Reference
$[Co(qdt)_2]^{2-}$	+0.12	-	MeCN	111a
$[Ni(qdt)_2]^{2-}$	+0.12	-	dmf	111b
$[Cu(qdt)_2]^{2-}$	−0.18	−1.28	dmf	111c

4.2.3.2 Tris(qdt) complexes

Apart from minor information on the redox aptitude of $[M(qdt)_3]^{n-}$ (M = Co, n = 3; M = Fe, n = 2) [111a], the study most pertinent to the present review is that

Table 50. Selected bond distances (average values; Å) and twista angle (°) in the couple $[Mo(qdt)_3]^{2-/-}$

Complex	Mo-S	S-C	C=C	C-N	ϕ	Cation	Reference
$[Mo(qdt)_3]^-$	2.39	1.74	1.43	1.32	14.6	$[PPh_4]^+$	112c
$[Mo(qdt)_3]^{2-}$	2.39	1.74	1.44	1.32	4.5	$[PPh_4]^+$	112b

devoted to $[Mo(qdt)_3]^{n-}$ [112]. The dianion $[Mo(qdt)_3]^{2-}$ undergoes, in MeCN solution, either a reversible one-electron oxidation ($E^{o\prime}_{2-/-}$ = –0.19 V, *vs.* Fc/Fc$^+$), or a reversible one-elecron reduction ($E^{o\prime}_{2-/3-}$ = –1.70 V) [112a,b].

The crystal structures of the couple $[Mo(qdt)_3]^{2-/-}$ substantially show that, upon electron removal, the MoS_6 core passes from a almost perfect to a octahedrally distorted trigonal prism, Table 50.

4.2.4 diotte Complexes

4.2.4.1 Bis(diotte) complexes

Complex $[Ni(diotte)_2]^-$ has been recently prepared [113]. In MeCN solution, it displays a one-electron oxidation, which is affected by electrode adsorption (E_p = +0.42 V, *vs.* AgAgCl), and a reversible one-electron reduction (E°' = –0.56 V). Chemical oxidation (by I_2) affords the neutral $[Ni(diotte)_2]$ [113]. No crystal structures are available.

4.3 1,2-Dithiolates forming lateral tetrathiafulvalene rings

4.3.1 R_2-dtttfdt Complexes

4.3.1.1 Bis(R_2-dtttfdt) complexes

The redox activity of a few complexes of general formula $[M(R_2\text{-dtttfdt})_2]^{n-}$ (M = Co, R = Bu, C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$, n = 1; M = Ni, R = Et, n = 2; M = Cu,

Table 51. Formal electrode potentials (V, *vs.* SCE) for the redox processes exhibited by $[M(R_2\text{-dtttfdt})_2]^{n-}$

Complex	$E^{o\prime}_{2-/-}$	$E^{o\prime}_{-/0}$	Solvent	Ref.
$[Co(Bu_2\text{-dtttfdt})_2]^-$	–0.61	–0.32	thf	114a
$[Co\{(C_6H_{13})_2\text{-dtttfdt}\}_2]^-$	–0.62	–0.26	thf	114a
$[Co\{(C_8H_{17})_2\text{-dtttfdt}\}_2]^-$	–0.56	–0.27	thf	114a
$[Co\{(C_{10}H_{21})_2\text{-dtttfdt}\}_2]^-$	–0.60	–0.27	thf	114a
$[Ni(Et_2\text{-dtttfdt})_2]^{2-}$	–0.45	–0.07[a]	CH_2Cl_2	114b
$[Cu(Me_2\text{-dtttfdt})_2]^-$	+0.25	+0.64	dmf	114c
$[Zn(Me_2\text{-dtttfdt})_2]^{2-}$	+0.15	+0.18	dmf	114c
$[Hg(Et_2\text{-dtttfdt})_2]^{2-}$	–0.04	+0.07[b]	CH_2Cl_2	114d
$[Pt\{(C_{10}H_{21})_2\text{-dtttfdt}\}_2]^{2-}$	–0.03	+0.38[a]	CH_2Cl_2	114e
$[Pt\{(C_{14}H_{29})_2\text{-dtttfdt}\}_2]^{2-}$	–0.25	+0.25	thf	114e
$[Pt\{(C_{14}H_{29})_2\text{-dtttfdt}\}_2]^{2-}$	–0.25	+0.05	thf	114e

[a] Peak-potential value for processes affected by adsorption; [b] followed by further oxidation processes

R = Me, n = 1; M = Zn, R = Me, n = 2; M = Hg, R = Et, n = 2; M = Pt, R = $C_{10}H_{21}$, $C_{14}H_{29}$, $C_{18}H_{37}$, n = 2) has been examined. As usual, they undergo the 2–/–/0 sequence, Table 51.

[Ni(Et_2-dtttfdt)$_2$] (obtained by chemical oxidation of the corresponding dianion) [114a] and [Pt{($C_{10}H_{21}$)$_2$-dtttfdt}$_2$]$^{2-}$ [114d] have a planar geometry, whereas [Hg(Et_2-dtttfdt)$_2$]$^{2-}$ has a tetrahedral geometry [114c].

4.3.2 endtttfdt Complexes

4.3.2.1 Bis(endtttfdt) complexes

[Au(endtttfdt)$_2$]$^-$ shows in dmf solution a quasireversible one-electron oxidation ($E^{\circ\prime}_{-/0}$ = +0.12 V, *vs.* SCE) [115], whereas [Co(endtttfdt)$_2$]$^-$ in thf solution exhibits either a quasireversible reduction ($E^{\circ\prime}_{-/2-}$ = –0.58 V, *vs.* SCE) or a quasireversible oxidation ($E^{\circ\prime}_{-/0}$ = –0.24 V) [114a].

4.3.3 pndtttfdt Complexes

4.3.3.1 Bis(pndtttfdt) complexes

Figure 19 shows the crystal structure of [Ni(pndtttfdt)$_2$]$^-$ [116a].

In MeCN solution, it exhibits the (usual) reversible one-electron reduction ($E^{\circ\prime}_{-/2-}$ = –0.45 V, *vs.* Ag/Ag$^+$) and the reversible one-electron oxidation ($E^{\circ\prime}_{-/0}$ = –0.15 V). As a matter of fact, the one-electron oxidised complex maintains the original planar geometry [116b]. Table 52 compares the bond lengths of the neutral complex with those of the corresponding monoanion.

It is evident that the electron transfer is essentially centred on the ligand.

The dianion [Cu(pndtttfdt)$_2$]$^{2-}$ exhibits a redox behaviour qualitatively similar to that of [Ni(pndtttfdt)$_2$]$^-$ ($E^{\circ\prime}_{-/2-}$ = –0.73 V, $E^{\circ\prime}_{-/0}$ = –0.08 V) [116a], but, at variance with the square planar geometry of this latter, has a tetrahedrally distorted geometry [116a,c].

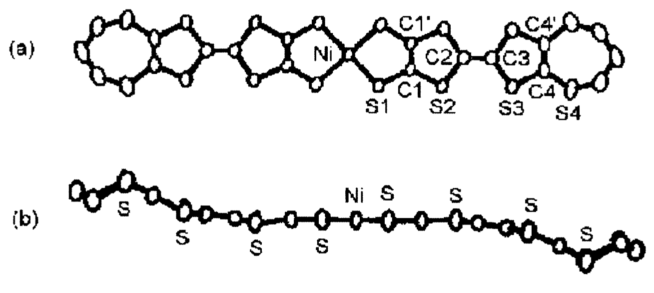


Figure 19. (a) ORTEP drawing and (b) side view of [Ni(pndtttfdt)$_2$]$^-$ ([PPh_4]$^+$ cation).

Table 52. Selected bond distances (average values; Å) in the square planar couple $[Ni(pndtttfdt)_2]^{-/0}$ (atomic labellings are referred to Figure 19)

Complex	Ni-S1	S1-C1	C1=C1'	C2=C3	C4=C4'	Cation	Reference
$[Ni(pndtttfdt)_2]^-$	2.16	1.72	1.34	1.32	1.36	$[PPh_4]^+$	116a
	2.17	1.71	1.36	1.35	1.34	$[NMe_4]^+$	116a,c
$[Ni(pndtttfdt)_2]^0$	2.18	1.73	1.38	1.38	1.34	-	116b

4.3.4 dmttfdt Complexes (originally named "dmdt")

4.3.4.1 Bis(dmttfdt) Complexes

$[Ni(dmttfdt)_2]^{2-}$ undergoes, in MeCN solution, two reversible one-electron oxidations ($E^{\circ\prime}_{2-/-} = -0.79$ V; $E^{\circ\prime}_{-/0} = -0.48$ V, *vs.* Ag/Ag^+) followed by a further irreversible anodic process ($E_p = +0.40$ V) [117]. Both the neutral and the dianionic derivatives have been chemically, but not yet crystallographically, characterised [117].

4.3.5 tmettfdt Complexes (originally named "tmdt")

4.3.5.1 Bis(tmettfdt) Complexes

Like the related $[Ni(dmttfdt)_2]^{2-}$, the dianion $[Ni(tmettfdt)_2]^{2-}$ undergoes, in MeCN solution, two reversible one-electron oxidations ($E^{\circ\prime}_{2-/-} = -0.80$ V; $E^{\circ\prime}_{-/0} = -0.46$ V, *vs.* Ag/Ag^+) followed by a further irreversible anodic process ($E_p = +0.55$ V) [117].

The neutral congener $[Ni(tmettfdt)_2]$ possesses a square planar geometry [118].

5 FINAL REMARKS

A systematic examination of the structural consequences of the redox changes exhibited by the homoleptic, mononuclear metal complexes of a wide variety of dithiolene ligands points out that they do not constitute a homogeneous class of redox active derivatives. In fact, depending upon the overall frame of each dithiolene ligand (in terms of geometrical and inductive effects), the relative electrochemical responses cover the whole range of classical electron transfer processes, *i.e.* essentially metal centered, essentially ligand centered, or metal-ligand centered. This means that too often the multiple redox processes exhibited by metallodithiolenes are quickly solved as ligand (or metal) centred. In reality, the precise and accurate attribution of their nature (if wished) would always need structural and theoretical supports.

ACKNOWLEDGEMENTS

Piero Zanello gratefully acknowledges the financial support of the University of Siena (PAR), which since a long time allows him to carry out multiple research investigations.

ABBREVIATIONS

atedt = 1,2-di(alkylthio)-1,2-ethenedithiolate
bdt = benzene-1,2-dithiolate
bdtodt = 2-oxobenzo[d]-1,3-dithiole-5,6-dithiolate
bdttdt = 2-thionebenzo[d]-1,3-dithiole-5,6-dithiolate
cnedt = 2-cyano-1,2-ethenedithiolate
dcmdtcr = 2-dicyanomethylene-4,5-disulfanylcyclopent-4-ene-1,3-dionate
dcmedt = 1,2-dicarbomethoxy-1,2-ethenedithiolate
dcnedt = 1,2-dicyano-1,2-ethenedithiolate
dcnpzdt = 2,3-dicyano-pyrazine-5,6-dithiolate
dfcdtdt = 2,3-diferrocenyl-1,4-dithiin-5,6-dithiolate
dfcedt = 1,2-diferrocenyl-1,2-ethenedithiolate
dfpndtdt = 2,2-difluoro-1,3-propanediyldithioethylene-1,2-dithiolate
dhdtdt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate
dhtpdt = 2,3-dihydro-4,5-thiophenedithiolate
dibzedt = 1,2-diiminobenzyl-1,2-ethenedithiolate
dichedt = 1,2-diiminocyclohexyl-1,2-ethenedithiolate
diotte = 1,3-dioxolane-tetrathiaethylene
dmedt = 1,2-dimethyl-1,2-ethenedithiolate
dmttfdt = dimethyltetrathiafulvalenedithiolate
dodt = 1,2-dioxo-1,2-dithiolate
doedt = 2-(1',3'-dithiole-2'-one)-1,2-ethenedithiolate
dphdtdt = 5,6-diphenyl-1,4-dithiin-2,3-dithiolate
dphedt = 1,2-diphenyl-1,2-ethenedithiolate
dt = ethane-1,2-dithiolate
dtcr = dithiocroconate = 4,5-disulfanylcyclopent-4-ene-1,2,3-trionate
dtdt = 1,4-dithiin-2,3-dithiolate
dtodt = 1,3-dithiole-2-one-4,5-dithiolate
dtsq = dithiosquarate

dttdt = 1,3-dithiole-2-thione-4,5-dithiolate
edt = ethene-1,2-dithiolate
endtttfdt = ethylenedithiotetrathiafulvalenedithiolate
fcdtdt = 2-ferrocenyl-1,4-dithiin-5,6-dithiolate
fcedt = ferrocenyl-1,2-ethenedithiolate
Hedt = unsubstituted ethene-1,2-dithiolate
idttdt = 1,2-dithiole-3-thione-4,5-dithiolate
mdtdt = 1,3-dithiole-4,5-dithiolate
mehdtdt = 5-methyl-6-hydro-1,4-dithiin-2,3-dithiolate
mpndtdt = 6,7-dihydro-6-methylene-5H-1,4-dithiepine-2,3-dithiolate
mtadt = mercaptothioacetate-1,2-dithiolate
nordt = norbornane-1,2-dithiolate
nqdt = naphthoquinonedithiolate
odtdt = 1,4-dithia-6-oxa-2,3-dithiolate = 1,2,6-oxadithiepin-4,5-dithiolate
phedt = 2-phenyl-1,2-ethenedithiolate
phhdtdt = 5-phenyl-6-hydro-1,4-dithiin-2,3-dithiolate
pndtdt = 1,3-propanediyldithioethylene-1,2-dithiolate = 6,7-dihydro-5H-1,4-dithiepine-2,3-dithiolate
pndtttfdt = propylenedithiotetrathiafulvalene-dithiolate
pyedt = pyridin-X-yl-1,2-ethenedithiolate (X = 2, 3, 4)
qdt = quinoxaline-2,3-dithiolate
qedt = quinoxalin-2-yl-1,2-ethenedithiolate
R_2-dtttfdt = 2,3-dialkylthiotetrathiafulvalene-6,7-dithiolate
R'-hdtdt = 5-substituted-6-hydro-1,4-dithiin-2,3-dithiolate
R-phedt = 1-substituted-2-phenyl-1,2-ethenedithiolate
R_2-pipdt = N,N'-dialkyl-piperazine-2,3-dithione
R_2-timdt = 1,3-dialkylimidazoline-2,4,5-trithionate
tfmedt = 1,2-di(trifluoromethyl)-1,2-ethenedithiolate
thdtdt = 5,7-dihydro-1,4,6-trithiin-2,3-dithiolate
thedt = 1,2-di(2-thienyl)-1,2-ethenedithiolate
tmettfdt = trimethylenetetrathiafulvalenedithiolate
tpdt = 3,4-thiophenedithiolate
ttpdt = 3,4-terthiophenedithiolate
X-bdt = benzene-substituted-1,2-dithiolate

REFERENCES

1. Clark, R.E.D. *Analyst, 60*, 242 (1936).
2. (a) Gray, H.B. *Transition Met.Chem., 1*, 240 (1965); (b) McCleverty, J.A. *Prog.Inorg.Chem., 10*, 49 (1968); (c) Schrauzer, G.N. *Acc.Chem.Res., 2*, 72 (1969); (d) Hoyer, E.; Dietzsch, W.; Schroth, W. *Z.Chem. 11*, 41 (1971); (e) Burns, R.P.; McAuliffe, C.A. *Adv.Inorg.Chem., 22*, 303 (1979); (f) Mueller-Westerhoff, U.T.; Vance, B. in "Comprehensive Coordination Chemistry", Pergamon Press, Oxford, Vol. 2, 1987, 595-631; (g) Clemenson, P.I. *Coord.Chem.Rev., 106*, 171 (1990); (h) Mueller-Westerhoff, U.T.; Vance, B.; Yoon, D.I. *Tetrahedron, 47*, 909 (1991); (i) Cassoux, P.; Valade, L.; Kobayashi, H.; Kobayashi, A.; Clark, R.A.; Underhill, A.E. *Coord.Chem.Rev., 110*, 115 (1991); (l) Olk, R.-M.; Olk, B.; Dietzsch, W.; Kirmse, R.; Hoyer, E. *Coord.Chem.Rev., 117*, 99 (1992); (m) Fourmigué, M. *Coord.Chem.Rev., 178-180*, 823 (1998); (n) Pullen, A.E.; Olk, R.-M. *Coord.Chem.Rev., 188*, 211 (1999); (o) Pilato, R.S.; Stiefel, E.I.; in "Bioinorganic Catalysis", Reedijk, J.; Bouwman, E.; Eds.; Marcel Dekker, New York, 1999, 81-152; (p) Robertson, N.; Cronin, L. *Coord.Chem.Rev., 227*, 93 (2002).
3. Ward M.D.; McCleverty, J.A. *J.Chem.Soc., Dalton Trans.*, 275 (2002).
4. (a) Costa, T; Dorfman, J.R.; Hagen, K.S.; Holm, R.H. *Inorg.Chem., 22*, 4091 (1983); (b) Dorfman, J.R.; Rao, Ch.P.; Holm, R.H. *Inorg.Chem., 24*, 453 (1985); (c) Rao, Ch.P.; Dorfman, J.R.; Holm, R.H. *Inorg.Chem., 25*, 428 (1986); (d) Snyder, B.S.; Rao, Ch.P.; Holm, R.H. *Aust. J.Chem. 39*, 963 (1986).
5. (a) Szeymies, D.; Krebs, B.; Henkel, G. *Angew.Chem.Int.Ed.Engl., 23*, 804 (1984); (b) Money, J.A.; Huffman, J.C.; Christou, G. *Inorg.Chem., 24*, 3297 (1985); (c) Wiggins, R.W.; Huffman, J.C.; Christou, G. *J.Chem.Soc., Chem.Commun.*, 1313 (1983).
6. (a) Davison, A.; Orvig, C.; Trop, H.S.; Sohn, M.; DePamphilis, B.V.; Jones, A.G. *Inorg.Chem., 19*, 1988 (1980); (b) Blower, P.J.; Dilworth, J.R.; Hutchinson, J.P.; Zubieta, J.A. *Inorg.Chim.Acta, 65*, L225 (1982); (c) Smith, J.E.; Byrne, E.F.; Cotton, F.A.; Sekutowski, J.C. *J.Am.Chem.Soc., 100*, 5571 (1978);.
7. Tatsumi, K.; Sekiguchi, Y.; Nakamura, A.; Cramer, R.E.; Rupp, J.J. *Angew.Chem.Int.Ed.Engl., 25*, 86 (1986).
8. Gama, V; Belo, D; Rabaça S.; Santos, I.C.; Alves, H.; Waerenborgh, J.C.; Duarte, M.T.; Henriques, R.T. *Eur.J.Inorg.Chem.*, 2101 (2000).
9. Hoyer, E.; Dietzsch, W.; Hennig, H.; Schroth, W. *Chem.Ber., 102*, 603 (1969).
10. Herman,Z.S.; Kirchner,R.F.; Loew,G.H.; Mueller-Westerhoff, U.T.; Nazzal, A; Zerner, M.C. *Inorg.Chem. 21*, 46 (1982).
11. Browall, K.W.; Bursch, T.; Interrante, L.V.; Kasper, J.S. *Inorg.Chem., 11*, 1800 (1972).
12. Donahue, J.P.; Goldsmith, C.R.; Nadiminti, U.; Holm, R.H. *J.Am.Chem.Soc., 120*, 12869 (1998).
13. Davies, E.S.; Beddoes, R.L.; Collison, D.; Dinsmore, A.; Docrat, A.; Joule, J.A.; Wilson, C.R.; Garner, C.D. *J.Chem.Soc., Dalton Trans.*, 3985 (1997)
14. Fourmigué, M.; Bertran, J.N. *Chem.Commun.*, 2111 (2000).
15. Keefer, C.E.; Purrington, S.T.; Bereman, R.D.; Boyle, P.D. *Inorg.Chem., 38*, 5437 (1999).

16. Wilkes, S.B.; Butler, I.R.; Underhill, A.E.; Kobayashi, A.; Kobayashi, H. *J.Chem.Soc., Chem.Commun.*, 53 (1994).
17. B.S.Lim, D.V.Fomitchev, and R.H.Holm, *Inorg.Chem.*, *40*, 4257 (2001).
18. (a) Lim, B.S.; Donahue, J.P.; Holm, R.H. *Inorg.Chem.*, *39*, 263 (2000); (b) Goddard, C.A.; Holm, R.H. *Inorg.Chem.*, *38*, 5389 (1999).
19. Fomitchev, D.V., Lim, B.S.; Holm, R.H. *Inorg.Chem.*, *40*, 645 (2001).
20. (a) Bowmaker, G.A.; Boyd, P.D.W.; Campbell, G.K. *Inorg.Chem.*, *22*, 1208 (1983); (b) Hill, C.A.S.; Charlton, A.; Underhill, A.E.; Malik, K.M.A.; Hursthouse, M.B.; Karaulov, A.I.; Oliver, S.N.; Kershaw, S.V. *J.Chem.Soc., Dalton.Trans.*, 587 (1995); (c) Sung, K.-M.; Holm, R.H. *J.Am.Chem.Soc.*, *124*, 4312 (2002).
21. (a) Mahadevan, C.; Seshasayee, M.; Kuppusamy, P.; Manoharan, P.T. *J.Cryst.Spectros.Res.*, *14*, 179 (1984); (b) Rajalakshmi, A.; Radha, A.; Seshasayee, M.; Kuppusamy, P.; Manoharan, P.T. *Z.Kristallogr.*, 159 (1988).
22. Koz'min, P.A.; Larina, T.B. *Koord.Khim. (Engl.Trans.)*, *5*, 464 (1979).
23. Megnamisi-Belombe, M.; Nuber, B. *Bull.Chem.Soc.Jpn.*, *62*, 4092 (1989).
24. (a) Wing, R.M.; Schlupp, R.L. *Inorg.Chem.*, *9*, 471 (1970); (b) Singhabhandhu, A.; Robinson, P.D.; Fang, J.H.; Geiger, W.E. *Inorg.Chem.*, *14*, 318 (1975); (c) Miller, J.S.; Calabrese, J.C.; Epstein, A.J. *Inorg.Chem.*, *28*, 4230 (1989).
25. Schmitt, R.D.; Wing, R.M.; Maki, A.H. *J.Am.Chem.Soc.*, *91*, 4394 (1969).
26. Geiger, W.E.; Mines, T.E.; Senftleber, F.C. *Inorg.Chem.*, *14*, 2141 (1975).
27. Wang, K.; McConnachie, J.M.; Stiefel, E.I. *Inorg.Chem.*, *38*, 4334 (1999).
28. Heuer, W.B.; Mountford, P.; Green, M.L.H.; Bott, S.G.; O'Hare, D.; Miller, S.J. *Chem.Mater.*, *2*, 764 (1990).
29. (a) Brown, R.K.; Bergendahl, T.J.; Wood, J.S.; Waters, J.H. *Inorg.Chim.Acta*, *68*, 79 (1983); (b) Baudron, S.A.; Batail, P. *Acta Cryst.*, *C58*, m575 (2002).
30. (a) Coucouvanis, D.; Hadjikyriacou, A.; Toupadakis, A.; Koo, S.-M.; Ileperuma, O.; Draganjac, M.; Salifoglou, A. *Inorg.Chem.*, *30*, 754 (1991); (b) Bandoli, G.; Nicolini, M; Mazzi, U.; Spies, H.; Munze, R. *Transition Met.Chem.*, *9*, 127 (1984); (c) Draganjac, M.; Coucouvanis, D. *J.Am.Chem.Soc.*, *105*, 139 (1983).
31. Beswick, C.L.; Terroba, R.; Greaney, M.A.; Stiefel, E.I. *J.Am.Chem.Soc.*, *124*, 9664 (2002).
32. Kean, C.L.; Pickup. P.G. *Chem.Commun.*, 815 (2001).
33. (a) Keller, C.; Walther, D.; Reinhold, J.; Hoyer, E. *Z.Chem.*, *11*, 410 (1988); (b) Vance,T.; Bereman, R.D. *Inorg.Chim.Acta*, *149*, 229 (1988).
34. (a) Charlton, A.; Hill, C.A.S.; Underhill, A.E.; Malik, K.M.A.; Hursthouse, M.B.; Karaulov, A.I.; Møller, J. *J.Mater.Chem.*, *4*, 1861 (1994); (b) Charlton, A.; Kilburn, J.D.; Underhill, A.E.; Webster, M. *Acta Cryst. C52*, 2441 (1996).
35. Mueller-Westerhoff, U.T.; Yoon, D.I.; Plourde, K. *Mol.Cryst.Liq.Cryst.*, *183*, 291 (1990)
36. Barrière, F.; Camire, N.; Geiger, W.E.; Mueller-Westerhoff, U.T.; Sanders, R. *J.Am.Chem.Soc.*, *124*, 7262 (2002).
37. (a) Kisch, H.; Nüsslein, F.; Zenn, I. *Z.Anorg.Allg.Chem.*, *600*, 67 (1991); (b) Persaud, L.; Langford, C.H. *Inorg.Chem.*, *24*, 3562 (1985); (c) Senftleber, F.C.; Geiger, W.E. *J.Am.Chem.Soc.*, *97*, 5018 (1975); (d) Fitzmaurice, J.C.; Slawin, A.M.Z.; Williams, D.J.; Woolins, J.D.; Lindsay, A.J. *Polyhedron*, *9*, 1561 (1990);

38. (a) Eisenberg, R.; Ibers, J.A. *Inorg.Chem.*, *4*, 605 (1965); (b) Eisenberg, R.; Ibers, J.A.; Clark, R.J.H.; Gray, H.B. *J.Am.Chem.Soc.*, *86*, 113 (1964); (c) Hove, M.J.; Hoffman, B.M.; Ibers, J.A. *J.Chem.Phys.*, *56*, 3490 (1972); (d) Dance, I.G.; Solstad, P.J.; Calabrese, J.C. *Inorg.Chem.*, *12*, 2161 (1973); (e) Coucouvanis, D.; Baenziger, N.C.; Johnson, S.M. *Inorg.Chem.*, *13*, 1191 (1974); (f) Kobayashi, A.; Sasaki, Y. *Bull.Chem.Soc. Jpn.*, *50*, 2650 (1977); (g) Endres, H.; Keller, H.J.; Moroni, W.; Nöthe, D. *Acta Cryst.*, *B35*, 353 (1979); (h) Kisch, H.; Fernández, A.; Wakatsuki, Y.; Yamazaki, H. *Z.Naturforsch.*, *40B*, 292 (1985); (i) Schmauch, G.; Knoch, F.; Kisch, H. *Chem.Ber.*, *127*, 287 (1994); (l) Handrosch, C.; Dinnebier, R.; Bondarenko, G.; Bothe, E.; Heineman, F.; Kisch, H. *Eur.J.Inorg.Chem.*, 1259 (1999); (m) Yang, L.-F.; Peng, Z.-H.; Cheng, G.-Z.; Peng, S.-M. *Polyhedron*, *22*, 3547 (2003).
39. (a) Fritchie, C.J. *Acta Cryst.*, *20*, 107 (1966); (b) Manoharan, P.T.; Noordik, J.H.; de Boer, E.; Keijzers, C.P. *J.Chem.Phys.*, *74*, 1980 (1981); (c) Ramakrishna, B.L.; Manoharan, P.T. *Inorg.Chem.*, *22*, 2113 (1983); (d) Mahadevan, C.; Seshasayee, M.; Murthy, B.V.R.; Kuppusamy, P.; Manoharan, P.T. *Acta Cryst.*, *C39*, 1335 (1983); (e) Brunn, K.; Endres, H.; Weiss, J. *Z.Naturforsch.*, *42B*, 1222 (1987); (f) Hobi, M.; Zürcher, S.; Gramlich, V.; Burckhardt, U.; Mensing, C.; Spahr, M.; Togni, A. *Organometallics*, *15*, 5342 (1996); (g) Zürcher, S.; Gramlich, V.; von Arx, D.; Togni, A *Inorg.Chem.*, *37*, 4015 (1998); (h) Robertson, N.; Bergemann,C.; Becker, H.; Agarwal, P.; Julian, S.R.; Friend, R.H.; Hatton, N.J.; Underhill, A.E.; Kobayashi, A. *J.Mater.Chem.*, *9*, 1713 (1999); (i) Ribera, E.; Rovira, C.; Veciana, J.; Tarrés, J.; Canadell, E.; Rousseau, R.; Molins, E.; Mas, M.; Schoeffel, J.-P.; Pouget, J.-P.; Morgado, J.; Henriques, R.T.; Almeida, M. *Chem.Eur.J.*, *5*, 2025 (1999); (l) Robertson, N.; Roehrs, S.; Akutagawa, T.; Nakamura, T.; Underhill, A.E. *J.Chem.Res.*, *(S)* 54 (1999); (m) Ren, X.; Lu, C.; Liu, Y.; Zhu, H.; Li, H.; Hu, C.; Meng, Q. *Transition Met.Chem.* *26*, 136 (2001); (n) Ren, X-M.; Li, H.-F.; Wu, P.-H.; Meng, Q.-J. *Acta Cryst.*, *C57*, 1022 (2001); (o) Xie, J.; Ren, X.; Song, Y.; Zou, Y.; Meng, Q. *J.Chem.Soc., Dalton Trans.*, 2868 (2002); (p) Xie, J.; Ren, X.; Song, Y.; Zhang, W.; Liu, W.; He, C.; Meng, Q. *Chem.Commun.*, 2346 (2002); (q) Ren, X.; Chen, Y.; He, C.; Gao, S. *J.Chem.Soc., Dalton Trans.*, 3915 (2002); (r) Xie, J.; Ren, X.; Gao, S.; Zang, W.; Liu, W.; Meng, Q.; Yao, Y. *Eur.J.Inorg.Chem.*, 2393 (2003).
40. (a) Mines, T.E.; Geiger, W.E. *Inorg.Chem.*, *12*, 1189 (1973); (b) Geiger, W.E.; Allen, C.S.; Mines, T.E.; Senftleber, F.C. *Inorg.Chem.*, *16*, 2003 (1977).
41. (a) Lemke, M.; Knoch, F.; Kisch, H. *Acta Cryst.*, *C49*, 1630 (1993); (b) Batsanov, A.S.; Moore, A.J.; Robertson, N.; Green, A.; Bryce, M.R.; Howard, J.A.K.; Underhill, A.E. *J.Mater.Chem.*, *7*, 387 (1997); (c) Bois, H.; Connelly, N.G.; Crossley, J.G.; Guillorit, J.-C.; Lewis, G.R.; Orpen, G.; Thornton, P. *J.Chem.Soc., Dalton Trans.*, 2833 (1998).
42. (a) Domingos, A.; Henriques, R.T.; Gama, V.; Almeida, M.; Vieira, A.L.; Alcacer, L. *Synth.Met.*, *27*, B411 (1988); (b) Hursthouse, M.B.; Short, R.L.; Clemenson, P.I.; Underhill, A.E. *J.Chem.Soc., Dalton Trans.*, 67 (1989).
43. (a) Güntner, W.; Gliemann, G.; Klement, U.; Zabel, M. *Inorg.Chim.Acta*, *165*, 51 (1989); (b) Clegg, W.; Birkby, S.L.; Banister, A.J.; Rawson, J.M.; Wait, S.T.; Rizkallah, P.; Harding, M.M.; Blake, A.J. *Acta Cryst.*, *C50*, 28 (1994); (c) Bigoli,

F.; Deplano, P.; Mercuri, M.L.; Pellinghelli, M.A.; Pilia, L.; Pintus, G.; Serpe, A.; Trogu, E.F. *Inorg.Chem.*, *41*, 5241 (2002); (d) Bremi, J.; Gramlich, V.; Caseri, W.; Smith, P. *Inorg.Chim.Acta*, *322*, 23 (2001).

