Coordination Chemistry Reviews, 54 (1984) 23–98
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

ELECTROCHEMISTRY AND REDOX BEHAVIOUR OF TRANSITION METAL DITHIOCARBAMATES

A.M. BOND

Division of Chemical and Physical Sciences, Deakin University, Victoria, 3217 (Australia)

R.L. MARTIN

Monash University, Clayton, Victoria 3168 (Australia)

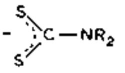
(Received 27 April 1983)

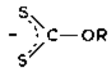
CONTENTS

0010-8545/84/$22.80

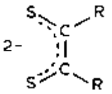
A. INTRODUCTION

The chemical redox behaviour of 1,1-dithio ligands such as dithiocarbamates (**1**) and xanthates (**2**) has been studied in aqueous media since the last century. However, water is generally a poor solvent for these complexes and organic solvents, such as acetone, acetonitrile, dichloromethane, benzene, etc. are usually required to achieve adequate solubility. Hence the detailed electrochemical characterization of the chelates discussed in this review had to await the introduction of instrumentation capable of performing well in high-resistance non-aqueous solvents. Such instrumentation, based on the use of a three-electrode potentiostatic or galvanostatic system, is now widely available [1] and electrochemical investigations of organometallic complexes can now be undertaken routinely.

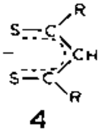

1


2

The first sulphur chelates to be studied from a combined chemical and electrochemical point of view were the 1,2-dithiochelates (**3**). Dithiolene complexes have been studied extensively over the past 20 years, a period which not surprisingly coincided with the advent of the potentiostat into electrochemical instrumentation [1]. The interest in their electrochemistry has been heightened by the ease with which many dithiolene complexes undergo sequential one-electron transfer reactions and the many interesting structural and spectral changes which accompany the electron transfer have also attracted the attention of inorganic chemists [2–5].


3

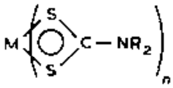
Two other classes of dithio complexes whose redox properties have been studied in detail more recently [6–9] are the 1,1- and 1,3-dithiochelates. The former include the dithiocarbamates (**1**) and xanthates (**2**) and the latter the dithio-β-diketonates (**4**).


4

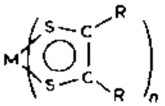
The review component of the present work is confined to the redox chemistry of dithiocarbamate complexes. The recent and extensive studies available enable a detailed picture of the systematic nature of dithiochelate chemistry to be achieved, and extrapolations can be made to related dithio complexes using data reviewed elsewhere.

(i) Nomenclature

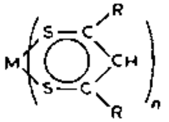
The three types of dithiochelates considered in this review are readily divided into three classes by both their structural and chemical redox properties. From the structural aspect the complexes form either 4-, 5- or 6-membered chelate rings (**5**, **6** and **7**). As classes, the complexes are referred to as 1,1-, 1,2- and 1,3-dithiochelates. Substituents on xanthates, dithiocarbamates and dithioacetylacetonates are readily discerned from the systematic abbreviations used. However, it has long been the practice to give 1,2-dithiochelates trivial abbreviations. These abbreviations will be used in this review and, where necessary, the nomenclature will be explained in the text. As a class, the 1,2-dithiochelates are referred to as dithiolenes, a term which in no way reflects the oxidation state of the ligand.



5



6



7

(ii) Preliminary considerations

Historically there are good reasons to compare and contrast the redox behaviour of 1,1-, 1,2- and 1,3-dithiochelates. Schrauzer in his early review [4] and again more recently [10] has summarized theoretical findings and made predictions as to the types of ligand which would be expected to give dithiolene-type redox behaviour. In particular, he concluded that the peculiar properties of the metal dithiolenes are essentially a consequence of their high covalency and the special type of electronic ground state delocalization that is present. He stated that, "this delocalization results from the interaction of the lowest occupied π-MOs of the ligands, with the metal p-orbitals of appropriate symmetry, producing a low-lying molecular orbital delocalized over the whole molecule or complex". Based on this rationalization, Schrauzer predicted that dithiolene-type behaviour could result from ligands with "even" π-electron systems in their neutral state. On the other hand, ligands with "odd" π-electron systems should not have any low-lying π-molecular orbitals to accept additional electrons and thus such systems should behave normally. Schrauzer concluded that the complexes of 1,2-bidentate unsaturated sulphur ligands form a very distinct group of compounds whose properties and unusual structures are not likely to be duplicated by other ligand systems such as the 1,1- and 1,3-dithiolates.

From Schrauzer's argument it follows, for example, that dithiochelating ligands which form 5-, 7-, or 9-membered ring systems are classifiable as "even" π-systems and should exhibit "normal" behaviour. McCleverty [3], however, has expressed a diametrically opposed point of view by suggesting that 1,3-dithio complexes "may be oxidized or reduced in much the same way as 1,2-dithiolenes" whilst acknowledging that other members of the "odd" class such as the 1,1-dithiochelates may be unable to engage in electron transfer reactions.

One experimental pathway for evaluating Schrauzer's predictions would be to study the electrochemical behaviour of assumed "odd" π-electron systems and then to compare this with the well-documented behaviour of the dithiolene complexes. Unfortunately, early electrochemical measurements on various "odd" systems provided conflicting experimental evidence on the "odd" versus "even" question. For example, using polarographic techniques, Van der Linden and Van der Roer noted the redox reversibility of some 1,1-dithiolate complexes [11,12] and regarded this evidence of one-electron transfer steps as showing that Schrauzer's classification "is not as clear as proposed". On the other hand, the irreversible reduction of the 1,3-metal dithioacetylacetonates in acetonitrile and DMF, reported by Furuhashi et al. [13] could have been interpreted as evidence in support of the "odd" classification assigned by Schrauzer. However, it has subsequently been reported that the same 1,3-dithio species actually undergo stepwise reversible reduction in acetone when kinetic perturbations are taken into account [14,15].

Another important and similarly confused aspect of the electrochemistry of these and related chelate compounds has been the effect of ligand substituents on the redox couples. The large substituent effect on the redox potentials of a series of substituted 1,2-dithiochelates was suggested "to clearly reflect the ligand π-orbital origin of the orbitals which become occupied during the reduction" [3,4,16]. This type of argument has caused confusion in discussion of the large substituent dependence of the redox couple of a series of $Ru(acac)_3/[Ru(acac)_3]^-$ complexes. Patterson and Holm [17], although recognizing that this couple should involve Ru(III)/Ru(II) species, were misled to the conclusion that the redox orbital "must possess appreciable ligand character", due to rationalizations of the kind presented by Schrauzer.

The broad aim of this review is to present a unifying survey of the redox properties of dithiocarbamate complexes rather than provide a comprehensive compilation of all the redox data available on these and related systems. Rationalizations emerging from this review of the 1,1-dithio complexes when applied to the 1,2- and 1,3- analogues, help to explain the conflicting interpretations presented above, both in regard to the nature and ability of "odd" and "even" dithiochelate complexes to participate in redox reactions and the relevance of reversibility and substituent effects in deducing the true nature of the redox process under study.

(iii) Definitions of chemical and electrochemical redox reversibility

A detailed knowledge of the "reversibility" or otherwise of redox processes is essential to understanding the significance of electrochemical data. In order to standardise the usage of the term, the following brief description of the two types of reversibility, i.e. chemical and electrochemical, will be presented.

(a) Chemical redox reversibility

Chemical redox reversibility pertains when two chemical species can be quantitatively changed into one another by chemical oxidants (ox) and reductants (red)

$$A \overset{\text{ox}}{\rightarrow} B \qquad (1)$$

$$B \overset{\text{red}}{\rightarrow} A \qquad (2)$$

An illustration of this type of process is the oxidation of ferrocene, Cp_2Fe, with, for example, silver, mercury or ferric salts to give the ferrocinium cation, $[Cp_2Fe]^+$. The latter species can be reduced by mild reductants to regenerate ferrocene

$$Cp_2Fe \overset{\text{ox}}{\rightarrow} [Cp_2Fe]^+ \qquad (3)$$

$$[Cp_2Fe]^+ \overset{\text{red}}{\rightarrow} Cp_2Fe \qquad (4)$$

Standard redox potentials for the ferrocene/ferrocinium couple can therefore be measured potentiometrically [18] using reactions of the kind given in eqn. 5 or from the reversible electrode process [19,20]

$$Cp_2Fe + Fe(III) \rightleftharpoons [Cp_2Fe]^+ + Fe(II) \qquad (5)$$

(b) Electrochemical redox reversibility

With the exception of potentiometry, most commonly used electrochemical (i.e. voltammetric) methods for measuring redox potentials involve nonequilibrium situations because, as part of the measurement procedure, they inherently perturb the system being examined. Rationalizations in this work are mainly based on thermodynamic (i.e. the equilibrium situation) principles and so, if the electrochemical measurements are to be useful, they must be capable of furnishing thermodynamically significant data.

Most redox couples have a finite and measurable standard heterogeneous charge transfer rate constant, k_s, which describes the rate of the electron transfer step (1) for a simple electrode process that can be defined as,

$$A + ne \overset{k_s}{\rightleftharpoons} B \tag{6}$$

For any given value of k_s, the degree of departure from the equilibrium situation observed in any measurement depends on the time-scale of the measuring technique. If the time-scale of the electron transfer step is very much shorter than the time-scale of the technique of measurement, the measured datum is not significantly different from the thermodynamic or equilibrium situation. An electrode process complying with this condition is regarded as having an electrochemically reversible charge transfer step. If the time-scale of the measurement is shorter than the electron transfer time-scale, the directly measured parameters will have kinetic rather than thermodynamic significance, despite the fact that the system may be chemically reversible and obey the Nernst equation under potentiometric (zero current flow) conditions. An electrode process observed to have these characteristics and where the rate of the back reaction can be assumed to be negligible would then be termed electrochemically irreversible. The term quasi-reversible is sometimes used for intermediate situations where both the forward and reverse reaction rates need to be included in the theoretical description of the heterogeneous charge transfer step.

An alternative type of kinetic complication may arise if the product of a fast electron transfer process is unstable. In this case the electrode process and following chemical reaction may be represented as,

$$A + ne \overset{k_s}{\rightleftharpoons} B \xrightarrow{k_1} C \tag{7}$$

where C represents the final product and k_1 the usual homogeneous chemical rate constant. In a long time-scale experiment (e.g. controlled potential electrolysis), the chemical reaction, $B \rightarrow C$, following the electron transfer would go to completion. The inference that the electrode process is,

$$A + ne \rightarrow C \tag{8}$$

would be incorrect. In contrast, if a relatively short time-scale technique compared with the chemical rate constant k_1 was used, the electrode process would simplify to eqn. 6 since the influence of the chemical step is effectively eliminated. Hence the short time-scale experiment reflects the simple reversible charge transfer step (k_s fast) and the data have direct thermodynamic significance.

The oxidation of ferrocene was given previously as an example of a chemically reversible electrode process. However, the reduction is an excellent example of a reaction with an unstable product [20].

$$Cp_2Fe + e \overset{k_s}{\rightleftharpoons} [Cp_2Fe]^- \xrightarrow{k_1} \text{products} \tag{9}$$

With short time-scale electrochemical techniques and low temperatures the chemical step can be quenched and the reversible one-electron step be observed. At higher temperatures the reduction becomes irreversible and actually involves two electrons [20].

Many classes of electrode processes are observed with dithiochelate systems. Clearly many combinations of electron transfer (reversible and irreversible) and coupled chemical reactions (reversible and irreversible) are possible and these will be considered where relevant.

B. ELECTROCHEMISTRY OF NON-COMPLEXED DITHIO LIGANDS

A knowledge of the electrochemistry of the free ligand is a necessary prerequisite for understanding the redox behaviour of coordinated dithiochelates. For example, understanding the relatively complex reduction mechanism for a series of cyclopentadienyl vanadium(IV) dithiolate complexes [21–23] at mercury electrodes was facilitated by the observation of a wave due to the presence of the free ligand [24,25]. Similarly, interpretation of the electrochemistry of manganese and iron dithiocarbamate complexes was aided by the occurrence of an oxidation wave of the ligand at a platinum electrode [26,27].

(i) Mercury electrodes

Generally, redox behaviour associated with a ligand is extremely dependent on the nature of the electrode, the solvent and the experimental conditions used. At a mercury electrode, the formation of mercury complexes is usually involved. That is, oxidation of the mercury electrode occurs in preference to oxidation of the ligand. The ultimate products from the oxidation step depend on the relative stability of the complexes in the different oxidation states of mercury. Dithiocarbamates [21,28–31] are predominantly involved in the electrode processes described by the equations

$$2\,Hg + 2\,[dtc]^- \rightleftharpoons 2\,Hgdtc + 2\,e \tag{10}$$

$$2\,Hgdtc \rightleftharpoons Hg + Hg(dtc)_2 \tag{11}$$

where the initial oxidation product Hg(I) undergoes spontaneous and rapid disproportionation to Hg(II) and Hg. Problems arising from adsorption and/or insolubility of $Hg(dtc)_2$ add to the complexity of the electrode process. In the presence of hydrogen ion the acid/base properties [30,32,33] of the system

$$\mathrm{Hdtc} \overset{K_a}{\rightleftharpoons} \mathrm{H}^+ + [\mathrm{dtc}]^- \tag{12}$$

also influence the electrochemistry. The equilibria (10–12) are generally applicable to the electrochemistry of other ligands at mercury electrodes.

In non-aqueous media, xanthates [25] and some other 1,1-dithiolates [24], including dialkyldithiophosphates and dimethyldithioarsinate, exhibit the following electrode processes as deduced from the observation and characterization of two polarographic waves

$$2\,\mathrm{Hg} + 6\,\mathrm{xan}^- \rightleftharpoons 2[\mathrm{Hg(xan)_3}]^- + 4\,\mathrm{e} \quad \text{Wave 1} \tag{13}$$

$$2[\mathrm{Hg(xan)_3}]^- + \mathrm{Hg} \rightleftharpoons 3\,\mathrm{Hg(xan)_2} + 2\,\mathrm{e} \quad \text{Wave 2} \tag{14}$$

The polarography of xanthate in aqueous and other media is extremely complex [34–36]. However, HgL_2 (L = 1,1-dithiolate) seems to be the commonly observed final product of oxidation of Hg in the presence of sulphur chelates.

The polarography of the 1,3-dithioligand, *O*-ethylthioacetothioacetate (OEt–SacSacH) has also been studied [37]. The overall electrode process can be described by the equation

$$\mathrm{Hg} + 2\,\mathrm{OEt{-}SacSacH} \rightarrow \mathrm{Hg(OEt{-}SacSac)_2} + 2\,\mathrm{H}^+ + 2\,\mathrm{e} \tag{15}$$

The mechanism is complicated and includes steps such as

$$\mathrm{Hg} + \mathrm{OEt{-}SacSacH} \rightleftharpoons [\mathrm{Hg(OEt{-}SacSac)}]^+ + \mathrm{H}^+ + 2\,\mathrm{e} \tag{16}$$

$$\mathrm{OEt{-}SacSacH} + [\mathrm{HgOEt{-}SacSac}]^+ \rightarrow \mathrm{Hg(OEt{-}SacSac)_2} + \mathrm{H}^+ \tag{17}$$

Reaction 17 does not influence the polarography but on longer time-scales $Hg(OEt–SacSac)_2$ is formed. The polarography of dithiomalonamide (4, $R = NH_2$) has also been studied briefly and appears to parallel that for OEt–SacSacH in that it is complex and ultimately leads to formation of the analogous mercury complex [38].

(ii) Platinum and other inert electrodes

At platinum and other inert electrodes, the 1,1-, 1,2- and 1,3-dithio ligands are themselves oxidized and either the formation of dimeric species or other reactions involving the formation of sulphur–sulphur bonds predominate.

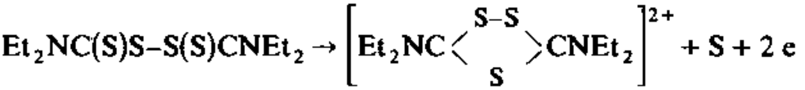
On oxidation, dithiocarbamates have been reported [39] to undergo a quasi-reversible oxidation to the neutral radical ($k_s \simeq 3 \times 10^{-2}$ cm s^{-1} at room temperature for $[Et_2dtc]^-$ at Pt in acetonitrile). The coupled dimerization to give the tetraethylthiuramdisulphide [39] is irreversible and the rate constant k_f was estimated to be 2×10^5 mol^{-1} l s^{-1}.

$$[Et_2NCS_2]^- \overset{k_s}{\rightleftharpoons} Et_2NCS_2\cdot + e \tag{18}$$

$$2\,Et_2NCS_2\cdot \overset{k_f}{\rightarrow} Et_2NC(S)S\text{–}S(S)CNEt_2 \tag{19}$$

Whilst there is no doubt that thiuramdisulphide is the final product of the oxidation, pathways other than dimerization of the radical could lead to its formation. Whether electrochemical data can distinguish between alternative mechanisms when the reactions are so fast is open to question.