44. (a) Ahmad, M.M.; Turner, D.J.; Underhill, A.E.; Kobayashi, A.; Sasaki, Y.; Kobayashi, H. *J.Chem.Soc., Dalton Trans.*, 1759 (1984); (b) Clemenson, P.I.; Underhill, A.E.; Hursthouse, M.B.; Short, R.L. *J.Chem.Soc., Dalton Trans.*, 61 (1989); (c) Bremi, J.; d'Agostino, E.; Gramlich, V.; Caseri, W.; Smith, P. *Inorg.Chim.Acta*, *335*, 15 (2002).
45. Forrester, J.D.; Zalkin, A.; Templeton, D.H. *Inorg.Chem.*, *3*, 1507 (1964).
46. (a) Plumlee, K.W.; Hoffman, B.M.; Ratjack, M.T.; Kannewurf, R.C. *Solid State Commun.*, *15*, 1651 (1974); (b) Plumlee, K.W.; Hoffman, B.M.; Ibers, J.A. *J.Chem.Phys.*, *63*, 1926 (1975); (c) Snaathorst, D.; Doesburg, H.M.; Perenboom, J.A.A.; Keijzers, C.P. *Inorg.Chem.*, *20*, 2526 (1981); (d) Kuppusamy, P.; Ramakrishna, B.L.; Manoharan, P.T. *Inorg.Chem.*, *23*, 3886 (1984); (e) Mahadevan, C.; Seshasayee, M. *J.Cryst.Spectrosc.Res.*, *14*, 215 (1984); (f) Fettouhi.M.; Ouahab, L.; Hagiwara, M.; Codjovi, E.; Kahn, O.; Constant-Machado, H.; Varret, F. *Inorg.Chem.*, *34*, 4152 (1995).
47. (a) Stach, J.; Kirmse, R.; Sieler, J.; Abram, U.; Dietzsch, W.; Böttcher, R.; Hansen, L.K.; Vergoossen, H.; Gribnau, M.C.M.; Keijzers, C.P. *Inorg.Chem.*, *25*, 1369 (1986); (b) Lahner, S.; Wakatsuki, Y.; Kish, H. *Chem.Ber.*, *120*, 1011 (1987).
48. Noordik, J.H.; Beurskens, P.T. *J.Cryst.Mol.Struct.*, *1*, 339 (1971).
49. Vlček, Jr.,A.; Vlček, A.,A. *J.Electroanal.Chem.*, *125*, 481 (1981)
50. (a) Forrester, J.D.; Zalkin, A.; Templeton, D.H. *Inorg.Chem.*, *3*, 1500 (1964); (b) Schmauch, G.; Knoch, F.; Kisch, H. *Chem.Ber.*, *128*, 303 (1995); (c) Schmauch, G.; Chihara, T.; Wakatsuki, Y.; Hagiwara, M.; Kisch, H. *Bull.Chem.Soc.Jpn.*, *69*, 2573 (1996).
51. Götz, B.; Knoch, F.; Kisch, H. *Chem.Ber.*, *129*, 33 (1996).
52. Das, S.K.; Biswas, D.; Maiti, R.; Sarkar, S. *J.Am.Chem.Soc.*, *118*, 1387 (1996).
53. (a) McCleverty, J.A.; Locke, J.; Ratcliff, B.; Wharton, E.J. *Inorg.Chim.Acta*, *3*, 283 (1969); (b) Das, S.K.; Chaudhury, P.K.; Biswas, D.; Sarkar, S. *J.Am.Chem.Soc.*, *116*, 9061 (1994).
54. Stiefel, E.I.; Bennett, L.E., Dori, Z.; Crawford, T.H.; Simo, C.; Gray, H.B. *Inorg.Chem.*, *9*, 281 (1970).
55. (a) Sequeira, A.; Bernal, I. *J.Cryst.Mol.Struct.*, *3*, 157 (1973); (b) Stiefel, E.I.; Dori, Z.; Gray, H.B. *J.Am.Chem.Soc.*, *89*, 3353 (1967); (c) Brown, G.F.; Stiefel, E.I. *Inorg.Chem.*, *12*, 2140 (1973).
56. Lewis, G.R.; Dance, I. *J.Chem.Soc., Dalton Trans.*, 3176 (2000).
57. (a) Maiti, R.; Shang, M.; Lappin, A.G. *Chem.Commun.*, 2349 (1999); (b) Maiti, R.; Shang, M.; Lappin, A.G. *J.Chem.Soc., Dalton Trans.*, 244 (2002).
58. Antolini, L.; Fabretti, A.C.; Franchini, G.; Menabue, L.; Pellacani, G.C.; Desseyen, H.O.; Dommisse, R.; Hofmans, H.C. *J.Chem.Soc., Dalton Trans.*, 1921 (1987).
59. DePamphilis, B.V., Jones, A.G., Davis, M.A.; Davison, A. *J.Am.Chem.Soc.*, *100*, 5570 (1978).
60. (a) Coucouvanis, D.; Baenziger, N.C.; Johnson, S.M. *J.Am.Chem.Soc.*, *95*, 3875 (1973); (b) Bellitto, C.; Bonamico, M.; Fares, V.; Imperatori, P.; Patrizio, S.

J.Chem.Soc., Dalton Trans., 719 (1989); (c) Golič, L.; Bulc, N.; Dietzsch, W. *Acta Cryst., C42*, 811 (1986); (d) Imamura, T.; Ryan, M.; Gordon, G.; Coucouvanis, D. *J.Am.Chem.Soc., 106*, 984 (1984); (e) Knatzidis, M.G.; Baenziger, N.C.; Coucouvanis, D. *Inorg.Chem., 24*, 2680 (1985); (f) Mennemann, K.; Mattes, R. J.Chem.Res. (S), 102 (1979); (g) Mattes, R.; Weber, H. *Z.Anorg.Allg.Chem., 474*, 216 (1981); (h) Butler, K.R.; Snow, M.R. *Inorg.Nucl.Chem.Letters, 8*, 541 (1972).

61. (a) Coucouvanis, D.; Hollander, F.J.; West, R.; Eggerding, D. *J.Am.Chem.Soc., 96*, 3006 (1974); (b) Coucouvanis, D.; Holah, D.G.; Hollander, F.J. *Inorg.Chem., 14*, 2657 (1975); (c) Bellitto, C.; Bonamico, M.; Fares, V.; Serino, P. *Inorg.Chem., 35*, 4070 (1996); (d) Bonnet, J.-J.; Cassoux, P.; Castan, P.; Laurent, J.-P.; Soules, R. *Mol.Cryst.Liq.Cryst., 142*, 113 (1987); (e) Arrizabalaga, Ph.; Bernardinelli, G.; Geoffroy, M.; Castan, P. *Inorg.Chim.Acta, 154*, 35 (1988); (f) Arrizabalaga, Ph.; Bernardinelli, G.; Castan, P.; Geoffroy, M.; Soules, R. *C.R.Acad.Sc.Paris* Série II, 559 (1987).
62. (a) Heuer, W.B.; Pearson, W.H. *J.Chem.Soc., Dalton Trans.*, 3507 (1996); (b) Heuer, W.B.; Pearson, W.H. *Polyhedron*, 15, 2199 (1996).
63. Venkatalakshmi, N.; Varghese, B.; Lalitha, S.; Williams, R.F.X.; Manoharan, P.T. *J.Am.Chem.Soc., 111*, 5748 (1989).
64. Belo, D.; Alves, H.; Lopes, E.B.; Duarte, M.T.; Gama, V.; Henriques, R.T.; Almeida, M.; Pérez-Benítez, A.; Rovira, C.; Veciana, J. *Chem.Eur.J., 7*, 511 (2001).
65. Pozo-Gonzalo, C.; Berridge, R.; Skabara, P.J.; Cerrada, E.; Laguna, M.; Coles, S.J.; Hursthouse, M.B. *Chem.Commun.*, 2408 (2002).
66. Veldhuizen, Y.S.J.; Veldman, N.; Spek, A.L.; Cassoux, P.; Carlier, R.; Mulder, M.J.J.; Haasnoot, J.G.; Reedijk, J *J.Chem.Soc., Dalton Trans.*, 2989 (1998).
67. (a) Sun, S.Q.; Zhang, B.; Wu, P.J.; Zhu, D.B. *J.Chem.Soc., Dalton Trans.*, 227 (1997); (b) Olk, R.-M.; Dietzsch, W.; Köhler, K.; Kirmse, R.; Reinhold, J.; Hoyer, E.; Golič, L.; Olk, B. *Z.Anorg.Allg.Chem. 567*, 131 (1988); (c) Liu, S.-G.; Wu, P.-J.; Li, Y.-F.; Zhu, D.-B. *Phosphorus, Sulfur and Silicon, 90*, 219 (1994); (d) Liu, S.-G.; Liu, Y.-Q.; Liu, S.-H.; Zhu, D.-B. *Synth. Met., 74*, 137 (1995); (e) Vicente, R.; Ribas, J.; Zanchini, C.; Gatteschi, D.; Legros, J.-P., Faulmann, C.; Cassoux, P. *Z.Naturforsch., 43b*, 1137 (1988); (f) Fettouhi, M.; Ouahab, L.; Codjovi, E.; Kahn, O. *Mol.Cryst.Liq.Cryst., 273*, 29 (1995); (g) Faulmann, G.; Rivière, E.; Dorbes, S.; Senocq, F.; Coronado, E.; Cassoux, P. *Eur.J.Inorg.Chem.*, 2393 (2003).
68. Yang, X.; Freeman, G.K.W.; Rauchfuss, T.B.; Wilson, S.R. *Inorg.Chem., 30*, 3034 (1991).
69. Tanaka, S.; Matsubayashi, G. *J.Chem.Soc., Dalton Trans.*, 2837 (1992).
70. Matsuda, F.; Tamura, H.; Matsubayashi, G. *Inorg.Chim.Acta, 235*, 239 (1999).
71. (a) Faulmann, C.; Errami, A.; Donnadieu, B.; Malfant, I.; Legros, J.-P.; Bowlas, C.; Cassoux, P.; Rovira, C.; Canadell, E. *Inorg.Chem., 35*, 3856 (1996); (b) Kato, R.; Kobayashi, H.; Kobayashi, A.; Sasaki, Y. *Bull.Chem.Soc.Jpn., 59*, 627 (1986); (c) Tommasino, J.-B.; Pomarede, B.; Medus, D.; de Montauzon, D.; Cassoux, P. *Mol.Cryst.Liq.Cryst., 237*, 445 (1993); (d) Nunn, I.; Eisen, B.; Benedix, R.; Kish, H. *Inorg.Chem., 33*, 5079 (1994); (e) Olk, R.-M.; Röhr, A.; Sieler, J.; Köhler, K.; Kirmse, R.; Dietzsch, W.; Hoyer, E.; Olk, B. *Z.Anorg.Allg.Chem., 577*, 206 (1989);

72. (a) Lindqvist, O.; Sjölin, L.; Sieler, J.; Steimecke, G.; Hoyer, E. *Acta Chem.Scand.*, *A33*, 445 (1979); (b) Steimecke, G.; Sieler, H.-J.; Kirmse, R.; Hoyer, E. *Phosphorus Sulfur*, *7*, 49 (1979); (c) Kushch, N.; Faulmann, C.; Cassoux, P.; Valade, L.; Malfant, I.; Legros, J.-P.; Bowlas, C.; Errami, A.; Kobayashi, A.; Kobayashi, H. *Mol.Cryst.Liq.Cryst.*, *284*, 247 (1996); (d) Bryce, M.R.; Moore, A.J.; Batsanov, A.S.; Howard, J.A.K.; Goldenberg, L.M.; Pearson, C.; Petty, M.C.; Tanner, B.K. *Synth.Met.*, *86*, 1839 (1997); (e) Cronin, L.; Clark, S.J.; Parsons, S.; Nakamura, T.; Robertson, N. *J.Chem.Soc., Dalton Trans.*, 1347 (2001).
73. (a) Lindqvist, O.; Andersen, L.; Sieler, J.; Steimecke, G.; Hoyer, E. *Acta Chem.Scand.*, *A36*, 855 (1982); (b) Kato, R.; Kobayashi, H.; Kobayashi, A.; Sasaki, Y. *Chem.Lett.*, 131 (1985); (c) Kobayashi, H.; Kato, R.; Kobayashi, A.; Sasaki, Y. *Chem.Lett.*, 191 (1985); (d) Groeneveld, L.R.; Schuller, B.; Kramer, G.J.; Haasnoot, J.G.; Reedijk, J. *Recl.Trav.Chim.Pays-Bas.*, *105*, 507 (1986); (e) Mentzafos, D.; Hountas, A.; Terzis, A. *Acta Cryst.*, *C44*, 1550 (1988); (f) van Diemen, J.H.; Groeneveld, L.R.; Lind, A.; de Graaff, R.A.G.; Haasnoot, J.G.; Reedijk, J. *Acta Cryst.*, *C44*, 1898 (1988); (g) Broderick, W.E.; Thompson, J.A.; Godfrey, M.R.; Sabat, M.; Hoffman, B.M. *J.Am.Chem.Soc.*, *111*, 7656 (1989); (h) Reefman, D.; Cornelissen, J.P.; Haasnoot, J.G.; de Graaff, R.A.G.; Reedijk, J. *Inorg.Chem.*, *29*, 3933 (1990); (i) Strzelecka, H,; Vicente, R.; Ribas, J.; Legros, J.-P.; Cassoux, P.; Petit, P.; Andre, J.-J. *Polyhedron*, *10*, 687 (1991); (l) Qi, F.; Xiao-Zeng, Y.; Jin-Hua, C.; Mei-Yun, H. *Acta Cryst.*, *C49*, 1347 (1993); (m) Kochurani; Singh, H.B.; Jasinski, J.P.; Paight, E.S.; Butcher, R.J. *Polyhedron*, *16*, 3505 (1997); (n) Sun, S.; Wu, P.; Zhu, D.; Ma, Z.; Shi, N. *Inorg.Chim.Acta*, *268*, 103 (1998); (o) Malfant, I.; Andreu, R.; Lacroix, P.G.; Faulmann, C.; Cassoux, P. *Inorg.Chem.*, *37*, 3361 (1998); (p) Takamatsu, N.; Akutagawa, T.; Hasegawa, T.; Nakamura, T.; Inabe, T.; Fujita, W.; Awaga, K. *Inorg.Chem.*, *39*, 870 (2000); (q) Mukai, K.; Hatanaka, T.; Senba, N.; Nakayashiki, T.; Misaki, Y.; Tanaka, K.; Ueda, K.; Sugimoto, T.; Azuma, N. *Inorg.Chem.*, *41*, 5066 (2002); (r) Liu, G.; Xue, G.; Yu, W.; Xu, W. *Acta Cryst.*, *C58*, m436 (2002).
74. Valade, L.; Legros, J.-P.; Bousseau, M.; Cassoux, P.; Garbauskas, M.; Interrante, L.V. *J.Chem.Soc., Dalton Trans.*, 783 (1985).
75. Sakamoto, Y.; Matsubayashi, G.-E.; Tanaka, T. *Inorg.Chim.Acta*, *113*, 137 (1986).
76. Matsubayashi, G.-E.; Takahashi, K.; Tanaka, T. *J.Chem.Soc., Dalton Trans.*, 967 (1988).
77. (a) Matsubayashi, G.-E.; Yokozawa, A. *J.Chem.Soc., Dalton Trans.*, 3535 (1990); (b) Nagapetyan, S.S.; Arakelova, E.R.; Belousava, L.V.; Struchkov, Yu.T.; Ukhin, L.Yu.; Shklover, V.E. *Russ.J.Inorg.Chem.*, *33*, 88 (1988); (c) Matsubayashi, G.-E.; Yokozawa, A. *Inorg.Chim.Acta 193*, 137 (1992); (d) Swaminathan, K.; Carroll, P.J.; Kochurani; Singh, H.B.; Bhargava, H.D. *Acta Cryst. C49*, 1243 (1993); (e) Takahashi, M.; Robertson, N.; Kobayashi, A.; Becker, H.; Friend, R.H.; Underhill, A.E. *J.Mater.Chem.*, *8*, 319 (1998).
78. (a) Chohan, Z.H.; Howie, R.A.; Wardell, J.L.; Wilkens, R.; Doidge-Harrison, S.M.S.V. *Polyhedron*, *16*, 2689 (1997); (b) Harrison, W.T.A.; Howie, R.A.; Wardell, J.L.; Wardell, S.M.S.V.; Comerlato, N.M.; Costa, L.A.S.; Silvino, A.C.; de Oliveira, A.I.; Silva, R.M. *Polyhedron*, *19*, 821 (2000).
79. Matsubayashi, G.-E.; Nojo, T.; Tanaka, T. *Inorg.Chim.Acta*, *154*, 133 (1988).

80. Matsubayashi, G.-E.; Maikawa, T.; Nakano, M. *J.Chem.Soc., Dalton Trans.*, 2995 (1993).
81. (a) Matsubayashi, G.-E.; Akiba, K.; Tanaka, T. *Inorg.Chem.*, *27*, 4744 (1988); (b) Broderick, W.E.; McGhee, E.M.; Gofrey, M.R.; Hoffman, B.M. *Inorg.Chem.*, *28*, 2904 (1989).
82. (a) Matsubayashi, G.-E.; Douki, K.; Tamura, H. *Chem.Lett.*, 1251 (1992); (b) Matsubayashi, G.-E.; Douki, K.; Tamura, H., Nakano, M.; Mori, W. *Inorg.Chem.*, *32*, 5990 (1993).
83. (a) Steimecke, G.; Sieler, H.-J., Kirmse, R.; Dietzsch, W.; Hoyer, E., *Phosphorus and Sulfur*, *12*, 237 (1982); (b) Lindqvist, O.; Sjölin, L.; Sieler, J.; Steimecke, G.; Hoyer E. *Acta Chem.Scand.*, *A36*, 853 (1982); (c) Kisch, H.; Nüsslein, F.; Zenn, I *Z.Anorg.Allg.Chem.*, *600*, 67 (1991).
84. Olk, R.-M.; Dietzsch, W.; Kirmse, R.; Stach, J.; Hoyer, E.; Golič, L. *Inorg.Chim.Acta*, *128*, 251 (1987).
85. (a) Bigoli, F.; Deplano, P.; Devillanova, F.A.; Lippolis, V.; Lukes, P.J.; Mercuri, M.L.; Pellinghelli, M.A.; Trogu, E.F. *J.Chem.Soc., Chem.Commun.*, 371 (1995); (b) Bigoli, F; Deplano, P.; Devillanova, F.A.; Ferraro, J.R.; Lippolis, V.; Lukes, P.J.; Mercuri, M.L.; Pellinghelli, M.A.; Trogu, E.F.; Williams, J.M. *Inorg.Chem.*, *36*, 1218 (1997); (c) Arca, M.; Demartin, F.; Devillanova, F.A.; Garau, A.; Isaia, F.; Lelj, F.; Lippolis, V.; Pedraglio, S.; Verani, G. *J.Chem.Soc., Dalton Trans.*, 3731 (1998); (d) Grigiotti, E.; Laschi, F.; Zanello, P.; Arca, M.; Denotti, C.; Devillanova F.A. *Portugaliae Electrochimica Acta*, in press; (e) Bigoli, F.; Deplano, P.; Mercuri, M.L.; Pellinghelli, M.A.; Pintus, G.; Trogu, E.F.; Zonnedda, G.; Wang, H.H.; Williams, J.M. *Inorg.Chim.Acta*, *273*, 175 (1998).
86. (a) Dyachenko, O.A.; Konovalikhin, S.V.; Kotov, A.I.; Shilov, G.V.; Yagubskii, E.B.; Faulmann, C.; Cassoux, P. *J.Chem.Soc., Chem.Commun.*, 508 (1993); (b) Hawkins, I.; Underhill, A.E. *J.Chem.Soc., Chem.Commun.*, 1593 (1990); (c) Schenk, S.; Hawkins, I.; Wilkes, S.B.; Underhill, A.E.; Kobayashi, A.; Kobayashi, H. *J.Chem.Soc., Chem.Commun.*, 1648 (1993); (d) Awaga, K.; Okuno, T.; Maruyama, Y.; Kobayashi, A.; Kobayashi, H.; Schenk, S.; Underhill, A.E. *Inorg.Chem.*, *33*, 5598 (1994).
87. (a) Sellmann, D.; Fünfgelder, S.; Knoch, F.; Moll, M. *Z.Naturforsch.* *B46*, 1601 (1991); (b) Mahadevan, C.; Seshasayee, M.; Kuppusamy, P.; Manoharan, P.T. *J.Crys.Spectrosc.Res.*, *15*, 305 (1985); (c) Xie, J.-L.; Ren, X-M.; He, C.; Song, Y. Duan, C.-Y.; Gao, S.; Meng, Q-J. *Polyhedron*, *22*, 299 (2003).
88. Rindorf, G.; Thorup, N.; Bjørnholm, T.; Bechgaard, K. *Acta Cryst.* *C46*, 1437 (1990).
89. (a) Boyde, S.; Ellis, S.R.; Garner, C.D.; Clegg, W. *J.Chem.Soc., Chem.Commun.*, 1541 (1986); (b) Oku, H.; Ueyama, N.; Kondo, M.; Nakamura, A. *Inorg.Chem.*, *33*, 209 (1994); (c) Ueyama, N.; Oku, H.; Nakamura, A. *J.Am.Chem.Soc.*, *114*, 7310 (1992); (d) Colmanet, S.F.; Mackay, M.F. *Austr. J.Chem.*, 40, 1301 (1987).
90. (a) Cowie, M.; Bennett, M.J. *Inorg.Chem.*, *15*, 1595 (1976); (b) Cowie, M.; Bennett, M.J. *Inorg.Chem.*, *15*, 1589 (1976); (c) Martin, J.L.; Takats, J. *Inorg.Chem.* *14*, 1358 (1975); (d) Colmanet, S.F.; Williams, G.A.; Mackay, M.F. *J.Chem.Soc., Dalton Trans.*, 2305 (1997).

91. Martin, J.L.; Takats, J. *Inorg.Chem. 14*, 73 (1975).
92. (a) Cervilla, A.; Llopis, E.; Marco, D.; Pérez, F. *Inorg.Chem.*, *40*, 6525 (2001); (b) Cowie, M.; Bennett, M.J. *Inorg.Chem.*, *15*, 1584 (1976).
93. (a) Burrow, T.E.; Morris, R.H.; Hills, A.; Hughes, D.L.; Richards, R.L. *Acta Cryst.*, *C49*, 1591 (1993); (b) Knock, F.; Sellmann, D.; Kern, W. *J.Kristallogr.*, *202*, 326 (1992); (c) Lorber, C.; Donahue, J.P.; Goddard, C.A.; Nordlander, E.; Holm, R.H. *J.Am.Chem.Soc.*, *120*, 8102 (1998); (d) Knock, F.; Sellmann, D.; Kern, W. *J.Kristallogr.*, *205*, 300 (1993).
94. (a) Sawyer, D.T.; Srivatsa, G.S.; Bodini, M.E.; Schaefer, W.P.; Wing, R.M. *J.Am.Chem.Soc.*, *108*, 936 (1986); (b) Henkel, G.; Greiwe, K.; Krebs, B. *Angew.Chem.Int.Ed.Engl.*, *24*, 117 (1985); (c) Greiwe, K.; Krebs, B.; Henkel, G. *Inorg.Chem.*, *28*, 3713 (1989); (d) Eisenberg, R.; Dori, Z.; Gray, H.B.; Ibers, J.A. *Inorg.Chem.*, *7*, 741 (1968); (e) Mazid, M.A.; Razi, M.T.; Sadler, P.J. *Inorg.Chem.*, *20*, 2872 (1981); (f) Bustos, L.; Khan, M.A.; Tuck, D.G. *Can.J.Chem.*, *61*, 1146 (1983).
95. Sellmann, D.; Binder, H.; Häußinger, D.; Heinemann, F.W.; Sutter, J. *Inorg. Chim.Acta*, *300-302*, 829 (2000).
96. (a) Welch, J.H.; Bereman, R.D.; Singh, P. *Inorg.Chem.*, *27*, 3680 (1988); (b) Vance, C.T.; Bereman, R.D.; Bordner, J.; Hatfield, W.E.; Helms, J.H. *Inorg.Chem.*, *24*, 2905 (1985); (c) Faulmann, C.; Cassoux, P.; Yagubskii, E.B.; Vetoshkina, L.V. *New J.Chem.*, *17*, 385 (1993); (d) Tian-Ming, Y.; Jing-Lin, Z.; Xiao-Zeng, Y.; Xiao-Ying, H. *Polyhedron*, *14*, 1487 (1995); (e) Noh, D.-Y.; Lee, H.-J.; Underhill, A.E. *Synth.Met.*, *86*, 1837 (1997); (f) Lee, H.J.; Noh, D.Y. *Polyhedron*, *19*, 425 (2000); (g) Vance, C.T.; Welch, J.H.; Bereman, R.D. *Inorg.Chim.Acta*, *164*, 191 (1989); (h) Schultz, A.J.; Wang, H.H.; Soderholm, L.C.; Sifter, T.L.; Williams, J.M.; Bechgaard, K.; Whangbo, M.-H. *Inorg.Chem.*, *26*, 3757 (1987).
97. (a) Welch, J.H.; Bereman, R.D.; Singh, P.; Haase, D.; Hatfield, W.E.; Kirk, M.L. *Inorg.Chim.Acta*, *162*, 89 (1989); (b) Kim, H.; Kobayashi, A.; Sasaki, Y.; Kato, R.; Kobayashi, H. *Bull.Chem.Soc.Jpn.*, *61*, 579 (1988).
98. (a) Welch, J.H.; Bereman, R.D.; Singh, P.; *Inorg.Chim.Acta*, *163*, 93 (1989); (b) Gritsenko, V.V.; Dyachenko, O.A.; Cassoux, P.; Kotov, A.L.; Laukhina, E.E.; Faulmann, C.; Yagubskii, E.B. *Izv.Akad.Nauk. SSR, Ser.Khim.*, 1207 (1993); (c) Geiser.U.; Schultz, A.J.; Wang, H.H.; Beno, M.A.; Williams, J.M. *Acta Cryst.*, *C44*, 259 (1988).
99. (a) Welch, J.H.; Bereman, R.D.; Singh, P. *Inorg.Chem.*, *27*, 2862 (1988); (b) Livage, C.; Formigué, M.; Batail, P.; Canadell, E.; Coulon, C. *Bull.Soc.Chim.Fr.*, *130*, 761 (1993); (c) Welch, J.H.; Bereman, R.D.; Singh, P. *Inorg.Chem.*, *29*, 68 (1990).
100. (a) Zuo, J.-L.; You, F.; Fun, H.-K. *Polyhedron*, *16*, 1465 (1997); (b) Zuo, J.-L.; Yao, T.-M.; You, F.; You, X.-Z.; Fun, H.-K.; Yip, B.-C. *J.Mater.Chem.*, *6*, 1633 (1996).
101. (a) Nakamura, T.; Nogami, T.; Shirota, Y. *Bull.Chem.Soc.Jpn.*, *60*, 3447 (1987); (b) Kim, H.; Kobayashi, A.; Sasaki, Y.; Kato, R.; Kobayashi, H.; Nakamura, T.; Nogami, T.; Shirota, Y. *Bull.Chem.Soc.Jpn. 61*, 2559 (1988).
102. (a) Lee, H.J.; Noh, D.Y. *J.Mater.Chem.*, *10*, 2169 (2000); (b) Lee, H.J.; Noh, D.Y. *Synth.Met.*, *102*, 1696 (1999).
103. (a) Tomura, M.; Tanaka, S.; Yamashita, Y. *Synth.Met.*, *64*, 197 (1994).

104. (a) Bigoli, F.; Chen, C.-T.; Wu, W.-C.; Deplano, P.; Mercuri, M.L.; Pellinghelli, M.A.; Pilia, L.; Pintus, L.; Serpe, A.; Trogu, E.F. *Chem.Commun.*, 2246 (2001); (b) Bigoli, F.; Deplano, P.; Mercuri, M.L.; Pellinghelli, M.A.; Pintus, L.; Serpe, A.; Trogu, E.F. *J.Am.Chem.Soc.*, *123*, 1788 (2001).
105. (a) Bereman, R.D.; Lu, H. *Inorg.Chim.Acta*, *204*, 53 (1993); (b) Dautel, O.J.; Fourmigué, M. *Inorg.Chem.*, *40*, 2083 (2001); (c) Yao, T.-M.; You, X.-Z.; Li, C.; Li, L.-F. *Acta Cryst.*, *C50*, 67 (1994); (d) Geiser, U.; Tytko, S.F.; Allen, T.J.; Wang, H.H.; Kini, A.M.; Williams, J.M. *Acta Cryst.*, *C47*, 1164 (1991).
106. (a) Charlton, A.; Underhill, A.E.; Kobayashi, A.; Kobayashi, H. *J.Chem.Soc., Dalton Trans.*, 1285 (1995); (b) Charlton, A.; Underhill, A.E.; Malik, K.M.A.; Hursthouse, M.B.; Jørgensen, T.; Becher, J. *Synth.Met.*, 68, 221 (1995).
107. (a) Robertson, N.; Parkin, D.L.; Underhill, A.E.; Hursthouse, M.B.; Hibbs, D.E.; Malik, K.M.A. *J.Mater.Chem.*, *5*, 1731 (1995); (b) Cleary, C.F.; Robertson, N.; Takahashi, M.; Underhill, A.E.; Hibbs, D.E.; Hursthouse, M.B.; Malik, K.M.A. *Polyhedron*, *16*, 1111 (1997); (c) Underhill, A.E.; Robertson, N.; Parkin, D.L. *Synth.Met.*, *71*, 1955 (1995).
108. Fox, S.; Wang, Y.; Silver, A.; Millar, M. *J.Am.Chem.Soc.*, *112*, 3218 (1990).
109. (a) Larsen, J.; Bechgaard, K. *J.Org.Chem.*, *52*, 3285 (1987); (b) Noh, D.-Y.; Mizuno, M.; Choy, J.-H. *Inorg.Chim.Acta*, *216*, 147 (1994).
110. Eduok, E.E.; Krawiec, M.; Buisson, Y.-S.L.; O'Conner, C.J.; Sun, D.; Watson, W.H. *J.Chem.Cryst.*, *26*, 621 (1996).
111. (a) Ganguli, K.K.; Carlisle, G.O.; Hu, H.J.; Theriot, L.J.; Bernal, I. *J.Inorg. Nucl.Chem.*, *33*, 3579 (1971); (b) Mukhopadhyay, S.; Ray, D. *J.Chem.Soc., Dalton Trans.*, 1159 (1993); (c) Boyde, S.; Garner, C.D.; Clegg, W. *J.Chem.Soc., Dalton Trans.*, 1083 (1987); (d) Pignedoli, A.; Peyronel, G.; Antolini, L. *Acta Cryst.*, *B30*, 2181 (1974).
112. (a) Boyde, S.; Garner, C.D.; Enemark, J.H.; Ortega, R.B. *Polyhedron*, *5*, 377 (1986); (b) Boyde, S.; Garner, C.D.; Enemark, J.H.; Ortega, R.B. *J.Chem.Soc., Dalton Trans.*, 297 (1987); (c) Boyde, S.; Garner, C.D.; Enemark, J.H.; Bruck, M.A.; Kristofzki, J.G. *J.Chem.Soc., Dalton Trans.*, 2267 (1987).
113. Kisch, H.; Eisen, B.; Dinnebier, R.; Shankland, K.; David, W.I.F.; Knoch, F. *Chem.Eur.J.*, *7*, 738 (2001).
114. (a) Kubo, K.; Nakano, M.; Hamaguchi, S.; Matsubayashi, G. *Inorg.Chim.Acta*, *346*, 43 (1993); (b) Le Narvor, N.; Robertson, N.; Weyland, T.; Kilburn, J.D.; Underhill, A.E.; Webster, M.; Svenstrup, N.; Becher, J. *Chem.Commun.*, 1363 (1996); (c) Ueda, K.; Goto, M.; Sugimoto, T.; Endo, S.; Toyota, N.; Yamamoto, K.; Fujita, H. *Synth.Met.*, *85*, 1679 (1997); (d) Le Narvor, N.; Robertson, N.; Wallace, E.; Kilburn, J.D.; Underhill, A.E.; Bartlett, P.N.; Webster, M. *J.Chem.Soc., Dalton Trans.*, 823 (1996); (e) Nakazono, T.; Nakano, M.; Tamura, H.; Matsubayashi, G. *J.Mater.Chem.*, *9*, 2413 (1999).
115. (a) Nakano, M.; Kuroda, A.; Maikawa, T.; Matsubayashi, G. *Mol.Cryst.Liq.Cryst.*, *284*, 301 (1996); Nakano, M.; Kuroda, T.; Matsubayashi, G. *Inorg.Chim.Acta*, *254*, 189 (1997).
116. (a) Kumasaki, M.; Tanaka, H.; Kobayashi, A. *J.Mater.Chem.*, *8*, 301 (1998); (b) Kobayashi, A.; Tanaka, H.; Kumasaki, M.; Torii, H.; Narymbetov, B.; Adachi, T.

J.Am.Chem.Soc., *121*, 10763 (1999); (c) Kobayashi, A.; Kumasaki, M.; Tanaka, H. *Synth.Met.*, *102*, 1768 (1999).
117. Kobayashi, A.; Tanaka, H.; Kobayashi, H. *J.Mater.Chem.*, *11*, 2078 (2001).
118. Tanaka, H.; Okano, Y.; Kobayashi, H.; Suzuki, W.; Kobayashi, A. *Science*, *291*, 285 (2001).

References

1 CHAPTER 1: HOMOLEPTIC, MONONUCLEAR TRANSITION METAL COMPLEXES OF 1,2-DITHIOLENES: UPDATING THEIR ELECTROCHEMICAL-TO-STRUCTURAL PROPERTIES

REFERENCE S

1. Clark, R.E.D. Analyst, 60, 242 (1936).

2. (a) Gray, H.B. Transition Met.Chem., 1, 240 (1965); (b) McCleverty, J.A. Pwg.lnorg.Chem., 10,49 (1968); (c) Schrauzer, G.N. Acc.Chem.Res., 2, 72 (1969); (d) Hoyer, E.; Dietzsch, W.; Schroth, W. Z.Chem. 11, 41 (1971); (e) Burns, R.P.; McAuliffe , C.A. Adv.InorgChem., 22, 303 (1979); (f) Mueller-Westerhoff, U.T.; Vance, B. in "Comprehensive Coordination Chemistry", Pergamon Press, Oxford, Vol. 2, 1987, 595-631; (g) Clemenson, P.I. CoordChem.Rev, 106, 111 (1990); (h) Mueller-Westerhoff, U.T. ; Vance, B.; Yoon, D.I. Tetrahedron, 47, 909 (1991); (i) Cassoux, P.; Valade, L.; Kobayashi, H.; Kobayashi, A.; Clark, R.A.; Underhill, A.E. CoordChem.Rev, 110,115 (1991); (1) Oik, R.-M.; Oik, B.; Dietzsch, W.; Kirmse, R.; Hoyer, E . Coord. Chem.Rev, 117, 99 (1992); (m) Fourmigué, M. CoordChem.Rev., 178-180, 823 (1998); (n) Pullen, A.E.; Oik, R.-M. CoordChem.Rev, 188, 211 (1999); (o) Pilato, R.S.; Stiefel, E.I.; in "Bioinorganic Catalysis", Reedijk, J.; Bouwman, E.; Eds.; Marcel Dekker, New York, 1999, 81-152; (p) Robertson, N.; Cronin, L . CoordChem.Rev, 227, 93 (2002).

3. Ward M.D.; McCleverty, J.A. J.Chem.Soc, Dalton Trans., 275 (2002).

4. (a) Costa, T; Dormían, J.R.; Hagen, K.S.; Holm, R.H. Inorg.Chem., 22, 4091 (1983); (b) Dormían, J.R.; Rao, Ch.R; Holm, R.H. Inorg.Chem., 24,453 (1985); (c) Rao, Ch.R; Dorfman, J.R.; Holm, R.H. Inorg.Chem., 25, 428 (1986); (d) Snyder, B.S.; Rao , Ch.P; Holm, R.H. Aust. J.Chem. 39, 963 (1986).

5. (a) Szeymies, D.; Krebs, B.; Henkel, G. Angew.Chem.Int.Ed.Engl, 23, 804 (1984); (b) Money , J.A.; Huffman, J.C.; Christou, G. Inorg.Chem., 24, 3297 (1985); (c) Wiggins, R.W.; Huffman, J.C; Christou, G. J.Chem.Soc., Chem.Commun., 1313 (1983) .

6. (a) Davison, A.; Orvig, C ; Trop, H.S.; Sohn, M.; DePamphilis, B.V.; Jones, A.G. Inorg.Chem., 19, 1988 (1980); (b) Blower, P.J.; Dilworth, J.R.; Hutchinson, J.P.;

Zubieta, J.A. Inorg.Chim.Acta, 65, L225 (1982); (c) Smith, J.E.; Byrne, E.R; Cotton, F.A.; Sekutowski, J.C. J.Am.Chem.Soc., 100, 5571 (1978);.

7. Tatsumi, K.; Sekiguchi, Y.; Nakamura, A.; Cramer, R.E.; Rupp, J.J. Angew.Chem.Int.Ed.Engl, 25, 86 (1986).

8. Gama, V; Belo, D; Rabaça S.; Santos, I.C.; Alves, H.; Waerenborgh, J.C; Duarte, M.T. ; Henriques, R.T. Eur.J.Inorg.Chem., 2101 (2000).

9. Hoyer, E.; Dietzsch, W.; Hennig, H.; Schroth, W. Chem.Ber., 102, 603 (1969).

10. Herman,Z.S.; Kirchner,R.R; Loew,G.H.; Mueller-Westerhoff, U.T.; Nazzal, A; Zerner, M.C. Inorg.Chem. 21, 46 (1982).

11. Browall, K.W.; Bursch, T.; Interrante, L.V; Kasper, J.S. Inorg.Chem., 11, 1800 (1972).

12. Donahue, J.P.; Goldsmith, C.R.; Nadiminti, U.; Holm, R.H. J.Am.Chem.Soc, 120, 12869(1998).

13. Davies, E.S.; Beddoes, R.L.; Collison, D.; Dinsmore, A.; Docrat, A.; Joule, J.A.; Wilson, C.R.; Garner, CD. J.Chem.Soc., Dalton Trans., 3985 (1997)

14. Fourmigué, M.; Bertrán, J.N. Chem.Commun., 2111 (2000).

15. Keefer, CE.; Purrington, S.T.; Bereman, R.D.; Boyle, P.D. Inorg.Chem., 38, 5437 (1999).

16. Wilkes, S.B.; Butler, I.R.; Underhill, A.E.; Kobayashi, A.; Kobayashi, H. J.Chem.Soc, Chem.Commun., 53 (1994).

17. B.S.Lim , D.V.Fomitchev, and R.H.Holm, Inorg.Chem., 40, 4257 (2001).

18. (a) Lim, B.S.; Donahue, J.P.; Holm, R.H. Inorg Chem., 39,263 (2000); (b) Goddard, C.A.; Holm, R.H. Inorg.Chem., 38, 5389 (1999).

19. Fomitchev, D.V., Lim, B.S.; Holm, R.H. Inorg.Chem., 40, 645 (2001).

20. (a) Bowmaker, G.A.; Boyd, P.D.W.; Campbell, G.K. Inorg.Chem., 22, 1208 (1983); (b) Hill , C.A.S.; Charlton, A.; Underhill, A.E.; Malik, K.M.A.; Hursthouse, M.B.; Karaulov, A.I.; Oliver, S.N.; Kershaw, S.V. J.Chem.Soc.,

Dalton.Trans., 587 (1995); (c) Sung, K.-M; Holm, R.H. J.Am.Chem.Soc., 124, 4312 (2002).

21. (a) Mahadevan, C; Seshasayee, M.; Kuppusamy, R; Manoharan, RT. J.Cryst.Spectros.Res., 14, 179 (1984); (b) Rajalakshmi, A.; Radha, A.; Seshasayee, M.; Kuppusamy , P.; Manoharan, RT. Z.Kristallogr, 159 (1988).

22. Koz'min, P.A.; Larina, T.B. Koord.Khim. (Engl.Trans.), 5, 464 (1979).

23. Megnamisi-Belombe, M.; Nuber, B. Bull.Chem.Soc.Jpn., 62, 4092 (1989).

24. (a) Wing, R.M.; Schlupp, R.L. Inorg.Chem., 9, All (1970); (b) Singhabhandhu, A.; Robinson, P.D.; Fang, J.H.; Geiger, W.E. Inorg.Chem., 14, 318 (1975); (c) Miller, J.S.; Calabrese, J.C.; Epstein, A.J. Inorg.Chem., 28, 4230 (1989).

25. Schmitt, R.D.; Wing, R.M.; Maki, A.H. J.Am.Chem.Soc, 91, 4394 (1969).

26. Geiger , W.E.; Mines, T.E.; Senftleber, F.C. Inorg.Chem., 14, 2141 (1975).

27. Wang , K.; McConnachie, J.M.; Stiefel, E.I. Inorg.Chem., 38, 4334 (1999).

28. Heuer, W.B.; Mountford, P.; Green, M.L.H.; Bott, S.G.; O'Hare, D.; Miller, S.J. Chem.Mater, 2, 764 (1990).

29. (a) Brown, R.K.; Bergendahl, T.J.; Wood, J.S.; Waters, J.H. Inorg.Chim.Acta, 68, 79 (1983); (b) Baudron, S.A.; Batail, P. Acta Cryst., C58, m575 (2002).

30. (a) Coucouvanis, D.; Hadjikyriacou, A.; Toupadakis, A.; Koo, S.-M.; Ileperuma, O.; Draganjac, M.; Salifoglou, A. Inorg.Chem., 30, 754 (1991); (b) Bandoli, G.; Nicolini, M; Mazzi, U.; Spies, H.; Munze, R. Transition Met.Chem., 9, 127 (1984); (c) Draganjac , M.; Coucouvanis, D. J.Am.Chem.Soc, 105, 139 (1983).

31. Beswick, C.L.; Terroba, R.; Greaney, M.A.; Stiefel, E.I. J.Am.Chem.Soc, 124, 9664 (2002).

32 . Kean, C.L.; Pickup. P.G. Chem.Commun., 815 (2001).

33. (a) Keller, C; Walther, D.; Reinhold, J.; Hoyer, E. Z.Chem., 11, 410 (1988); (b) Vance,T.; Bereman, R.D.

Inorg.Chim.Acta, 149, 229 (1988).

34. (a) Charlton, A.; Hill, C.A.S.; Underhill, A.E.; Malik, K.M.A.; Hursthouse, M.B.; Karaulov, A.I.; M0ller, J. JMater.Chem., 4, 1861 (1994); (b) Charlton, A.; Kilburn, J.D.; Underhill, A.E.; Webster, M. Acta Cryst. C52, 2441 (1996).

35. Mueller-Westerhoff, U.T.; Yoon, D.I.; Plourde, K. Mol.Cryst.Liq.Cryst, 183, 291 (1990)

36. Barrière, F.; Camire, N.; Geiger, W.E.; Mueller-Westerhoff, U.T.; Sanders, R. J.Am.Chem.Soc, 124, 7262 (2002).

37. (a) Kisch, H.; Nüsslein, R; Zenn, I. Z.Anorg.Allg.Chem., 600, 61 (1991); (b) Persaud, L.; Langford, C.H. Inorg.Chem., 24, 3562 (1985); (c) Senftleber, F.C; Geiger, W.E. J.Am.Chem.Soc, 97, 5018 (1975); (d) Fitzmaurice, J.C.; Slawin, A.M.Z.; Williams, D.J.; Woolins, J.D.; Lindsay, A.J. Polyhedron, 9, 1561 (1990);

38. (a) Eisenberg, R.; Ibers, J.A. Inorg.Chem., 4, 605 (1965); (b) Eisenberg, R.; Ibers, J.A.; Clark , R.J.H.; Gray, H.B. JAm.Chem.Soc, 86, 113 (1964); (c) Hove, M.J.; Hoffman, B.M. ; Ibers, J.A. JChem.Phys., 56,3490 (1972); (d) Dance, I.G.; Solstad, P.J.; Calabrese, J.C. Inorg.Chem., 12,2161 (1973); (e) Coucouvanis, D.; Baenziger, N.C.; Johnson, S.M. Inorg.Chem., 13, 1191 (1974); (f) Kobayashi, A.; Sasaki, Y. Bull.Chem.Soc. Jpn., 50, 2650 (1977); (g) Endres, H.; Keller, H.J.; Moroni, W.; Nome , D. Acta Cryst.,B35,353 (1979); (h) Kisch, H.; Fernández, A.; Wakatsuki, Y.; Yamazaki, H. Z.Naturforsch., 40B, 292 (1985); (i) Schmauch, G.; Knoch, R; Kisch, H. Chem.Ber., 127, 287 (1994); (1) Handrosch, C; Dinnebier, R.; Bondarenko, G.; Bothe, E. ; Heineman, R; Kisch, H. Eur.J.Inorg.Chem., 1259 (1999); (m) Yang, L.R; Peng, Z.-H.; Cheng, G.-Z.; Peng, S.-M. Polyhedron, 22, 3547 (2003).

39. (a) Fritchie, C.J. Acta Cryst, 20, 107 (1966); (b) Manoharan, P.T.; Noordik, J.H.; de Boer, E.; Keijzers, C.R JChem.Phys., 74, 1980 (1981); (c) Ramakrishna, B.L.; Manoharan, P.T. Inorg.Chem., 22, 2113 (1983); (d) Mahadevan, C; Seshasayee, M.; Murthy, B.V.R.; Kuppusamy, P.; Manoharan, P.T. Acta Cryst., C39, 1335 (1983); (e) Brunn, K.; Endres, H.; Weiss, J. Z.Naturforsch., 42B, 1222 (1987); (f) Hobi, M.; Zürcher, S.; Gramlich, V.; Burckhardt, U.; Mensing, C ; Spahr, M.; Togni, A . Organometallics, 15, 5342 (1996); (g) Zürcher, S.;

Gramlich, V.; von Arx, D.; Togni, A Inorg.Chem., 37, 4015 (1998); (h) Robertson, N.; Bergemann,C; Becker, H. ; Agarwal, P.; Julian, S.R.; Friend, R.H.; Hatton, N.J.; Underhill, A.E.; Kobayashi, A. J.Mater.Chem., 9, 1713 (1999); (i) Ribera, E.; Rovira, C; Veciana, J.; Tarrés , J.; Canadell, E.; Rousseau, R.; Molins, E.; Mas, M.; Schoeffel, J.-R; Pouget, J.-R; Morgado, J.; Henriques, R.T.; Almeida, M. Chem.Eur.J, 5, 2025 (1999); (1) Robertson, N.; Roehrs, S.; Akutagawa, T.; Nakamura, T.; Underhill, A.E. JChem.Res., (S) 54 (1999); (m) Ren, X.; Lu, C; Liu, Y; Zhu, H.; Li, H.; Hu, C; Meng, Q. Transition Met.Chem. 26, 136 (2001); (n) Ren, X-M.; Li, H.-R; Wu, RH.; Meng, Q.-J. Acta Cryst, C57, 1022 (2001); (o) Xie, J.; Ren, X.; Song, Y; Zou, Y; Meng, Q. JChem.Soc, Dalton Trans., 2868 (2002); (p) Xie, J.; Ren, X.; Song, Y ; Zhang, W.; Liu, W.; He, C; Meng, Q. Chem.Commun., 2346 (2002); (q) Ren, X.; Chen, Y; He, C ; Gao, S. JChem.Soc, Dalton Trans., 3915 (2002); (r) Xie, J.; Ren, X.; Gao, S.; Zang, W.; Liu, W.; Meng, Q.; Yao, Y Eur.J.Inorg.Chem., 2393 (2003).

40. (a) Mines, T.E.; Geiger, W.E. Inorg.Chem., 12, 1189 (1973); (b) Geiger, W.E.; Allen, C.S.; Mines, T.E.; Senftleber, RC. Inorg.Chem., 16, 2003 (1977).

41. (a) Lemke, M.; Knoch, R; Kisch, H. Acta Cryst., C49, 1630 (1993); (b) Batsanov, A.S.; Moore, A.J.; Robertson, N.; Green, A.; Bryce, M.R.; Howard, J.A.K.; Underhill, A.E. J.Mater.Chem., 7, 387 (1997); (c) Bois, H.; Connelly, N.G.; Crossley, J.G.; Guillorit, J.-C; Lewis, G.R.; Orpen, G.; Thornton, P. JChem.Soc, Dalton Trans., 2833 (1998).

42. (a) Domingos, A.; Henriques, R.T.; Gama, V.; Almeida, M.; Vieira, A.L.; Alcacer, L. Synth.Met., 27, B411 (1988); (b) Hursthouse, M.B.; Short, R.L.; Clemenson, P.I.; Underhill, A.E. JChem.Soc, Dalton Trans., 67 (1989).

43. (a) Güntner, W.; Gliemann, G.; Klement, U.; Zabel, M. Inorg.Chim.Acta, 165, 51 (1989); (b) Clegg, W.; Birkby, S.L.; Banister, A.J.; Rawson, J.M.; Wait, S.T.; Rizkallah, P.; Harding, M.M.; Blake, A.J. Acta Cryst, C50, 28 (1994); (c) Bigoli, R; Deplano, R; Mercuri, M.L.; Pellinghelli, M.A.; Pilia, L.; Pintus, G.; Serpe, A.; Trogu , E.F. Inorg.Chem., 41, 5241 (2002); (d) Bremi, J.; Gramlich, V.; Caseri, W.; Smith, P . Inorg.Chim.Acta, 322, 23 (2001).

44. (a) Ahmad, M.M.; Turner, D.J.; Underhill, A.E.; Kobayashi, A.; Sasaki, Y; Kobayashi, H. JChem.Soc, Dalton Trans., 1759 (1984); (b) Clemenson, P.I.; Underhill, A.E.; Hursthouse, M.B.; Short, R.L. J.Chem.Soc, Dalton Trans., 61 (1989); (c) Bremi, J.; d'Agostino, E.; Gramlich, V.;

Caseri, W.; Smith, P. Inorg.Chim.Acta, 335, 15 (2002).

45. Forrester, J.D.; Zalkin, A.; Templeton, D.H. Inorg.Chem., 3, 1507 (1964).

46. (a) Plumlee, K.W.; Hoffman, B.M.; Ratjack, M.T.; Kannewurf, R.C. Solid State Commun., 15, 1651 (1974); (b) Plumlee, K.W.; Hoffman, B.M.; Ibers, J.A. J.Chem.Phys., 63, 1926 (1975); (c) Snaathorst, D.; Doesburg, H.M.; Perenboom, J.A.A.; Keijzers , C.P. Inorg.Chem., 20, 2526 (1981); (d) Kuppusamy, R; Ramakrishna, B.L. ; Manoharan, RT. Inorg.Chem., 23,3886 (1984); (e) Mahadevan, C; Seshasayee, M. J.Cryst.Spectrosc.Res., 14,215 (1984); (f) Fettouhi.M.; Ouahab, L.; Hagiwara, M.; Codjovi, E.; Kahn, O.; Constant-Machado, H.; Varret, F. Inorg.Chem., 34, 4152 (1995).

47. (a) Stach, J.; Kirmse, R.; Sieler, J.; Abram, U.; Dietzsch, W.; Bõttcher, R.; Hansen, L.K.; Vergoossen, H.; Gribnau, M.C.M.; Keijzers, C.P. Inorg.Chem., 25, 1369 (1986); (b) Lahner, S.; Wakatsuki, Y.; Kish, H. Chem.Ber., 120, 1011 (1987).

48. Noordik, J.H.; Beurskens, P.T. J.Cryst.Mol.Struct, 1, 339 (1971).

49. Vlcek , Jr.,A.; Vlcek, A.,A. J.Electroanal.Chem., 125, 481 (1981)

50. (a) Forrester, J.D.; Zalkin, A.; Templeton, D.H. Inorg.Chem., 3, 1500 (1964); (b) Schmauch, G. ; Knoch, R; Kisch, H. Chem.Ber., 128, 303 (1995); (c) Schmauch, G.; Chihara, T.; Wakatsuki, Y; Hagiwara, M.; Kisch, H. Bull.Chem.Soc.Jpn., 69, 2573 (1996).

51. Gõtz, B.; Knoch, R; Kisch, H. Chem.Ber., 129, 33 (1996).

52. Das, S.K.; Biswas, D.; Maiti, R.; Sarkar, S. J.Am.Chem.Soc., 118, 1387 (1996).

53. (a) McCleverty, J.A.; Locke, J.; Ratcliff, B.; Wharton, E.J. Inorg.Chim.Acta, 3,283 (1969); (b) Das, S.K.; Chaudhury, P.K.; Biswas, D.; Sarkar, S. J.Am.Chem.Soc, 116, 9061 (1994).

54. Stiefel, E.I.; Bennett, L.E., Dori, Z.; Crawford, T.H.; Simo, C; Gray, H.B. Inorg.Chem., 9, 281 (1970).

55. (a) Sequeira, A.; Bernai, I. J.Cry st.Mol.Struct., 3,157 (1973); (b) Stiefel, E.I.; Dori, Z.; Gray, H.B.

J.Am.Chem.Soc, 89, 3353 (1967); (c) Brown, G.R; Stiefel, E.I. Inorg.Chem., 12, 2140 (1973).

56. Lewis, G.R.; Dance, I. J.Chem.Soc, Dalton Trans., 3176 (2000).

57. (a) Maiti, R.; Shang, M.; Lappin, A.G. Chem.Commun., 2349 (1999); (b) Maiti, R.; Shang, M.; Lappin, A.G. J.Chem.Soc., Dalton Trans., 244 (2002).

58. Antolini, L.; Fabretti, A.C.; Franchini, G.; Menabue, L.; Pellacani, G.C.; Desseyen, H.O.; Dommisse, R.; Hofmans, H.C. J.Chem.Soc., Dalton Trans., 1921 (1987).

59. DePamphilis, B.V., Jones, A.G., Davis, M.A.; Davison, A. J.Am.Chem.Soc, 100, 5570(1978).

60. (a) Coucouvanis, D.; Baenziger, N.C.; Johnson, S.M. J.Am.Chem.Soc., 95, 3875 (1973); (b) Bellitto, C; Bonamico, M.; Fares, V.; Imperatori, P.; Patrizio, S. J.Chem.Soc, Dalton Trans., 719 (1989); (c) Golic, L.; Bule, N.; Dietzsch, W. Acta Cryst, C42, 811 (1986); (d) Imamura, T.; Ryan, M.; Gordon, G.; Coucouvanis, D. J.Am.Chem.Soc, 106, 984 (1984); (e) Knatzidis, M.G.; Baenziger, N.C.; Coucouvanis, D . Inorg.Chem., 24, 2680 (1985); (f) Mennemann, K.; Mattes, R. J.Chem.Res. (S), 102 (1979); (g) Mattes, R.; Weber, H. Z.Anorg.Allg.Chem., 474, 216 (1981); (h) Butler, K.R.; Snow, M.R. Inorg.Nucl.Chem.Letters, 8, 541 (1972).

61. (a) Coucouvanis, D.; Hollander, F.J.; West, R.; Eggerding, D. J.Am.Chem.Soc, 96, 3006 (1974); (b) Coucouvanis, D.; Holah, D.G.; Hollander, F.J. Inorg.Chem., 14, 2657 (1975); (c) Bellitto, C ; Bonamico, M.; Fares, V.; Serino, P. Inorg.Chem., 35, 407 0 (1996); (d) Bonnet, J.-J.; Cassoux, P.; Castan, P.; Laurent, J.-P; Soûles, R. Mol.Cryst.Liq.Cryst, 142, 113 (1987); (e) Arrizabalaga, Ph.; Bernardinelli, G.; Geoffroy, M. ; Castan, P. Inorg.Chim.Acta, 154, 35 (1988); (f) Arrizabalaga, Ph.; Bernardinelli, G.; Castan, P.; Geoffroy, M.; Soûles, R. C.R.Acad.Sc.Paris Série II, 559(1987).

62. (a) Heuer, W.B.; Pearson, W.H. J.Chem.Soc., Dalton Trans., 3507 (1996); (b) Heuer, W.B.; Pearson, W.H. Polyhedron, 15, 2199 (1996).