Oxidation of the tetraethylthiuramdisulphide generated at the electrode surface can then occur at more positive potentials to produce the relatively stable 3,5-bis(*N*,*N*-diethyliminium 1,2,4-trithiolane) dication $[bitt]^{2+}$ [40]



$$Et_2NC(S)S\text{–}S(S)CNEt_2 \rightarrow \left[Et_2NC \left\langle \begin{matrix} S\text{–}S \\ \\ S \end{matrix} \right\rangle CNEt_2 \right]^{2+} + S + 2\,e \tag{20}$$

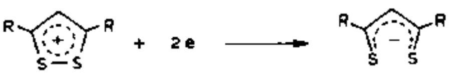
In aqueous media, the oxidation process is complicated by adsorption of dithiocarbamate over a wide potential range at carbon paste electrodes [41], but thiuramdisulfide remains as the product of the first oxidation step. Electrochemical oxidation of sodium dimethyldithiocarbamate to produce tetramethylthiuramdisulphide produces a 95% yield of high-purity material and has been the subject of a patent [42].

Xanthates, because of their importance as flotation reagents in mineral technology have been subjected to detailed investigations [43,44]. On electrochemical oxidation, dixanthogen (R = alkyl) is the final product

$$2\,[ROCS_2]^- \rightarrow ROC(S)S\text{–}S(S)COR + 2\,e \tag{21}$$

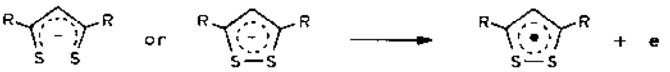
Chemical oxidation of xanthates and dithiocarbamates also affords dixanthogens and thiuramdisulphides, respectively [6], paralleling the electrochemical data at inert electrodes.

Although alkyl or aryl substituted 1,3-dithio ligands [R–Sac R–Sac]$^-$ have not been isolated, Bechgaard et al. [45] have carefully characterized the voltammetric behaviour of these ligands at platinum by electrochemically generating the 1,3-dithio anions in situ from the 1,3-dithiolium cations



(22)

Cyclic voltammetry indicates that the oxidation of [Ph–Sac Ph–Sac]$^-$ to the neutral radical is chemically irreversible probably because of the ring opening and closing which accompanies the reaction


(23)

The radical very rapidly dimerizes to an extent depending on the temperature and bulkiness of the substituents at the dimerization point, with dimerization being favoured by low temperatures and the less bulky substituents [46].


(24)

This dimerization differs from that observed with 1,1-dithio species where dimerization of the radicals formed by oxidation occurs by S–S bonding.

A further one-electron oxidation of the neutral radical affords the 1,2-dithiolium cation, a product which also results from the chemical and electrochemical oxidation of 1,3-dithio metal chelates. Oxidation in acetone of Zn(OEt–SacSac)$_2$ and Cd(OEt–SacSac)$_2$ at mercury electrodes also gives a substituted 1,2-dithiolium cation [47].

$$\mathrm{M(OEt{-}SacSac)_2 \rightarrow M^{2+} + 2\,[OEt{-}SacSac]^+ + 4\,e} \quad (25)$$

Similarly, oxidation of first-row transition metal complexes of dithioacetylacetone by Br_2 and I_2 yields the 3,5-dimethyl-1,2-dithiolium halometallates [48,49]. Thus, even though no direct information is available on the oxidation of the parent [SacSac]$^-$ ligand, it seems likely it would be oxidized to the dithiolium cation at an inert electrode such as platinum.

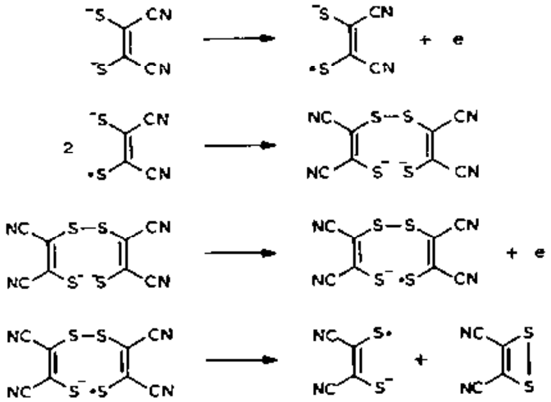
The deep red [Ph–Sac Ph–Sac]$^-$ species can be reversibly reduced at Pt in acetonitrile to the dianion radical at −1.75 V vs. SCE [45]. The dianion is not stable on the coulometric time-scale. This reduction step was not reported for compounds possessing only alkyl substituents. Nevertheless, the possibility of obtaining 1,3-dithio radical dianions in chelating arrangements cannot be overlooked, particularly in those complexes where metal-based reductions are expected to be difficult.

Unfortunately, no completely definitive voltammetry appears to be available for the non-complexed 1,2-dithio ligands. In view of the extensive electrochemical redox series for complexes containing the mnt (maleonitrile dithiolate) ligand [16,50], and the fact that many of these redox processes are ligand based, one might anticipate a series of one-electron steps

$$\mathrm{mnt} \overset{\pm e}{\rightleftharpoons} [\mathrm{mnt}]^- \overset{\pm e}{\rightleftharpoons} [\mathrm{mnt}]^{2-} \quad (26)$$

However, other pathways analogous to the 1,1- and 1,3-dithio systems involving S–S bond formation and dimerization are also possible and irreversible electrode processes have generally been reported [16,51].

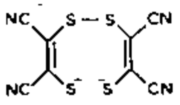
The electrochemical data have been interpreted in terms of reactions such as



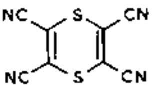
(27)

Chemical oxidations with halogens, thionyl chloride, etc., also give rise to a range of dimeric species [51] such as (**8**) and (**9**).

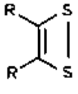
The cyclic oxidation product (**10**) is unstable with R = CN, but reasonably stable with R = CF_3. The CF_3 analogue does dimerize to (**11**) although at high temperatures this reverts [52] to the monomer (**10**). It is interesting to note that the monomeric species is related to (**12**) by a two-electron reduction as is the stable 1,3-dithiolium cation to the 1,3-dithio anion. The analogous 1,1-dithio cyclic species (**13**) is not known.



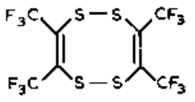
8



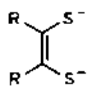
9



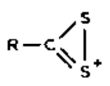
10



11



12



13

The redox behaviour of the free ligand is thus frequently different to that observed when it is coordinated to a metal. Single one-electron steps can then occur due to stabilization of the ligand through chelation to the metal ion. More work on the delicate balance between ligand-based and metal-based processes and on the stability of the oxidized or reduced complexes to further degradation needs to be undertaken to obtain a complete understanding of the electrochemistry of dithio complexes.

C. REDOX BEHAVIOUR OF MANGANESE, IRON, RUTHENIUM AND OSMIUM DITHIOCARBAMATES

As noted in the introduction, the redox behaviour of 1,1-, 1,2- and 1,3-dithio complexes has been the subject of much speculation, especially in the context of "odd" and "even" π-ligand systems. Much of this speculation has been based on an inadequate knowledge of the electrochemistry and its interpretation. For example, in respect of the electrochemistry of copper and iron dithiocarbamate complexes, the following kind of discussion appears in the earlier literature.

The observation of a reversible one-electron oxidation of $Cu(Bu^n_2dtc)_2$ suggested, "Schrauzer's classification for sulphur-containing ligands was not as clear as was proposed" [11], i.e. a reversible oxidation step was not anticipated by the authors. On the other hand, the observation by McCleverty et al. [53] that $Fe(Et_2dtc)_3$ exhibited poorly defined voltammetric behaviour added to the confusion since reversible electrochemistry was expected, at least with respect to a metal-based Fe(III)/Fe(II) couple. Other examples of this kind were also alluded to in the introduction and it is only now that a reasonably comprehensive picture of the redox chemistry has emerged. In particular, a comprehensive study of the electrochemistry of the first-row transition metal dithiocarbamates in non-aqueous media [54] has confirmed that reversible redox processes are common and that the measured potentials are dependent on both the metal and the substituents R in (**1**).

In an endeavour to provide a unifying picture we have highlighted data on selected transition metal dithiocarbamates. Each datum chosen is to emphasise an important feature which is characteristic of either a group of dithiocarbamates or an electrochemical response. Thus, some transition metals are discussed at length while others are mentioned only briefly or not at all. In the last section, relevant data from 1, 2- and 1,3-dithio systems are compared with the behaviour of the 1,1- systems. In this context, the present review is not comprehensive but complements other publications [2–10].

(i) Manganese dithiocarbamates

(a) Chemistry

The chemistry of manganese dithiocarbamates has been extensively studied, and thereby provides a variety of data to demonstrate the consistency between chemical and electrochemical observations. Cambi and Cagnasso [55] isolated the yellow divalent $Mn(R_2dtc)_2$ and commented on the ready oxidation to the dark-violet trivalent complexes $Mn(R_2dtc)_3$. Subsequent investigations [56–58] have confirmed these early observations and established that the complexes are monomeric in solution and are relatively unstable to moisture and light. There is strong evidence that $[Mn(dtc)_3]^-$ exists in solution [27]. However, attempts to isolate $[Mn(dtc)_3]^-$ have proved unsuccessful although the corresponding ethyl xanthate $[Mn(EtXant)_3]^-$ is readily obtained [59].

The X-ray crystal structure of $Mn(Et_2dtc)_3$ establishes the six-coordinate MnS_6-core and the gross asymmetry attributed to Jahn–Teller distortions of the high-spin d^4 ion [60].

Isolation and characterization of the oxidized moiety $[Mn(R_2dtc)_3]^+$ as $[ClO_4]^-$ and $[BF_4]^-$ salts [61–64] show the salts to be 1 : 1 electrolytes with a room temperature magnetic moment of 3.8 BM which is consistent with a high spin $3d^3$ Mn(IV) compound. The X-ray structural data [64] on $[Mn(pipdtc)_3]ClO_4 \cdot CHCl_3$ are also consistent with a formally Mn(IV) species. On comparison with $Mn(Et_2dtc)_3$ the Mn–S bond lengths are shorter and a higher symmetry of chelation is associated with the oxidized species. Little is known of the redox chemistry of the Mn(IV) complexes, although they oxidize free dithiocarbamate ligands, presumably [27] to produce thiuram disulphide, R_4dts, and $Mn(dtc)_3$.

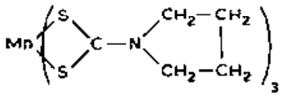
$$[Mn(R_2dtc)_3]^+ + [R_2dtc]^- \rightarrow Mn(R_2dtc)_3 + \tfrac{1}{2}R_4dts \qquad (28)$$

(b) Electrochemical oxidation of $Mn(R_2dtc)_3$

Sixteen Mn(III) dithiocarbamates undergo a relatively facile oxidation in acetone [27] with half-wave potentials (approx. E^0) in the range $+0.25$ to $+0.53$ V vs. Ag/AgCl (0.1 M LiCl in acetone) reference electrode. Studies employing AC, normal pulse and cyclic voltammetry, and the long time-scale technique of controlled potential electrolysis (coulometry) confirm a reversible one-electron oxidation step

$$Mn(R_2dtc)_3 \rightleftharpoons [Mn(R_2dtc)_3]^+ + e \qquad (29)$$

The spectrum of a solution of $Mn(pyrrdtc)_3$ (**14**) in CH_2Cl_2 (0.1 M



14

$[Bu^n_4N]BF_4$) monitored throughout the electrochemical oxidation illustrates, by the presence of isosbestic points, the simple nature of the oxidation of the complex (Fig. 1). The final spectrum is characteristic of a $[Mn(R_2dtc)_3]^+$ species and identical to the spectrum of chemically prepared $[Mn(pyrrdtc)_3]BF_4$.

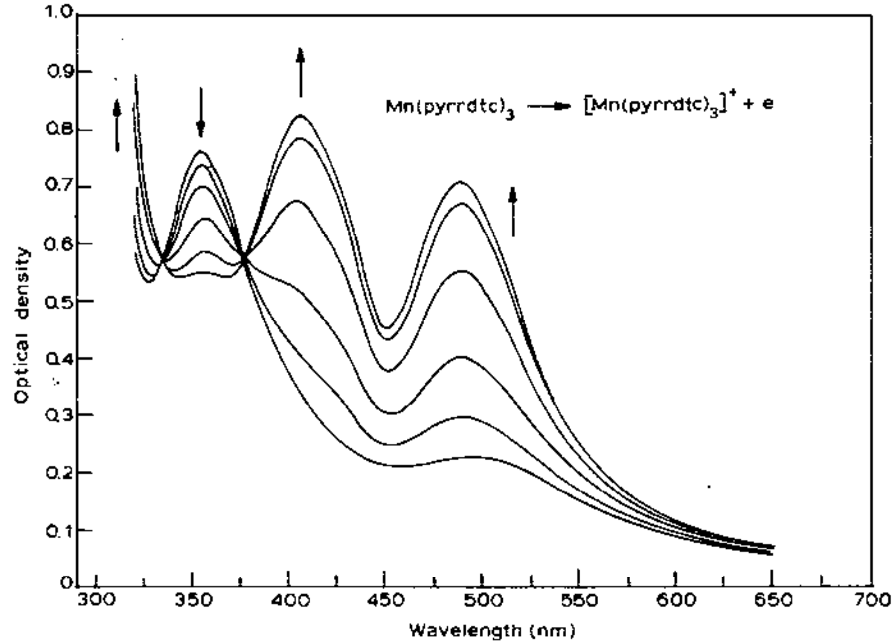


Fig. 1. Oxidative electrolysis of Mn(pyrrdtc)$_3$ in CH_2Cl_2 (0.1 M n-Bu_4NBF_4) as monitored spectrophotometrically. Arrows indicate the progress of electrolysis with the initial and final spectra corresponding to Mn(pyrrdtc)$_3$ and [Mn(pyrrdtc)$_3$]$^+$, respectively. Reproduced by courtesy: Inorg. Chem., 13 (1974) 1933.

(c) Electrochemical reduction of Mn(R$_2$dtc)$_3$

The reduction of Mn(R$_2$dtc)$_3$ at a platinum electrode in acetone or dichloromethane is a facile, reversible, one-electron process [27] occurring at $E_{1/2}$ values in the range +0.06 to −0.23 V vs. Ag/AgCl,

$$\mathrm{Mn(R_2dtc)_3 + e \rightleftharpoons [Mn(R_2dtc)_3]^-} \tag{30}$$

Titration of Mn^{2+} with [pyrrdtc]$^-$ exhibits observable (electrochemical) end-points at ratios of Mn^{2+} : [pyrrdtc]$^-$ of 1 : 2 and 1 : 3. The solution behaviour of Mn(pyrrdtc)$_2$ was compared with that of an analytically pure sample and found to be simply related to [Mn(pyrrdtc)$_3$]$^-$ by the following equilibria:

$$\mathrm{Mn(pyrrdtc)_2 + [pyrrdtc]^- \rightleftharpoons [Mn(pyrrdtc)_3]^-} \tag{31}$$

$$\mathrm{2\,[Mn(pyrrdtc)_3]^- + Mn^{2+} \rightleftharpoons 3\,Mn(pyrrdtc)_2} \tag{32}$$

The very pale colour of a [Mn(pyrrdtc)$_3$]$^-$ solution, its direct formation from Mn^{2+}, as well as by reduction of Mn(pyrrdtc)$_3$, are all consistent with its formulation as a Mn(II) complex. Hence Mn(R$_2$dtc)$_3$ is the central member

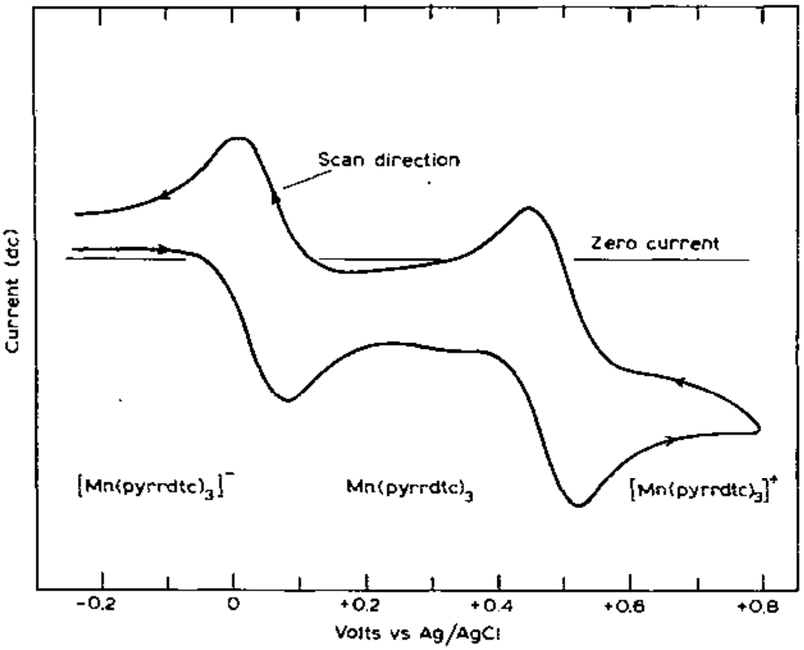


Fig. 2. Cyclic voltammogram of $[Mn(pyrrdtc)_3]^-$ in acetone (0.1 M Et_4NClO_4) showing the existence of the electron transfer series: $[Mn(dtc)_3]^- \overset{\pm e}{\rightleftharpoons} Mn(dtc)_3 \overset{\pm e}{\rightleftharpoons} [Mn(dtc)_3]^+$. Reproduced by courtesy: Inorg. Chem., 13 (1974) 1933.

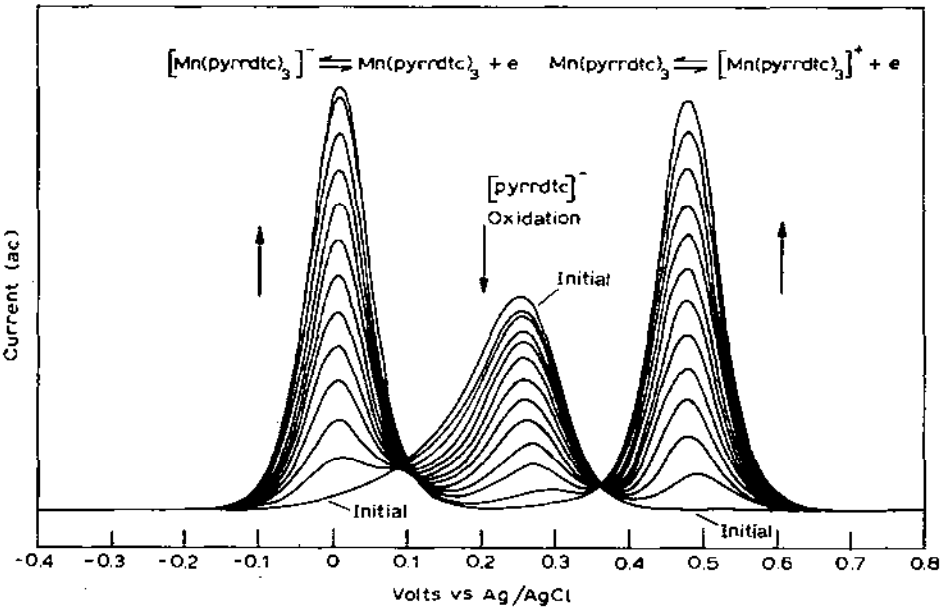


Fig. 3. A.c. voltammetric scans of the titration of Mn^{2+} into $[pyrrdtc]^-$ solution up to the 1 : 3 endpoint illustrating the disappearance of $[pyrrdtc]^-$ and the complete generation of the a.c. voltammogram of $[Mn(pyrrdtc)_3]^-$. Reproduced by courtesy: Inorg. Chem., 13 (1974) 1933.

of a three-membered one-electron transfer series

$$[Mn(R_2dtc)_3]^+ \overset{\pm e}{\rightleftharpoons} Mn(R_2dtc)_3 \overset{\pm e}{\rightleftharpoons} [Mn(R_2dtc)_3]^- \qquad (33)$$

Figures 2 and 3 show cyclic voltammograms and titration data based on a.c. voltammetry which clearly illustrate and confirm the above conclusions.

Polagraphic data on $Mn(R_2dtc)_3$ at a dropping mercury electrode in dimethylformamide [65,66] indicate that reduction of electrochemically produced $[Mn(R_2dtc)_3]^-$ occurs. Presumably, $E_{1/2}$ values are too negative to be observed in similar studies at a platinum electrode in the more readily reduced solvents such as acetone and dichloromethane. The products are manganese metal and the free dithiocarbamate ligand. Thus, two d.c. polarographic waves are observed for reduction of $Mn(R_2dtc)_3$, the more negative having a limiting current per unit concentration value of twice that of the reversible one-electron reduction step described above for platinum electrodes in acetone and dichloromethane. Reaction scheme (34) summarizes the polarographic data

$$Mn(R_2dtc)_3 + e \rightleftharpoons [Mn(R_2dtc)_3]^- \quad \text{Wave 1}$$

$$[Mn(R_2dtc)_3]^- + 2\,e \rightarrow Mn + 3\,[R_2dtc]^- \quad \text{Wave 2} \qquad (34)$$

Measurements of k_s values for wave 1 at a mercury electrode [65] ($> 10^{-2}$ cm s^{-1}) are consistent with the characterization of this electrode process as reversible under polarographic conditions.

In summary, the electrochemical data provided no evidence of Mn(I) or Mn(0) complexes so that stabilization of "unusual" oxidation states by dithiocarbamate appears to be confined to higher rather than lower ones for manganese.

(ii) Iron, ruthenium and osmium dithiocarbamates

Both the electrochemistry and the chemistry of manganese dithiocarbamates illustrate the behaviour to be expected for a relatively simple redox system. The iron, ruthenium and osmium triad involves the introduction of progressively more complicated chemistry to explain the redox data observed when moving from the first row transition metal iron (which has many similarities with manganese) through to the third row transition metal osmium. Systematic electrochemical studies have proved to be extremely valuable in unravelling the more complicated processes which determine the redox chemistry of ruthenium and osmium dithiocarbamates.

(a) Iron dithiocarbamates

Chemistry of iron dithiocarbamates. The general chemistry of iron dithiocarbamate complexes has been very widely studied and the oxidation states (II), (III) and (IV) are observed. $Fe(R_2dtc)_2$ is extremely air-sensitive and oxidizes rapidly to $Fe(R_2dtc)_3$ [6,8]. The air sensitivity and oxidation pathway are similar to those of $Mn(R_2dtc)_2$. The molecular structure of $Fe(Et_2dtc)_2$ in the solid state is based on a five-coordinate dimer [67]. Iron(II) dithiocarbamate in the presence of excess ligand forms the anion $[Fe(R_2dtc)_3]^-$ [68] which is also air-sensitive, the stability depending on the associated cation. With $[Et_4N]^+$ the complex readily transforms to $Fe(R_2dtc)_2$, whereas with $[PPh_4]^+$ greater stability is observed. These data are consistent with the equilibrium

$$[Fe(R_2dtc)_3]^- \rightleftharpoons Fe(R_2dtc)_2 + [R_2dtc]^- \qquad (35)$$

The inability of other workers [59] to isolate the $[Fe(R_2dtc)_3]^-$ salts is therefore not surprising.

The general chemistry of the monomeric tris-chelated $Fe(R_2dtc)_3$ complexes has been very widely studied [6–8,69], although it is only relatively recently that the extended redox properties of the tris chelates have been recognized and investigated. X-ray crystal structure data [70–73] show the expected D_3 molecular symmetry with a twist angle depending on the R group.

Aerial oxidation of $Fe(R_2dtc)_3$ in benzene in the presence of BF_3 enabled Pasek and Straub to isolate and characterize salts of composition $[Fe(R_2dtc)_3]BF_4$ [61]. Much evidence has been obtained culminating in the crystal structure of $[Fe(pyrrdtc)_3]ClO_4$, confirming the existence of an Fe(IV) complex [74]. The marked shortening of the Fe–S bond distances (0.11 Å) of $[Fe(pyrrdtc)_3]^+$ compared with those of $Fe(pyrrdtc)_3$ is consistent with depopulation of the antibonding e_g orbitals on oxidation from the configuration Fe(III) ($t_2^3e^2$) to Fe(IV) (t_2^4) with a further small contribution from the increased oxidation state of the metal ion. Geometry and bond lengths in the Fe(IV) complex are unexceptional for the dithiocarbamate ligand. Alternative synthetic methods are now available to form these iron(IV) dithiocarbamates employing $FeCl_3$ [63], $Fe(ClO_4)_3 \cdot 6H_2O$ [63], perchloric acid [27], and electrochemical methods [75] to oxidize $Fe(R_2dtc)_3$. Oxidation with halogens (Cl_2 and Br_2) of either $Fe(Et_2dtc)_3$ or $Fe(Et_2dtc)_2X$ results in ligand oxidation [76] forming the 3,5-bis(*N*,*N*-diethyliminium)-1,2,4-trithiolone ion (eqn. 20) and the $[FeX_4]^-$ anion [77]. Reaction of $Fe(R_2dtc)_3$ with the milder oxidant iodine produces $Fe(R_2dtc)_2I$ and thiuram disulphide [78].

In the presence of excess $[R_2dtc]^-$ the redox reaction

$$[Fe(R_2dtc)_3]^+ + [R_2dtc]^- \rightarrow Fe(R_2dtc)_3 + \tfrac{1}{2}R_4tds \tag{36}$$

occurs [27] so that the Fe(IV) cation can act as an oxidant in the same manner as $[Mn(R_2dtc)_3]^+$. Halide ions have been found to react with $[Fe(R_2dtc)_3]^+$ [27] which precludes its formation by halogen oxidation of $Fe(R_2dtc)_3$. The products of this reaction are $Fe(R_2dtc)_2X$ and R_4tds [79]. Thus, substitution as well as redox reactions occur with the reactive Fe(IV) complexes as is also demonstrated in other work [80].

Electrochemical oxidation of $Fe(R_2dtc)_3$. Despite the comment by McCleverty et al. [53] that $Fe(Et_2dtc)_3$ "exhibited poorly defined voltammetric behaviour", many workers have since confirmed that ferric dithiocarbamates are readily oxidized and reduced by electrochemical methods in a range of solvents [17,27,54,75,81–85].

At a platinum working electrode, voltammetric, coulometric and con-

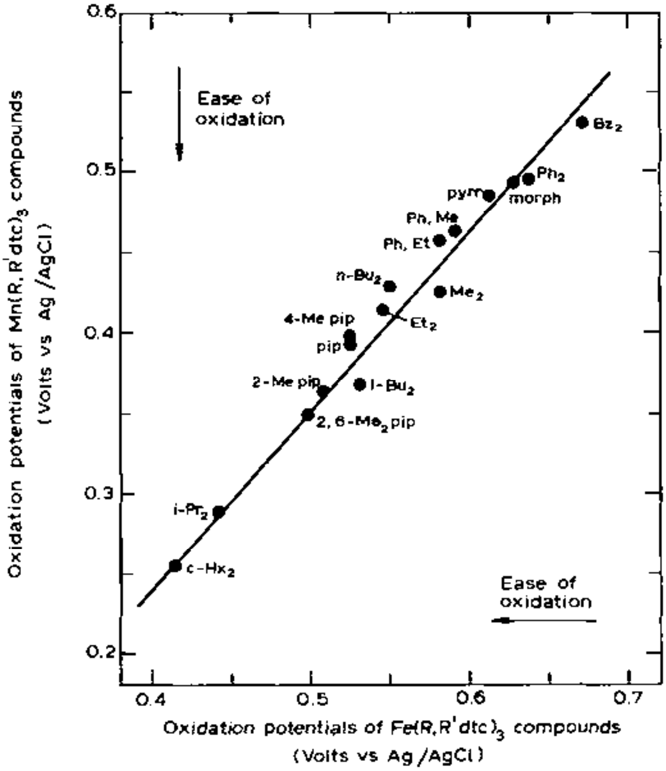


Fig. 4. The relationship between the oxidation potentials of the complexes $Fe(RR'dtc)_3$ and $Mn(RR'dtc)_3$. Reproduced by courtesy: Inorg. Chem., 14 (1975) 1894.

trolled potential electrolysis studies coupled with spectrophotometric measurements define the oxidation of $Fe(R_2dtc)_3$ as a one-electron reversible process [27,75]

$$Fe(R_2dtc)_3 \rightarrow [Fe(R_2dtc)_3]^+ + e \quad (37)$$

In acetonitrile the product shows some instability which has been attributed to residual water in the solvent [75].

Voltammetric measurements on the reduction of chemically prepared $[Fe(R_2dtc)_3]^+$ salts including half-wave potentials and coulometric values for the number of electrons involved in the relationship further attest to the reversibility of the Fe(III)/Fe(IV) couple [27]. The $E_{1/2}$ values for the oxidation of 20 ferric dithiocarbamates (approximately equal to E^0) span the range from +0.42 to +0.67 vs. Ag/AgCl (0.1 M LiCl in acetone) [27]. These results have been confirmed with the report of the $E_{1/2}$ values for a similar series of ferric complexes [81].

A substantial substituent effect on the redox potentials is observed. An excellent correlation with the substituent effect found for $Mn(R_2dtc)_3$ is obtained as shown in Fig. 4.

Electrochemical measurements on the oxidation of mixed ligand species

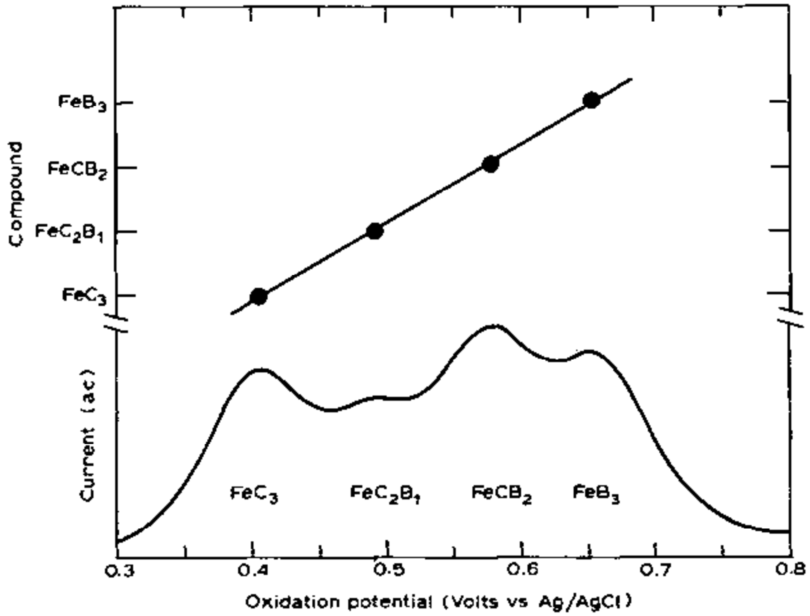


Fig. 5. Bottom curve: a.c. voltammogram (oxidation) of a solution containing a mixture of mixed-ligand species FeC_3, FeC_2B, $FeCB_2$, and FeB_3 where C = dicyclohexyldithiocarbamate and B = dibenzyldithiocarbamate. Top curve: relationship between complex composition and a.c. peak potential. Reproduced by courtesy: Inorg. Chem., 14 (1975) 1894.

indicate that a kinetically labile system is associated with the charge transfer [27]. Mixed dithiocarbamate species with the ligands *N,N*-dibenzyldithiocarbamate and *N,N*-dicyclohexyldithiocarbamate are prepared in situ by simply mixing solutions of pure $Fe(c\text{-}Hx_2dtc)_3$ and $Fe(Bz_2dtc)_3$ in the voltammetric vessel at room temperature. Ligand-exchange equilibrium is established rapidly and a.c. voltammetry shows both the reduction and oxidation steps expected for the four compounds (see Fig. 5), viz., $Fe(c\text{-}Hx_2dtc)_3$, $Fe(c\text{-}Hx_2dtc)_2(Bz_2dtc)$, $Fe(c\text{-}Hx_2dtc)(Bz_2dtc)_2$ and $Fe(Bz_2dtc)_3$.