63. Venkatalakshmi, N.; Varghese, B.; Lalitha, S.; Williams, R.F.X.; Manoharan, P.T. J.Am.Chem.Soc, Ill, 5748 (1989).

64. Belo , D.; Alves, H.; Lopes, E.B.; Duarte, M.T.; Gama, V.; Henriques, R.T.; Almeida, M.; Pérez-Benîtez, A.; Rovira, C; Veciana, J. Chem.Eur.J, 7, 511 (2001).

65. Pozo-Gonzalo, C ; Berridge, R.; Skabara, P.J.; Cerrada, E.; Laguna, M.; Coles, S.J.; Hursthouse, M.B. Chem.Commun., 2408 (2002).

66. Veldhuizen, Y.S.J.; Veldman, N.; Spek, A.L.; Cassoux, P.; Carlier, R.; Mulder, M.J.J.; Haasnoot , J.G.; Reedijk, J J.Chem.Soc, Dalton Trans., 2989 (1998).

67. (a) Sun, S.Q.; Zhang, B.; Wu, P.J.; Zhu, D.B. J.Chem.Soc., Dalton Trans., 227 (1997); (b) Olk, R.-M.; Dietzsch, W.; Kõhler, K.; Kirmse, R.; Reinhold, J.; Hoyer, E.; Golic , L.; Olk, B. Z.Anorg.Allg.Chem. 567, 131 (1988); (c) Liu, S.-G.; Wu, PJ.; Li, Y.-F.; Zhu, D.-B. Phosphorus, Sulfur and Silicon, 90, 219 (1994); (d) Liu, S.-G.; Liu , Y.-Q.; Liu, S.-H.; Zhu, D.-B. Synth. Met., 74, 137 (1995); (e) Vicente, R.; Ribas, J.; Zanchini, C ; Gatteschi, D.; Legros, J.-R, Faulmann, C; Cassoux, P. Z.Naturforsch., 43b, 1137 (1988); (f) Fettouhi, M.; Ouahab, L.; Codjovi, E.; Kahn, O. Mol.Cryst.Liq.Cryst, 273, 29 (1995); (g) Faulmann, G.; Riviêre, E.; Dorbes, S.; Senocq, F.; Coronado, E.; Cassoux, P. Eur.J.Inorg.Chem., 2393 (2003).

68. Yang, X.; Freeman, G.K.W.; Rauchfuss, T.B.; Wilson, S.R. Inorg.Chem., 30, 3034 (1991).

69. Tanaka, S.; Matsubayashi, G. J.Chem.Soc, Dalton Trans., 2837 (1992).

70. Matsuda, F.; Tamura, H.; Matsubayashi, G. Inorg.Chim.Acta, 235, 239 (1999).

71. (a) Faulmann, C; Errami, A.; Donnadieu, B.; Malfant, I.; Legros, J.-P; Bowlas, C; Cassoux, P.; Rovira, C; Canadell, E. Inorg.Chem., 35, 3856 (1996); (b) Kato, R.; Kobayashi, H.; Kobayashi, A.; Sasaki, Y Bull.Chem.Soc. Jpn., 59, 627 (1986); (c) Tommasino, J.-B.; Pomarede, B.; Medus, D.; de Montauzon, D.; Cassoux, P. Mol.Cryst.Liq.Cryst, 237, 445 (1993); (d) Nunn, I.; Eisen, B.; Benedix, R.; Kish, H. Inorg.Chem., 33, 5079 (1994); (e) Olk, R.-M.; Rõhr, A.; Sieler, J.; Kõhler, K.; Kirmse, R.; Dietzsch, W.; Hoyer, E.; Olk, B. Z.Anorg.Allg.Chem., 577, 206 (1989);

72. (a) Lindqvist, O.; Sjõlin, L.; Sieler, J.; Steimecke, G.; Hoyer, E. Acta Chem.Scand., A33,445 (1979); (b) Steimecke, G.; Sieler, H.-J.; Kirmse, R.; Hoyer, E.

Phosphorus Sulfur, 7, 49 (1979); (c) Kushch, N.; Faulmann, C; Cassoux, P.; Valade, L.; Malfant, I.; Legros, J.-R; Bowlas, C ; Errami, A.; Kobayashi, A.; Kobayashi, H. Mol.Cryst.Liq.Cryst, 284, 247 (1996); (d) Bryce, M.R.; Moore, A.J.; Batsanov, A.S.; Howard, J.A.K.; Goldenberg, L.M.; Pearson, C.; Petty, M.C.; Tanner, B.K. Synth.Met, 86, 1839 (1997); (e) Cronin, L.; Clark, S.J.; Parsons, S.; Nakamura, T.; Robertson, N . J.Chem.Soc, Dalton Trans., 1347 (2001).

73. (a)Lindqvist,O.;Andersen,L.; Sieler,J.; Steimecke,G.;Hoyer,E.ActaChem.Scand, A36, 855 (1982); (b) Kato, R.; Kobayashi, H.; Kobayashi, A.; Sasaki, Y. Chem.Lett, 131 (1985) ; (c) Kobayashi, H.; Kato, R.; Kobayashi, A.; Sasaki, Y. Chem.Lett, 191 (1985) ; (d) Groeneveld, L.R.; Schuller, B.; Kramer, G.J.; Haasnoot, J.G.; Reedijk, J. Recl.Trav.Chim.Pays-Bas., 105, 507 (1986); (e) Mentzafos, D.; Hountas, A.; Terzis, A. Acta Cryst., C44, 1550 (1988); (f) van Diemen, J.H.; Groeneveld, L.R.; Lind , A.; de Graaff, R.A.G.; Haasnoot, J.G.; Reedijk, J. Acta Cryst, C44, 1898 (1988) ; (g) Broderick, W.E.; Thompson, J.A.; Godfrey, M.R.; Sabat, M.; Hoffman, B.M. J.Am.Chem.Soc, 111, 1656 (1989); (h) Reefman, D.; Cornelissen, J.P.; Haasnoot , J.G.; de Graaff, R.A.G.; Reedijk, J. Inorg.Chem., 29, 3933 (1990); (i) Strzelecka, H,; Vicente, R.; Ribas, J.; Legros, J.-P; Cassoux, P.; Petit, P.; Andre, J.-J. Polyhedron, 10, 687 (1991); (1) Qi, R; Xiao-Zeng, Y; Jin-Hua, C; Mei-Yun, H. Acta Cryst, C49, 1347 (1993); (m) Kochurani; Singh, H.B.; Jasinski, J.P.; Paight, E.S.; Butcher , R.J. Polyhedron, 16, 3505 (1997); (n) Sun, S.; Wu, P.; Zhu, D.; Ma, Z.; Shi, N. Inorg.Chim.Acta, 268, 103 (1998); (o) Malfant, I.; Andreu, R.; Lacroix, P.G.; Faulmann, C; Cassoux, P. Inorg.Chem., 37, 3361 (1998); (p) Takamatsu, N.; Akutagawa , T.; Hasegawa, T.; Nakamura, T.; Inabe, T.; Fujita, W.; Awaga, K. Inorg.Chem., 39, 870 (2000); (q) Mukai, K.; Hatanaka, T; Senba, N.; Nakayashiki, T; Misaki, Y; Tanaka, K.; Ueda, K.; Sugimoto, T; Azuma,N. Inorg.Chem., 41,5066 (2002); (r) Liu, G.; Xue, G.; Yu, W.; Xu, W. Acta Cryst, C58, m436 (2002).

74. Valade , L.; Legros, J.-P; Bousseau, M.; Cassoux, P.; Garbauskas, M.; Interrante, L.V J.Chem.Soc, Dalton Trans., 783 (1985).

75. Sakamoto , Y; Matsubayashi, G.-E.; Tanaka, T. Inorg.Chim.Acta, 113, 137 (1986).

76. Matsubayashi, G.-E.; Takahashi, K.; Tanaka, T. J.Chem.Soc, Dalton Trans., 967 (1988).

77. (a) Matsubayashi, G.-E.; Yokozawa, A. J.Chem.Soc, Dalton Trans., 3535 (1990); (b) Nagapetyan, S.S.; Arakelova, E.R.; Belousava, L.V; Struchkov, Yu.T.; Ukhin, L.Yu.; Shklover , VE. Russ.J.Inorg.Chem., 33, 88 (1988); (c) Matsubayashi, G.-E.; Yokozawa, A. Inorg.Chim.Acta 193, 137 (1992); (d) Swaminathan, K.; Carroll, P.J.; Kochurani; Singh, H.B.; Bhargava, H.D. Acta Cryst. C49, 1243 (1993); (e) Takahashi, M.; Robertson, N.; Kobayashi, A.; Becker, H.; Friend, R.H.; Underhill, A.E. J.Mater.Chem., 8, 319 (1998).

78. (a) Chohan, Z.H.; Howie, R.A.; Wardell, J.L.; Wilkens, R.; Doidge-Harrison, S.M.S.V Polyhedron, 16,2689 (1997); (b) Harrison, W.T.A.; Howie, R.A.; Wardell, J.L.; Wardell, S.M.S.V; Comerlato, N.M.; Costa, L.A.S.; Silvino, A.C.; de Oliveira, A.I.; Silva, R.M. Polyhedron, 19, 821 (2000).

79. Matsubayashi, G.-E.; Nojo, T.; Tanaka, T. Inorg.Chim.Acta, 154, 133 (1988).

80. Matsubayashi, G.-E.; Maikawa, T.; Nakano, M. J.Chem.Soc, Dalton Trans., 2995 (1993).

81. (a) Matsubayashi, G.-E.; Akiba, K.; Tanaka, T. Inorg.Chem., 27, 4744 (1988); (b) Broderick, W.E.; McGhee, E.M.; Gofrey, M.R.; Hoffman, B.M. Inorg.Chem., 28, 2904(1989).

82. (a) Matsubayashi, G.-E.; Douki, K.; Tamura, H. Chem.Lett., 1251 (1992); (b) Matsubayashi, G.-E.; Douki, K.; Tamura, H., Nakano, M.; Mori, W. Inorg.Chem., 52,5990(1993).

83. (a) Steimecke, G.; Sieler, H.-J., Kirmse, R.; Dietzsch, W.; Hoyer, E., Phosphorus and Sulfur, 12, 237 (1982); (b) Lindqvist, O.; Sjõlin, L.; Sieler, J.; Steimecke, G.; Hoyer E . Acta Chem.Scand., A36, 853 (1982); (c) Kisch, H.; Nüsslein, R; Zenn, I Z.Anorg.Allg.Chem., 600, 67 (1991).

84. Oik,R.-M.; Dietzsch,W.; Kirmse,R.; Stach, J.; Hoyer, E.; Golic, L.Inorg.Chim.Acta, 725,251(1987).

85. (a) Bigoli, F.; Deplano, R; Devillanova, F.A.; Lippolis, V.; Lukes, P.J.; Mercuri, M.L.; Pellinghelli , M.A.; Trogu, E.F. J.Chem.Soc, Chem.Commun., 371 (1995); (b) Bigoli, F; Deplano, P.; Devillanova, F.A.; Ferraro, J.R.; Lippolis, V.; Lukes, P.J.; Mercuri , M.L.; Pellinghelli, M.A.; Trogu, E.F.; Williams, J.M. Inorg.Chem., 36, 1218 (1997); (c) Area, M.; Demartin, E; Devillanova, F.A.;

Garau, A.; Isaia, F.; Lelj, F.; Lippolis, V.; Pedraglio, S.; Verani, G. J.Chem.Soc, Dalton Trans., 3731 (1998); (d) Grigiotti, E.; Laschi, F.; Zanello, P.; Area, M.; Denotti, C ; Devillanova F.A. Portugaliae Electrochimica Acta, in press; (e) Bigoli, E; Deplano, P.; Mercuri, M.L.; Pellinghelli , M.A.; Pintus, G.; Trogu, E.F.; Zonnedda, G.; Wang, H.H.; Williams, J.M. Inorg.Chim.Acta, 273, 175 (1998).

86. (a) Dyachenko, O.A.; Konovalikhin, S.V.; Kotov, A.I.; Shilov, G.V.; Yagubskii, E.B.; Faulmann , C; Cassoux, P. J.Chem.Soc, Chem.Commun., 508 (1993); (b) Hawkins, I.; Underhill, A.E. J.Chem.Soc, Chem.Commun., 1593 (1990); (c) Schenk, S.; Hawkins, I.; Wilkes, S.B.; Underhill, A.E. ; Kobayashi, A.; Kobayashi, H. J.Chem.Soc, Chem.Commun., 1648 (1993); (d) Awaga, K.; Okuno, T.; Maruyama, Y.; Kobayashi, A.; Kobayashi, H.; Schenk, S.; Underhill, A.E. Inorg.Chem., 33, 5598 (1994) .

87. (a) Sellmann, D.; Fünfgelder, S.; Knoch, E; Moll, M. Z.Naturforsch. B46, 1601 (1991); (b) Mahadevan, C; Seshasayee, M.; Kuppusamy, P.; Manoharan, P.T. J.Crys.Spectrosc.Res., 15, 305 (1985); (c) Xie, J.-L.; Ren, X-M.; He, C; Song, Y. Duan, C.-Y; Gao, S.; Meng, Q-J. Polyhedron, 22, 299 (2003).

88. Rindorf, G.; Thorup, N.; Bjornholm, T.; Bechgaard, K. Acta Cryst. C46, 1437 (1990).

89. (a) Boyde, S.; Ellis, S.R.; Garner, CD.; Clegg, W. J.Chem.Soc, Chem.Commun., 1541 (1986); (b) Oku, H.; Ueyama, N.; Kondo, M.; Nakamura, A. Inorg.Chem., 33, 209 (1994); (c) Ueyama, N.; Oku, H.; Nakamura, A. J.Am.Chem.Soc, 114, 7310 (1992); (d) Colmanet, S.F.; Mackay, M.F. Austr. J.Chem., 40, 1301 (1987).

90. (a) Cowie, M.; Bennett, M.J. Inorg.Chem., 15, 1595 (1976); (b) Cowie, M.; Bennett, M.J. Inorg.Chem., 15,1589 (1976); (c) Martin, J.L.; Takats, J. Inorg.Chem. 14, 1358 (1975); (d) Colmanet, S.F.; Williams, G.A.; Mackay, M.F. J.Chem.Soc, Dalton Trans., 2305 (1997).

91. Martin , J.L.; Takats, J. Inorg.Chem. 14, 73 (1975).

92. (a) Cervilla, A.; Llopis, E.; Marco, D.; Pérez, F. Inorg.Chem., 40, 6525 (2001); (b) Cowie, M. ; Bennett, MJ. Inorg.Chem., 15, 1584 (1976).

93. (a) Burrow, T.E.; Morris, R.H.; Hills, A.; Hughes, D.L.; Richards, R.L. Acta Cryst., C49, 1591 (1993); (b)

Knock, F.; Sellmann, D.; Kern, W. J.Kristallogr., 202, 326 (1992); (c) Lorber, C; Donahue, J.P.; Goddard, C.A.; Nordlander, E.; Holm, R.H. J.Am.Chem.Soc, 120, 8102 (1998); (d) Knock, F.; Sellmann, D.; Kern, W. J.Kristallogr, 205, 300 (1993).

94. (a) Sawyer, D.T.; Srivatsa, G.S.; Bodini, M.E.; Schaefer, W.P.; Wing, R.M. J.Am.Chem.Soc, 108, 936 (1986); (b) Henkel, G.; Greiwe, K.; Krebs, B. Angew.Chem.Int.Ed.Engl, 24, 117 (1985); (c) Greiwe, K.; Krebs, B.; Henkel, G. Inorg.Chem., 28, 3713 (1989); (d) Eisenberg, R.; Dori, Z.; Gray, H.B.; Ibers, J.A. Inorg.Chem., 7, 741 (1968); (e) Mazid, M.A.; Razi, M.T.; Sadler, P.J. Inorg.Chem., 20, 2872 (1981); (f) Bustos, L.; Khan, M.A.; Tuck, D.G. Can.J.Chem., 61, 1146 (1983).

95 . Sellmann, D.; Binder, H.; Hauflinger, D.; Heinemann, F.W.; Sutter, J. Inorg. Chim.Acta, 300-302, 829 (2000).

96. (a) Welch, J.H.; Bereman, R.D.; Singh, P. Inorg.Chem., 27, 3680 (1988); (b) Vance, C.T.; Bereman , R.D.; Bordner, J.; Hatfield, W.E.; Helms, J.H. Inorg.Chem., 24, 2905 (1985); (c) Faulmann, C; Cassoux, P.; Yagubskii, E.B.; Vetoshkina, L.V. New J.Chem., 17, 385 (1993); (d) Tian-Ming, Y; Jing-Lin, Z.; Xiao-Zeng, Y; Xiao-Ying, H . Polyhedron, 14, 1487 (1995); (e) Noh, D.-Y; Lee, H.-J.; Underhill, A.E. Synth.Met., 86, 1837 (1997); (f) Lee, H.J.; Noh, D.Y. Polyhedron, 19, 425 (2000); (g) Vance, C.T.; Welch, J.H.; Bereman, R.D. Inorg.Chim.Acta, 164, 191 (1989); (h) Schultz, A.J.; Wang, H.H.; Soderholm, L.C.; Sifter, T.L.; Williams, J.M.; Bechgaard, K. ; Whangbo, M.-H. Inorg.Chem., 26, 3757 (1987).

97. (a) Welch, J.H.; Bereman, R.D.; Singh, P.; Haase, D.; Hatfield, W.E.; Kirk, M.L. Inorg.Chim.Acta, 162, 89 (1989); (b) Kim, H.; Kobayashi, A.; Sasaki, Y; Kato, R.; Kobayashi, H . BullChem.SocJpn., 61, 579 (1988).

98. (a) Welch, J.H.; Bereman, R.D.; Singh, P.; Inorg.Chim.Acta, 163, 93 (1989); (b) Gritsenko, V.V.; Dyachenko, O.A.; Cassoux, P.; Kotov, A.L.; Laukhina, E.E.; Faulmann, C; Yagubskii, E.B. Izv.Akad.Nauk. SSR, Ser.Khim., 1207 (1993); (c) Geiser.U.; Schultz, A.J.; Wang, H.H.; Beño, M.A.; Williams, J.M. Acta Cryst., C44, 259(1988).

99. (a) Welch, J.H.; Bereman, R.D.; Singh, P. Inorg.Chem., 27,2862 (1988); (b) Livage, C; Formigue, M.; Batail, P.; Canadell, E.; Coulon, C. Bull.Soc.Chim.Fr, 130,16\ (1993); (c) Welch, J.H.; Bereman, R.D.; Singh, P. Inorg.Chem., 29, 68 (1990).

100. (a) Zuo, J.-L.; You, F.; Fun, H.-K. Polyhedron, 16,1465 (1997); (b) Zuo, J.-L.; Yao, T.-M.; You, F.; You, X.-Z.; Fun, H.-K.; Yip, B.-C. J.Mater.Chem., 6, 1633 (1996).

101. (a) Nakamura, T.; Nogami, T.; Shirota, Y BullChem.SocJpn., 60, 3447 (1987); (b) Kim, H.; Kobayashi, A.; Sasaki, Y; Kato, R.; Kobayashi, H.; Nakamura, T.; Nogami, T.; Shirota, Y BullChem.SocJpn. 61, 2559 (1988).

102. (a) Lee, H.J.; Noh, D.Y. J.Mater.Chem., 10, 2169 (2000); (b) Lee, H.J.; Noh, D.Y. Synth.Met, 102, 1696 (1999).

103. (a) Tomura, M.; Tanaka, S.; Yamashita, Y Synth.Met., 64, 197 (1994).

104. (a) Bigoli, R; Chen, C.-T.; Wu, W.-C; Deplano, P.; Mercuri, M.L.; Pellinghelli, M.A.; Pilia, L.; Pintus, L.; Serpe, A.; Trogu, E.F. Chem.Commun., 2246 (2001); (b) Bigoli , F.; Deplano, P.; Mercuri, M.L.; Pellinghelli, M.A.; Pintus, L.; Serpe, A.; Trogu, E.F. JAm.Chem.Soc, 123, 1788 (2001).

105. (a) Bereman, R.D.; Lu, H. Inorg.Chim.Acta, 204, 53 (1993); (b) Dautel, O.J.; Fourmigué, M. Inorg.Chem., 40, 2083 (2001); (c) Yao, T.-M.; You, X.-Z.; Li, C ; Li, L.-F. Acta Cryst, C50, 61 (1994); (d) Geiser, U.; Tytko, S.F.; Allen, T.J.; Wang, H.H.; Kini, A.M.; Williams, J.M. Acta Cryst, C47, 1164 (1991).

106. (a) Charlton, A.; Underhill, A.E.; Kobayashi, A.; Kobayashi, H. J.Chem.Soc, Dalton Trans., 1285 (1995); (b) Charlton, A.; Underhill, A.E.; Malik, K.M.A.; Hursthouse, M.B.; Jorgensen, T.; Bêcher, J. Synth.Met., 68, 221 (1995).

107. (a) Robertson, N.; Parkin, D.L.; Underhill, A.E.; Hursthouse, M.B.; Hibbs, D.E.; Malik, K.M.A. J.Mater.Chem., 5, 1731 (1995); (b) Cleary, CF.; Robertson, N.; Takahashi, M. ; Underhill, A.E.; Hibbs, D.E.; Hursthouse, M.B.; Malik, K.M.A. Polyhedron, 16, 1111 (1997); (c) Underhill, A.E.; Robertson, N.; Parkin, D.L. Synth.Met, 71, 1955 (1995).

108. Fox , S.; Wang, Y; Silver, A.; Millar, M. J.Am.Chem.Soc, 112, 3218 (1990).

109. (a) Larsen, J.; Bechgaard, K. J.Org.Chem., 52, 3285 (1987); (b) Noh, D.-Y; Mizuno, M. ; Choy, J.-H. Inorg.Chim.Acta, 216, 147 (1994).

110. Eduok, E.E.; Krawiec, M.; Buisson, Y.-S.L.; O'Conner, C.J.; Sun, D.; Watson, W.H. J.Chem.Cryst, 26, 621 (1996).

111. (a) Ganguli, K.K.; Carlisle, G.O.; Hu, H.J.; Theriot, L.J.; Bernai, I. J.lnorg. Nucl.Chem., 33, 3579 (1971); (b) Mukhopadhyay, S.; Ray, D. J.Chem.Soc, Dalton Trans., 1159 (1993); (c) Boyde, S.; Garner, CD.; Clegg, W. J.Chem.Soc, Dalton Trans., 1083 (1987); (d) Pignedoli, A.; Peyronel, G.; Antolini, L. Acta Cryst, B30, 2181 (1974).

112. (a) Boyde, S.; Garner, CD.; Enemark, J.H.; Ortega, R.B. Polyhedron, 5, 377 (1986); (b) Boyde, S.; Garner, CD.; Enemark, J.H.; Ortega, R.B. J.Chem.Soc, Dalton Trans., 297 (1987); (c) Boyde, S.; Garner, CD.; Enemark, J.H.; Bruck, M.A.; Kristofzki, J.G. J.Chem.Soc, Dalton Trans., 2267 (1987).

113. Kisch, H.; Eisen, B.; Dinnebier, R.; Shankland, K.; David, W.I.F.; Knoch, F. Chem.Eur.J, 7, 73S (2001).

114. (a) Kubo, K.; Nakano, M.; Hamaguchi, S.; Matsubayashi, G. Inorg.Chim.Acta, 346, 43 (1993); (b) Le Narvor, N.; Robertson, N.; Weyland, T.; Kilburn, J.D.; Underhill, A.E.; Webster, M.; Svenstrup, N.; Bêcher, J. Chem.Commun., 1363 (1996); (c) Ueda, K.; Goto, M.; Sugimoto, T.; Endo, S.; Toyota, N.; Yamamoto, K.; Fujita, H. Synth.Met, 85, 1679 (1997); (d) Le Narvor, N.; Robertson, N.; Wallace, E.; Kilburn, J.D.; Underhill, A.E.; Bartlert, P.N.; Webster, M. J.Chem.Soc, Dalton Trans., 823 (1996); (e) Nakazono, T.; Nakano, M.; Tamura, H.; Matsubayashi, G. J.Mater.Chem., 9, 2413 (1999).

115. (a) Nakano, M.; Kuroda, A.; Maikawa, T.; Matsubayashi, G. Mol.Cryst.Liq.Cryst, 284, 301 (1996); Nakano, M.; Kuroda, T.; Matsubayashi, G. Inorg.Chim.Acta, 254, 189(1997).

116. (a) Kumasaki, M.; Tanaka, H.; Kobayashi, A. J.Mater.Chem., 8, 301 (1998); (b) Kobayashi, A.; Tanaka, H.; Kumasaki, M.; Torii, H.; Narymbetov, B.; Adachi, T. JAm.Chem.Soc, 121, 10763 (1999); (c) Kobayashi, A.; Kumasaki, M.; Tanaka, H. Synth.Met, 102, 1768 (1999).

117. Kobayashi, A.; Tanaka, H.; Kobayashi, H. JMater.Chem., 11, 2078 (2001).

118. Tanaka, H.; Okano, Y.; Kobayashi, H.; Suzuki, W.; Kobayashi, A. Science, 291, 285 (2001).

4 CHAPTER 4: FROM ELECTRON TRANSFER TO CHEMISTRY: ELECTROCHEMICAL ANALYSIS OF ORGANOMETALLIC REACTION CENTERS AND OF THEIR INTERACTION ACROSS LIGAND BRIDGES

1. Creutz, C; Taube, H. J. Am. Chem. Soc, 95, 1086 (1973).

2. Creutz, C. Prog. Inorg.Chem., 30, 1 (1983).

3. Kaim , W.; Bruns, W.; Poppe, J.; Kasack, V. J. Mol Struct, 292, 221 (1993).

4. Kaim, W.; Klein, A.; Glõckle, M. Ace. Chem. Res., 33, 755 (2000).

5. (a) Stout, D.M.; Meyers, A.I. Chem. Rev, 82, 223 (1982). (b) Lee, I.-S. H.; Jeoung, E. H.; Kreevoy, M. M. J. Am. Chem. Soc, 119, 2722 (1997).

6. Kõlle, U. New J. Chem., 16, 157 (1992).

7. (a) Kõlle, U.; Grãtzel, M. Angew. Chem., 99, 572 (1987); Angew. Chem. Int. Ed. Engl, 26, 568 (1987). (b) Kõlle, U.; Kang, B.-S.; Infelta, P.; Compte, P.; Grãtzel, M. Chem. Ber., 112, 1869 (1989).

8. (a) Westerhausen, D.; Hermann, S.; Hummel, W.; Steckhan, E. Angew. Chem., 104, 1496 (1992); Angew. Chem. Int. Ed. Engl.,31, 1529 (1992). (b) Steckhan, E.; Hermann, S.; Ruppert, R.; Thõmmes, J.; Wandrey, C. Angew. Chem., 102, 445 (1990); Angew. Chem. Int. Ed. Engl.,29, 388 (1990). (c)

9. (a) Ziessel, R. J. Am.Chem.Soc, 115, 118 (1993). (b) Ziessel, R. Angew. Chem., 103, 863 (1991); Angew. Chem. Int. Ed. Engl, 30, 844 (1991). (c) Ziessel, R.; Noblat-Chardon, S.; Deronzier, A.; Matt, D.; Toupet, L.; Balgroune, F.; Grandjean, D. Acta Cry st., B49, 515 (1992).

10. Cosnier, S.; Deronzier, A.; Vlachopoulos, N. J. Chem. Soc, Chem. Commun., 1259 (1989). Rodriguez, M; Romero, I.; Llobet, A., Deronzier, A.; Biner, M.; Parella, T.; Stoeckli-Evans, H. Inorg. Chem., , 40, 4150 (2001). Laguitton-Pasquier, H.; Martre, A. ; Deronzier, A. J. Phys. Chem. B, 105, 4801 (2001). Chardon-Noblat, S.; Deronzier, A.; Ziessel, R. Collect. Czech. Chem. Commun., 66, 207 (2001). Chardon-Noblat, S.; Deronzier, A.; Haiti, F.; Van Slageren, J.; Mahabiersing, T. Eur. J. Inorg. Chem., 613 (2001). Chardon-Noblat, S.; Cripps, G. H.; Deronzier, A.; Field, J. S.; Gouws, S.; Haines, R.; Southway, F. Organometallics, 20, 1668 (2001). Romero, I.; Collomb,

M.-N.; Deronzier, A.; Llobet, A.; Perret, E.; Pecaut, J.; Le Pape, L.; Latour, J.-M. Eur. J. Inorg. Chem., 69 (2001).

11. Ladwig,. M.; Kaim, W. J. Organomet. Chem., 419, 233 (1991).

12. Ladwig, M.; W. Kaim, W. J. Organomet. Chem., 439, 79 (1992).

13. Kaim, W.; Reinhardt, R.; Sieger, M. Inorg. Chem., 33, 4453 (1994).

14. Kaim, W.; Reinhardt, R.; Waldhõr, E.; Fiedler, J. J. Organomet. Chem., 524, 195 (1996).

15. Zalis, S.; Sieger, M.; Greulich, S.; Stoll, H; Kaim, W. Inorg. Chem., 42, 5185 (2003).

16. Reinhardt, R.; Kaim, W. Z Anorg. Allg. Chem., 619, 1998 (1993).

17. Greulich, S.; Kaim, W.; Stange, A.; Stoll, H.; Fiedler, J.; Zalis, S. Inorg. Chem., 35, 3998(1996).

18. Berger, S.; Baumann, F.; Scheiring, T.; Kaim, W. Z. Anorg. Allg. Chem. 627 (2001) 620 (2001).

19. Greulich, S.; Klein, A.; Knoedler, A.; Kaim, W. Organometallics, 21, 765 (2002).

20. Heilmann, O.; Hausen, H.-D.; Kaim, W. Z Naturforsch., 49b, 1554 (1994).

21. Heilmann, O.; Hornung, F. M.; Kaim, W.; Fiedler, J. J. Chem. Soc, Faraday Trans., 92,4233(1996) .

22. Heilmann, O; Hornung, F. M.; Fiedler, J.; Kaim, W. J. Organomet. Chem., 589, 2 (1999).

23. Baumann, F.; Stange, A.; Kaim, W. Inorg. Chem. Commun., 1, 305 (1998).

24. Kaim, W.; Reinhardt, R.; Greulich, S.; Fiedler, J. Organometallics, 22, 2240 (2003).

25. Berger, S.; Scheiring, T.; Fiedler, J.; Kaim, W., manuscript in preparation.

26. Reinhardt , R.; Fees, J.; Klein, A.; Sieger, M.; Kaim, W. in Wasserstoff als Energietrager,

VDI-Verlag,Dusseldorf, 1994, p. 133.