Electrochemical reduction of $Fe(R_2dtc)_3$. The electrochemical reduction of $Fe(R_2dtc)_3$ at platinum electrodes has been studied in two solvents, acetone [27] and acetonitrile [75], with the following results being common to both studies. By cyclic voltammetry the process is almost reversible. However, controlled potential electrolysis affords n values ranging up to 1.3. The pale-yellow solution generated from the reduction suggests Fe(II) species are formed. Cauquis and Lachenal [75] have presented evidence to suggest that there is a slow release of free ligand, $[Et_2dtc]^-$ from the electro-generated iron(II) complex. The electrode process is therefore defined as

$$Fe(R_2dtc)_3 + e \rightleftharpoons [Fe(R_2dtc)_3]^- \tag{38}$$

with some evidence of instability associated with the reduced anion. Titrimetric studies of Fe(II) and $[R_2dtc]^-$ provides at the 1 : 3 end-point, a species in solution with the electrochemical properties predicted from the electrochemistry of $Fe(R_2dtc)_3$ and $[Fe(R_2dtc)_3]^+$ viz., two reversible oxidations corresponding to

$$[Fe(R_2dtc)_3]^- \rightleftharpoons Fe(R_2dtc)_3 + e \tag{39}$$

$$Fe(R_2dtc)_3 \rightleftharpoons [Fe(R_2dtc)_3]^+ + e \tag{40}$$

The recent isolation of the bright yellow, air-sensitive complexes of the stoichiometry $[Fe(R_2dtc)_3]^-$ and their characterization by Mössbauer and electronic spectra led de Vries et al. [68] to suggest that the complexes are high-spin complexes of iron(II). Hence, it appears that tris-dithiocarbamates of Fe(IV), Fe(III) and Fe(II) may be classed as low-spin (d^4), intermediate-spin (d^5) and high-spin (d^6), respectively, although some Fe(III) dithiocarbamates exhibit high- or low-spin behaviour (80–300 K) depending on the substituents on the dithiocarbamate ligand [86]. The influence of magnetism on the thermodynamically significant parameter $E_{1/2}$ would appear to be very small [27]. It is also pertinent to note that in the presence of water, $[Fe(R_2dtc)_3]^-$ is in dissociative equilibrium with $Fe(R_2dtc)_2$ by ligand loss [68]. This equilibrium is consistent with the electrochemical results of Cauquis and Lachenal [75].

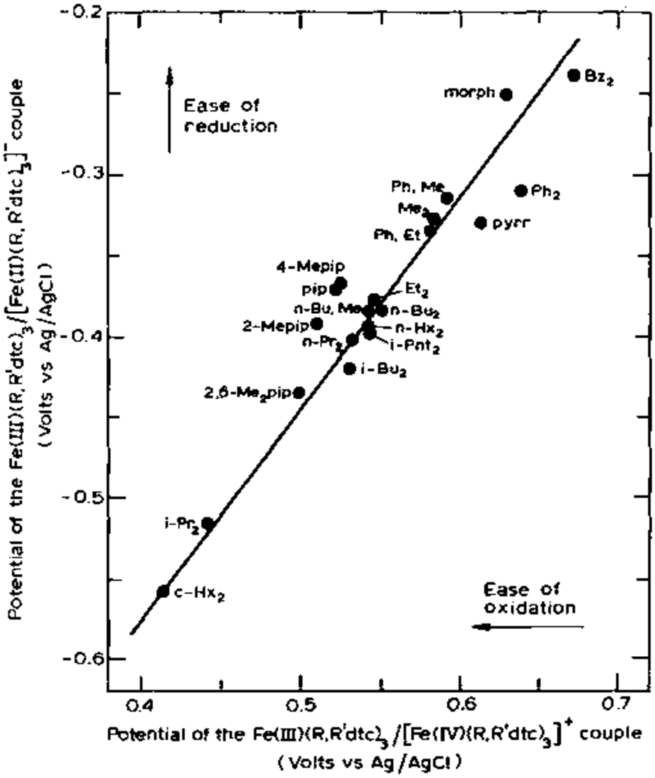


Fig. 6. Relation between the oxidation and reduction potentials of Fe(RR'dtc)$_3$ complexes. Reproduced by courtesy: Inorg. Chem., 14 (1975) 1894.

The $E_{1/2}$ values associated with eqns. 39 and 40, and the substituent effects correlate with each other, as well as with the Mn(R$_2$dtc)$_3$ redox data (Figs. 4 and 6). Thus the substituent effect is of far greater importance than any contribution to $E_{1/2}$ from magnetism or minor instability of [M(R$_2$dtc)$_3$]$^{-,0,+}$ (M = Mn or Fe). Indeed similar substituent effects are observed with all transition metal dithiocarbamates.

The above electrochemical data were all obtained at platinum electrodes. At mercury electrodes, the large negative potential range available enables additional reduction processes to be observed [66,85]. Three one-electron reduction steps are observed for Fe(R$_2$dtc)$_3$. The first is the reversible one-electron step observed at platinum electrodes to produce [Fe(R$_2$dtc)$_3$]$^-$. Subsequent steps are chemically irreversible and are accompanied by loss of [R$_2$dtc]$^-$ as demonstrated by cyclic voltammetry and the monitoring of peaks for the [R$_2$dtc]$^-$/Hg(R$_2$dtc)$_2$ couple (see Section B). The reduction steps at mercury have been explained in terms of the reactions

$$\mathrm{Fe(R_2dtc)_3 + e \rightleftharpoons [Fe(R_2dtc)_3]^- \rightleftharpoons Fe(R_2dtc)_2 + [R_2dtc]^-} \tag{41}$$

$$\mathrm{Fe(R_2dtc)_2 + e \rightleftharpoons [Fe(R_2dtc)_2]^-} \tag{42}$$

$$\mathrm{[Fe(R_2dtc)_2]^- + e \rightleftharpoons [Fe(R_2dtc)_2]^{2-} \rightarrow Fe + 2\,[R_2dtc]^-} \tag{43}$$

An oxidation wave for $\mathrm{Fe(R_2dtc)_3}$ at mercury electrodes has also been reported [85]. The potential of this step does not correspond to that for the $\mathrm{[Fe(R_2dtc)_3]^+/Fe(R_2dtc)_3}$ process observed at platinum and presumably involves ligand exchange and mercury compound formation. $\mathrm{Hg(R_2dtc)_2}$ complexes are extremely stable [87] and $\mathrm{[R_2dtc]^-}$ at mercury electrodes results in oxidation of mercury of produce $\mathrm{Hg(R_2dtc)_2}$ (see Section B).

The instability of $\mathrm{[Fe(R_2dtc)_3]^-}$ towards dissociation has been elegantly demonstrated by examining the electrode processes in the presence of π-acceptor ligands such as 2,2-bipyridine [85]. $\mathrm{Fe(R_2dtc)_2(bipy)}$ is a well-characterized compound and the electrochemistry in the presence of bipy clearly occurs according to the following reaction scheme (eqn. 44).

$$\begin{aligned}
&\mathrm{Fe(R_2dtc)_3 + e \rightleftharpoons [Fe(R_2dtc)_3]^-}\\
&\mathrm{[Fe(R_2dtc)_3]^- + bipy \xrightarrow{k_1} Fe(R_2dtc)_2(bipy) + [R_2dtc]^-}\\
&\mathrm{Fe(R_2dtc)_2(bipy) + e \rightleftharpoons [Fe(R_2dtc)_2(bipy)]^-}\\
&\mathrm{[Fe(R_2dtc)_2(bipy)]^- \rightleftharpoons Fe(R_2dtc)_2 + [bipy]^-}\\
&\mathrm{Fe(R_2dtc)_2 + bipy \xrightarrow{k_2} Fe(R_2dtc)_2(bipy)}
\end{aligned} \tag{44}$$

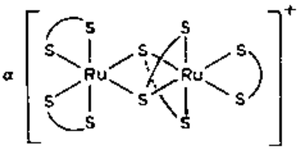
The formation of the radical anion $\mathrm{[bipy]^-}$, in this reaction scheme was confirmed by electron spin resonance spectroscopy.

(b) Ruthenium dithiocarbamates

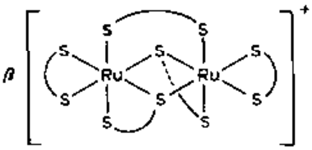
Chemistry of ruthenium dithiocarbamates. As indicated in the sections on manganese and iron dithiocarbamates, the electrochemical behaviour is entirely consistent with the known chemistry of these elements. Ruthenium dithiocarbamate chemistry is extremely rich in the number and nature of compounds that can be formed and the various interconversions that are possible. It is therefore not surprising that the electrochemistry is equally as rich and fascinating.

A number of Ru(II), Ru(III) and Ru(IV) dithiocarbamate complexes have been well-characterized by X-ray analysis [88–93]. Interesting chemical and photoredox reactions have been used in the synthesis of many of these complexes. Tris-dithiocarbamate $Ru(R_2dtc)_3$ complexes, first reported by Cambi and Malatesta [94,95], are low-spin monomeric complexes with a molecular geometry intermediate between trigonal prismatic and trigonal antiprismatic [88,89].

Oxidation of $Ru(R_2dtc)_3$ in the presence of BF_3 was originally suggested to lead to formation of the ruthenium(IV) complex $[Ru(R_2dtc)_3]BF_4$ [96]. However, subsequent detailed studies show that a ruthenium(III) dimer $[Ru_2(R_2dtc)_5]BF_4$ and the 3,5-bis(*N*,*N*-diethyliminium)-1,2,4-trithiolane dication is produced [91]. $[Ru_2(R_2dtc)_5]^+$ can exist in two isomeric forms, α and β (**15** and **16**). The β-form is prepared from the BF_3 reaction in the presence of air and the α-form from reaction of $RuCl_3$ with $[R_2dtc]^-$ in aqueous solution [89]. Other synthetic methods, including electrochemical oxidation, are also available for the preparation of $[Ru_2(dtc)_5]^+$ [97,98]. Reduction of $[Ru_2(dtc)_5]^+$ with $NaBH_4$ produces the uncharged mixed oxidation state complex $Ru_2(dtc)_5$ [97,98].

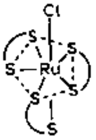


15



16

Reaction of $Ru(Et_2dtc)_3$ with anhydrous HCl in benzene yields the ruthenium(IV) complex, $ClRu(Et_2dtc)_3$ as well as (**16**) [92,99]. Compounds (**16**) and (**17**) can also be synthesized by photolysis of $Ru(R_2dtc)_3$ in chlorine-containing solvents [99].



17

Relatively little is known about unsubstituted Ru(II) dithiocarbamate complexes, although many mixed ligand species of the kind $Ru(R_2dtc)_2X$ ($X = CO$, PPh_3, etc.) have been well characterized [6,100]. Electrochemical reduction [97] of $Ru(Me_2dtc)_3$ produces an orange-red solution which is likely to be $[Ru(Me_2dtc)_3]^-$. This species, like $[Fe(R_2dtc)_3]^-$ and $[Mn(R_2dtc)_3]^-$, is air-sensitive and reacts rapidly with atmospheric oxygen to re-form $Ru(Me_2dtc)_3$.

Electrochemical oxidation of $Ru(R_2dtc)_3$. A substantial number of electrochemical studies on the oxidation of $Ru(dtc)_3$ have been reported since

Patterson and Holm [17] suggested that the Ru(IV) cation $[Ru(R_2dtc)_3]^+$ should be accessible synthetically. These authors noted that a "reversible" one-electron oxidation occurred in *N,N*-dimethylformamide at +0.38 V versus the saturated calomel electrode (SCE) for $Ru(Et_2dtc)_3$ compared with +0.42 V vs. SCE for $Fe(Et_2dtc)_3$ where $[Fe(dtc)_3]^+$ is well-known (see Section C(ii) a).

However, $[Ru(R_2dtc)_3]^+$ has yet to be isolated and more detailed electrochemical data demonstrate the instability of this species. At platinum electrodes in acetone [97], the electrochemical oxidation of $Ru(R_2dtc)_3$ is generally not reversible by cyclic voltammetry at a scan rate of 200 mV s^{-1}. Oxidation for a range of $Ru(R_2dtc)_3$ complexes occurs at 0.47 to 0.67 V vs. Ag/AgCl (0.1 M LiCl in acetone). Thus the $E_{1/2}$ value for oxidation is similar to that for the reversible oxidation of $Fe(R_2dtc)_3$. However, for $Ru(R_2dtc)_3$ there is a marked substituent-dependence on the degree of reversibility; e.g. the pyrrolidyl derivative showed no current on the return sweep after oxidation employing cyclic voltammetry with a scan rate of 200 mV s^{-1} whilst oxidation of $Ru(MePhdtc)_3$ is close to reversible in acetone when using a scan rate of only 100 mV s^{-1}. Other substituents examined showed intermediate behaviour.

The data for $Ru(MePhdtc)_3$ suggest that the electrode process is

$$Ru(R_2dtc)_3 \rightleftharpoons [Ru(R_2dtc)_3]^+ + e \qquad (45)$$

with the formally ruthenium(IV) species exhibiting various degrees of instability to further reaction or decomposition depending on the substituents. On exhaustive oxidative electrolysis of $Ru(Me_2dtc)_3$ the resulting solution did not contain $[Ru(Me_2dtc)_3]^+$ (cyclic and a.c. voltammetry). When this solution was worked-up by chromatography, $Ru(Me_2dtc)_3$ and a diruthenium complex $[Ru_2(Me_2dtc)_5]^+$ were isolated although neither species was originally present in the oxidized solution.

In a later electrochemical investigation, when the chemistry of ruthenium(IV) complexes was better understood, rationalization of the chemical irreversibility associated with eqn. 45 became possible. In the work of Pignolet and co-workers [98] the electrochemical behaviour of $Ru(Et_2dtc)_3$ was examined by conventional d.c., a.c. and cyclic voltammetry using the solvents acetonitrile, propylene carbonate and dichloromethane. A reversible one-electron reduction wave (Fig. 6) with an $E_{1/2}$ value of −0.74 V vs. SCE was observed in all three solvents and corresponds to the reduction

$$Ru(R_2dtc)_3 + e \rightleftharpoons [Ru(R_2dtc)_3]^- \qquad (46)$$

A one-electron oxidation wave was also observed at approximately +0.40 V vs. SCE as shown in Fig. 7. This wave has been assigned to eqn. 45 in other

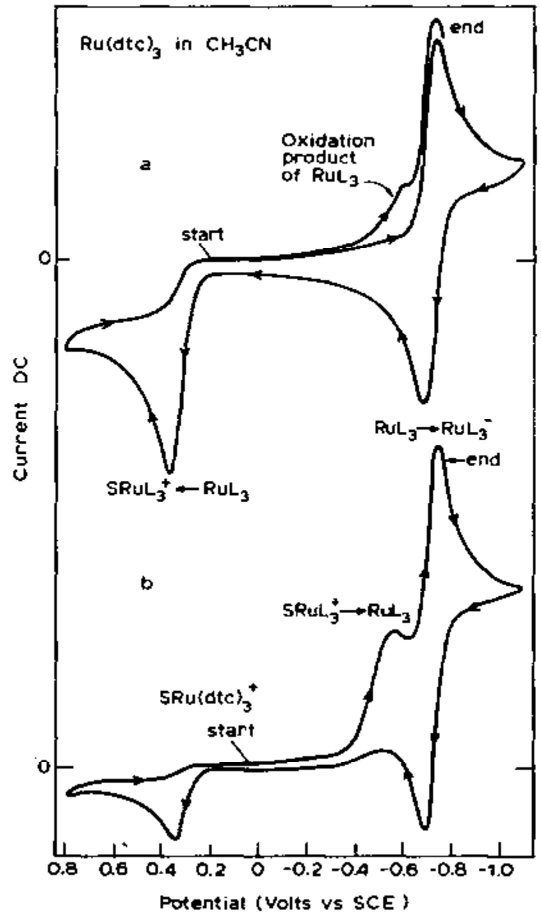


Fig. 7. (a) Cyclic voltammogram of Ru(Et$_2$dtc)$_3$ in CH$_3$CN (ca. 0.1 M Et$_4$NClO$_4$) (scan rate 200 mV s^{-1}). (b) Cyclic voltammogram of the above solution in (a) after controlled-potential electrolysis at 0.50 V vs. SCE. Approximately 85% of the Ru(Et$_2$dtc)$_3$ has been oxidized. Reproduced by courtesy: Inorg. Chem., 17 (1978) 340.

studies [17,97]. However, the wave is not reversible by cyclic voltammetry (Fig. 7) and the cationic complex [Ru(Et$_2$dtc)$_3$]$^+$ is not observed or isolated after controlled potential oxidation in acetonitrile. With Ru(Et$_2$dtc)$_3$ in acetonitrile, the immediate oxidation product after electrolysis is the diamagnetic seven-coordinate Ru(IV) complex [(CH$_3$CN)Ru(Et$_2$dtc)$_3$]$^+$. Evidence for this complex is mainly based on the use of cyclic voltammetry. Examination of the second scan of the cyclic voltammogram of Ru(Et$_2$dtc)$_3$ in CH$_3$CN solvent (see Fig. 7a) reveals a new wave at about −0.60 V vs. SCE which appears only after oxidation of Ru(Et$_2$dtc)$_3$. After controlled-potential electrolysis of $Ru(Et_2dtc)_3$ at +0.50 V, so that about 85% of the $Ru(Et_2dtc)_3$ was oxidized, the cyclic voltammogram shown in Fig. 7b was recorded. The new wave at −0.60 V is now present in the initial scan. Since the complex $[(CH_3CN)Ru(Et_2dtc)_3]^+$ is isolated from this solution in good yield, the new reduction wave must result from process (47)

$$\left[(CH_3CN)Ru(Et_2dtc)_3\right]^+ + e \rightarrow Ru(Et_2dtc)_3 + CH_3CN \tag{47}$$

The entire voltammetric cycle in CH_3CN solvent is shown in Fig. 7 and is described by eqn. 48.

$$\begin{tikzcd}
\left[Ru(Et_2dtc)_3\right]^+ \arrow[r, shift left, "\pm e"] \arrow[d, "CH_3CN"', "fast"] & \left[Ru(Et_2dtc)_3\right] \arrow[l, shift left] \arrow[r, shift left, "\pm e"] & \left[Ru(Et_2dtc)_3\right]^- \arrow[l, shift left] \\
\left[(CH_3CN)Ru(Et_2dtc)_3\right]^+ \arrow[ur, "+e", "-CH_3CN"'] & &
\end{tikzcd} \tag{48}$$

The chemical step which converts $[Ru(Et_2dtc)_3]^+$ into the diamagnetic CH_3CN adduct must be fast since the reverse reduction wave expected for a reversible process is completely absent in CH_3CN even for a scan rate of 200 $V\ s^{-1}$. The isolated cationic complex of Ru(IV), $[(CH_3CN)Ru(Et_2dtc)_3]^+$, is moderately stable in the solid state as a $[BF_4]^-$ salt, but is not stable in solvents other than CH_3CN and its decomposition products have not been identified.

Cyclic voltammograms of $Ru(Et_2dtc)_3$ using the weakly co-ordinating solvent propylene carbonate, $C_4H_6O_3$ at 25°C are qualitatively similar to those in CH_3CN. However, the new wave which appears after oxidation of $Ru(Et_2dtc)_3$ is shifted to ca. −0.19 V vs. SCE from its value of −0.60 V vs. SCE in CH_3CN.

Controlled-potential oxidation at +0.50 V leads to growth of the −0.19 V oxidation wave of $Ru(Et_2dtc)_3$. This wave could be due to the process (49)

$$\left[(C_4H_4O_3)Ru(Et_2dtc)_3\right]^+ + e \rightarrow Ru(Et_2dtc)_3 + C_4H_6O_3 \tag{49}$$

where coordinated $C_4H_6O_3$ stabilizes the Ru(IV) cation in a similar fashion to CH_3CN. However, it is also possible that the seventh coordination site is occupied by either $[ClO_4]^-$ or H_2O especially since the corresponding cathodic wave in noncoordinating CH_2Cl_2 and acetone solvents occurs at −0.20 and −0.17 V, respectively. Alternatively, the formation of dimeric $[Ru_2(R_2dtc)_6]^{2+}$ as an intermediate would also seem plausible in the light of the behaviour of osmium dithiocarbamates described in the following section.

The mechanism for the formation of electrochemically generated $[Ru_2(R_2dtc)_5]^+$ is not known. The data of Hendrickson et al. [97] in acetone show that $[Ru_2(R_2dtc)_5]^+$ is formed via a secondary rather than the primary electrochemical process.

Intermediates such as monomeric $[Ru(R_2dtc)_3(solvent)]^+$ or dimeric $[Ru_2(R_2dtc)_6]^{2+}$ are likely electrochemical precursors. It should be noted that $[Ru_2(R_2dtc)_5]^+$ can also be formed by direct chemical means from $Ru(R_2dtc)_3$ via a mechanism not involving oxidation [97,98].

Electrochemical reduction of $Ru(R_2dtc)_3$. Voltammetric reduction data for the series of $Ru(R_2dtc)_3$ complexes have been reported in acetone at a platinum electrode [97]. The process has been characterized as a reversible one-electron reduction

$$Ru(R_2dtc)_3 + e \rightleftharpoons [Ru(R_2dtc)_3]^- \tag{50}$$

for R = Me and appears to be the same for all the other 11 substituents examined. For $Ru(Me_2dtc)_3$ exhaustive electrolysis produced an orange-red solution of $[Ru(Me_2dtc)_3]^-$ and afforded an *n* value of 1.0. This anion undergoes reversible oxidation (by cyclic voltammetry) at an a.c. peak potential coincident with the reduction potential of $Ru(Me_2dtc)_3$. The $[Ru(Me_2dtc)_3]^-$ anion has a similar $E_{1/2}$ value to $[Fe(R_2dtc)_3]^-$ and reacts rapidly with atmospheric oxygen reverting to $Ru(Me_2dtc)_3$. Spectral monitoring of the electrolytic reduction of $Ru(Me_2dtc)_3$ in CH_2Cl_2 saturated with $[NEt_4][ClO_4]$ displays growth of the spectrum of $[Ru(Me_2dtc)_3]^-$ with well-defined isosbestic points at 557 and 413 nm. This is analogous to the reduction behaviour of $Fe(R_2dtc)_3$ and $Mn(R_2dtc)_3$.

For both oxidation and reduction, the effect of substituents on the redox potential is virtually identical to that found for other transition metal complexes, with the dibenzyl-substituted complexes being the most difficult to oxidize and the α-branched substituents di-isopropyl and dicyclohexyl being the easiest to oxidize. The reverse order holds for reduction, with the difference between the oxidation and reduction potentials for any substituent being approximately constant at 1.2 V.

Polarographic reduction of a series of $Ru(R_2dtc)_3$ complexes has also been examined in dimethylsulphoxide [101]. The reduction step represented by eqn. 50 is observed at a mercury electrode, although some evidence for dissociation of $[Ru(R_2dtc)_3]^-$ is found. Generation of $Hg(R_2dtc)_2$ is assumed to occur at the electrode surface via release of $[R_2dtc]^-$ in a manner analogous to that described in detail by Bond et al. [21–23] for some vanadium complexes. Clearly the mercury electrode is not "inert" in this instance and this feature appears to be a characteristic of many electrochemical studies of dithiocarbamate complexes at mercury electrodes. The extraordinary stability of mercury dithiocarbamate complexes noted earlier would appear to enable exchange reactions to occur at the electrode surface.

Electrochemistry of $[Ru_2(R_2dtc)_5]^+$ dimers. Pignolet and co-workers have examined the electrochemistry of $[Ru_2(R_2dtc)_5]^+$ and $Ru(R_2dtc)_5$ (β-form) in acetonitrile at platinum electrodes [91]. Their results indicate the existence of a four-membered electron transfer series

$$[Ru_2(R_2dtc)_5]^{2+} \overset{\pm e}{\rightleftharpoons} [Ru_2(R_2dtc)_5]^+ \overset{\pm e}{\rightleftharpoons} Ru_2(R_2dtc)_5 \overset{\pm e}{\rightleftharpoons} [Ru_2(R_2dtc)_5]^- \tag{51}$$

The one-electron nature of these processes was established for R = Et by comparing current per unit concentration for known one-electron processes associated with $Fe(R_2dtc)_3$ and $Mn(R_2dtc)_3$ (see Section C) and by isolation of $Ru_2(Et_2dtc)_5$, and demonstrating that it has the same $E_{1/2}$ values as $[Ru_2(Et_2dtc)_5]^+$. No attempts were made to isolate the $[Ru_2(R_2dtc)_5]^{2+}$ or $[Ru_2(R_2dtc)_5]^-$ species. Hendrickson et al. [97], in their work using acetone, were aware of the existence of α- and β-forms of $[Ru_2(R_2dtc)_5]^+$. They have

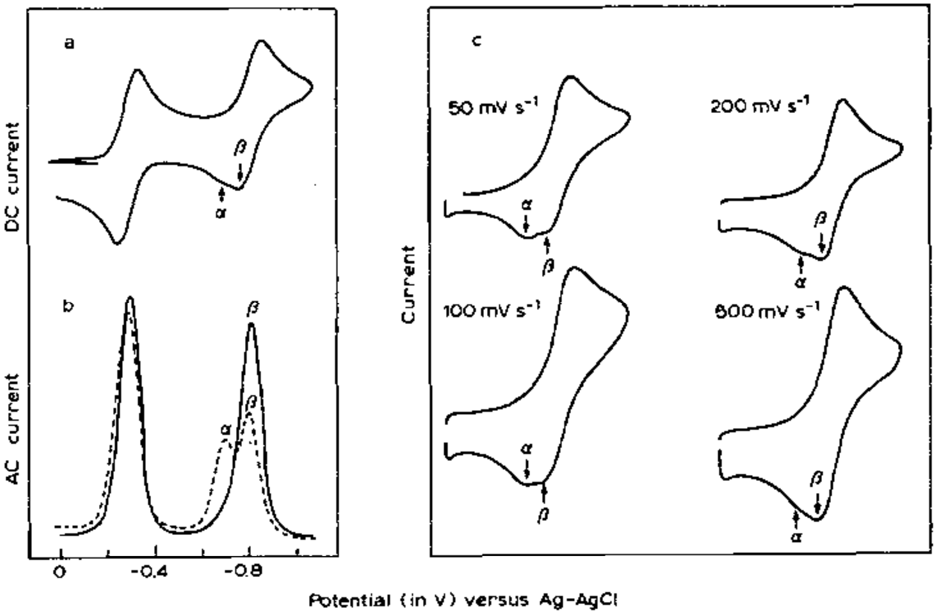


Fig. 8. (a) Cyclic voltammogram of β-$[Ru_2(Me_2dtc)_3][BF_4]$ in acetone (0.1 M Et_4NClO_4) (scan rate 200 mV s^{-1}). (b) Cyclic a.c. voltammogram (solution as in (a)): (———), negative scan; (— — —), positive scan obtained by holding a negative potential for ca. 10 s. Scan rate 100 mV s^{-1}. In both (a) and (b) the second reduction process displays the $\beta^- \rightarrow \alpha^-$ isomerization of the anion. (c) Effect of scan rate on the $\beta^- \rightarrow \alpha^-$ isomerization of $[Ru_2(Me_2dtc)_5]^-$ Complex added to acetone (0.1 M Et_4NClO_4) solution as β-$[Ru_2(Me_2dtc)_5]Cl$. Redox processes centered at ca. −0.75 V vs. Ag/AgCl. Reproduced by courtesy: J. Chem. Soc., Dalton Trans. (1976) 2032.

provided a more extensive account of the electrochemistry, although only a three-membered electron transfer series was reported with no mention of the $[Ru_2(R_2dtc)_5]^{2+}/[Ru_2(R_2dtc)_5]^+$ couple being made.

According to Hendrickson et al. [97], both the α- and β-diruthenium(III) species are electroactive and behave similarly. Interestingly, α-$[Ru_2(Me_2dtc)_5]^+$ is slightly easier (by 35 mV) to reduce than β-$[Ru_2(Me_2dtc)_5]^+$, a trend which becomes more pronounced for the second reduction step where the reduction potentials for the two isomers differ by 105 mV. Furthermore, the reduction of β-$Ru_2(Me_2dtc)_5$ results in a rapid conversion of β-$[Ru_2(Me_2dtc)_5]^-$ into the α-anion. The reduction product of α-$[Ru_2(Me_2dtc)_5]^-$ does not isomerize. These factors are illustrated by the cyclic voltammograms in Fig. 8. When this information is coupled with the fact that, from NMR data, the more stable cationic isomer is the β-form, the relative orders of stability can be determined. The equilibrium position for α-$Ru_2Me_2dtc_5$ and β-$Ru_2Me_2dtc_5$ has been determined in CH_2Cl_2 solution saturated with $[Et_4N][ClO_4]$ at 20°C. Solutions obtained from the electrolytic reduction of separate solutions of α- and β-$[Ru_2(Me_2dtc)_5]^+$ were allowed to equilibrate and the concentration of each isomeric form was monitored by a.c. voltammetry of the $Ru_2(Me_2dtc)_5/[Ru_2(Me_2dtc)_5]^-$ couples. The ratios of a.c. peak currents at equilibrium yield

$$k(\beta^0/\alpha^0) = [\beta\text{-}Ru_2(Me_2dtc)_5]/[\alpha\text{-}Ru_2(Me_2dtc)_5] = 5.6 \tag{52}$$

From the additional redox data it can be shown that

$$k(\beta^+/\alpha^+) = 22 \tag{53}$$

$$k(\beta^-/\alpha^-) = 0.09 \tag{54}$$

The stability order of the two isomers, as a function of ruthenium oxidation state, is dependent on the electronic and steric requirements of d^5 ruthenium(III) and d^6 ruthenium(II). The proximity of the ruthenium(III) atoms in the low-spin cation (2.787 Å) favours the unique bridging ligand β-structure. The absence of Ru–Ru bonding in the anion is associated with a Ru–Ru distance which is too long to favour this type of unique bridging ligand (e.g. the Rh–Rh distance [102] in the isoelectronic complex $[Rh_2(Me_2dtc)_5]^+$ is 3.556 Å).

It is also worth noting the difference in the rates of the reactions (55) and (56)

$$\beta\text{-}[Ru_2(Me_2dtc)_5]^- \xrightarrow{k_1} \alpha\text{-}[Ru_2(Me_2dtc)_5]^- \tag{55}$$

$$\beta\text{-}[Ru_2(Me_2dtc)_5]^+ \xrightarrow{k_2} \alpha\text{-}[Ru_2(Me_2dtc)_5]^+ \tag{56}$$

where the Ru–Ru bonded cation isomerizes rather slowly at 60°C (first order rate constant approximately 10^{-4} s^{-1}), whereas the anionic species isomerizes rapidly, even at room temperature. The rate of conversion of β-$[Ru_2(Me_2dtc)_5]^-$ into α-$[Ru_2(Me_2dtc)_5]^-$ was estimated from the cyclic voltammograms of the $[Ru_2(Me_2dtc)_5]/[Ru_2(Me_2dtc)_5]^-$ couple (Fig. 8) using the working curve of Nicholson and Shain [103] for a first order chemical reaction with a rate constant of k_1 occurring after the electron transfer step. For this purpose the $\beta^- \overset{k_1}{\rightleftharpoons} \alpha^-$ conversion was considered to be irreversible. Approximate k_1 values of 0.04, 0.06, 0.16, 0.38, 0.50 and 1.48

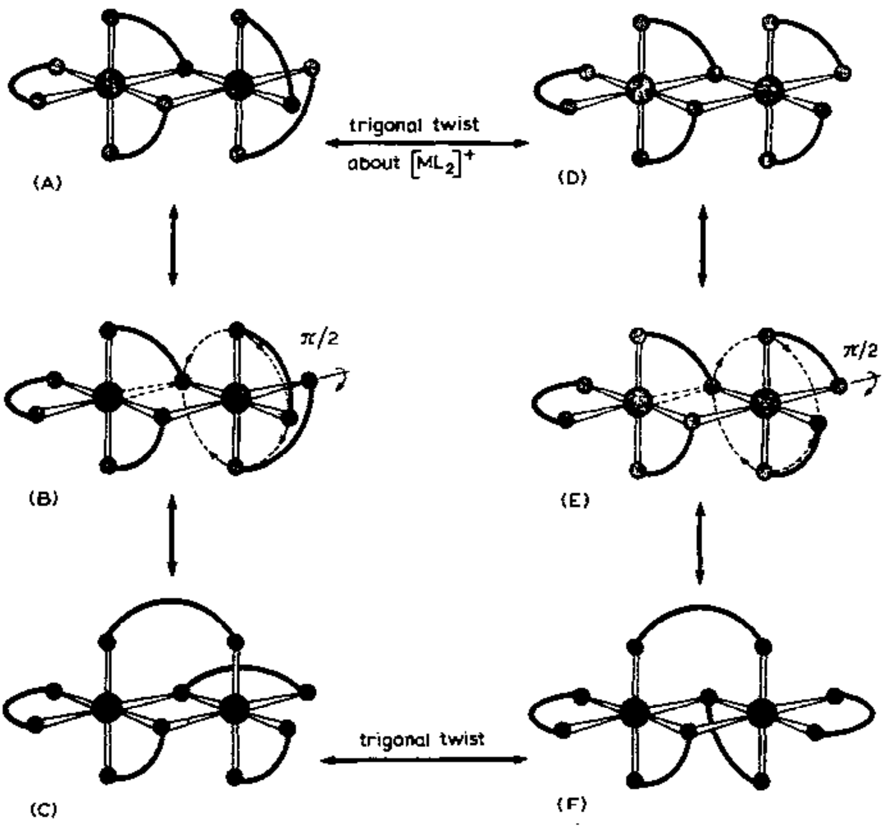


Fig. 9. A proposed mechanism for the interrelation of geometrical isomers for known binuclear cations of the type $[M_2(R_2dtc)_5]^+$. Structure (A), in which the two metal centres have opposite chiralities, may be converted into (D), where the metal chiralities are the same, by trigonal twist mechanism operating on the $(ML_2)^+$ segment of the cation. Rupture of a M–S bond (dotted), followed by a $\pi/2$ rotation along the indicated axis (structure (E)), and the reforming of a M–S(bridging) bond orthogonal to the ligand plane, affords isomeric structure (F). The presence of the metal–metal bond in the binuclear d^5 ruthenium cation may facilitate the spanning of the metal atoms by the unique $[R_2dtc]^-$ ligand in structure (F). Reproduced by courtesy: Aust. J. Chem., 29 (1976) 269.

s^{-1} obtained at 5, 15, 25, 35, 45 and 55°C were used in a plot of log k_1 against $1/T$ to obtain a projected value for the isomerization at 60°C of $k_1 = 2 \pm 1\ s^{-1}$. An intramolecular mechanism has been proposed for the $\alpha \rightarrow \beta$ isomerization [102] as shown in Fig. 9.