27. Ernst, S.; Kaim, W. J. Am. Chem. Soc, 108, 3578 (1986).

28. Fees, J.; Kaim, W.; Moscherosch, M.; Matheis, W.; Klima, J.; Krejcik, M.; Zalis, S. Inorg. Chem., 32, 166 (1993).

29. Kaim, W. Coord. Chem. Rev., 219-221, 463 (2001).

30. Astruc, D. Electron Transfer and Radical Processes in Transition Metal Chemistry, VCH, New York, 1995.

31. Bruns, W.; Kaim, W.; Ladwig, M.; Olbrich-Deussner, B.; Roth, T.; Schwederski, B. in Molecular Electrochemistry of Inorganic, Bioinorganic and Organometallic Compounds, (Pombeiro, A.J.L.; McCleverty, J., eds.), Kluwer Academic Publishers, Dordrecht (Nat o ASI Series C 385), 1993, p. 255.

32. Greulich, S.; Reinhardt, R.; Fiedler, J.; Kaim, W., unpublished results.

33. Haim , A. Prog. Inorg. Chem., 30, 273 (1983).

34. Kaim , W.; Kohlmann, S. Inorg. Chem., 25, 3306 (1986).

35. Kaim, W.; Kohlmann, S.; Jordanov, J.; Fenske, D. Z. Anorg. Allg. Chem., 598/599, 217(1991).

36. Kaim, W.; Reinhardt, R.; Fiedler, J. Angew. Chem., 109, 2600 (1997); Angew. Chem. Int. Ed. Engl., 36, 2493 (1997).

37. Kaim, W.; Berger, S.; Greulich, S.; Reinhardt, R.; Fiedler, J. J. Organomet. Chem., 582, 153 (1999).

38. Berger, S.; Klein, A.; Wanner, M.; Fiedler, J.; Kaim, W. Inorg. Chem., 39, 2516 (2000).

39. Kaim, W.; Reinhardt, R.; Greulich, S.; Sieger, M.; Klein, A.; Fiedler, J. Collect. Czech. Chem. Commun., 66,291 (2001).

40. Glõckle , M.; Fiedler, J.; Kaim, W. Z Anorg. Allg. Chem., 627, 1441 (2001).

41. Frantz, S.; Reinhardt, R.; Greulich, S.; Wanner, M.; Kaim, W.; Fiedler, J.; DubocToia, C , Dalton Trans., 3370 (2003).

42. Baumann, F.; Kaim, W.; Sarkar, B.; Denninger, G.; Kümmerer, H.-J.; Fiedler, J., unpublished results.

43. Kaim, W. Coord Chem. Rev., 76, 187 (1987).

44. Robin, M. B., Day, P. Adv. Inorg. Chem. Radiochem., 10, 247 (1967).

45. Ernst, S.; Kasack, V.; Kaim, W. Inorg. Chem., 27, 1146 (1988).

46. Scheiring, T.; Fiedler, J.; Kaim, W. Organometallics, 20, 1437 and 3209 (2001).

47. Frantz, S.; Weber, M.; Scheiring, T.; Fiedler, J.; Duboc, C; Kaim, W., Inorg. Chim. Acta, in print.

48. Hawecker, J.; Lehn, J. M.; Ziessel, R. Helv. Chim. Acta, 69, 1900 (1986). Sullivan, B. P.; Meyer, T. J. J. Chem. Soc, Chem. Commun., 1244 (1984).

49. Scheiring , T.; Klein, A.; Kaim, W. J. Chem. Soc, Perkin Trans. 2, 2569 (1997).

50. Tributsch, H. J. Electroanal. Chem., 331, 783 (1992).

5 CHAPTER 5: BOND AND STRUCTURE ACTIVATION BY ANODIC ELECTRON-TRANSFER:METAL-HYDROGEN BOND CLEAVAGE AND cis/trans ISOMERIZAHON IN COORDINATION COMPOUNDS

1. Vlcek, A., Jr. Chemtracts-Inorg. Chem., 5, 1 (1993).

2. Geiger, W.E. Ace. Chem. Res., 28, 351 (1995).

3. Bond, A.M.; Colton, R. Coord Chem. Rev., 166, 161 (1997).

4. Battaglini, F.; Calvo, E.J.; Doctorovich, F. J. Organometal. Chem., 547, 1 (1997)

5. Pombeiro, A.J.L.; A.J.L.; Guedes da Silva, M.F.C.; Lemos, M.A.N.D.A. Coord. Chem. Rev., 219-221, 53 (2001).

6. Pombeiro, A.J.L. Portugaliae Electrochim. Acta, 1,19 (1983).

7. Pombeiro, A.J.L.; McCleverty, J. (Eds.) Molecular Electrochemistry of Inorganic, Bioinorganic and Organometal lie Compounds, NATO ASI Series, Kluwer Academic, Dordrecht , 1993.

8. Astruc, D. Electron Transfer and Radical Processes in Transition-Metal Chemistry, VCH, New York, 1995.

9. Savéant, J.-M. Advances in Physical Organic Chemistry, 35, Academic Press, London, 2000, pp. 117-192.

10. Crabtree, R.H. The Organometallic Chemistry of the Transition Elements, 3 rd éd., John Wiley, Toronto, 2001.

11. Astruc, D. Chimie Organométallique, EDP Sciences, Les Ulis, 2000.

12. Mathey , F.; Sevin, A. Molecular Chemistry of the Transition Elements, John Wiley, Chichester, 1996.

13. Fraústo da Silva, J.J.R.; Williams, R.J.P. The Biological Chemistry of the Elements, Oxford Univ. Press, 2 nd éd., 2001.

14. Kaim, W.; Schwederski, B. Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life, John Wily, Chichester, 1994.

15. Peruzzini, M.; Poli, R. (Eds.) Recent Advances in

Hydride Chemistry, Elsevier, Amsterdam, 2001 .

16. (a) Ruiz, J; Ogliaro, F.; Saillard, J.-Y; Halet, J.-F; Varret, E; Astruc, D. J. Am. Chem. Soc, 120, 11693 (1998). (b) Roth, T.; Kaim, W. Inorg. Chem., 31, 1930 (1992).

17. (a)Geiger, W.E.; Shaw, M.J.; Wünsch, M; Barnes, CE.; Foersterling, F.H. J. Am. Chem. Soc. 119, 2804 (1997). (b) Delville-Desbois, M.-H.; Mross, S.; Astruc, D.; Linares, J. ; Varret, F.; Rabaâ, H.; Le Beuze, A.;. Saillard, J.-Y; Culp, R.D.; Atwood, D.A.; Cowley, A.H. J. Am. Chem. Soc. 118, 4133 (1996). (c) Delville-Desbois, M.H.; Mross, S.; Astruc, D. Organometallics, 15, 5598 (1996). (d) Powell, D.W.; Lay, P.A. Inorg. Chem., 31, 3542 (1992).

18. (a) Szczepura, L.F.; Kubow, S.A.; Leising, R.A.; Perez, W.J.; Huynh, M.H.V.; Lake, C.H.; Churchill, D.G.; Churchill, M.R.; Takunchi, K.J., J. Chem. Soc. Dalton Trans., 1463 (1996) . (b) Tomita, A.; Sano, M., Inorg. Chem., 33, 5825 (1994). (c) Sano, M.; Taube, H . Inorg. Chem., 33, 705 (1994). (d) Sano, M.; Taube, H. J. Am. Chem. Soc, 113, 2327 (1991). (e) Roth, T.; Kaim, W. Inorg. Chem., 31, 1930 (1992).

19. (a) Pierce, D.T.; Hatfield, T.L.; Billo, E.J.; Ping, Y. Inorg. Chem., 36, 2950 (1997). (b) Villeneuve, N.M.; Schroeder, R.R.; Ochrymowycz, L.A.; Rorabacher, D.B. Inorg. Chem. 36, 4475 (1997). (c) Robandt, P.V.; Schroeder, R.R.; Rorabacher, D.B. Inorg. Chem., 32, 3957 (1993). (d) Cárdenas, D.J.; Livoreil, A.; Sauvage, J.-P. J. Am. Chem. Soc, 118, 11980 (1996). (e) Livoreil, A.; Dietrich-Buchecker, CO.; Sauvage, J.-P . J. Am. Chem. Soc, 116, 9393 (1994).

20. Wytko, J.A.; Boudon, C; Weiss, J.; Gross, M. Inorg. Chem., 35, 4469 (1996).

21. Jacq, J. J. Electroanal. Chem. Interfacial Electrochem., 29, 149 (1971).

22 . (a) Evans, D.E. Chem. Rev., 90, 739 (1990). (b) Astruc, D. Angew Chem. Int. Ed. Engl., 27, 643 (1988). (c) Geiger, W.E. Progress Inorg. Chem., 33, 275 (1985). (d) Vallat, A.; Person, M.; Roullier, L.O.; Laviron, E. Inorg. Chem., 26, 332 (1987).

23. Pombeiro, A.J.L. Inorg. Chem. Commun., 4, 585 (2001).

24. Pombeiro , A.J.L. ; Guedes da Silva, M.F.C J.

Organometal. Chem., 617-618, 65 (2001)

25. Almeida, S.S.P.R.; Guedes da Silva, M.F.C; Fraústo da Silva, J.J.R.; Pombeiro, A.J.L. J. Chem. Soc, Dalton Trans., 467 (1999).

26. Guedes da Silva, M.F.C; Lemos, M.A.N.D.A.; Fraústo da Silva, J.J.R.; Pombeiro, A.J.L.; Pellinghelli, M.A.; Tiripicchio, A. J. Chem. Soe, Dalton Trans., 373 (2000).

27. Lemos, M.A.N.D.A.; Guedes da Silva, M.F.C; Pombeiro, A.J.L. Inorg. Chim. Acta, 226,9(1994).

28. (a) Ryan, O.B.; Tilset, M.; Parker, V.D. J. Am. Chem. Soc, 112, 2618 (1990). (b) Tilset, M. J. Am. Chem. Soe, 114, 2740 (1992). (c) Skagestad, V; Tilset, M. J. Am. Chem. Soc, 115, 5077 (1993). (d) Tilset, M.; Hamon, J.-R; Hamon, P. Chem. Commun., 765 (1998). (e) Tilset, M.; Fjeldahl, L; Hamon, J.-R.; Hamon, P.; Toupet, L.; Saillard, J.-Y; Costuas, K.; Haynes, A. J. Am. Chem. Soc, 123, 9984 (2001).

29. Marken, R; Bond, A.M.; Colton, R. Inorg. Chem., 34, 1705 (1995).

30. Wang, D.; Angelici, R.J. J. Am. Chem. Soc, 118, 935 (1996).

31. Berning, D.E.; Noll, B.C.; DuBois, D.L., J. Am. Chem. Soc. 121, 11432 (1999).

32. Lemos, M.A.N.D.A.; Pombeiro, A.J.L. J. Organometal. Chem., 438, 159 (1992).

33. Lemos, M.A.N.D.A.; Pombeiro, A.J.L. J. Organometal Chem., 332, C17 (1987)

34. Venancio, A.I.F.; Kuznetsov, M.L.; Guedes da Silva, M.F.C.; Martins, L.M.D.R.S.; Fraústo da Silva, J.J.R.; Pombeiro, A.J.L. Inorg. Chem., 41, 6456 (2002).

35. Klinger, R.J.; Huffman, J.C.; Kochi, J.K. J. Am. Chem. Soc., 102, 208 (1980).

36. Pedersen , A.; Tilset, M. Organometallics, 13, 4887 (1994).

37. Ryan, O.B.; Tilset, M. J.Am. Chem. Soc., 113, 9554 (1991).

38. Zlota, A.A.; Tilset, M.; Caulton, K.G. Inorg. Chem., 32, 3816 (1993).

39. Smith , K.-T.; Tilset, M.; Kuhlman, R.; Caulton, K.G. J. Am. Chem. Soc, 117, 9473 (1995).

40. Westerberg, D.E.; Rhodes, L.F.; Edwin, J.; Geiger, W.E.; Caulton, K.G. Inorg. Chem.,30,\\01(\99\).

41. Smith , K.-T.; Romming, C ; Tilset, M. J. Am. Chem. Soc., 115, 8681 (1993).

42. Detty, M.R.; Jones, W.D. J. Am. Chem. Soc, 109, 5666 (1987).

43. Amatore, C; Fraûsto da Silva, J.J.R.; Guedes da Silva, M.F.C.; Pombeiro, A.J.L. ; Verpeaux, J.-N. J. Chem. Soc, Chem. Commun., 1289 (1992).

44. Guedes da Silva, M.F.C.; Fraûsto da Silva, J.J.R.; Pombeiro, A.J.L., Inorg. Chem., 41,2X9(2002).

45. Baptista A.A.; Cordeiro, L.A.C.; Oliva, G. Inorg. Chim. Acta, 203, 185 (1993).

46. Menglet, D.; Bond, A.M.; Coutinho, K.; Dickson, R.S.; Lazarev, G.G.; Olsen, S.A.; Pilbrow, J.P . J.Am. Chem. Soc, 120, 2086 (1998).

47. Bianchini, C ; Peruzzini, M.; Ceccanti, A.; Laschi, F.; Zanello, P. Inorg. Chim. Acta, 61,259(1991).

48. Guedes da Silva, M.F.C.; Hitchcock, P.B.; Hughes, D.L.; Marjani, K.; Pombeiro, A.J.L.; Richards, R.L. J. Chem. Soe, Dalton Trans., 3725 (1997).

49. Bond, A.M.; Colton, R.; Cooper, J.B.; Traeger, J.C.; Walter, J.N.; Way, D.M. Organometallics, 13, 3434 (1994).

50. Bond, A.M.; Grabaric, B.S.; Jackowski, J.J. Inorg. Chem., 17, 2153 (1978).

51. Cummings, D.A.; McMaster, J.; Rieger, A.L.; Rieger, P.H. Organometallics, 16, 4362 (1997).

52. Wimmer, F.L.; Snow, M.R.; Bond, A.M. Inorg. Chem. 13, 1617 (1974).

53. Abdel-Hamid, R.; El-Samahy, A.A.; Rabia, M.K.M.; Taylor, N.; Shaw, B.L. Bull. Chem. Soc. Jpn., 67, 321

(1994).

54. Bond , A.M.; Colton, R.; Humphrey, D.G.; Mahon, P.J.; Snook, G.A.; Tedesco, V.; Walter, J.N. Organometallics 17, 2977 (1998).

55. Bond, A.M.; Colton, R.; Gable, R.W.; Mackay, M.F.; Walter, J.N. Inorg. Chem. 36, 1181 (1997).

56. Conner, K.A.; Walton, R.A., Inorg. Chem., 25, 4422 (1986).

57. Carriedo, G.A.; Connelly, N.G.; Crespo, M.C.; Quarmby, I.C.; Riera, V.; Worth, G.H. J. Chem. Soc, Dalton Trans., 315 (1991).

58. Carriedo, G.A.; Connelly, N.G.; Crespo, M.C.; Quarmby, I.C.; Riera, V. J. Chem. Soc, Chem. Commun. 1806(1987).

59. Barrado, G.; Carriedo, G.A.; Diaz-Valenzuela, C; Riera, V. Inorg. Chem., 30, 4416 (1991).

60. Bursten, B.E. J. Am. Chem. Soc, 104, 1299 (1982).

61. Bond, A.M.; Colton, R.; Kevekordes, J.E. Inorg., Chem., 25, 749 (1986).

62. (a) Menon, M.; Pramanik, A.; Bag, N.; Chakravorty, A. J. Chem. Soe, Dalton Trans., 1543, (1995). (b) Bag, N.; Lahiri, G.K.; Chakravorty, A. J. Chem. Soc, Dalton Trans., 1557 (1990).

63. Pramanik, A.; Bag, N.; Chakravorty, A. J. Chem. Soe, Dalton Trans., 237 (1993).

64. Guedes da Silva, M.F.C. ; Fraústo da Silva, J.J.R.; Pombeiro, A.J.L.; Amatore, C; Verpeaux, J.-N. Inorg. Chem., 37, 2344 (1998).

65. Guedes da Silva, M.F.C; Fraústo da Silva, J.J.R.; Pombeiro, A.J.L., J. Organometal. Chem., 526,237 (1996).

66. Guedes da Silva, M.F.C. ; Duarte, M.T.; Galvão, A.M.; Fraústo da Silva, J.J.R.; Pombeiro, A.J.L . J. Organometal. Chem., 433, C14 (1992).

67. Guedes da Silva, M.F.C. ; Pombeiro, A.J.L.; Hills, A.; Hughes, D.L.; Richards, R.L. J. Organometal. Chem., 403, Cl (1991).

68. Kuznetsov M.L.; Pombeiro, A.J.L. Dalton Trans., 738 (2003).

69. Guedes da Silva, M.F.C; Fraústo da Silva, J.J.R.; Pombeiro, A.J.L.; Amatore, C; Verpeaux, J. -N. Organometallics, 13, 3943 (1994).

70. Anson, F.C.; Collins, T.J.; Gipson, S.L.; Keech, J.T.; Krafft, T.E.; Prake, G.T. J. Am. Chem. Soc, 108, 6593 (1986).

71. Rich , R.L.; Taube, H. J. Am. Chem. Soc, 76, 2608 (1954).

72. Basôlo, F.; Pearson, R.G. Mechanisms of Inorganic Reactions, John Wiley, New York, 196 7 and refs. therein.

73. Feldberg, S.W.; Jeftic, L. J. Phys. Chem., 76, 2439 (1972), and refs. therein.

74 . (a) Savéant, J.M. Ace. Chem. Res., 13, 323 (1980). (b) Amatore, C ; Pinson, J.; Savéant, J.M.; Thiébault, A. J. Electroanal. Chem., Interfacial Electrochem., 107, 59 (1980). (c) Amatore, C ; Pinson, J.; Savéant, J.M.; Thiébault, A. J. Am. Chem. Soc, 104, 817 (1982), and refs. therein.

75. Guede s da Silva, M.F.C; Ferreira, C. M.P.; Fraústo da Silva, J.J.R.; Pombeiro, A.J.L. J. Chem. Soc, Dalton Trans., 4139 (1998).

76. (a) Geiger, W.E., in: Zuckermann, J.J. (Ed.) Inorganic Reactions and Methods, Vol. 15, VCH, New York, 1986, p. 88. (b) Connelly, N.G.; Raven, S.J.; Carriedo, G.A.; Riera, V. J. Chem. Soc. Chem. Commun., 992 (1986).(c) Acewgoda, G.M.; Robinson, B.H.; Simpson, J. J. Chem. Soc, Chem. Commun., 284 (1982). (d) Rieke, R.D.; Kojima, H.; Õfele, K. Angew. Chem. Int. Ed. Engl., 19, 538 (1980).

6 CHAPTER 6: TOWARDS EXPLOITING THE ELECTROCHEMISTRY OF CYTOCHROME P450

1. Guengerich, F. P., Nat. Rev. Drug Discov, 1, 359, (2002).

2. Gelboin, H. V., Physiol. Rev, 60, 1107, (1980).

3. Ortiz de Montellano, P. R., Cytochrome P-450: Structure, mechanism and biochemistry, Plenum Press, New York, (1995).

4. Honeychurch, M. J., Hill, H. A. O. & Wong, L.-L., FEBSLett., 451, 351, (1999).

5. Poulos, T. L., in Cytochrome P-450, Eds. Ortiz de Montellano, P. R., Plenum Publishing Corporation, New York, (1986).

6. Poulos, T. L., Finzel, B. C. & Howard, A. J., Biochemistry, 25, 5314, (1986).

7. Hasemann, C. A., Kurumbail, R. G., Boddupali, S. S., Peterson, J. A. & Diesenhofer, J., Structure, 3,41,(1995).

8. Sonnenfeld, R. & Hansma, P. K., Science, 232, 211, (1986).

9. Liu, H. Y., Fan, F R. F, Lin, C. W. & Bard, A. J., J. Am. Chem. Soc, 108, 3838, (1986).

10. Lindsay, M. S., Thundat, T., Nagahara, L., Knipping, U. & Rill, R. L., Science, 244, 1063,(1989).

11. Lindsay, M. S., Tao, N. J., DeRose, J. A., Oden, P. I., Lyubchenko, Y. L., Harrington, R. E. & Shlyakhtenko, L., Biophys. J., 61, 1570, (1992).

12. Wandlowski, T., Lampner, D. & Lindsay, S. M., J. Electroanal. Chem., 404, 215, (1996).

13. Srinivasan, R., Murphy, J. C, Fainchtein, R. & Pattabiraman, N., J. Electroanal. Chem., 312,293, (1991).

14. Tao, N. J. & Shi, Z., J. Phys. Chem., 98, 1464, (1994).

15. Katsumata, S. & Ide, A., Jpn. J. Appl Phys., 33, 3723, (1994).

16. Katsumata, S. & Ide, A., Jpn. J. Appl. Phys., 34, 3360, (1995).

17. Salmerón, M., Beebe, T., Odriozola, J., Wilson, T., Ogletree, D. F. & Siekhaus, W., J. Vac. Technol. A, 8, 635, (1990).

18. Navaz, Z., Cataldi, T. R. I., Smekh, J. K. R. & Pethica, J. B., Surf. Sci., 265, 139, (1992).

19. Rao, S. V., Anderson, K. W. & Bâchas, L. G., Microchim. Acta, 128, 111, (1998).

20. Davis, J. J., Halliwell, C. M., Hill, H. A. O., Canters, G. W., van Amsterdam, M. C. & Verbeet, M. P., New J. Chem., 10, 1119, (1998).

21. Pethig , R., Dielectric and Electronic Properties of Biological Materials, J. Wiley and Sons, New York, (1979).

22. Morgan, H. & Pethig, R., J. Chem. Soc, Faraday Trans., 82, 143, (1986).

23. Bruni, F., Careri, G. & Leopold, A. C, Phys. Rev. A, 40, 2803, (1989).

24. Yuan , J., Shao, Z. & Gao, C , Phys. Rev. Lett, 67, 7863, (1991).

25. Lindsay, S. M., Jing, T. W., Pan, J., Vaught, A. & Rekesh, D., Nanobiology, 3, 17, (1994).

26. Garcia, R. & Garcia, N., Chem. Phys. Lett, 173, 44, (1990).

27. Eddowes , M. J. & Hill, H. A. O., J. Chem. Soc, Chem Commun., 771, (1977).

28. Yeh, P. & Kuwana, T., Chem. Lett, 1145, (1977).

29. Scheller, F., Renneberg, R., Strnad, G., Pommerening, K. & Mohr, P., Bioelectrochem. Bioenerg., 4, 500, (1977).

30. Vilker, V. L., Khan, F., Shen, D., Baizer, M. M. & Nobe, K., in Redox Chemistry and Interfacial Behaviour of Biological Molecules, Eds. Dryhurst, G. and Niki, K., Plenum, Ne w York, (1988).

31. Faulkner, K. M., Shet, M. S., Fisher, C. W. & Estabrook, R. W., Proc. Natl. Acad. Sci. USA, 92, 7705, (1995).

32. Reipa, V., Mayhew, M. P. & Vilker, V. L., Proc. Natl. Acad. Sci. USA, 94, 13554, (1997).

33. Kazlauskaite, J., Westlake, A. C. G., Wong, L.-L. & Hill, H. A. O., Chem. Commun., 75,2189,(1996).

34. Di Gleria, K., Nickerson, D. P., Hill, H. A. O., Wong, L.-L. & Fulop, V, J. Am. Chem. Soc, 120, 46, (199S).

35. Lo, K. K.-W., Wong, L.-L. & Hill, H. A. O., FEBSLett, 451, 342, (1999).

36. Davis, J. J., Djuricic, D., Lo, K. K. W., Wallace, E. N. K., Wong, L.-L. & Hill, H. A. O., Faraday Discuss., 116, 15, (2000).

37. Rusling, J. F. & Nassar, A.-E. F., J. Am. Chem. Soc, 115, 11891, (1993).

38. Lvov, Y M., Lu, Z., Schenkman, J. B., Zu, X. & Rusling, J. F., J. Am. Chem. Soc, 120, 4073, (1998).

39. Lei, C , Wollenberger, U., Jung, C. & Scheller, F. W., Biochem. Biophys. Res. Commun., 268, 740, (2000).

40. Zhang, Z., Nassar, A.-E. F., Lu, Z., Schenkman, J. B. & Rusling, J. F., J. Chem. Soc, Faraday Trans., 93, 1769, (1997).

41. Rusling, J. F., Ace Chem. Res., 31, 363, (1998).

42. Koo, L. S., Immos, C. E., Cohen, M. S., Farmer, P. J. & Ortiz de Montellano, P. R., J. Am. Chem. Soc, 124, 5684, (2002).

43. Aguey-Zinsou, K.-F., Bernhardt, P. V., De Voss, J. J. & Slessor, K. E., Chem. Commun., 418, (2003).

44. Iwuoha, E., Kane, S., Ania, C. O., Smyth, M. R., Ortiz de Montellano, P. R. & Fuhr, U., Electroanalysis, 12, 980, (2000).

45. Shumyantseva, V. V., Bulko, T. V., Usanov, S. A., Schmid, R. D., Nicolini, C. & Archakov, A. I., J. Inorg. Biochem., 87, 185, (2001).

46. Iwuoha, E. I., Joseph, S., Zhang, Z., Smyth, M. R., Fuhr, U. & Ortiz de Montellano, P. R. , J. Pharm. Biomed. Anal, 17, 1101, (1998).

47. Zu, X., Lu, Z., Zhang, Z., Schenkman, J. B. & Rusling, J. F., Langmuir, 15, 7372, (1999).

48. Munge, B., Estavillo, C , Schenkman, J. B. & Rusling, J. F., ChemBioChem, 4, 82, (2003).

49. Sligar, S. G., Cinti, D. L., Gibson, G. G. & Schenkman, J. B., Biochem. Biophys. Res. Commun., 90, 925, (1979).

50. Castro , C. E., Wade, R. S. & Belser, N. O., Biochemistry, 24, 204, (1985).

51. Li, S. & Wackett, L. P., Biochemistry, 32, 9355, (1993).

52. Xie, W., Jones, J. P., Wong, L.-L. & Hill, H. A. O., Chem. Commun., 2370, (2001).

7 CHAPTER 7: CHEMISTRY, ELECTROCHEMISTRY AND ALL-IRONHYDROGENASE

1. Nicolet, Y; Piras, C ; LeGrand, P.; Hatchikian, C.E.; Fontecilla-Camps, J.C. Structure, 7, 13, (1997).

2. Peters, J.W.; Lanzilotta, W.N.; Lemon, B.J.; Seefeldt, L.C. Science, 282, 1853, (1998).

3. Pierik, A.J.; Hulstein, M.; Hagen, W.R.; Albracht, S.P.J. Eur J. Biochem., 258, 572, (1998); De Lacey, A.L.; Stadler, C ; Cavazza, C; Hatchikian, E.C.; Fernandez, V.M. JAm.Chem.Soc, 122, 11232, (2000); Nicolet, Y.; De Lacey, A.L.; Vernede, X.; Fernandez , V.M.; Hatchikian, E.C.; Fontecilla-Camps, J.C. J. Am. Chem. Soc, 725,1596,(2001).

4. Pereira, A.S.; Tavares, P.; Moura, I.; Moura, J.J.G.; Huynh, B.H., J. Am. Chem. Soc, 725,2771,(2001).

5. Popescu, C.V.; Munck, E. J. Am. Chem. Soc, 121,1%11, (1999).

6. Surerus, K.K.; Chen, M.; Vanderzwaan, J.W.; Rusnak, F.M.; Kolk, M.; Duin, E.C.; Albracht, S.P.J. ; Munck, E. Biochemistry, 33, 4980, (1994).

7. DeLacey, A.L.; Stadler, C ; Cavazza, C; Hatchikian, E.C.; Fernandez, V.M. J. Am. Chem. Soc, 122, 11232, (2000).

8. Razavet, M.; Borg, S.J.; George, S.J.; Best, S.P.; Fairhurst, S.A.; Pickett, C.J. Chem. Commun., 700,(2002).

9. Cao, Z.X.; Hall, M.B. J. Am. Chem. Soc, 123, 3734, (2001).

10. Nicolet, Y; Lemon, B.J.; Fontecilla-Camps, J.C; Peters, J.W. Trends Biochem. Set, 25, 138, (2000).

11. Peters, J.W. personal communication.

12. Reihlen, H.; Gruhl, A.; Hessling, G. Liebigs Annalen Der Chemie, 472, 268, (1929).

13. Seyferth, D.; Womack, G.B.; Archer, CM.; Dewan, J.C. Organometallics, 8, 430, (1989).

14. Lyon, E.J.; Georgakaki, LP.; Reibenspies, J.H.; Darensbourg, MY. Angew. Chem., In.Ed, 38, 3178, (1999).

15. Schmidt, M.; Contakes, S.M.; Rauchfuss, T.B. J. Am. Chem. Soc, 121, 9736, (1999).

16. Le Cloirec, A.; Best, S.P.; Borg, S.; Davies, S.C; Evans, D.J.; Hughes, D.L.; Pickett, C.J. Chem. Commun., 2285, (1999).

17. Lawrence, D.; Li,H.X.; Rauchfuss,T.B.; Benard, M.; Rohmer, M.M.Angew.Chem., Int. Ed., 40, 1768, (2001).

18. Lyon, E.J.; Georgakaki, LP.; Reibenspies, J.H.; Darensbourg, MY. J. Am. Chem. Soc, 123, 3268, (2001).

19. Gloaguen, F.; Lawrence, J.D.; Schmidt, M.; Wilson, S.R.; Rauchfuss, T.B. JAm.Chem.Soc, 123, 12518, (2001).

20. George, S.J.; Cui, Z.; Razavet, M.; Pickett, C.J. Chemistry: A European Journal, 8, 4037, (2002).

21. Razavet, M.; Davies, S.C; Hughes, D.L.; Pickett, C.J. Chem. Commun., 847, (2001).

22. Razavet, M.; Davies, S.C; Hughes, D.L.; Barclay, J.E.; Evans, D.J.; Fairhurst, S.A.; Liu, X.; Pickett, C.J. JChem.Soc, Dalton Trans., 586, (2003).

23. Liu, Z.R; Hu, P. J. Am. Chem. Soc, 124, 5175, (2002).

24. Chart, J.; Kan, C.T.; Leigh, G.J.; Pickett, CJ.; Stanley, D.R. J.C.S Dalton, 2032, (1980).

25. Teo, B.K.; Hall, M.B.; Fenske, R.R; Dahl, L.F. Inorg. Chem., 14, 3103-3117, (1975).

26. Zhao, X.; Georgakaki, LR; Miller, M.L.; Yarbrough, J.C.; Darensbourg, M.Y. J. Am. Chem. Soc, 123, 9710, (2001).

27. Coliman, J.R; Wagenknect, P.S.; Hembre, R.T.; Lewis, N.S.; J. Am. Chem. Soc, 772,1294,(1990).

28. Zhao, X.; Georgakaki, LR; Miller, MX.; Mejia-Rodriguez, R.; Chiang, C.Y; Darensbourg, M.Y . Inorg.Chem., 41, 3917, (2002).

29. Gloaguen, R; Lawrence, J.D.; Schmidt, M.; Wilson, S.R.; Rauchfuss, T.B. J. Am. Chem. Soc, 123, 12518, (2001).

30. Best , S.R; Borg, S.; Razavet, M.; Liu, X.; Tard, C; Pickett, CJ. unpublished results

31. Evans, D.J.; Pickett, CJ. Chem.Soc.Rev., inpress, 2003.

9 CHAPTER 9: ELECTROCHEMISTRY AND ELECTRON-TRANSFER CHEMISTRY OF METALLODENDRIMERS

1. For a recent book, see: Newkome, G. R.; Moorefield, C. N.; Vogtle, F. "Dendrimers andDendrons. Concept, Syntheses, Applications", Wiley-VCH, Weinheim (2001).

2. Balzani, V.; Campana, S.; Denti, G.; Juris, A.; Serroni, S.; Venturi, M. Ace. Chem. Res., 31, 26 (1998).

3. For a comprehensive review, see: Ardoin, N.; Astruc, D. Bull. Soc. Chim. Fr., 132, 875 (1995) .

4. Hamon, J.-R.; Saillard, J.-Y.; Le Beuze, A.; McGlinchey, M; Astruc, D. J. Am. Chem. Soc, 104, 3755 (1982).

5. a) Moulines, F.; Astruc, D. Angew. Chem. Int. Ed. Engl, 27, 1347 (1988); b) Moulines, F. ; Astruc, D. J. Chem. Soc. Chem. Commun., 614 (1989).

6. Alonso, B.; Biais, J.-C; Astruc, D. Organometallics, 21, 1001 (2000).

7. a) Fillaut, J.-L.; Linares, J.; Astruc, D. Angew. Chem. Int. Ed. Engl, 33, 2460 (1994); b) Fillaut, J.-L.; Boese, R.; Astruc, D. Synlett, 55 (1992); c) Fillaut, J.-L.; Astruc, D . New J. Chem., 20, 945 (1996).

8. Moulines , F.; Gloaguen, B.; Astruc, D. Angew. Chem. Int. Ed. Engl, 28, 458 (1992).

9. Marx, H. W.; Moulines, F.; Wagner, T.; Astruc, D. Angew. Chem. Int. Engl, 35, 1701 (1996).

10. Moulines, F.; Djakovitch, L.; Boese, R.; Gloaguen, B.; Thiel, W.; Fillaut, J.-L.; Delville, M.-H.; Astruc, D. Angew. Chem. Int. Ed. Engl, 105, 1132 (1993).

11. Trujillo, H.; Casado, C; Ruiz, J.; Astruc, D. J. Am. Chem. Soc, 121, 5674 (1999).

12. a) Alonso, B.; Cuadrado, L; Moran, M.; Losada, J. J. Chem. Soc, Chem. Commun., 2575 (1994); b) Garcia, B.; Casado, C; Cuadrado, L; Alonso, B.; Mora, M.; Losada, J. Organometallics, 18, 2349 (1999).

13. Alonso , B.; Moran, M.; Casado, C. M.; Lobete, F.; Losada, J.; Cuadrado, I. Chem. Mater., 7, 1440 (1995).

14 . Losada, J.; Cuadrado, L; Moran, M.; Casado, C. M.; Alonso, B.; Barranco, M. Anal. Chim. Acta., 251, 5 (1996); 338, 191 (1997).

15. Casado, C. M.; Alonso, B.; Moran, M.; Cuadrado, L; Losada, J. J. Electroanal Chem., 463, 87 (1999).

16. Cuadrado, L; Casado, C. M.; Alonso, B.; Moran, M.; Losada, J.; Belsky, V. J. Am. Chem. Soc, 119,7613 (1997).

17. a) Takada, K.; Diaz, D. J.; Abruña, H.; Cuadrado, L; Casado, C. M.; Alonso, B.; Moran,M.;Losada,J.J.Am. Chem. Soc, 119,10763 (1997);b)Cuadrado,L;Moran, M.; Casado, C. M.; Alonso, B.; Lobete, F.; Garcia, B.; Losada, J. Organometallics, 15, 5278 (1996).

18. a) Castro, R.; Cuadrado, L; Alonso, B.; Casado, C. M.; Moran, M.; Kaifer, A. J. Am. Chem. Soc, 119, 5760 (1997); b) Kaifer, A. E.; Gomez-Kaifer, M. Supramolecular Electrochemistry, Wiley-VCH, Weinheim, (1999).

19. a) Gonzãlez, B.; Casado, C. M.; Alonso, B.; Cuadrado, L; Moran, M.; Wang, Y.; Kaifer, A. E. Chem. Commun., 2569 (1998); b) Valerio, C ; Ruiz, J.; Fillaut, J.-L.; Astruc, D. C. R. Acad. Sel, Paris, 2, sẽrie II c, 79 (1999).

20. a) Casado, C. M.; Gonzales, B.; Cuadrado, I.; Alonso, B.; Moran, M.; Losada, J. Angew. Chem. Int. Ed. Engl, 39, 2135 (2000); (b) Gonzales, B.; Cuadrado, I.; Casado, C . M.; Alonso, B.; Pastor, C. Organometallic, 19, 5518 (2000).

21. Cardona, C. M.; Kaifer, A. E. J. Am. Chem. Soc., 120, 4023 (1998).

22. Newkome, G. R.; Behera, R. K.; Moorefield, C. N.; Baker, G. R. J. Org. Chem., 56, 7126(1991).

23. a) Wang, Y.; Cardona, C ; Kaifer, A. E. J. Am. Chem. Soc., 121, 9756 (1999); b) Kaifer, A . E.; Gomez-Kaifer, M. Supramolecular Electrochemistry, Wiley-VCH: Weinheim(1999).

24. Togni, A.; Hayashi, T., Eds.; Ferrocenes, VCH: Weinheim (1995).

25. a) Kõllner, C; Pugin, B.; Togni, A. J. Am. Chem. Soc, 120, 10274 (1998); b) Schneider, R. ; Kollner, C; Weber, I.; Togni, A. Chem Commun., 2415 (1999); c) Oosterom, E . G.; van Haaren, R. J.; Reek, J. N. H.; Kamer, P. C. J.; van Leewen, P. W. N. M. Chem. Commun., 1119 (1999).

26. Shu , C.-R; Shen, H.-M. J. Mater. Chem., 7, 47 (1997).

27. Achar, S.; Immoos, C. E.; Hill, M. G.; Catalano, V. J. Inorg. Chem., 36, 2314 (1997).

28. a) Deschenaux, R.; Serrano, E.; Levelut, A.-M. Chem. Commun., 1577 (1997); b) Dardel, B.; Descheneaux, R.; Even, M.; Serrano, E. Macromolecules, 32, 5193, (1999).

29. Turrin, C.-O.; Chiffre, J.; de Montauzon, D.; Daran, J.-C; Caminade, A.-M.; Manoury, E.; Balavoine, G.; Majorai, J.-P. Macromolecules, 33, 7328 (2000).

30. Mosbach, M.; Schuhman, W. Patent W DE 19917052, CA 133:293175 (1999).

31. Yoon, H. C; Hong, M.-Y.; Kim, H.-S. Anal. Chem., 72,4420 (2000).

32. Yoon, H. C; Hong, M.-Y; Kim, H.-S. Anal. Biochem., 282, 121 (2000).

33. Valentini, M.; Pregosin, P. S.; Ruegger, H. Organometallics, 19, 2551 (2000).

34. McCarley , T. D.; DuBois, C. J. Jr; McCarley, R. L.; Cardona, C. M.; Kaifer, A. E. Polym. Prepr. (Am. Chem. Soc, Div. Polym. Chem.), 41, 674 (2000).

35. Cardona, C; McCarley, T. D.; Kaifer, A. E. J. Org. Chem., 65, 1857 (2000).

36. Ipatschi, J.; Hosseinzadeh, R.; Schlaf, P. Angew. Chem. Int. Ed. Engl, 38, 1658 (1999).

37. Casado, C; Cuadrado, I.; Moran, M.; Alonso, B.; Barranco, M.; Losada, J. Appl. Organomet. Chem., 14, 245 (1999).

38. Tokuhisa, H.; Zhao, M.; Baker, L. A.; Phan, V. T.; Dermody, D. L.; Garcia, M. E.; Peez, R. R; Crooks, R. M.; Mayer, T. M. J. Am. Chem. Soc, 120, 4492 (1998).

39. Marciniec, B. In "Applied Homogeneous Catalysis with Organometallic Compounds" (Eds.: B. Cornils, W. A. Herrmann), VCH, Weinheim, Vol. 1, Chap. 2.6(1996).

40. Lewis, L. N.; Stein, J.; Smith, K. A. In Progress in Organosilicon Chemistry (Eds.: Marciniec, B.; Chojnowski, J.) Gordon and Breach, Langhorne, USA, p. 263 (1995).

41. Nlate, S.; Neto, Y; Biais, J.-C; Ruiz, J.; Astruc, D. Chemistry Eur. J., 8, 171 (2002).

42. Nlate, S.; Ruiz, J.; Astruc, D. Chem. Commun., 417 (2000).

43. Nlate, S.; Ruiz, J.; Sartor, V.; Navarro, R.; Biais, J.-C; Astruc, D. Chemistry Eur. J., 6, 2544 (2000).

44. a) Sartor, V; Djakovitch, L.; Fillaut, J.-L.; Moulines, F.; Neveu, F.; Marvaud, V.; Guittard, J.; Biais, J.-C; Astruc, D. J. Am. Chem. Soc, 121, 2929 (1999); b) Sartor, V.; Nlate , S.; Fillaut, J.-L.; Djakovitch, L.; Moulines, F.; Marvaud, V.; Neveu, F.; Biais, J.-C. NewJ. Chem., 24, 351 (2000).

45. Pannel, K. H.; Sharma, H. Organometallics, 10, 954 (1991).

46. Jutzi, R; Batz, C; Neumann, B.; Stammler, H. G. Angew. Chem. Int. Engl, 35,2118 (1996).

47. Flanagan, J. B.; Margel, S.; Bard, A. J.; Anson, F. C. J. Am. Chem. Soc, 100, 4248 (1978).

48. Valerio, C; Fillaut, J-L.; Ruiz, J.; Guittard, J.-C; Biais, J.-C; Astruc, D. J. Am. Chem. Soc, 777,2588(1997).

49. a) Astruc, D.; Valerio, C; Fillaut, J.-L.; Hamon, J.-R.; Varret, F. In Magnetism, a Supramolecular Function (Ed.: O. Kahn), NATO ASAI Series, Kluver, Dordrecht, p. 1107 (1996); b) Valerio, C. PhD Thesis, Université Bordeaux I, (1996).

50. a) Cuadrado, L; Moran, M.; Casado, C. M.; Alonso, B.; Lobete, F.; Garcia, B.; Losada, J . Organometallics, 15, 5278 (1996); b) Takada, K.; Diaz, D. J.; Abruña, H.; Cuadrado, L; Casado, C. M.; Alonso, B.; Moran, M.; Losada, J. J. Am. Chem. Soc, 119, 10763 (1997).

51. Reviews : a) Casado, C. M.; Cuadrado, L; Moran, M.; Alonso, B.; Garcia, B.; Gonzales, B.; Losada, J. Coord. Chem. Rev., 185-6, 53 (1999); b) Cuadrado, L; Moran, M.; Casado, C. M.; Alonso, B.; Losada, J. Coord. Chem. Rev., 189, 123 (1999); c) Hershaw, M. A.; Moss, J. R. Chem. Commun., 1 (1999); d) Newkome, G. R.; He, E.; Moorefield, C. N. Chem. Rev., 99, 1689 (1999).

52. Ruiz , J.; Astruc, D. C. R. Acad. Sci. Paris, t. 1,

Série II c, 21 (1998).

53. Collins, R. L. J. Chem. Phys., 42, 1072 (1965).

54. Green , S. J.; J. J. Pietron, J. J. Stokes, M. J. Hostetler, H. Vu, W. P. Wuelfing, R. W. Murray, Langmuir, 14, 5612 (1998).

55. Gorman, C B.; Smith, J. C; Hager, M. W.; Parhurst, B. L.; Sierzputowska-Gracz, H.; Haney, C. A. J. Am. Chem. Soc, 121, 9958 (1999).

56. Murray, R. In Molecular Design of Electrode Surfaces (Ed.: Murray, R.), Wiley, New York, p. 1(1992).

57. Dandliker, P. J.; Diederich, F.; Gross, M.; Knobler, B.; Louati, A.; Stanford, E. M. Angew. Chem. Int. Ed. Engl, 33, 1739 (1994).

58. Newkome, G. R.; Güther, R.; Moorefield, C. N.; Cardullo, F.; Echegoyen, L.; PérezCordero, F.; Luftmann, H. Angew. Chem. Int. Ed. Engl., 34, 2023 (1995).

59. Chow, H.-F.; Chan, I. Y.-K.; Chan, D. T. W.; Kwok, R. W. M.; Chem. Eur. J., 2,1085 (1996).

60. Dandliker, P. J.; Diederich, F.; Chow, H.-F.; Chan, I. Y.-K.; Kwok, R. W. M. ; Chem. Eur.J., 2, 1085(1996).

61. Issberner, J.; Võgtle, F.; De Cola, L. ; Balzani, V Chem. Eur. J., 3, 706 (1997).

62. Gorman, C. B.; Parkhurst, B. L.; Su, W. Y; Chen, K. Y J. Am. Chem. Soc, 119, 1141(1997).

63. Smith, D. K.; Diederich, F. Chem. Eur. J., 4, 2353 (1998).

65. Ruiz, J.; Ogliaro, F.; Saillard, J.-Y.; Halet, J.-F.; Varret, F.; Astruc, D. J. Am. Chem. Soc, 120, 11693(1998).

66. Rajasekharan , M. V; Giesynski, S.; Ammeter, J. H.; Oswald, N.; Hamon, J.-R.; Michaud, P.; Astruc, D. J. Am. Chem. Soc, 104, 129 (1982).

67. Astruc, D.; Hamon, J.-R.; Althoff, G.; Roman, E.; Batail, P.; Michaud, P. ; Mariot, J.-R; Varret, F.; Cozak, D. J. Am. Chem. Soc, 101, 5445 (1979). This paper also reports the first $CpFe^+$ -induced iterative starburst hexa-alkylation of C_6Me_6 .

68. Hamon, J.-R.; Astruc, D.; Michaud, P. J. Am. Chem. Soc, 103, 758 (1981).

69. Ruiz, J.; Pradet, C ; Varret, F.; Astruc, D. Chem. Commun., 1108 (2002).

70. Bossard, C ; Rigaut, S.; Astruc, D.; Delville, M.-H. ; Félix, G. ; Février-Bouvier, A.; Amiell, J.; Flandrois, S.; Delhaès, P. J. Chem. Soc, Chem. Commun., 333 (1993).

71. Rigaut, S.; Delville, M.-H.; Astruc, D. J. Am. Chem. Soc, 119, 1132 (1997).

72. Astruc, D. Ace Chem. Res., 33, 287 (2000).

73. Astruc, D. In Electron Transfer in Chemistry (Ed.: Balzani, V), Vol II (Matay, J.; Astruc, D . Vol. Eds), Wiley, Weinheim, pp 714-803 (2001).

74. Tokuaka, M. Collect. Czech. Chem. Commun., 4, 444 (1932); 6, 339 (1934).

75. Buet, A.; Darchen, A.; Moinet, C. J. Chem. Soc, Chem. Commun., 447 (1979).

76. Rigaut, S.; Delville, M.-H.; Losada, J.; Astruc, D. Inorg. Chim. Acta, 334, 225 (2000), (issue dedicated to Andrew Wojcicki).

77. Alonso, E.; Astruc, D. J. Am. Chem. Soc, 122, 3222 (2000).

78. a) Bruce, M. I.; Kehoe, D. C; Matisons, J. G.; Nicholson, B. K.; Rieger, P. H.; Williams, M . L. J. J. Chem. Soc. Chem. Commun., 442 (1982); b) Bruce, M. I.; Mattisons, J. G. ; Nicholson, B. K. J. Organomet. Chem., 247, 321 (1983).

79. a) Reetz, M. T.; Lohmer, G.; Scwickardi, R. Angew. Chem. Int. Ed. Engl, 36, 1526 (1997); b) de Brabander-van den Berg, E. M. M.; Meijers, E. W. Angew. Chem. Int. Ed. Engl, 32, 1308(1993).

80. First example of recognized ETC catalysis: Rich, R.; Taube, H. J. Am. Chem. Soc, 7(5,2608(1954).

81. Comprehensive review on ETC catalyzed reactions: Astruc, D. Angew. Chem. Int. Ed. Engl, 27, 643 (1988). See also ref. 82.

82. a) Astruc, D. "Electron Transfer and Radical Processes in Transition-Metal Chemistry", VCH, New York (1995); b) ref. 80 a), chapter 6: Chain Reactions, pp. 413-478.

83. Beer, P. D.; Gale, P. A. Angew. Chem. Int. Ed. Engl, 40, 486 (2001).

84. Lehn, J.-M.; Supramolecular Chemistry: Concepts and Perspectives VCH, Weinheim (1995).

85. Miller, S. R.; Gustowski, D. A.; Chen, Z.-H.; Gokel, G. W.; Echegoyen, L.; Kaifer, A. E. Anal. Chem., 60, 2021 (1988).

86. Valerio, C; Alonso, E.; Ruiz, J. ; Biais, J.-C; Astruc, D. Angew. Chem. Int. Ed. Engl., 38, 1747 (1999).

87. Ruiz, J.; Ruiz Medel, M.-J.; Daniel, M.-C; Astruc, D. Chem. Commun., 464 (2003).

88. Daniel, M.-C; Ruiz, J.; Astruc, D. Chem. Eur. J., 9, 4371 (2003).

89. Daniel, M.-C; Ruiz, J.; Astruc, D. J. Am. Chem. Soc, 125, 1150 (2003).

90. Labande, A.; Astruc, D. Chem. Commun., 1007 (2000).

91. Labande, A.; Ruiz, J.; Astruc, D. J. Am. Chem. Soc., 124, 1782 (2002)

92. Daniel, M.-C; Ruiz, J.; Nlate, S.; Biais, J.-C; Astruc, D. J. Am. Chem. Soc, 125, 2617(2003).

11 CHAPTER 11: SPECTROELECTROCHEMICAL TECHNIQUES

1. Russell, J.W.; Overend, J.; Scanlon, K.; Severson, M.W.; Bewick, A. J. Phys. Chem, 55,3066(1982).

2. Fiedler, J.; Nervi, C; Osella, D.; Calhorda, M.J.; Godinho, S.S.M.C.; Merkel, R.; Wadepohl, H. J. Chem. Soe, Dalton Trans. 3705 (2002).

3. Krejcik, M.; Danek, M.; Haiti, F. J. Electroanal. Chem. 317, 179 (1991).

4. Best, S.P.; Clark, R.J.H.; McQueen, R.C.S.; Clooney, R.P. Rev. Sci. Instrum. 58, 20711(1987).

5. Best, S.P.; Ciniawskii, S.A.; Humphrey, D.G. J. Chem. Soe., Dalton Trans. 2945 (1996).

6. al Dulaimi, J.P.; Bond, A.M.; Clark, R.J.H.; Harden, N.C.; Humphrey, D.G. J. Chem. Soe, Dalton Trans. 2541 (2002).

7. Bellec, V.; De Backer, M.G.; Levillain, E.; Sauvage, F.X.; Sombret, B.; Wartelle, C. Electrochem. Commun. 3, 483 (2001).

8. Rosenberg, E.; Abedin, M.J.; Rokhsana, D.; Osella, D.; Milone, L.; Nervi, C; Fiedler, J. Inorg. Chim. Acta 300-302, 769 (2000).

9. Büschel, M.; Stadler, C; Lambert, C; Beck, M.; Daub, J. J. Electroanal. Chem. 484, 24 (2000).

10. Kardash, D.; Huang, J.; Korzeniewski, C. J. Electroanal. Chem. 476, 95 (1999).

11. Mosier-Boss, P.A.; Newbery, R.; Szpak, S.; Lieberman, S.H.; Rovang, J.W. Anal. Chem. 68,3271 (1996).

12. Shaw, M.J.; Geiger, W.E. Organometallics 15, 13 (1996).

13. Atwood, C.G.; Geiger, W.E.; Bitterwolf, T.E. J. Electroanal. Chem. 397, 279 (1995).

14. Yu, J.S.; Zhou, T.Y. J. Electroanal. Chem. 504, 89 (2001).

15. Prenzler, P.D.; Bramley, R.; Downing, S.R.; Heath, G.A. Electrochem. Commun. 2, 516(2000).

16. Zhu, Y.; Cheng, G.; Dong, S. Biophys. Chem. 97, 129 (2002)

17. Jasperson, S.N.; Burge, D.K.; O'Handley, R.C. Surf. Sci. 37, 548 (1973).

18. Salbeck, J. J. Electroanal. Chem. 340, 169 (1992).

19. Hartl, F.; Stufkens, D.J.; Vlcek, A. Inorg. Chem. 31, 2869 (1992).

20. Lin, C-Y; Spiro, T.G. Inorg. Chem. 35, 5237 (1996).

21. Farley, N.R.S.; Gurman, S.J.; Hillman, A.R. Electrochem. Commun. 1, 449 (1999).

22. Soderholm, L.; Antonio, M.R.; Williams, C; Wasserman, S.R. Anal. Chem. 71, 4622 (1999).

23. Plieth, W.; Wilson, G.S.; Gutiérrez de la Fe, C. Pure and Appl. Chem. 70, 1395 (1998),

24. Plieth, W.; Wilson, G.S.; Gutiérrez de la Fe, C. Pure and Appl Chem. 70, 2409 (1998).

25. Iengo, E.; Mestroni, G.; Geremia, S.; Calligaris, M.; Alessio, E. J. Chem. Soc, Dalton Trans. 3361 (1999).

26. Baldwin, D.A.; Betterton, E.A.; Pratt, J.M. J. Chem. Soe, Dalton Trans. 217 (1983).

27. Ford, S.H.; Nichols, A.; Shambee, M.J. Inorg. Biochem. 41, 235 (1991).

28. Zou, X.; Evans, D.R.; Brown, K.L. Inorg. Chem. 34, 1634 (1995).

29 . Koetsier, M.J.; Craig, D.H.; Mackay, R; Daff, S.; Chapman, S.K. Flavins and Flavoproteins (Rudol f Weber), Chapman,S.K.; Perham, R.N.; Scrutton, N.S. eds., 587 (2002) .

30. Adams, C.J.; James, S.L.; Liu, X.M.; Raithby, P.R.; Yellowlees, L.J. J. Chem. Soc. f Dalton Trans. 63 (2000).

31. Barton, M.T.; Rowley, N.M.; Ashton, P.R.; Jones, C.J.; Spencer, N.; Tolley, M.S.; Yellowlees, L.J. New J. Chem.24, 555 (2000).

32. Mclnnes, E.J.L.; Welch, A.J.; Yellowlees, L.J. J. Chem. Soc, Chem. Commun. 2393 (1996).

33. McInnes,E.J.L.; Farley, R.D.; Rowlands, C.C.; Welch, A.J.; Rovatti, L.; Yellowlees, L.J. J. Chem. Soe, Dalton Trans. 4203 (1999).

34. Macgregor, S.A.; Mclnnes, E.J.L.; Sorbie, R.J.; Yellowlees, L.J. Molecular Electrochemistry of Inorganic, Bioinorganic and Organometallic Compounds (Kluwer, Netherlands), Pombeiro, A.J.L.; McCleverty, J.A. eds. 530 (1993).

35. Morse , P. Scientific Software Services, Bloomington, USA (1994).

36. Quantum CAChe version 3.2, Oxford Molecular Ltd. (1999).

37. WIN-EP R SimFonia, version 1.25, Bruker, Billerica, USA (1996).

38. Kuwana, T.; Heineman, W.R. Ace. Chem. Res. 9, 241 (1976).

39. Heineman, W.R.; Hawkridge, RM.; Blount, H.N. Electroanalytical Chemistry, Bard, A.J. (ed.) Marcel dekker, New York, 13, 1 (1984).

40. Szentrimay, R.; Yeh, P.; Kuwana, T. Electrochemical Studies of Biological Systems, Sawyer, D.T. (ed.) ACS Symp. Ser. 38, 143 (1977).

41. Murray , R.W.; Heineman, R.W. O'Dom, G.W. Anal. Chem. 39, 1666 (1967).

42. De Angelis, T.P.; Heineman, W.R. J. Chem. Educ. 53, 594 (1976).

43. Kirchhoff, J.R.; Allen, M.R.; Cheesman, B.V.; Okamoto, K.; Heinemaan, W.R.; Deutsch, E. Inorg. Chim. Acta 262, 195 (1997).

44. Toma, H.E.; Sernaglia, R.L. Talanta 42, 1867 (1995).

45. Bagatin, I.A.; Toma, H.E. Spectrosc. Letts. 29, 1409 (1996).

46. Toma, H.E.; Alexiou, A.D.P.; Dovidauskas, S. Eur. J. Inorg. Che. 3010 (2002).

47. Enemark, J.H.; Feltham, R.D. Coord. Chem. Rev. 13, 339 (1974).

48. Eisenberg, R. Meyer, CD. Ace. Chem. Res. 8, 26 (1975).

49. Bottomley, R Coord. Chem. Rev. 26,1 (1978).

50. Westcott, B.L.; Enemark, J.H. Transition Metal NitrosyIs, John Wiley & Sons, Inc., Vol. II: Applications and Case Studies (1999).