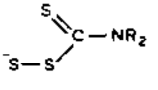
This marked difference in isomerization rates of a factor of 10^4 probably reflects the influence of the Ru–Ru bond on the energetics of rotation at the ruthenium centres although the requirement of rupturing a Ru–S bond for isomerization may also be more difficult for the cationic species. The difficulty of breaking the Ru–Ru bond in $[Ru_2(Me_2dtc)_5]^+$ is shown when a mixture of the two isomers was heated with $[Me_2dtc]^-$ under reflux in MeOH for 5 h in an attempt to cleave the dimer into two molecules of $Ru(Me_2dtc)_3$. Thin-layer chromatography showed that very little $Ru(Me_2dtc)_3$ was formed.

The electrochemical studies on the ruthenium dimers indicate the large amount of kinetic and thermodynamic data that can be obtained from careful use of the different electrochemical techniques.

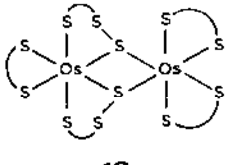
(c) Osmium dithiocarbamates

Chemistry of osmium dithiocarbamates. The chemistry of the osmium dithiocarbamates has recently been studied in detail and has proved to be extremely rich. Osmium forms all the classes of compound noted for both iron and ruthenium but in addition, an even wider range of dimers and oxidation states is found.

In 1972, Bozis [104] reported an $Os(R_2dtc)_3$ complex (R = pentamethylene). Subsequently, additional monomeric low-spin osmium(III) complexes were prepared by Dix et al. [105] and Pignolet and co-workers [106]. The $[Os_2(R_2dtc)_5]^+$ complexes analogous to the ruthenium dimers are also known [106]. An osmium(III) complex containing the sulphur-rich trithiocarbamate (Sdtc) ligand (**18**) was also isolated as a byproduct in the synthesis of $Os(R_2dtc)_3$ and $[Os_2(R_2dtc)_5]^+$ [106,107]. The structure (**19**) of $[Os_2(Et_2dtc)_3(Et_2Sdtc)_2]^+$ closely resembles that of an α-$[Ru_2(R_2dtc)_5]^+$ (**15**), except that each of the two bridging ligands of the osmium complex has been expanded by the addition of an extra sulphur atom and the details of the stereochemistry are somewhat different. The Os–Os distance of 2.79 Å is similar to the Ru–Ru distance in α-$[Ru_2(R_2dtc)_5]^+$ and indicates that



18



19

metal–metal bonding occurs. The stereochemistry of $[Os_2(R_2dtc)_5]^+$ itself is unknown but its chemical properties are similar to the ruthenium analogues.

In the (II) oxidation state, mixed ligand dithiocarbamate complexes with carbonyl and phosphine ligands have been prepared [108,109] and these have analogues in iron and ruthenium dithiocarbamate chemistry. No chemical evidence has been presented for the existence of $[Os(R_2dtc)_3]^-$ although electrochemical data (see later) suggest at least a transient existence.

The chemical oxidation of $Os(R_2dtc)_3$ with aerobic BF_3 resembles that of iron in that the osmium(IV) cation, $[Os(R_2dtc)_3]^+$, is formed [110]. By contrast, reaction with I_2 [110] follows the ruthenium pathway to produce $Os(R_2dtc)_3I$. This compound appears to be structurally identical with the analogous seven-coordinate ruthenium species and undergoes chemical reactions not unlike those of the analogous ruthenium compound. The same reaction with $Fe(dtc)_3$ produces $Fe(R_2dtc)_2I$ and thiuram disulphide as noted previously.

Reaction of $[Os(R_2dtc)_3]^+$ with chloride ion yields the seven-coordinate cation $Os(R_2dtc)_3Cl$, whereas reaction of chloride ion with $[Fe(R_2dtc)_3]^+$ leads to the complex, $Fe(R_2dtc)_2Cl$ with a diminished coordination number. Furthermore, $[Os(R_2dtc)_3]^+$ is readily converted into a wide range of other seven-coordinate complexes $Os(R_2dtc)_3X$ by the addition of I^-, CH_3CN or PPh_3 etc. [110]. This class of compound is known in ruthenium but not in iron dithiocarbamate chemistry.

A careful examination by low temperature NMR spectrometry and electrochemistry (see later) demonstrated that $[Os(R_2dtc)_3]^+$ exhibits a monomer–dimer equilibrium in dichloromethane solution [110]. The monomer is paramagnetic in solution. In the solid state, an X-ray crystal structure determination demonstrated that the compound exists exclusively as a diamagnetic dimer $[Os_2(R_2dtc)_6]^{2+}$. The geometry about each osmium atom is that of a distorted pentagonal bipyramid and is quite similar to the coordination geometry found in $Ru(R_2dtc)_3Cl$. Presumably, the tendency of osmium to form stronger bonds with sulphur and higher coordination numbers is important in the formation of the dimer.

A tetrakis osmium(IV) dithiocarbamate complex $Os(R_2dtc)_4$ is known and evidence for even higher oxidation state osmium dithiocarbamates is also available [105,111]. In summary, it can be seen that the chemistry of osmium dithiocarbamate is very rich, combining features of both iron and ruthenium plus characteristics that are unique to osmium.

Electrochemistry of $Os(R_2dtc)_3$*,* $[Os(R_2dtc)_3]^+$ *and* $[Os_2(R_2dtc)_6]^{2+}$. As is the case with other dithiocarbamate complexes, electrochemical pathways are consistent with the chemical behaviour summarized in the previous section. In acetone [105] and propylene carbonate [106], electrochemical data at platinum electrodes demonstrate the existence of a four-membered electron transfer series (three chemically reversible cyclic voltammograms) between tris-chelate complexes in four oxidation states, II, III, IV and V.

$$[Os(R_2dtc)_3]^- \overset{\pm e}{\rightleftharpoons} Os(R_2dtc)_3 \overset{\pm e}{\rightleftharpoons} [Os(R_2dtc)_3]^+ \overset{\pm e}{\rightleftharpoons} [Os(R_2dtc)_3]^{2+} \qquad (57)$$

Controlled-potential electrolysis of $Os(Et_2dtc)_3$ gives the purple cation $[Os(Et_2dtc)_3]^+$ which has spectral and electrochemical properties identical to samples prepared by the reaction of aerobic BF_3 with $Os(Et_2dtc)_3$. The one-electron nature of this oxidation has been verified by coulometry [106]. These electrochemical results strongly suggest that the one-electron oxidation product of $Os(Et_2dtc)_3$ is the six-coordinate tris-chelate $[Os(Et_2dtc)_3]^+$. This contrasts with the analogous ruthenium chemistry where the one-electron oxidation product of $Ru(Et_2dtc)_3$ in propylene carbonate is believed to produce a solvent or ligand-stabilized seven-coordinate complex. Furthermore, the +5 oxidation state with ruthenium is not observed.

The electrochemical results for $Os(Et_2dtc)_3$ in CH_3CN at 0°C are considerably different to the above results with propylene carbonate but they are very similar to the CH_3CN data observed with $Ru(Et_2dtc)_3$. The electro-

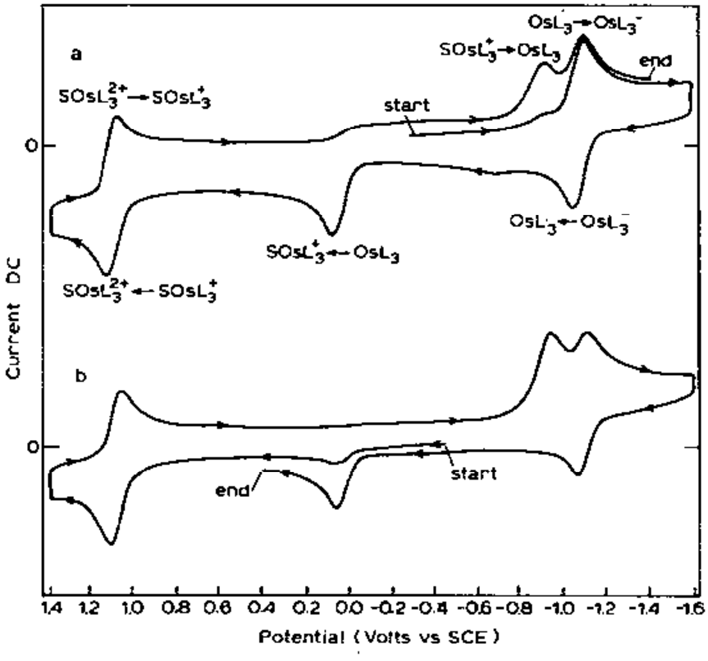


Fig. 10. (a) Cyclic voltammogram of $Os(Et_2dtc)_3$ in CH_3CN (ca. 0.1 M Et_4NClO_4) (at a scan rate = 100 mV s^{-1}). (b) Cyclic voltammogram of the above solution after controlled potential electrolysis at 0.3 V. Reproduced by courtesy: Inorg. Chem., 15 (1976) 1900.

chemical data are presented in Fig. 10. The overall cyclic voltammetric process in CH_3CN illustrated in Fig. 10 is best represented by eqn. 58

$$\begin{tikzcd}
\left[Os(Et_2dtc)_3\right]^+ \arrow[r, shift left, "\pm e"] \arrow[d, "CH_3CN"', "fast"] & Os(Et_2dtc)_3 \arrow[l, shift left] \arrow[r, shift left, "\pm e"] & \left[Os(Et_2dtc)_3\right]^- \arrow[l, shift left] \\
\left[(CH_3CN)Os(Et_2dtc)_3\right]^+ \arrow[ur, "+e", "-CH_3CN"'] \arrow[d, shift left] & & \\
\left[(CH_3CN)Os(Et_2dtc)_3\right]^{2+} \arrow[u, shift left, "\pm e"] & &
\end{tikzcd} \tag{58}$$

The one-electron reduction at $E_{1/2} = -1.10$ V vs. SCE is reversible while the oxidation at $E_{1/2} = 0.01$ V vs. SCE is irreversible with a new peak appearing at -0.93 V vs. SCE on the reverse scan. This peak appears only after oxidation of $Os(Et_2dtc)_3$ and is initially present after controlled-potential oxidative electrolysis of $Os(Et_2dtc)_3$. The cyclic voltammogram shown in Fig. 10 was recorded after exhaustive electrolysis at 0.3 V vs. SCE indicating that the parent species is $[Os(Et_2dtc)_3(CH_3CN)]^+$. The complex $[Os(Et_2dtc)_3(CH_3CN)]^+$ has identical spectral and electrochemical properties to $Os(Et_2dtc)_3Cl$ dissolved in CH_3CN, suggesting that Cl^- is displaced by CH_3CN. This chemistry is identical with that observed for the analogous ruthenium complex except for the additional reversible one-electron oxidation of $[Os(Et_2dtc)_3(CH_3CN)]^+$ to $[Os(Et_2dtc)_3(CH_3CN)]^{2+}$ at $E_{1/2} = 1.08$ V vs. SCE.

It is interesting to compare the reduction and oxidation half-wave potentials for $M(Et_2dtc)_3$ (M = Fe, Ru and Os). The trend is in the expected order for the reversible process $M(Et_2dtc)_3 + e \rightleftharpoons [M(Et_2dtc)_3]^-$ with iron being the easiest and osmium the hardest complex to reduce. The half-wave potentials for the process $M(Et_2dtc)_3 \rightleftharpoons [M(Et_2dtc)_3]^+ + e$ are nearly identical for Fe and Ru but much less positive for Os. It is expected that Os should be the easiest to oxidize but the similarity in potentials for Fe and Ru in unexpected. It should be emphasized, however, that the Ru oxidation is usually irreversible and therefore less certainty should be attached to the $E_{1/2}$ values in this case.

In dichloromethane, the presence of the monomer–dimer equilibrium

$$2\left[Os(R_2dtc)_3\right]^+ \rightleftharpoons \left[Os_2(R_2dtc)_6\right]^{2+} \tag{59}$$

influences the observed electrochemistry [110]. Thus at 0°C $[Os(R_2dtc)_3]^+$ shows reversible electrochemical behaviour of CH_2Cl_2 solution (Fig. 11a) consistent with that observed for oxidation of $Os(R_2dtc)_3$. However, at -78°C the cyclic voltammogram for $[Os(R_2dtc)_3]^+$ (Fig. 11b) is consistent with the presence of the dimeric species. The new peak which corresponds to

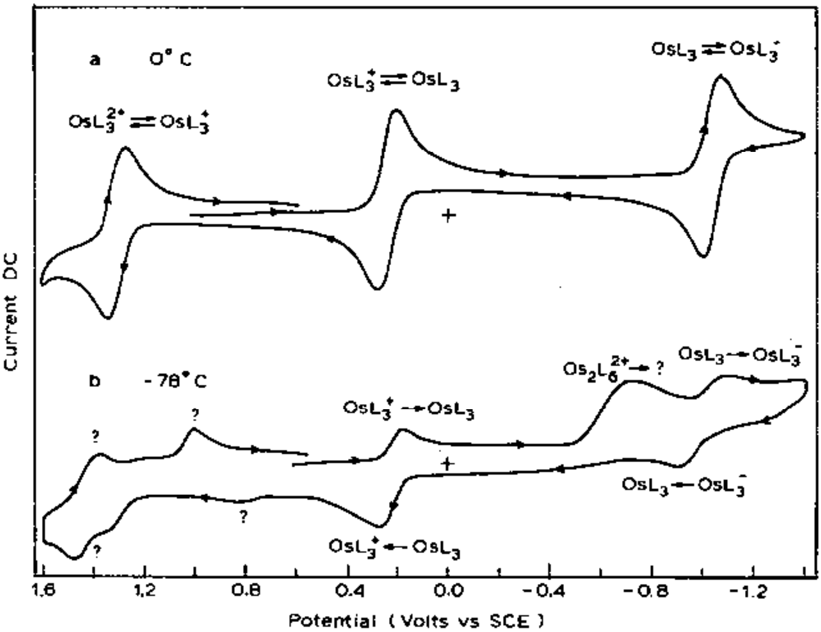


Fig. 11. Cyclic voltammograms of $[Os(dtc)_3]^+$ in CH_2Cl_2 at 0 and −78°C. The zero-current potential position is marked by a cross (scan rate 100 and 200 mV s^{-1} for (a) and (b), respectively). The cation was generated in situ by controlled-potential electrolysis of $Os(dtc)_3$. Reproduced by courtesy: Inorg. Chem., 19 (1980) 972.

the reduction of $[Os_2(R_2dtc)_6]^{2+}$ appears at −0.74 V vs. SCE. The new peaks at potentials more positive than 0.6 V vs. SCE which appear at −78°C (Fig. 11b) reveal complex non-reversible processes which have not been characterized.