51. Nunes, RS.; Toma, H.E. J. Coord. Chem. 36, 33 (1995).

52. Lõpez-Palacios, J.; Colina, A.; Herras, A.; Ruiz, V.; Fuente, L. Anal. Chem. 73, 2883 (2001).

53. Qian, W.; Zhu, S-M.; Luo, Q-H.; Hu, X-L.; Wang, Z-L Bioelectrochem, 58, 197 (2002).

54. Losada, J.; del Peso, I.; Beyer, L. Inorg. Chim. Acta 321, 107 (2001).

55. Dag, O.; Yaman, S.O.; Õnal, A.M.; Isci, H. J. Chem. Soe, Dalton Trans. 2819 (2001).

56. Hill, M.G.; Mann, K.R. Inorg. Chim. Acta 243, 219 (1996).

57. Hill, M.G.; Bailey, J.A.; Miskowski, V.M.; Gray, H.B. norg. Chem. 35, 4585 (1996).

58. Stinner, C; Wightman, M.D.; Kelly, S.O.; Hill, M.G.; Barton, J.K. Inorg. Chem. 40, 5245 (2001).

59. Jain, S.L.; Crayston, J.A.; Richens, D.T.; Woollins, J.D. Inorg. Chem. Commun. 5, 853 (2002) .

60. Haiti, R; Luyten, H.; Nieuwenhuis, H.A.; Schoemaker, G.C. Appl. Spectroscopy 48, 1522(1994).

61. Knõdler, A.; Wanner, M.; Fiedler, J.; Kaim, W. J. Chem. Soe, Dalton Trans. 3079 (2002).

62. Glõckle, M.; Kaim, W.; Katz, N.E.; Posse, M.G.; Cutin, E.H.; Fiedler, J. Inorg. Chem. 38,3210(1999).

63. Kaim, W.; Berger, S.; Greulich, S.; Reinhardt, R.; Fiedler, J. J. Organomet. Chem. 582, 1533 (1999).

64. Baumann, R; Kaim, W.; Olabe, J.A.; Parise, A.R.; Jordanov, J. J. Chem. Soc, Dalton Trans. 4455 (1997).

65. Baumann , R; Kaim, W.; Posse, M.G.; Katz, N.E. Inorg. Chem. 37, 658 (1998).

66. Berger, S.; Hartmann, H.; Wanner, M.; Fiedler, J.; Kaim, W. Inorg. Chim. Acta 314, 22(2001).

67. Kaim, W.; Sixt, T.; Weber, M.; Fiedler, J. J. Organomet. Chem. 637-639, 167 (2001).

68. Sixt, T.; Fiedler, J.; Kaim, W. Inorg. Chem. Commun.3, 80 (2000).

69. Farrell, I.R.; Haiti, R; Zâlis, S.; Wanner, M.; Kaim, W.; Vlcek Jr., A. Inorg. Chim. Acta 318, 143(2001).

70. Kaim, W.; Schwederski, B.; Dogan, A.; Fiedler, J.; Kuehl, C.J.; Stang, P.J. Inorg. Chem. 41, 4025 (2002).

71. Crespo, M.; Grande, C; Klein, A. J. Chem.Soc, Dalton Trans. 1629 (1999).

72. Lin, X.Q.; Kadish, K.M. Anal. Chem. 57, 1498 (1985).

73. Wei, Z.; Ryan, M.D. Inorg. Chim. Acta 314, 49 (2001).

74. Akiba , K.; Nadano, R.; Satoh, W.; Yamamoto, Y.; Hâgase, S.; Ou, Z.; Tan, X.; Kadish, K.M. Inorg. Chem. 40, 5533 (2001).

75. Chaudhuri, P.; Verani, C.N.; Bill, E.; Bothe, E.; Weyhermuller, T.; Wieghardt, K. J. Am. Chem. Soc. 123, 2213 (2001).

76. Sun, X.; Chun, H.; Hildenbrand, K.; Bothe, E.; Weyhermuller, T.; Neese, R; Wieghardt, K . Inorg. Chem. 41, 4295 (2002).

77. Chun, H.; Verani, C.N.; Chaudhuri, P.; Bothe, E.; Bill, E.; Weyhermuller, T.; Wieghardt, K. Inorg. Chem. 40, 4157 (2001).

78. Barthram, A.M.; Ward, M.D. New J. Chem. 501 (2000).

79. Behrendt, A.; Couchman, S.M.; Jeffrey, J.C.; McCleverty, J.A.; Ward, M.D. J. Chem. Soc, Dalton Trans. 4349 (1999).

80. Lee, S-M.; Kowallick, R.; Marcaccio, M.; McCleverty, J.A.; Ward, M.D. J. Chem. Soc, Dalton Trans. 3443 (1998).

81. Lee, S-M.; Marcaccio, M.; McCleverty, J.A.; Ward, M.D. Chem. Mater. 10, 3272 (1998).

82. Chakraborty, S.; Laye, R.H.; Paul, R.L.; Gonnade, R.G.; Puranik, V.G.; Ward, M.D.; Lahiri, G.K. J. Chem. Soc, Dalton Trans. 1172 (2002).

83. Sakar, B.; Laye, R.H.; Mondai, B.; Chakraborty, S.; Paul, R.L.; Jeffrey, J.C.; Puranik, V.G.; Ward, M.D.; Lahiri, G.K. /. Chem. Soc, Dalton Trans. 2097 (2002).

84. Duff, CM.; Heath, G.A. Inorg. Chem. 30, 2528 (1991).

85. Arnold, D.R; Heath, G.A. J. Am. Chem. Soc. 115, 12197 (1993).

86. Arnold, D.R; Heath, G.A.; James, D.A. J. Porphyrins Phthalocyanines 3, 5 (1999).

87. Arnold, D.R; Hartnell, R.D.; Heath, G.A.; Newby, L.; Webster, R.D. J. Chem. Soc., Chem. Commun. 754 (2002).

88. Bruce, M.I.; Low, P.J.; Costuas, K.; Halet, J-R; Best, S.R; Heath, G.A. J. Am. Chem. Soc. 122, 1949 (2000).

89. Webster, R.D.; Heath, G.A.; Bond, A.M. J. Chem. Soc, Dalton Trans, 3189 (2001).

90. Marcaccio, M.; Paolucci, R; Paradisi, C ; Roffia, S.; Fontanesi, C ; Yellowlees, L.J.; Serroni, S.; Campagna, S.; Denti, G.; Balzani, V. J. Am. Chem. Soc. 121, 10081 (1999).

91. Robertson, N.; Liu, X.; Yellowlees, L.J. Inorg. Chem. Commun. 3, 424 (2000).

92. Araũjo, C.S.; Drew, M.G.B.; Jack, L.; Madureira, J.; Newell, M.; Roche, S.; Santos, T.M.; Thomas , J.A.; Yellowlees, L.J. Inorg. Chem. 41, 2250 (2002).

93. Nairn , A.K.; Bhalla, R.; Foxon, S.R; Liu, X.; Yellowlees, L.J.; Gilbert, B.C.; Walton, RH. J. Chem. Soc, Dalton Trans. 1253 (2002).

94. Marcaccio, M.; Paolucci, R; Paradisi, C ; Carano, M.; Roffia, S.; Fontanesi, C ; Yellowlees, L.J.; Serroni, S.; Campagna, S.; Balzani, V. J. Electroanal. Chem. 532, 99 (2002).

95. Brown, A.R.; Taylor, K.J.; Yellowlees, L.J. J. Chem. Soc, Dalton Trans. 2401 (1998).

96. Kennedy, B.J.; Heath, G.A. Inorg. Chim. Acta 195, 101 (1992).

97. Creutz, C; Taube, H. J. Am. Chem. Soc. 91, 3988 (1969).

98. Robin, M.B.; Day, P. Adv. Inorg. Radiochem. 10, 247 (1967).

99. Fürholz, U.; Bürgi, H-B.; Wagner, F.E.; Stebler, A.; Ammeter, H.H.; Krausz, E.; Clark, R.J.H.; Stead, M.J.; Ludi, A. J. Am. Chem. Soc. 106, 121 (1984).

100. Richardson, D.E.; Taube, H. J. Am. Chem. Soc. 105, 40 (1983).

101. Sutton, J.E.; Taube, H. Inorg. Chem. 20, 3125 (1981).

102. Callahan, R.W.; Keene, F.R.; Meyer, T.J.; Salmon, D.J. J. Am. Chem. Soc. 99,1064 (1977).

103. Creutz, C; Chou, M.H. Inorg. Chem. 26, 2995 (1987).

104. Callahan, R.W. PhD Dissertation, University of North Carolina, Chapel Hill, 1975.

105. Coe, B.J.; Meyer, T.J.; White, RS. Inorg. Chem. 34, 593 (1995).

106. Hornung, F.M.; Baumann, R; Kaim, W.; Olabe, J.A.; Slep, L.D.; Fiedler, J. Inorg. Chem. 57,311(1998).

107. Lay, P.A.; Magnuson, R.H.; Taube, H. Inorg. Chem. 37, 2364 (1988).

108. Balducci, G.; Mestroni, G.; Alessio, E. Current Topics in Electrochemistry, 2, 323 (1993).

109. Alessio, E.; Balducci, G.; Calligaris, M.; Costa, G.; Attia, W.M.; Mestroni, G. Inorg. Chem. 30, 609 (1991).

110. Gutmann, V. The Donor-Acceptor Approach to Molecular Interactions, Plenum Press, New York (1980). Chapter 11

111. Hush , N.S. Prog. Inorg. Chem. 8, 391 (1967).

112. Gutmann, V.; Resch, G.; Linert, W. Coord Chem. Rev.

43, 133 (1982).

113. Creutz, C; Chou, M.H. Inorg. Chem. 31, 3170 (1992).

114. Creutz , C. Prog. Inorg. Chem. 30, 29 (1983).

115. Powers, M.J.; Meyer, T.J. Inorg. Chem. 17, 2955 (1978).

116. Powers, M.J.; Meyer, T.J. J. Am. Chem. Soc. 102, 1289 (1980).

117. Richardson , D.E.; Taube, H. Inorg. Chem. 20, 1278 (1981).

118. Taboy, C.H.; Bonaventura, C; Crumbliss, A.L. Bioelectrochem. Bioenerg, 48, 79 (1999).

119. Ding, X.D.; Weichsel, A.; Andersen, J.F.; Shokhieeva, T.K.; Balfour, C ; Pierik, A.J.; Averill , B.A.; Montfort, W.R.; Walker, F.A. J. Am. Che. Soc. 121, 128 (1999).

120. Borrsari, M.; Benini, S.; Marchesi, D.; Ciurli, S. Inorg. Chim. Acta 263, 379 (1997).

121. Niki, K.; Vrána, O.; Brabec, V. Experimental Techniques in Bioelectrochemistry (Birkháuserr Verlag) Brabec, V.; Walz, D.; Milazzo, G. (eds.) Basel (1996).

122. Comtat, M; Durliat, H. Biosensors Bioelectronics 9, 663 (1994).

123. Heineman, W.R.; Norris, B.J.; Goelz, J.F. Anal. Chem. 47, 79 (1975).

124. Norris, B.J.; Meckstroth, M.L.; Heineman, W.R. Anal. Chem. 48, 630 (1976).

125. Kreishman, G.P.; Anderson, C.W.; Su, C-H.; Halshall, H.B.; Heineman, W.R. Bioelectrochem. Bioenerg. 5, 196 (1978).

126. Anderson, C.W.; Halsall, H.B.; Heineman, W.R. Anal. Biochem. 93, 366 (1979).

127. Taniguchi , V.T.; Sailasuta-Scott, N.; Anson, F.C., Gray, H.B. PureAppl. Chem. 52, 2275 (1980).

128. Heineman, W.R.; Meckstroth, M.L.; Norris, B.J.; Su, C-H. Bioelectrochem. Bioenerg. 6, 511 (1979).

129. Sailasuta , N.; Anson, F.C.; Gray, H.B. J. Am. Chem. Soc. 101, 455 (1979).

130. Fan, K.J.; Akutsu, H.; Niki, K.; Higuchi, N.; Kyogoku, Y. J. Electroanal. Chem. 275,295(1990).

131. Pratt, J.M. Chemistry and Biochemistry ofB 12 (Wiley) Banerjee, R. (ed.) New York, 73 (1999).

132. Lexa, D.; Saveant, J-M.; Zickler, J. J. Am. Chem. Soc. 102, 4851 (1980).

133. Sano, M.; Taube, H. J. Am. Chem. Soc. 113, 2327 (1991).

134. Sano , M.; Taube, H. Inorg. Chem. 33, 705 (1994).

135. Koppenhofer, A.; Turner, K.L.; Allen, J.W.A.; Chapman, S.K.; Ferguson, S.J. Biochemistry 39, 4243 (2000).

136. Daff, S. N.; Chapman, S. K.; Turner, K.L.; Holt, R.A.; Govindaraj, S.; Poulos, T.L.; Munro, A.W. Biochemistry, 36, 13816 (1997).

137. Webster, R.D.; Heath, G.A.; Bond, A.M. J. Chem. Soc. Dalton Trans. 31189 (2001).

138. van Staveren, D.R.; Bothe, E.; Weyhermiiller, T.; Metzler-Nolte,N. Eur. J. Inorg. Chem. 1518(2002).

139. Winter, R.F. Eur. J. Inorg. Chem. 2121 (1999).

140. Lomoth, R.; Huang, P.; Zheng, J.; Sun, L.; Hammarstrõm, L.; Akermark, N.; Styring, S. Eur. J. Inorg. Chem. 2965 (2002).

141. Robben, M.P.; Reiger, P.H.; Geiger, W.E. J. Am. Chem. Soc. 121, 367 (1999).

142. McKinney, T.M. Electroanalytical Chemistry Vol 10: Electron Spin Resonance and Electrochemistry Bard, A.J. (ed) (Marcel Dekker) New York, 97 (1977).

143. Bard, A.J.; Faulkner, L.R. Electrochemical Methods: Fundamentals and Applications (John Wiley and Sons) New York, 615 (1980).

144. Compton, R.G.; Waller, A.M. Spectroelectrochemistry: Theory and Practise Gale, R.J. (ed.) (Plenum Press) New York 349 (1988).

145. Goldberg , LB.; McKinney, T.M. Laboratory techniques in Electroanalytical Chemistry, Kissinger, P.T.; Heineman, W.R. (eds) (Marcel Dekker) New York, 901 (1996).

146. Haiti, R; Vlcek, Jr. A. Inorg. Chem. 30, 3048 (1991).

147. Haiti , R; Groenestein, R.P.; Mahabiersing, T. Collect. Czech. Chem. Commun. 66, 52 (2001).

148 . Allendoerfer, R.D.; Martinchek, G.A.; Bruckenstein, S. Anal. Chem. 47, 890 (1975).

149. Farrell, I.R,; Hartl, R; Zalis, S.; Mahabiersing, T.; Vlcek Jr. A. J. Chem. Soc. Dalton Trans. 4323 (2000).

150. Fiedler, D.A.; Koppenol, M.; Bond, A.M. J. Electrochem Soc. 142, 863 (1995).

151. Bond, A.M.; Dyson, P.J.; Humphrey, D.G.; Lazarev, G.; Suman, P. J. Chem. Soc, Dalton Trans. 443 (1999).

152. Coles, B.A.; Compton, R.G. J. Electroanal. Chem. 144, 87 (1983).

153 . Webster, R.D.; Bond, A.M.; Coles, B.A.; Compton, R.G. J. Electroanal. Chem. 404,(1996).

154. Kaim, W.; Ernst, S.; Kasack, V. J. Am. Chem. Soc. 112, 173 (1990).

155. Scheiring, T.; Fiedler, J.; Kaim, W. Organometallics 20, 1437 (2001).

156. Hartmann , H.; Scheiring, T.; Fiedler, J.; Kaim, W. J. Organomet. Chem. 604, 267 (2000).

157. Rapta, P.; Stasko, A.; Gromov, A.V.; Bartl, A.; Dunsch, L. Electrochem. Soc. Proceed. 10 (2000).

158. Rapta, P.; Kress, L.; Hapiot, P.; Dunsch, L. Phys. Chem. Chem. Phys. 4, 4181 (2002).

159. Rapta, P.; Dunsch, L. J. Electroanal. Chem. 507, 287 (2001).

160. Rapta, P.; Fâber, R.; Dunsch, L.; Neudeck, A.; Nuyken, O. Spectrochim. Acta Part A 56, 357 (2000).

161. Neudeck, A.; Petrr, A.; Dunsch, L. Synth. Mets. 107, 143 (1999).

162. Wilgocki, M.; Rybak, W.K. Portugalie Electrochim. Acta 13, 211 (1995).

163. McConnell, H.M. J. Chem. Phys. 24, 764 (1958).

164. Long, Y-T.; Yu, Z-H.; Chen, H-Y Electrochem. Commun. 1, 194 (1999).

12 CHAPTER 12: ELECTROCHEMISTRY AT ULTRAMICROELECTRODES: SMALL AND FAST MAY BE USEFUL

1. Bard, A.J.; Faulkner, L.R. "Electrochemical Methods ", J. Wiley & Sons, New York (1980).

2. Amatore C, in "Physical Electrochemistry", Rubinstein L, Ed., M. Dekker, New York, Chapter 4 (1995).

3. Amatore C; Lefrou C. J. Electroanal Chem., 296, 335 (1990).

4. P.T. Kissinger; W.R. Heineman, Eds., Laboratory Techniques in Electroanalytical Chemistry, M. Dekker, New York (1984).

5. Wipf D.O.; Wightman R.M. Anal Chem., 60, 2460 (1988).

6. Andrieux C.P.; Garreau D.; Hapiot P.; Pinson J.; Savéant J.M. J. Electroanal Chem., 243,321 (1988).

7. Amatore C; Lefrou C; Pflüger F. J. Electroanal Chem., 270, 43 (1989).

8. Amatore C; Lefrou C. J. Electroanal. Chem., 324, 33 (1992).

9. Amatore C; Maisonhaute E.; Simonneau G. Electrochem. Commun., 2, 81 (2000).

10. Amatore C; Maisonhaute E.; Simonneau G. J. Electroanal Chem., 486, 141 (2000).

11. Amatore C; Lefrou C. J .Electroanal Chem., 325, 239 (1992).

12. Masnovi J.M.; Sankararaman S.; Kochi J.K. J. Phys. Chem., Ill, 2263 (1989).

13. Amatore C; Jutand A.; Pfliiger F. J. Electroanal Chem., 218, 361 (1987).

14. Amatore C; Arbault S., unpublished results.

15. Kawata H.; Suzuki Y.; Nuzuma S. Tetrahedron Lett, 27, 4489 (1986).

16. Amatore C; Jutand A.; Pflüger F.; Jallabert C ; Strzelecka H.; Veber M. Tetrahedron Lett, 30, 1383(1989).

17. Amatore C; Lefrou C. J. Electroanal. Chem., 324, 33 (1992).

18. Takada K.; Stonier G.D.; Moran M.; Abruña H.D. Langmuir, 15, 7333 (1999).

19. Díaz D. J.; Stonier G.D.; Bernhard S.; Takada K.; Abruña H.D. Langmuir, 15, 7351 (1999).

20. Munay R. W. Phil. Trans. R. Soc. London A, 302, 253 (1981).

21. Dahms H.J. J. Phys. Chem., 72, 362 (1968).

22. Ruff I.; Friedrich V.J. J. Phys. Chem., 75, 3297 (1971).

23. Ruff L; Friedrich V.J.; Demeter K.; Csillag K. J. Phys. Chem., 75, 3303 (1971).

24. Andrieux CR; Savéant J.M. J. Electroanal. Chem., Ill, 311 (1980).

25. Laviron E. J. Electroanal. Chem., 112, 1 (1980).

26. Facci J.; Munay R.W. J. Phys. Chem., 85, 2870 (1981).

27. Blauch D.N.; Savéant J.M. J. Phys. Chem., 97, 6444 (1993).

28. Amatore C; Bouret Y.; Maisonhaute E.; Goldsmith J.I.; Abruña H.D. Chem. Eur. J., 7,2206(2001).

29. Amatore C; Bouret Y; Maisonhaute E.; Goldsmith J.I.; Abruña H.D. ChemPhysChem Eur. J., 2,, 130 (2001).

30. Stonier G.D.; Takada K.; Abruña H.D. Langmuir, 15 , 872 (1999).

31. Sutin N.; Creutz C , PureAppl. Chem., 52, 2717 (1980).

32. Chance B.; DeVault D.; Frauenfelder H.; Marcus R.A.; Schrieffer J.R.; Sutin N., Eds., "Tunneling in Biological Systems", Acad. Press, New York (1979).

33. Mayo S.; Ellis W.R.; Crutchley R.J.; Gray H.B. Science, 233,, 948 (1986).

34. Miller C.J., in "Physical Electrochemistry", Rubinstein, L, Ed., M. Dekker: New York, Chapter 2 (1995),

and refs. therein.

35. Engstrom R.C.; Weber M.; Wunder D.J.; Burgess R.; Winquist S. Anal. Chem., 58, 844(1986).

36. Engstrom R.C.; Meaney T.; Tople R.; Wightman R.M. Anal. Chem., 59, 2005 (1987).

37. Jan C.C.; McCreery R.L. Anal. Chem., 58, 2771 (1986).

38. Bard A.J.; Fan F.F.; Kwak J.; Lev O. Anal. Chem., 61,132 (1989).

39. For a recent book on SECM, see: Bard, A.J.; Mirkin, M.V., Eds., "Scanning Electrochemical Microscopy", Marcel Dekker, New York (2001).

41. Slevin C.J.; Unwin PR. Langmuir, 13, 4799 (1997).

42. Slevin C.J.; Macpherson J.V.; Unwin PR. J. Phys.Chem. B, 101, 10851 (1997).

43. Zhang J.; Slevin C.J.; Unwin P Chem. Com., 1501 (1999).

44. Slevin C.J.; Unwin PR. Langmuir, 15, 7361 (1999).

45. Honocks B.R.; Mirkin M.V.; Pierce D.T.; Bard A.J. Anal. Chem., 65, 1213 (1993).

46. Wei C; Bard A.J.; Nagy G.; Toth K. Anal. Chem., 67, 1346 (1995).

47. Kupper M.; Schultze J.W. Electrochimica Acta, 42, 3023 (1997).

48. Kupper M.; Schultze J.W. Electrochimica Acta, 42, 3085 (1997).

49. Klusmann E.; Schultze J.W Electrochimica Acta, 42, 3123 (1997).

50. Amatore C; Bonhomme F.; Bruneel J.-L.; Servant L.; Thouin L. Electrochem. Commun., 2, 235 (2000).

51. Amator e C; Bonhomme F.; Bruneel J.-L.; Servant L.; Thouin L. J. Electroanal. Chem., 484, 1 (2000).

52. Amatore C; Szunerits S.; Thouin L. Electrochem. Commun., 2, 248 (2000).

53. Amator e C; Szunerits S.; Thouin L.; Warkocz J.S. Electrochem. Commun., 2, 353 (2000).

54. Amatore C; Szunerits S.; Thouin L.; Warkocz J.S. J. Electroanal. Chem., 500, 62 (2001).

55. Lund H.; Michel M.A.; Simonet J. Acta. Chem. Scand., B28, 901 (1974).

56. Andrieux CR; Savéant J.M., in "Investigations of rates and mechanisms of reactions", Bernasconi F., Ed., Vol. 6, 4/E, Part 2, John Wiley & Sons, Inc., p. 305 (1986).

57. Lund H.; Daasbjerg K.; Lund T.; Pedersen S. Ace. Chem. Res., 28, 313 (1995).

58. Amator e C; Szunerits S.; Thouin L.; Warkocz J.-S. Electroanalysis., 13, 646 (2001).

59. Amatore C, Pebay C, Scialdone O., Szunerits S., Thouin L.. Chem. Eur. J., 7,2933 (2001).

60 Andrieux C.P.; Blocman C; Dumas-Bouchiat J.M.; Savéant J.M. J. Am. Chem. Soc, 76^ 7, 3431 (1979).

61. Andrieux C. P.; Savéant J.M.; Su K.B. J. Phys. Chem., 90, 3815 (1986).

62. Andrieux C. P.; Savéant J.M. J. Am. Chem. Soc, 115, 8044 (1993).

63. Watkin s J.J.; Chen J.; White H.S.; Abruna H.D.; Maisonhaute E.; Amatore C. Anal. Chem., 75, 3962 (2003).

14 CHAPTER 14: ILLUSTRATION OF EXPERIMENTAL AND THEORETICAL PROBLEMS ENCOUNTERED IN CYCLIC VOLTAMMETRIC STUDIES OF CHARGED SPECIES WITHOUT ADDED SUPPORTING ELECTROLYTE

1. Heyrovsky, J. Chem. Listy, 16,256 (1922).

2. Heyrovsky, J.; Kuta, J. Principles of Polography, Academic Press, New York, 1966.

3. Slendyk, I. Coll. Czech Chem. Commun., 3, 385 (1931).

5. Oldham, K.B. Microelectrodes; Theory and Applications. Montenegro, M.I.; Queirós, M.A. ; Daschbach, J.L. (eds) Kluwer Academic Publishers, Dordrecht, 1991, p 83.

6. Oldham, K.B.; Feldberg, S.W. J. Phys. Chem. B., 103, 1699 (1999).

7. Oldham, K.B. J. Electroanal. Chem., 337, 91 (1992).

8. Microelectrodes: Theory and Applications. Montenegro, M.I.; Queirós, M.A.; Daschbach, J.L. (eds) Kluwer Academic Publishers, Dordrecht, 1991.

9. Wightman, R.M.; Wipf, D.O. Electroanal. Chem., 15, 267 (1989).

10. Cooper, J.B.; Bond, A.M.; Oldham, K.B. J. Electroanal. Chem., 33, 887 (1992).

11. Bond , A.M. Broadening Electrochemical Horizons, Oxford University Press, 2002.

12. Bard, A.J.; Faulkner, L.R. Electrochemical Methods: Fundamentals and Applications, John Wiley, New York, 1 st edition 1980, 2 nd edition 2001.

13. Bond, A.M.; Coomber, D.C.; Feldberg, S.W.; Oldham, K.B.; Vu, T. Anal. Chem., 73, 352 (2001).

14 . Bond, A.M.; Feldberg, S.W. J. Phys. Chem. B., 102, 9966 (1998).

15. Stevens, N.S.C.; Bond, A.M. J. Electroanal. Chem., 538-539, 25 (2002).

16. He, P.; Avery, J.P.; Faulkner, L.R. Anal. Chem., 54, 1313A (1982).

17. Hawkridge, F.M. in Laboratory Techniques in Electroanalytical Chemistry, Kissinger, P.T. ; Heineman, W.R. (eds) Marcel Dekker, New York, 1984, Chapter 12.

18. Roe, D.K. in Laboratory Techniques in Electroanalytical Chemistry, Kissinger, P.T.; Heineman, W.R . (eds) Marcel Dekker, New York, 1986, Chapter 7.

19. Nicholson, R.S. Anal. Chem., 37, 661 (1965).

20. Nicholson, R.S. Anal. Chem., 37, 1351 (1965).

21. Nicholson, R.S.; Shain, I. Anal. Chem., 36, 706 (1964).

22. Rudolph, M.; Reddy, D.P.; Feldberg, S.W. Anal. Chem., 66, 589A (1994).

23. Way, D.M.; Bond, A.M.; Wedd, A.G. Inorg. Chem., 36, 2826 (1997).

24. Bond, A.M.; Coomber, D.C.; Harika, R.; Hultgren, V.M.; Rooney, M.B.; Vu, T.; Wedd, A.G. Electroanalysis, 13, 1475 (2001).

25. Rooney, M.B.; Coomber, D.C.; Bond, A.M. Anal. Chem., 72, 3486 (2000).

26. Stevens, N.P.C., Rooney, M.B.; Bond, A.M.; Feldberg, S.W. /. Phys. Chem. A, 105, 9085 (2001).

27. Lee, C ; Anson, F.C. J. Electronanal Chem., 323, 381 (1992).

28. Beriet, C ; Pletcher, D. J. Electroanal. Chem., 323, 381 (1992).

29. Kawiak, J.; Kulesza, P.J.; Galus, Z. J. Electroanal. Chem., 226, 305 (1987).

30. Amatore, C; Fosset, B.; Bartlet, J.; Deakin, M.R.; Lightman, R.M. J. Electroanal. Chem., 256, 255 (1988).

31. Oldham, K.B.; Myland, J.C. Fundamentals of Electrochemical Science, Academic Press, San Diego, 1994.

32. Gouy, M. J. Phys. Radium, 9, 457 (1910).

33. Hunter, R.J. Fundamentals of Colloid Science, Clarendon Press, Oxford, 1987, p 341.

34. Frumkin , A.N.; Florianovich, G.M. Doklady Akad NaukSSSR, 80, 907 (1951).

36. Heyrovsky, J. Actualits scientifigues et industrielles, Herman, Paris, 1934, p 90.

37. Heyrovsky , J. Polarographie, Springer, Wien, 1941, p 74.

38. Frumkin, A.N. Trans. Faraday Soc, 55, 156 (1959).

39. Eaton , W.A.; George, P.; Hanania, G.I.H. J. Phys. Chem., 71, 2016 (1967).

40. Hanania, G.H.I.; Irvine, D.H.; Eaton, W.A.; George, P. J. Phys. Chem., 71, 2022 (1967).

41. Campbell, S.A.; Peter, L.M. J. Electroanal. Chem., 364, 257 (1994).

42. Peter, L.M.; Durr, W.; Bindra, P.; Gerischer, H. J. Electroanal. Chem., 71, 31 (1976).

43. Mejman, N. Zh. Fiz. Khim., 22, 1454, (1948).

44. Koutecky, J. Chem. Listy, 47, 323 (1953).

45. Gavaghan, D.J.; Feldberg, S.W. J. Electroanal. Chem., 491, 103 (2000).

46. Aoki, K. Electroanalysis, 5, 627 (1993).

47. Eklund , J.C; Bond, A.M.; Alden, J.A.; Compton, R.G. Advances in Physical Organic Chemistry, 32, 1 (1999).

48. Rooney, M.B.; Gavaghan, D.J.; Coomber, D.C.; Feldberg, S.W.; Bond, A.M. Unpublished work containing data and concepts that were significantly used in preparation of Sections 4 and 5 of this Chapter.

15 CHAPTER 15: ELECTRON TRANSFER AT THE LIQUID-LIQUID INTERFACE

1. Cunnane, V. J. ; Murtomaki, L., Liquid/liquid interfaces. Theory and methods., A. G. Volkov and D. W. Deamer, Eds., CRC Press, Boca Raton, 1996.

2. Girault, H. H., Modern Aspects of Electrochemistry, J. O. M. Bockris et al., Eds., Plenum Press, New York and London, 1993.

3. Girault, H.; Schiffrin, D., Electroanalytical Chemistry. A Series of Advances, A. Bard, Ed., Marcel Dekker, INC., New York and Basel, 1989.

4. Koryta, J.; Vanysek, P., Advances in Electrochemistry and Electrochemical Engineering, 72, 113 (1981).

5. Schmickler, W., Annual Reports on the Progress of Chemistry, Sect. C, 95, 117 (1999).

6. Fermin, D.; Lahtinen, R., Surfactant Science Series, 95 (Liquid Interfaces in Chemical, Biological, and Pharmaceutical Applications), 179 (2001).

7. Benjamin, I., Progress in Reaction Kinetics and Mechanism - Science Reviews, 27, 87 (2002).

8. Gibbs , J. W., Collected works, Vol. 1, Langmans Green & Co, New York, 1928.

9. Nernst, W.; Riesenfeld, E. H., Ann.Phys., 8, 600 (1902).

10. Bell, R. P., J. Phys. Chem., 32, 882 (1928).

11. Brust , M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R., J. Chem. Soc, Chem. Commun., 801 (1994).

12. Faraday, M., Philos. Trans. R. Soc. London, 147-181, 145 (1857).

13. Guastalla, J., J. Chim.Phys., 53, 470 (1956).

14. Dupeyrat, M.; Guastalla, J., J. Chim. Phys., 53, 469 (1956).

15. Dupeyrat, M., J. Chim. Phys., 61, 306 (1964).

16. Dupeyrat, M., J. Chim. Phys., 61, 323 (1964).

17. Gavach, C , C. R. Acad. Sci. Paris, 269, 1356 (1969).

18. Samec, Z., J. Electroanal. Chem., 99, 197 (1979).

19. Koryta, J., Anal. Chim. Acta, 91, 1 (1977).

20. Lyons, M. E. G., Annual Reports on the Progress of Chemistry, Section C: Physical Chemistry (1991), 87, 119 (1990).

21. Watts, A.; Van der Noot, T. J., Liquid/liquid interfaces. Theory and methods, A. G. Volkov and D. W. Deamer, Eds., CRC Press, Boca Raton, 1996.

22. Benjamin, I., Annu. Rev. Phys. Chem., 48, 407 (1997).

23. Benjamin, I., Chem. Rev, 96, 1449 (1996).

24. Benjamin, I., Liquid/liquid interfaces. Theory and methods., A. G. Volkov and D. W. Deamer, Eds., CRC Press, Boca Raton, 1996.

25. Kakiuchi, T., Liquid/liquid interfaces. Theory and methods, A. G. Volkov and D. W. Deamer, Eds., CRC Press, Boca Raton, 1996.

26. Samec, Z., J. Electroanal. Chem., 103, 1 (1979).

27. Vanysek, P., Electrochemistry on Liquid-Liquid Interfaces, Springer-Verlag, Berlin, 1985. Chapter 15

28. Senda, M.; Yamamoto, Y., Liquid/liquid interfaces. Theory and methods, A. G. Volkov and D. W. Deamer, Eds., CRC Press, Boca Raton, 1996.

29. Samec , Z., Liquid/liquid interfaces. Theory and methods., A. G. Volkov and D. W. Deamer, Eds., CRC Press, Boca Raton, 1996.

30. Marcus, R. A., J. Chem. Phys., 43, 679 (1965).

31. Albery, W., Annu. Rev. Phys. Chem., 31, 227 (1980).

32. Marcus , R. A., J. Phys. Chem., 94, 4152 (1990).

33. Marcus, R. A., J. Phys. Chem., 94, 1050 (1990).

34. Marcus, R. A., J. Phys. Chem., 95, 2010 (1991).

35. Marcus, R. A., J. Electroanal. Chem., 438, 251 (1997).

36. Marcus, R. A., J. Phys. Chem. B, 102, 10071 (1998).

37. Marcus, R. A., J. Electroanal. Chem., 483, 2 (2000).

38. Kharkats, Y I.; Volkov, A. G., J.Electroanal.Chem., 184, 435 (1985).

39. Girault, H. H.; Schiffrin, D. J., J.Electroanal.Chem, 244, 15 (1988).

40. Sutin, N., Ace. Chem. Res., 15, 275 (1982).

41. Newton, M. D.; Sutin, N., Annu. Rev. Phys. Chem., 35, 437 (1984).

42. Schmickler, W., J. Electroanal. Chem., 428, 123 (1997).

43. Koryta, J.; Vanysek, P.; Brezina, M., J. Electroanal. Chem., 67, 263 (1976).

44. Slevin, C. J.; Unwin, P. R., Langmuir, 13,4799 (1997).

45. Zhang , J.; Slevin, C. J.; Murtomaki, L.; Kontturi, K. S.; Williams, D. E.; Unwin, P. R., Langmuir, 17, 821 (2001).

46. Zhang, J.; Unwin, P. R., Phys. Chem. Chem. Phys., 4, 3820 (2002).

47. Slevin, C. J.; Unwin, P. R., Langmuir, 15, 7361 (1999).

48. Slevin, C. J.; Zhang, J.; Unwin, P. R., J. Phys. Chem. B, 106, 3019 (2002).

49. Marken, F.; Webster, R. D.; Bull, S. D.; Davies, S. G., J. Electroanal. Chem., 437, 209(1997).

50. Fujihira, M.; Yanagisawa, M.; Kondo, T., Bull. Chem. Soc. Jpn, 66, 3600 (1994).

51. Shi, C ; Anson, F. C , J. Phys. Chem. B, 105, 8963 (2001).

52. Shi, C; Anson, F. C , J. Phys. Chem. B, 105, 1047 (2001).

53 . Shi, C; Anson, F. C, J. Phys. Chem. B, 103, 6283 (1999).

54. Shi, C; Anson, F. C , Anal. Chem., 70, 3114 (1998).

55. Shi, C ; Anson, F. C , J. Phys. Chem. B, 102, 9850 (1998).

56. Komorsky-Lovric, S.; Lovric, M.; Scholz, F., Collect. Czech. Chem. Commun., 66, 434 (2001).

57. Komorsky-Lovric, S.; Lovric, M.; Scholz, F., J. Electroanal. Chem., 508, 129 (2001).

58. Mirceski, V; Scholz, F., J. Electroanal. Chem., 522, 189 (2002).

59. Scholz, F.; Komorsky-Lovric, S.; Lovric, M., Electrochem. Commun., 2,112 (2000).

60. Wadhawan, J.; Schroder, U.; Neudeck, A.; Wilkins, S.; Compton, R. G.; Marken, F.; Consorti, S.; de Souza, R.; Dupont, J., J. Electroanal. Chem., 493, 75 (2000).

61. Wadhawan, J.; Compton, R. G.; Marken, F.; Bull, S.; Davies, S., J. Solid State Electrochem., 5, 301 (2001).

62. Taylor, G.; Girault, H. H., J. Electroanal. Chem., 208, 179 (1986).

63. Shao, Y. H.; Mirkin, M. V, Anal. Chem., 70, 3155 (1998).

64. Campbell, J.; Girault, H. H., J. Electroanal. Chem., 266, 465 (1989).

65. Peulon, S.; Guillou, V.; L'Her, M , J. Electroanal Chem., 514, 94 (2001).

66. Liu, B.; Mirkin, M. V., Electroanalysis, 12, 1433 (2000).

67. Liu, B.; Mirkin, M. V., Surfactant Science Series, 95, 373 (2001).

68. Homolka, D.; Hung, L. Q.; Hofmanova, A.; Khalil, M.; Koryta, J.; Marecek, V.; Samec, Z. ; Sen, S.; Vanysek, P.; Weber, J.; Brezina, M.; Janda, M.; Stibor, I., Anal Chem., 52, 1606(1980).

69. Marecek, V.; Samec, Z., J. Electroanal Chem., 185, 263 (1985).

70. Gavach, C ; Henry, F., J. Electroanal. Chem., 54, 361

(1974).

71. Makrlik, E., Collect. Czech. Chem. Commun., 50, 1636 (1985).

72. Stewart, A. A.; Campbell, J. A.; Girault, H. H.; Eddowes, M., Ber. Bunsen-Ges. Phys. Chem., 94, 83 (1990).

73. Makrlik, E., Z. Phys. Chem. (Leipzig), 268, 826 (1987).

74. Makrlik, E., Z. Phys. Chem. (Leipzig), 268, 59 (1987).

75. Makrlik, E., Z Phys. Chem. (Leipzig), 268, 507 (1987).

76. Koryta, J.; Vanysek, P.; Brezina, M., J. Electroanal. Chem., 75, 211 (1977).

77. Makrlik, E., Z Phys. Chem. (Leipzig), 268, 200 (1987).

78. Makrlik, E., Z. Phys. Chem. (Leipzig), 267, 851 (1986).

79. Maeda, K.; Kihara, S.; Suzuki, ML; Matsui, M., J.Electroanal.Chem., 303, 111 (1991).

80. Reid, J.; Vanysek, P.; Buck, R., J. Electroanal Chem., 161, 1 (1984).

81. Reid, J.; Vanysek, P.; Buck, R., J. Electroanal. Chem., 170, 109 (1984).

82. VanderNoot, T.; Schiffrin, D. J., J. Electroanal. Chem., 278, 137 (1990).

83. Marecek, V; Gratzl, M.; Janata, J., J. Electroanal. Chem., 296, 537 (1990).

84. Vanysek, P., Chimica Oggi, 8, 47 (1990).

85. Chen , Q. Z.; Iwamoto, K.; Seno, M., Electrochim. Acta, 36, 291 (1991).

86. Cheng, Y.; Schiffrin, D. J., J. Chem. Soc, Faraday Trans., 89, 199 (1993).

87. Ding, J.; Fermin, D.; Brevet, P.-R; Girault, H. H., J. Electroanal Chem., 458, 139 (1998).

88. Bard, A. J.; Fan, R R. R; Mirkin, M. V, Electroanalytical Chemistry, A. J. Bard, Ed., Marcel Dekker, Inc., New York, 1994.

89. Mirkin, M. V; Tsionsky, M., Scanning Electrochemical Spectroscopy, A. J. Bard and M . V. Mirkin, Eds., Marcel Dekker, Inc., New York, 2001.

90. Mirkin, M. V; Horrocks, B., Anal. Chim. Acta, 406, 119 (2000).

91. Martin, R.; Unwin, P. R., J. Electroanal Chem., 439, 123 (1997).

92. Mirkin, M. V, Mikrochim. Acta, 130, 127 (1999).

93. Barker, A.; Slevin, C; Unwin, P. R.; Zhang, J., Surfactant Science Series, 95, 283 (2001).

94. Tsionsky, M.; Zhou, J.; Amemiya, S.; Fan, R R. R; Bard, A. J.; Dryfe, R., Anal. Chem., 77,4300 (1999).

95. Amemiya, S.; Ding, Z.; Zhou, J.; Bard, A. J., J. Electroanal Chem., 483,1 (2000).

96. Kuzmin, M. G.; Soboleva, I. V; Kotov, N. A., Anal. Set, 15, 3 (1999).

97. Kotov, N. A.; Kuzmin, M. G., Liquid/liquid interfaces. Theory and methods, A. Volkov and D. Deamer, Eds., CRC Press, Boca Raton, 1996.

98. De Armond, M. K.; De Armond, A. H., Liquid/liquid interfaces. Theory and methods., A. Volkov and D. Deamer, Eds., CRC Press, Boca Raton, 1996.

99. Eisenthal, K. B., Chem. Rev., 96, 1343 (1996).

100. Eisenthal , K. B., J.Phys.Chem, 100, 12997 (1996).

101. Brevet, P. R; Girault, H. H., Liquid/liquid interfaces. Theory and methods., A. Volkov and D. Deamer, Eds., CRC Press, Boca Raton, 1996.

102. Brevet, P. R; Girault, H. H., Prog. Colloid Polym. Sci., 103, 1 (1997).

103. Webster, R. D.; Dryfe, R. A. W.; Coles, B. A.; Compton, R. G., Anal. Chem., 70,792 (1998).

104. Dryfe, R. A. W.; Webster, R. D.; Coles, B. A.; Compton, R. G., Chem. Commun., 779(1997).

105. Dryfe, R. A. W.; Ding, Z.; Wellington, R. G.; Brevet, P. R; Kuznetzov, A. M.; Girault, H. H., J. Phys. Chem. A, 101, 2519 (1997).

106. Webster, R., Phys. Chem. Chem. Phys., 2, 5660 (2000).

107. Bard, A. J.; Parsons, R.; Jordan, J., Marcel Dekker, Inc., New York, 1985.

108.Kihara, S. ; Suzuki, M.; Maeda, K.; Ogura, K.; Matsui, M.; Yoshida, Z., J. Electroanal. Chem., 271, 107 (1989).

109. Shafer , H.; Derback, T.; Koval, C , J. Phys. Chem. B, 104, 1025 (2000).

110. Bard , A. J.; Faulkner, L., Electrochemical Methods. Fundamentals and Applications, John Wiley & Sons, New York, 1980.

111. Connelly, N. G.; Geiger, W. E., Chem. Rev., 96, 877 (1996).

112. Cox , B. G.; Parker, A. J., J. Am. Chem. Soc, 95, 402 (1973).

113. Alfenaar, M., J. Phys. Chem., 79, 2200 (1975).

114. Kolthoff, I. M.; Chantooni, M. K., J. Am. Chem. Soc, 93, 7104 (1971).

115. Gritzner , G.; Kuta, J., PureAppl. Chem., 56, 461 (1984).

116. De Ligny, C. L.; Alfenaar, M.; Van Der Veen, N. G., Reel. Trav. Chim. Pays-Bas, 87, 585 (1968).

117. Bond, A. M.; McLennan, E. A.; Stojanovic, R. S.; Thomas, F. G., Anal. Chem., 59, 2853 (1987).

118. Quinn, B. M.; Liljeroth, P.; Kontturi, K., J. Am. Chem. Soc, 124, 12915 (2002).

119. Ding, Z.; Quinn, B. M.; Bard, A. J., J. Phys. Chem. B, 105, 6367 (2001).

120. Ulmeanu, S.; Lee, H.; Fermin, D.; Girault, H. H.; Shao, Y, Electrochem. Commun., 5,219(2001).

121. Quinn, B.; Kontturi, K. S., J. Electroanal. Chem., 483, 124 (2000).

122. Tsionsky, M.; Bard, A. J.; Mirkin, M. V, J. Am. Chem. Soc, 119, 10785 (1997).

123. Selzer, Y; Mandler, D., J. Electroanal. Chem., 409, 15 (1996).

124. Zhang, J.; Slevin, C. J.; Unwin, P. R., Chem. Commun., 1501 (1999).

125. Zhang, J.; Barker, A.; Unwin, P. R., J. Electroanal. Chem., 483, 95 (2000).

126. Barker, A.; Unwin, P. R.; Amemiya, S.; Zhou, J.; Bard, A. J., J. Phys. Chem. B, 103, 7260 (1999).

127. Georganopoulou, D.; Strutwolf, J.; Pereira, C; Silva, R; Unwin, P. R.; Williams, D., Langmuir, 17, 8348 (2001).

128. Zhang, J.; Unwin, P. R., J. Phys. Chem. B, 104, 2341 (2000).

129. Zhang, Z. Q.; Ye, J. Y; Sun, P.; Yuan, Y; Tong, Y H.; Hu, J. M.; Shao, Y H., Anal. Chem., 74, 1530(2002).

130. Zhang, Z. Q.; Tong, Y H.; Sun, P.; Shao, Y H., Chemical journal of chĭnese Universities Chineses, 22, 206 (2001).

131. Ding, Z.; Brevet, P.-R, Chem. Commun., 2059 (1997).

132. Samec, Z.; Marecek, V; Weber, J., J. Electroanal. Chem., 96, 245 (1979).

133. Samec, Z.; Marecek, V.; Weber, J., J. Electroanal. Chem., 103, 11 (1979).

134. Samec, Z.; Marecek, V.; Weber, J.; Homolka, D., J. Electroanal. Chem., 126, 105 (1981).

135. Cunnane, V.; Geblewicz, G.; Schiffrin, D. J., Electrochim. Acta, 40, 3005 (1995).

136. Quinn , B.; Lahtinen, R.; Murtomaki, L.; Kontturi, K. S., Electrochim. Acta, 44, 47 (1998).

137. Hotta, H.; Akagi, N.; Sugihara, T.; Ichikawa, S.; Osakai, T., Electrochem. Commun., 4, All (2002).

138. Yuan, Y.; Gao, Z.; Zhang, M. Q.; Zhang, Z. Q.; Shao,

Y. H., Sel China, Ser. B, 45, 494 (2002).

139. Geblewicz, G.; Schiffrin, D. J., J. Electroanal. Chem., 244, 27 (1988).

140. Cheng, Y; Schiffrin, D. J., J. Chem. Soc, Faraday Trans., 90, 2517 (1994).

141. Cunnane , V.; Schiffrin, D. J.; Beltran, C ; Geblewicz, G.; Solomon, T., J.Electroanal.Chem, 247, 203 (1988).

142. L'Her , M.; Rousseau, R.; L'Hostis, E.; Roue, L.; Laouenan, A., C. R. Acad. Sci. Paris, t.322, serie lib, 55 (1996).

143 . Solomon, T.; Bard, A. J.,Anal. Chem., 67, 2787 (1995).

144. Solomon, T.; Bard, A. J., J.Phys.Chem, 99, 17487 (1995).

145. Kihara, S.; Maeda, K.; Suzuki, M.; Sohrin, Y; Shirai, O.; Matsui, M., Anal. Sel, 7, 1415(1991).

146. Barker, A.; Unwin, R R.; Zhang, J., Electrochem. Commun., 3, 372 (2001).

147. Delville, M. H.; Tsionsky, M.; Bard, A. J., Langmuir, 14, 211A (1998).

148. Lahtinen, R.; Fermin, D.; Konrurri, K. S.; Girault, H. H., J. Electroanal. Chem., ^3,81(2000).

149. Liu, B.; Mirkin, M. V., J. Phys. Chem. B, 106, 3933 (2002).

150. Zhang, J.; Unwin, P. R., J. Electroanal. Chem., 494, Al (2000).

151. Liu, B.; Mirkin, M. V., J. Am. Chem. Soc, 121, 8352 (1999).

152. Tsionsky, M.; Bard, A. J.; Mirkin, M. V., High-Resolution Study of Charge Transfer Processes at the Liquid/liquid Interface, 1996, p 16.

153. Tsionsky, M.; Bard, A. J.; Mirkin, M. V., J. Phys. Chem., 100, 17881 (1996).

154. Ding, Z.; Wellington, R. G.; Brevet, P.-R; Girault, H.

H., J. Phys. Chem., 100, 10658(1996).

155. Brown, A. R.; Yellowlees, L. J.; Girault, H. H., J. Chem. Soc, Faraday Trans., 89, 207 (1993).

156. Kott, K. L.; Higgins, D. A.; McMahon, R. J.; Corn, R. M., J. Am. Chem. Soc, 115, 5342 (1993).

157. Wei, C; Bard, A. J.; Mirkin, M. V., J. Phys. Chem., 99, 16033 (1995).

158. Thomson, R L.; Yellowlees, L. J.; Girault, H. H., J. Chem. Soc, Chem. Commun., 1547(1988).

159. Kanoufi, R; Cannes, C ; Zu, Y; Bard, A. J., J. Phys. Chem. B, 105, 8951 (2001).

160. Zu, Y B.; Fan, R R. R; Bard, A. J., J. Phys. Chem. B, 103, 6272 (1999).

161. Dvorak, O.; De Armond, A. H.; De Armond, M. K., Langmuir, 8, 508 (1992).

162. Marecek, V.; De Armond, A. H.; De Armond, M. K., J.Am.Chem.Soc, 111, 2561 (1989).

163. Osakai , T.; Muto, K., J. Electroanal Chem., 496, 95 (2001).

164. Fermin, D. J.; Duong, H. D.; Ding, Z.; Brevet, P. F.; Girault, H. H., Electrochem. Commun., 1,29 (1999).

165. Fermin, D. J.; Duong, H. D.; Ding, Z.; Brevet, P.-F.; Girault, H. U., J. Am. Chem. Soc, 121, 1020 3 (1999).

166. Eugster, N.; Fermin, D. J.; Girault, H. H., J. Phys. Chem. B, 106, 3428 (2002).

167. Fermin, D. J.; Ding, Z.; Duong, H. D.; Brevet, P.-F.; Girault, H. H., J. Phys. Chem. 5,702,10334(1998).

168. Fermin, D. J.; Ding, Z.; Duong, H. D.; Brevet, P.-F.; Girault, H. H., Chem. Commun., 1125(1998).

169. Duong, H. D.; Brevet, P.-F.; Girault, H. H., J. Photochem. Photobiol. A, 117, 27 (1998).

170. Jensen, H.; Khakkassery, J.; Nagatani, H.; Fermin, D. J.; Girault, H. H., J. Am. Chem. Soc, 122, 10943 (2000).

171. Jensen, H.; Fermin, D. J.; Girault, H. H., Phys. Chem. Chem. Phys., 3, 2503 (2001).

172. Lillie, G. C; Holmes, S. M.; Dryfe, R. A. W., J. Phys. Chem. B, 106, 12101 (2002).

173. Ohde, H.; Maeda, K.; Yoshida, Y.; Kihara, S., Electrochim. Acta, 44, 23 (1998).

174. Osakai, T.; Jensen, H.; Nagatani, H.; Fermin, D. J.; Girault, H. H., J. Electroanal. Chem., 510,43 (2001).

175. Osakai , T.; Akagi, N.; Hotta, H.; Ding, J.; Sawada, S., J. Electroanal. Chem., 490, 85 (2000).

176. Suzuki, M.; Umetani, S.; Matsui, M.; Kihara, S., J. Electroanal. Chem., 420, 119 (1997).

177. Georganopoulou, D. G.; Caruana, D. J.; Strutwolf, J.; Williams, D. E., Faraday Discuss., 109(2000).

178. Ohde, H.; Maeda, K.; Yoshida, Y; Kihara, S., J. Electroanal. Chem., 483, 108 (2000).

179. Zhang, Z. Q.; Yuan, Y; Sun, P.; Su, B.; Guo, J. D.; Shao, Y H.; Girault, H. H., J. Phys. Chem. B, 106, 6713 (2002).

180. Donten, M.; Stojek, Z.; Scholz, F., Electrochem. Commun., 4, 324 (2002).

181. Noviandri , I.; Brown, K. N.; Fleming, D. S.; Gulyas, P. T.; Lay, P. A.; Masters, A. F.; Phillips, L., J. Phys. Chem. B, 103, 6713 (1999).

182. Cheng, Y; Schiffrin, D. J., J.Chem.Soc, Faraday Trans., 89, 199 (1993).

183. Zhang, J.; Unwin, P. R., J.Chem.Soc, Perkin Trans. 2, 1608 (2001).

184. Fermin, D. J.; Duong, H. D.; Ding, Z. R; Brevet, P.-R; Girault, H. H., Phys. Chem. Chem. Phys., 1, 1461(1999).

185. Guainazzi, M.; Silvestri, G.; Serravalle, G., J.Chem.Soc,Chem.Commun., 200 (1975).

186. Dehmlow, E. V., Angew. Chem., Int. Ed. Engl., 13, 170 (1974).

187. Hanzlik, J.; Samec, Z.; Hovorka, J., J. Electroanal. Chem., 216, 303 (1987).

188. Barker, A.; Unwin, P. R., J. Phys. Chem. B, 105, 12019 (2001).

189. Prins, R.; Korswagen, A. R.; Kortbeek, A. G. T. G.,J. Organometal. Chem., 39, 335 (1972).

190. Page, J. A.; Wilkinson, G., J. Am. Chem. Soc, 74, 6149 (1952).

191. Vaucher, S.; Charmant, J.; Sorace, L.; Gatteschi, D.; Mann, S., Polyhedron, 20, 2467 (2001).

192. Chen, Q.-Z.; Iwamoto, K.; Seno, M., Electrochim. Acta, 36, 291 (1991).

193. L'Her, M.; Pondaven, A., The Porphyrin Handbook; vol. 16; Phthalocyaniñes: spectroscopic and electrochemical characterization., Academic Press-Elsevier, Amsterdam, 2003 .

194. Kotov, N. A.; Kuzmin, M. G., J. Electroanal. Chem., 338, 99 (1992).

195. Kotov , N. A.; Kuzmin, M. G., J.Electroanal.Chem, 341, 47 (1992).

196. Eugster, N.; Fermin, D. J.; Girault, H. H., J. Am. Chem. Soc, 125, 4862 (2003).

197. Das , S.; Thanulingama, T. L.; Rajesha, C. S.; George, M. V., Tetrahedron Lett., 36, 1337(1995).

198. Rajesh, C; Thanulingam, T.; Das, S., Tetrahedron, 53, 16817 (1997).

199. Aoki, K.; Tasakorn, P.; Chen, J., J. Electroanal. Chem, 542, 51 (2003).

200. Tasakorn, P.; Chen, J.; Aoki, K., J. Electroanal. Chem., 533, 119 (2002).

201. Mirceski, V.; Gulaboski, R.; Scholz, F., Electrochem. Commun., 4, 814 (2002).

202. Komorsky-Lovric, S.; Lovric, M.; Scholz, F., Collect. Czech. Chem. Commun., 66, 434(2001).

203. Saczek-Maj, ML; Opallo, M., Electroanalysis, 14, 1060 (2002).

204. Opallo, M.; Saczek-Maj, M., Electrochem. Commun., 3, 206 (2001).

205. Cheng, Y; Murtomaki, L.; Corn, R., J. Electroanal. Chem., 483, 88 (2000).

206. Steiger, B.; Anson, F. C , Inorg. Chem., 39, 4579 (2000).

207. Chung, T.; Anson, F. C , Anal. Chem., 73, 337 (2001).

208. Myland, J. C ; Oldham, K. B., J. Electroanal. Chem., 530, 1 (2002).

209. Barker , A.; Unwin, P. R., J. Phys. Chem., 104, 2330 (2000).

210. Forssten, C; Strutwolf, J.; Williams, D. E., Electrochem. Commun., 3, 619 (2001).

211. Nakabayashi, S.; Aogaki, R.; Karantonis, A.; Iguchi, U.; Ushida, K.; Nawa, M., J. Electroanal. Chem., 473, 54 (1999).

212. Sathaye, S.; Patil, K.; Paranjape, D.; Padalkar, S., Mater. Res. Bull, 36, 1149 (2001).

213. Cheng, Y.; Schiffrin, D. J., J. Chem. Soc, Faraday Trans., 92, 3865 (1996).

214. Kassim , A.; Abdullah, A. H.; Idris, Z., Ultra Scientist of Physical Sciences, 13, 306 (2001).

215. Cunnane, V. J.; Evans, U., Chem. Commun., 2163 (1998).

216. Gorgy, K.; Fusalba, F.; Evans, U.; Kontturi, K. S.; Cunnane, V. J., Synth. Met, 125, 365 (2002).

217. Johans, C; Clohessy, J.; Fantini, S.; Kontturi, K. S.; Cunnane, V. J., Electrochem. Commun., 4, 227 (2002).

218. Johans, C; Kontturi, K. S.; Schiffrin, D. J., J. Electroanal. Chem., 526, 29 (2002).

219. Johans, C; Lahtinen, R.; Konturri, K. S.; Schiffrin, D. J., J. Electroanal. Chem., 488, 99 (2000).

220. Johans, C; Liljeroth, P.; Kontturi, K. S., Phis. Chem. Chem. Physics, 4, 1067 (2002).

221.Maeda, K.; Jãnchenova, H.; Lhotsky, A.; Stibor, I.; Budka, J.; Marecek, V., J. Electroanal. Chem., 516, 103 (2001).

222. Yunus, K.; Marks, C. B.; Fisher, A. C; Allsopp, D. W. E.; Ryan, T. J.; Dryfe, R. A. W.; Hill, S. S.; Roberts, E. P. L.; Brennan, C. M , Electrochem. Commun., 4, 579 (2002).

223. Solomon, T., Bull Chem. Soc. Ethiop., 11, 79 (1997).

224. Volkov, A. G.; Kharkats, Y., Kinetika i Kataliz, 26, 1322 (1985).

225. Volkov, A. G.; Gugeshashvili, M.; Deamera, D., Electrochim. Acta, 40, 2849 (1995).

226. Kharkats, Y.; Volkov, A. G., Biochimica et Biophysica Acta, 891, 56 (1987).

227. Volkov , A. G., J. Electroanal Chem., 483, 150 (2000).

228. Volkov , A. G., Electrochimica Acta, 44, 139 (1998).

229. Boguslavskii, L.; Volkov, A. G.; Kandelaki, M., FEBSLett, 65, 155 (1976).

230. Boguslavskii , L.; Volkov, A. G.; Kandelaki, M., Bioelectrochem. Bioenerg., 4, 68 (1977).

231. Kharkats, Y; Volkov, A. G.; Boguslavskii, L., J.Theor.Biol, 65, 379 (1977).

232. Volkov, A. G.; Mironov, A.; Boguslavskii, L., Elektrokhimiya, 12, 1326 (1976).

233. Volkov , A. G.; Deamer, D. W., Prog. ColloidPolym. Scl, 103, 21 (1997).

234. Boguslavskii , L.; Volkov, A. G.; Kandelaki, M.; Nizhnikovskii, E.; Bibikova, M., Biofizika, 22, 223 (1977).

235. Maeda, K.; Nishihara, M ; Ohde, H.; Kihara, S., Anal. Set, 14, 85 (1998).

236. Sortino, S.; Petralia, S.; Di Bella, S., J. Am. Chem. Soc, 125, 5610 (2003).

237. Katz, E.; Filanovsky, B.; Willner, I., New J. Chem., 23, 481 (1999).

238. Schmickler, W., Interfacial electrochemistry, Oxford University Press, Oxford, 1996.