The striking difference between the cyclic voltammograms for $[Os(R_2dtc)_3]^+$ recorded at 0 and −78°C (Fig. 11) clearly shows the value of low-temperature electrochemistry in the interpretation of complicated electrochemical behaviour.

Electrochemical data for some other osmium compounds are also available [106,110] and oxidation states II to V are readily accessible.

D. ELECTROCHEMICAL STUDIES ON SOME OTHER TRANSITION METAL DITHIOCARBAMATES

The data available on manganese and the Group VIII triad dithiocarbamates demonstrate their close relationship in chemical and electrochemical behaviour. Similar data are also available for dithiocarbamates of many

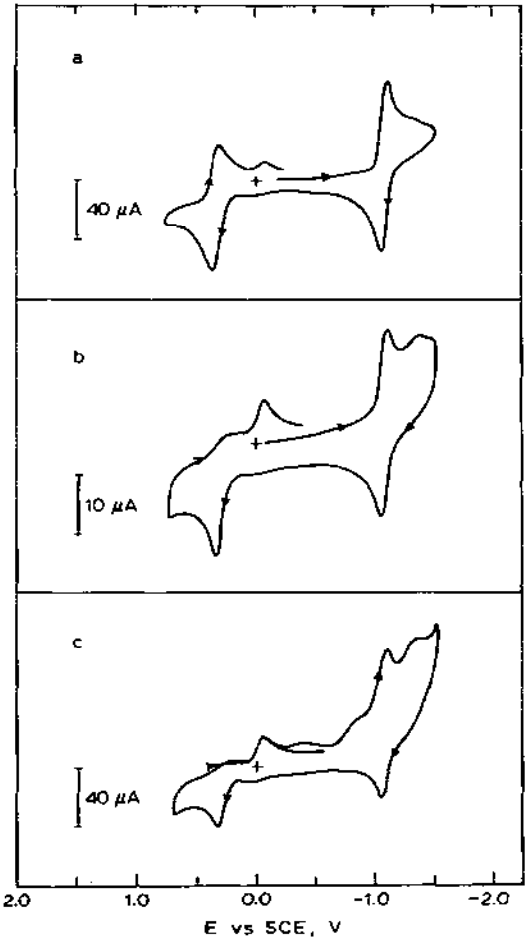


Fig. 12. Cyclic voltammograms of (a) 10^{-3} M $V(R_2dtc)_3$, (b) 2.5×10^{-4} M $V(R_2dtc)_3$, and (c) 10^{-3} M $V(R_2dtc)_3$, *after controlled-potential oxidation at* +0.50 V *vs.* SCE in acetonitrile; 0.1 M Et_4NClO_4 at a scan rate 200 mV s^{-1}. Reproduced by courtesy: Inorg. Chem., 15 (1976) 1900.

other transition metals and these are presented in the following section if they highlight some aspect of the electrochemical technique or are useful in the general discussion which concludes the review.

(i) Electrochemistry of $V(R_2dtc)_3$

Figure 12 shows a cyclic voltammogram of $V(R_2dtc)_3$ (R = Et) at two different concentrations and after controlled-potential oxidative electrolysis. Careful examination of the cyclic voltammetric data and the electrochemical response of a range of related compounds enable the electrode processes to be understood [112].

The cyclic voltammogram (Fig. 12a) for a 10^{-3} M solution of $V(R_2dtc)_3$ exhibits a reduction couple with an $E_{1/2}$ value of -1.075 V vs. SCE and an oxidation couple at $+0.35$ V. In both cases the peak-potential separations are near the theoretical value for an electrochemically reversible one-electron process (i.e. 56 mV at 25°C) and the ratio of oxidation to reduction peak heights is unity, as expected for a chemically reversible process.

The coulometric data from controlled potential reduction at -1.30 V confirm that the reduction is a one-electron process. A cyclic voltammogram of the product solution yields the -1.075 V couple (now oxidation). A subsequent controlled potential electrolysis at -0.90 V is a one-electron oxidation process. The cyclic voltammogram of this oxidized solution is essentially identical with the initial one (Fig. 12a). These results indicate that the electrochemical step is

$$V(R_2dtc)_3 + e \rightleftharpoons [V(dtc)_3]^- \tag{60}$$

The electrochemical step for the oxidation at $+0.35$ V can be formulated as

$$V(R_2dtc)_3 \rightleftharpoons [V(R_2dtc)_3]^+ + e \tag{61}$$

but the appearance of a reduction peak at -0.10 V in the cyclic voltammogram (Fig. 12a) indicates that a subsequent chemical reaction gives at least one additional product. The cyclic voltammogram (Fig. 12b) of a 2.5×10^{-4} M solution of $V(dtc)_3$ indicates that the reduction peak of the $+0.35$ V couple is almost negligible at this lower concentration but that significant reduction peaks are observed at -0.10 and -1.35 V. These latter peaks are visible in the cyclic voltammogram for a 10^{-3} M solution but are negligible in the cyclic scan for a 5×10^{-3} M solution. Although the $+0.35$ V couple is essentially irreversible for the 2.5×10^{-4} M solution, it is the dominant reaction for a 10^{-3} M solution and the only reaction for a 5×10^{-3} M solution. Thus the system appears simple at the higher concentration but at a concentration of 2.5×10^{-4} M, oxidation leads to at least three products.

Coulometric data for the controlled-potential oxidation of $V(R_2dtc)_3$ at $+0.50$ V indicate that the primary electrochemical step is as represented by eqn. 61. This conclusion is further supported by the observation that the ratio of the cathodic to anodic peak currents for the $+0.35$ V couple approaches unity with increasingly rapid scan rates.

The cyclic voltammogram that is observed after controlled-potential oxidation of $V(R_2dtc)_3$ at $+0.05$ V is essentially the same at all three concentrations; that for the 10^{-3} M solution is shown in Fig. 12c. For the initial scan a reduction peak is not observed at $+0.35$ V, which indicates that the $[V(R_2dtc)_3]^+$ species is not stable. When a small amount of water is added to a solution of $V(R_2dtc)_3$ the oxidation is not chemically reversible, which indicates that $[V(R_2dtc)_3]^+$ reacts rapidly with water

$$[V(R_2dtc)_3]^+ + H_2O \rightarrow [V(R_2dtc)_3(H_2O)]^+$$

$$[V(R_2dtc)_3(H_2O)]^+ \rightarrow V(OH)(R_2dtc)_3 + H^+ \qquad (62)$$

The resultant species, $V(OH)(R_2dtc)_3$ is reduced at -0.10 V.

$$V(OH)(R_2dtc)_3 + e \rightarrow [V(OH)(R_2dtc)_3]^- \qquad (63)$$

Proton reduction is responsible for the peak at -0.40 V. The reduction product quickly dissociates to give the initial tris complex

$$[V(OH)(R_2dtc)_3]^- \xrightarrow{\text{rapid}} V(R_2dtc)_3 + OH^- \qquad (64)$$

with a reversible couple at -1.075 V.

On the basis of other data [112], the reduction peaks at -0.90 and -1.35 V are believed to be due to $VO(R_2dtc)_3$, and $VO(R_2dtc)_2$, respectively. To account for these species in Fig. 12c, $V(OH)(R_2dtc)_3$ probably undergoes two reactions in addition to that given by eqn. 63. A disproportionation reaction would account for the $VO(R_2dtc)_3$ peak

$$2\,V(OH)(R_2dtc)_3 \rightarrow V(R_2dtc)_3 + VO(R_2dtc)_3 + H_2O \qquad (65)$$

and, when considered with eqn. 64, would explain how the $V(R_2dtc)_3$ reduction peak can be larger than that for $VO(R_2dtc)_3$. The $VO(R_2dtc)_2$ species presumably is produced by a dissociation reaction

$$V(OH)(R_2dtc)_3 \rightarrow VO(R_2dtc)_2 + H^+ + [R_2dtc]^- \qquad (66)$$

and is then reduced at -1.35 V.

On a second cyclic scan a small reduction peak at $+0.325$ V is observed because some $V(R_2dtc)_3$ has been regenerated and then oxidized at $+0.375$ V.

The relative peak heights for the reductions at -0.90, -1.075 and -1.35 V (after oxidative electrolysis) vary with the concentration of $V(R_2dtc)_3$ which indicates the relative dominance of the reactions that compete for the product species $V(OH)(R_2dtc)_3$. However, 10 min after controlled-potential oxidation experiments, the reduction peak for $V(OH)(R_2dtc)_3$ at -0.10 V has disappeared.

In summary, vanadium(III) tris-dithiocarbamate exhibits many similarities to other transition metals. Stabilization of high oxidation states is observed but these complexes can be fairly reactive with formation of seven-coordinate species being relatively common.

(ii) Electrochemistry of $Cr(R_2dtc)_3$

$Cr(R_2dtc)_3$ complexes are difficult to reduce and difficult to oxidize. However, data at a platinum electrode in dichloromethane [113] are consistent with the existence of a three-membered electron transfer series

$$[Cr(R_2dtc)_3]^+ \overset{\pm e}{\rightleftharpoons} Cr(R_2dtc)_3 \overset{\pm e}{\rightleftharpoons} [Cr(R_2dtc)_3]^- \qquad (67)$$

The formally chromium(IV) cation $[Cr(R_2dtc)_3]^+$ appears to be relatively stable, although attempts to isolate the compound were unsuccessful [113]. Data for reduction at platinum electrodes indicate [113] that $[Cr(R_2dtc)_3]^-$ is unstable as ligand oxidation processes (eqns. 18 and 19) producing thiuram disulfide are seen on reverse scans of the cyclic voltammograms.

The virtue of working at mercury in addition to platinum electrodes emerges from polarographic studies which enable a complete description of the reduction steps to be provided [85]. $Cr(R_2dtc)_3$ is characterized by reduction waves in dimethylformamide at 25°C with limiting currents in the ratio 1 : 2. The first (more positive) one-electron reduction process is close to being electrochemically reversible but there is evidence for loss of $[R_2dtc]^-$. The second reduction step is irreversible and is associated with a two-electron process. With lowering of temperature, the second reduction step (more negative) splits into two one-electron reduction waves (R = Et). The details of the reduction of $Cr(R_2dtc)_3$ can be summarized by the following reaction scheme

$$Cr(R_2dtc)_3 + e \rightleftharpoons [Cr(R_2dtc)_3]^- \rightarrow Cr(R_2dtc)_2 + [R_2dtc]^-$$

$$Cr(R_2dtc)_2 + e \rightarrow [Cr(R_2dtc)_2]^-$$

$$[Cr(R_2dtc)_2]^- + e \rightarrow [Cr(R_2dtc)_2]^{2-} \rightarrow Cr + 2\,[R_2dtc]^- \qquad (68)$$

Depending on the conditions, the second and third electron transfer step may or may not be resolved.

The instability of $[Cr(R_2dtc)_3]^-$ is confirmed by reactions with 1,10-phenanthroline (phen) and 2,2-bipyridine (bipy). On addition of phen to solutions of $Cr(R_2dtc)_3$, the d.c. limiting current for the first reduction step increases and cyclic voltammetry indicates a marked increase in the degree of chemical irreversibility

$$Cr(R_2dtc)_3 \overset{\pm e}{\rightleftharpoons} [Cr(R_2dtc)_3]^-$$

$$[Cr(R_2dtc)_3]^- + phen \xrightarrow{k_1} Cr(R_2dtc)_2(phen) + [R_2dtc]^-$$

$$Cr(R_2dtc)_2(phen) \overset{\pm e}{\rightleftharpoons} [Cr(R_2dtc)_2(phen)]^- \qquad (69)$$

i.e. a so-called ECE mechanism [1]. Values of k_1 have been computed using a range of electrochemical techniques [114–120].

When bipy is used instead of phen, values of k_1 are smaller but the overall mechanism is the same. Previously, examples have been provided to show that the combination of UV/visible spectroscopy and electrochemistry is most useful. The addition of ESR spectroscopy is also valuable in understanding the detailed nature of electrode processes, e.g. ESR work with the addition of bipy [121] verifies that the reaction scheme is probably correct.

The polarograms for chromium(III) dithiocarbamate in acetonitrile give three one-electron waves. When bipy is added to the solution, the first reduction wave shows an increase in height and becomes kinetically controlled as is the case with phen. The concentration and the scan rate dependence of cyclic voltammograms indicate that following the charge-transfer stage, a chemical reaction is taking place between the reduction product and one bipy molecule

$$\mathrm{Cr(R_2dtc)_3} \overset{\pm e}{\rightleftharpoons} [\mathrm{Cr(R_2dtc)_3}]^- \rightleftharpoons \mathrm{Cr(R_2dtc)_2} + [\mathrm{R_2dtc}]^-$$

$$\mathrm{Cr(R_2dtc)_2} + \mathrm{bipy} \rightarrow \mathrm{Cr(R_2dtc)_2(bipy)} \tag{70}$$

The resulting complex is reduced at a more positive potential than the original chromium(III) complex and this explains the increase in the limiting current of the first wave when bipy is added to the solution

$$\mathrm{Cr(R_2dtc)_2(bipy)} \overset{\pm e}{\rightleftharpoons} [\mathrm{Cr(R_2dtc)_2(bipy)}]^- \tag{71}$$

$$[\mathrm{Cr(R_2dtc)_2(bipy)}]^- \rightarrow \mathrm{Cr(R_2dtc)(bipy)} + [\mathrm{R_2dtc}]^- \tag{72}$$

The reversibility of eqn. 71 and the formation of the diethyldithiocarbamate anions in eqns. 70 and 72 was verified by cyclic voltammetry.

When a solution of chromium(III) diethyldithiocarbamate in acetonitrile is electrolyzed in the presence of bipy at the potential of the limiting current of the first wave, ESR spectra of paramagnetic species are observed, confirming that the oxidation state of the central atom is +1. The spectra show lines due to additional hyperfine splitting from the four nitrogen atoms of the two heterocyclic rings (Fig. 13). Further, two additional spectra containing a large number of hyperfine lines appear indicating the formation of two other paramagnetic species during electrolysis. It may be assumed that the main signal is due to the complex $\mathrm{Cr(R_2dtc)(bipy)_2}$ whereas the other two spectra which have lower line intensities can be assigned to the bipyridyl complexes $[\mathrm{Cr(bipy)_2}]^+$ and $[\mathrm{Cr(bipy)_3}]^+$. The low intensity of the ESR signals of the last two complexes and their superimposition on the spectrum of the main complex makes the analysis of the hyperfine splitting difficult. Since chromium(I) has a tendency to form octahedral complexes, it is assumed that under the conditions of the electrolysis, another bipy ligand is attached to the product of the two-electron reduction (72) leading to the formation of $Cr(R_2dtc)(bipy)_2$

$$Cr(R_2dtc)(bipy) + bipy \rightarrow Cr(R_2dtc)(bipy)_2 \quad (73)$$

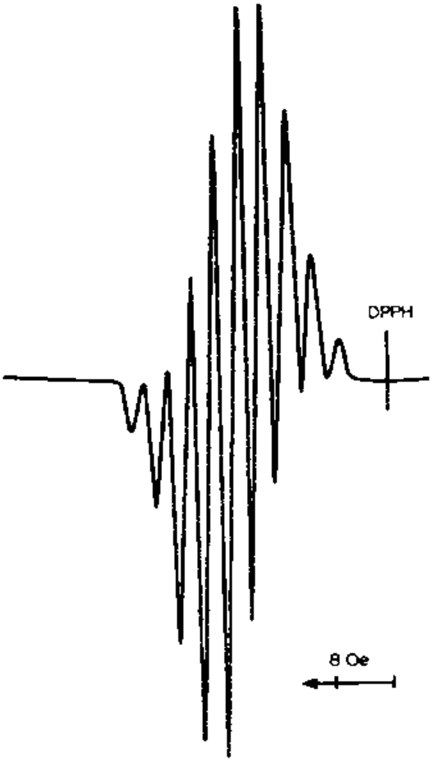


Fig. 13. ESR spectrum of an acetonitrile solution of $Cr(Et_2dtc)_3$ (5×10^{-3} M) in the presence of bipy (2×10^{-3} M) after electrolysis at a potential corresponding to the first reduction step and at −35°C. Reproduced by courtesy: Russ. J. Inorg. Chem., 21 (1976) 255.

In the absence of π-acceptors such as phen or bipy, the low oxidation state chromium dithiocarbamate complexes are unstable.

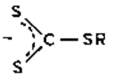
(iii) Electrochemistry of $Mo(R_2dtc)_4$ and $W(R_2dtc)_4$

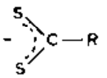
Tetrakis dithiocarbamate compounds of Mo and W can be synthesized both as $M(R_2dtc)_4$ and the cation $[M(R_2dtc)_4]^+$ [122–132]. Not surprisingly, therefore, a reversible

$$[M(R_2dtc)_4]^+ + e \rightleftharpoons M(R_2dtc)_4$$

couple exists [124,128,129] establishing that reversible electrochemistry can be associated with eight-coordinate complexes. There is some evidence for the existence of an extended electron transfer series [123] although $[Mo(R_2dtc)_4]^-$, $[W(R_2dtc)_4]^{2+}$ and $[Mo(R_2dtc)_4]^{2+}$ appear to be unstable and their existence as intermediates in redox processes is not well characterized. Accordingly, arguments for substituent and related effects based on these electrode processes [129] should be treated with caution.

The M(V)/M(IV) couple for Mo and W has been examined electrochemically for a number of sulphur-based ligands, and these processes are electrochemically and chemically reversible yielding thermodynamically significant data. Generally, the $E_{1/2}$ value for the Mo(V) and Mo(IV) dithiocarbamate couple occurs at very negative potentials relative to the corresponding complexes of thioxanthate (**20**) (RSxant) [133] and dithiocarboxylate (**21**) (Rdta) [131]. This reflects the considerable ability of dithiocarbamates to stabilize high oxidation states. Conversely, lower oxidation states are far more accessible with ligands used such as (**20**) and (**21**) and electrochemical evidence for the molybdenum(II) complexes $[Mo(RSxant)_4]^{2-}$ and $[Mo(Rdta)_4]^{2-}$ has been obtained. In contrast, no electrochemical evidence for molybdenum(II) or tungsten(II) dithiocarbamate complexes has been reported following the reduction of eight-coordinate M(IV) or M(V) species.


20


21

A number of dimers of molybdenum dithiocarbamate and related complexes, as well as oxo- and sulphide-bridged species and other monomeric oxo species, are also known [6,8,133,134]. Electrochemical studies have revealed the importance of monomer–dimer equilibria as well as the ready formation of oxygen-containing complexes (see refs. 133–139). These studies highlight the problem alluded to above of using $E_{1/2}$ values obtained from irreversible processes [129] in $M(R_2dtc)_4$ and assuming them to have thermodynamic significance. The $E_{1/2}$ values for the irreversible processes in molybdenum and tungsten chemistry could simply reflect either a dimerization rate constant or the formation of an oxo-bridged or oxygen-containing species from adventitious water etc.

(iv) Electrochemistry of $Co(R_2dtc)_3$

Tris-cobalt(III) dithiocarbamate complexes are kinetically inert. On reduction the lower oxidation state dithiocarbamates are prone to loss of $[R_2dtc]^-$. In dimethylformamide three one-electron reduction steps are observed polarographically and evidence for the presence of $[Co(R_2dtc)_3]^-$ and $[Co(R_2dtc)_3]^{2-}$ is provided [140]. Electrochemical data [66,140] in this solvent can be summarized by the reaction scheme (74)

$$\mathrm{Co(R_2dtc)_3} \overset{\pm e}{\rightleftharpoons} [\mathrm{Co(R_2dtc)_3}]^-$$

$$[\mathrm{Co(R_2dtc)_3}]^- \overset{\pm e}{\rightleftharpoons} [\mathrm{Co(R_2dtc)_3}]^{2-} \rightarrow [\mathrm{Co(R_2dtc)_2}]^- + [\mathrm{R_2dtc}]^-$$

$$[\mathrm{Co(R_2dtc)_2}]^- \overset{\pm e}{\rightleftharpoons} [\mathrm{Co(R_2dtc)_2}]^{2-} \rightarrow \mathrm{Co} + 2\,[\mathrm{R_2dtc}]^- \qquad (74)$$

In acetone, the chemical reversibility of the $Co(R_2dtc)_3/[Co(R_2dtc)_3]^-$ couple depends on the nature of R [141], whereas in dichloromethane this step is always chemically irreversible at both platinum and mercury electrodes. In dichloromethane and other solvents [141], a one-electron reduction followed by an irreversible two-electron reduction is observed in contrast to the three one-electron steps noted in dimethylformamide. In dichloromethane the electrode processes are consistent with reaction scheme (75).

$$\mathrm{Co(R_2dtc)_3} \overset{\pm e}{\rightleftharpoons} [\mathrm{Co(R_2dtc)_3}]^- \rightarrow \mathrm{Co(R_2dtc)_2} + [\mathrm{R_2dtc}]^-$$

$$\mathrm{Co(R_2dtc)_2} + 2\,e \rightarrow \mathrm{Co} + 2\,[\mathrm{R_2dtc}]^- \qquad (75)$$

Presumably, a delicate balance between the kinetic and thermodynamic relationships involved in the reaction $[Co(R_2dtc)_3]^- \rightleftharpoons [Co(R_2dtc)_2] + [R_2dtc]^-$ leads to the solvent-dependence of the electrochemical behaviour.

Originally it was claimed [96] that aerobic oxidation of $Co(R_2dtc)_3$ in the presence of BF_3 led to the formation of $[Co(R_2dtc)_3]^+$. Subsequent studies [142,143] indicated that a $[Co_2(R_2dtc)_5]^+$ dimer of the kind sketched in (**15**) had been formed. Controlled-potential electrolysis of $Co(R_2dtc)_3$ in acetone (R = cyclohexyl) [141] leads to the formation of $[Co_2(R_2dtc)_5]^+$. However, when the same experiment is undertaken in dichloromethane a species is generated which, (i) has a UV/visible spectrum different to $[Co_2(R_2dtc)_5]^+$, (ii) can be reduced back to $Co(R_2dtc)_3$, and (iii) produces a cyclic voltammogram which is essentially identical to that for oxidation of $Co(R_2dtc)_3$ (except for the sign of the current). All these properties suggest that the elusive cobalt(IV) species claimed originally [96] can be prepared for the bulky cyclohexyl derivative but its stability depends upon the solvent and the functional group R.

(v) Electrochemistry of $Ni(R_2dtc)_2$ and $[Ni(R_2dtc)_3]^+$

The electrochemical behaviour of nickel dithiocarbamates has been studied in numerous publications [11,12,54,66,121,138,144–151]. The different stereochemistries associated with nickel(II), $Ni(R_2dtc)_2$, and nickel(IV), $[Ni(R_2dtc)_3]^+$, enable two distinct electron transfer series to be characterized.

The polarographic reduction of $Ni(R_2dtc)_2$ in dimethylformamide [140] produces two one-electron reduction steps. The first step is essentially reversible from both a chemical and electrochemical viewpoint. The second reduction step is an irreversible process which occurs with loss of two dithiocarbamate ligands. At mercury and in dimethylformamide the electrode processes can be described by eqn. 76

$$Ni(R_2dtc)_2 + e \rightleftharpoons [Ni(R_2dtc)_2]^- + e \rightarrow Ni + 2[R_2dtc]^- \qquad (76)$$

The $[Ni(R_2dtc)_2]^-$ species has been investigated in considerable detail. In particular, the ready displacement of one $[R_2dtc]^-$ ligand is noted in the studies of Budnikov and Ulakhovich [148]. Thus in the presence of bipy, the electrode process is described by reaction scheme (77)

$$Ni(R_2dtc)_2 \overset{\pm e}{\rightleftharpoons} [Ni(R_2dtc)_2]^-$$

$$[Ni(R_2dtc)_2]^- + bipy \xrightarrow{k_1} Ni(R_2dtc)bipy + [R_2dtc]^- \qquad (77)$$

This kind of reaction with π-acceptor ligands appears to be typical of first row transition metal dithiocarbamates in formally low oxidation states. Considerable interest has also been devoted to the question of whether

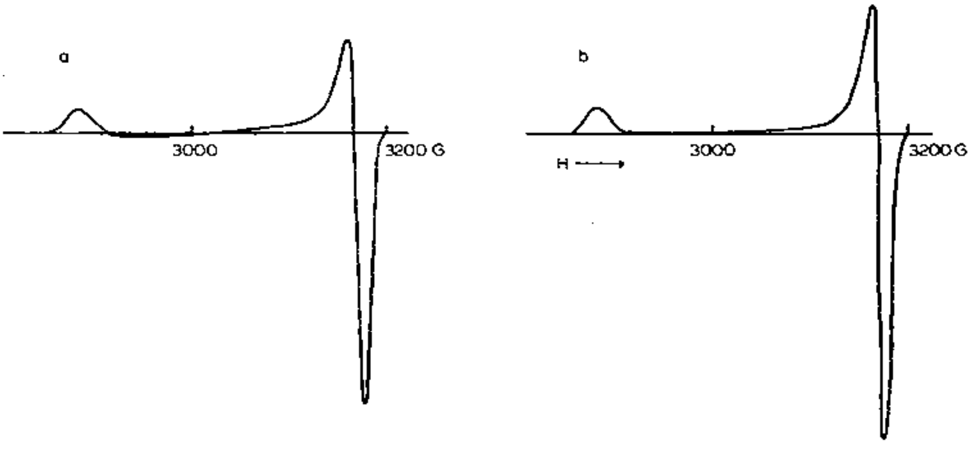


Fig. 14. (a) ESR spectrum (9.197 GHz) of reduced $Ni(Bu_2NCS_2)_2$ (species 1) in frozen acetone solution (77 K). The spectrum was obtained by rapid sampling of the product from controlled-potential electrolysis. (b) Simulated ESR spectrum for g values $g_\parallel = 2.272$ and $g_\perp = 2.062$ and line widths $\sigma_\parallel = 10.0$ G and $\sigma_\perp = 7.0$ G. Reproduced by courtesy; Inorg. Chem., 21 (1982) 1152.

$[Ni(R_2dtc)_2]^-$ is really a nickel(I) compound or a nickel(II) complex with a reduced ligand. A combination of electrochemical and ESR techniques [151] produced the spectrum shown in Fig. 14. Ni(I) complexes generally have an anisotropic *g*-value greater than 2.0 whereas Ni(II)-stabilized radical anions have *g*-values close to 2.0. The ESR behaviour demonstrated in Fig. 14 therefore is indicative of a planar Ni(I) complex. Furthermore, ^{61}Ni-enriched experiments and examination of relatively stable nickel(I) species such as $[Ni(dpe)_2]^+$, where dpe = 1,2-bis(diphenylphosphine)ethane, provide convincing evidence that $[Ni(R_2dtc)_2]^-$ is also a nickel(I) complex. Interestingly, the $Ni(R_2dtc)(dpe)$ complex disproportionates to $Ni(dpe)_2 + Ni(R_2dtc)_2$ confirming the instability of the d^9 configuration in $[Ni(R_2dtc)_2]^-$ with $[R_2dtc]^-$ as a bidentate ligand. In the absence of an alternative ligand such as bipy, dpe etc., $[Ni(R_2dtc)_2]^-$ has been postulated to "rearrange" to $Ni(R_2dtc)$ or $Ni_2(R_2dtc)_2$ [147] or alternatively to a three-coordinate complex with one monodentate rather than bidentate $[R_2dtc]^-$ ligand [151]. All studies assume that the "rearranged" species is also a d^9 nickel(I) complex. It is also possible that the reaction pathway at mercury electrodes may differ from platinum as generation of $Hg(R_2dtc)_2$ would appear to accompany the electron transfer in some of the studies [147].

The oxidation of $Ni(R_2dtc)_2$ has also produced some unexpected results. In all studies at platinum electrodes in a range of solvents, chemically irreversible oxidation of $Ni(R_2dtc)_2$ occurs [144,145]. Coulometric data and isolation of oxidation products are consistent with an overall process leading to formation of the well-characterized nickel(IV) complex, $[Ni(R_2dtc)_3]^+$.

$$3\ Ni(R_2dtc)_2 \rightarrow 2\ [Ni(R_2dtc)_3]^+ + Ni^{2+} + 4\ e \qquad (78)$$

The mechanism of the oxidation has been the subject of considerable speculation [144,145,149]. The data seem to be in agreement with the initial formation of a transient $[Ni(R_2dtc)_2]^+$ species. This may be followed by a rapid transformation to $Ni(R_2dtc)_3$ and a disproportionation step, although the exact nature of the subsequent steps has not been established. A possible alternative reaction scheme not involving disproportionation would be

$$\begin{gathered} Ni(R_2dtc)_2 \rightleftharpoons [Ni(R_2dtc)_2]^+ + e \\ 2\ [Ni(R_2dtc)_2]^+ + Ni(R_2dtc)_2 \rightarrow Ni^{2+} + 2\ Ni(R_2dtc)_3 \\ Ni(R_2dtc)_3 + [Ni(R_2dtc)_2]^+ \rightarrow Ni(R_2dtc)_2 + [Ni(R_2dtc)_3]^+ \qquad (79) \end{gathered}$$

Evidence from reduction of $[Ni(R_2dtc)_3]^+$ demonstrates [144,145] the considerable stability of $Ni(R_2dtc)_3$ relative to $[Ni(R_2dtc)_2]^+$ so that this postulated intermediate seems plausible. An alternative step would involve the direct electrochemical oxidation of $Ni(R_2dtc)_3$ to $[Ni(R_2dtc)_3]^+$ instead of disproportionation [145]. ESR data [149] provide evidence for an unstable intermediate which presumably is a nickel(III) species. The claim that this species is $[Ni(R_2dtc)_2]^+$ seems unsubstantiated. Low temperature electrochemical studies indicate [144] that intermediates other than or in addition to $Ni(R_2dtc)_3$ and $[Ni(R_2dtc)_2]^+$ are associated with the formation of Ni^{2+} and $[Ni(R_2dtc)_3]^+$ as the final products so that the exact mechanism is certainly far more complex than as presented in eqn. 79.

Electrochemical reduction of $[Ni(R_2dtc)_3]^+$ at a platinum electrode produces two reversible electron reduction steps [144,145] when short time-scale or low temperature studies are undertaken

$$[Ni(R_2dtc)_3]^+ \overset{\pm e}{\rightleftharpoons} Ni(R_2dtc)_3 \overset{\pm e}{\rightleftharpoons} [Ni(R_2dtc)_3]^- \qquad (80)$$

However, neither $Ni(R_2dtc)_3$ nor $[Ni(R_2dtc)_3]^-$ are stable on the controlled-potential electrolysis time-scale and a range of interesting reactions occur [145] after their electrochemical generation. Thus on addition of an electron, thiuram disulphide is generated

$$[Ni(R_2dtc)_3]^+ \overset{\pm e}{\rightleftharpoons} Ni(R_2dtc)_3 \rightarrow Ni(R_2dtc)_2 + \tfrac{1}{2}(R_4tds) \qquad (81)$$

If a sufficiently negative potential is applied to generate $[Ni(R_2dtc)_3]^-$, the reaction occurs according to scheme (82)

$$[Ni(R_2dtc)_3]^+ + 2\,e \rightleftharpoons [Ni(R_2dtc)_3]^-$$

$$[Ni(R_2dtc)_3]^- \rightleftharpoons Ni(R_2dtc)_2 + [R_2dtc]^-$$

$$[Ni(R_2dtc)_3]^+ + [R_2dtc]^- \rightarrow Ni(R_2dtc)_2 + R_4tds \qquad (82)$$

so that the overall reaction is

$$2\,[Ni(R_2dtc)_3]^+ + 2\,e \rightarrow 2\,Ni(R_2dtc)_2 + R_4tds \qquad (83)$$

A reaction of the kind

$$[Ni(R_2dtc)_3]^+ + [Ni(R_2dtc)_3]^- \rightarrow 2\,Ni(R_2dtc)_2 + R_4tds \qquad (84)$$

is also possible as thermodynamically the reaction

$$[Ni(R_2dtc)_3]^+ + [Ni(R_2dtc)_3]^- \rightarrow 2\,Ni(R_2dtc)_3 \qquad (85)$$

lies substantially to the right and this coupled with reaction (81) would lead to the same products.

An oxidation wave at very positive potentials has been reported in one study using a graphite electrode [149]. Few details are available but presumably this is a ligand-based step producing thiuram sulphide or its oxidation products (see Section B(ii)).

In summary, the nickel dithiocarbamate electrochemistry encompasses a wide range of oxidation and reduction pathways. Figure 15 demonstrates

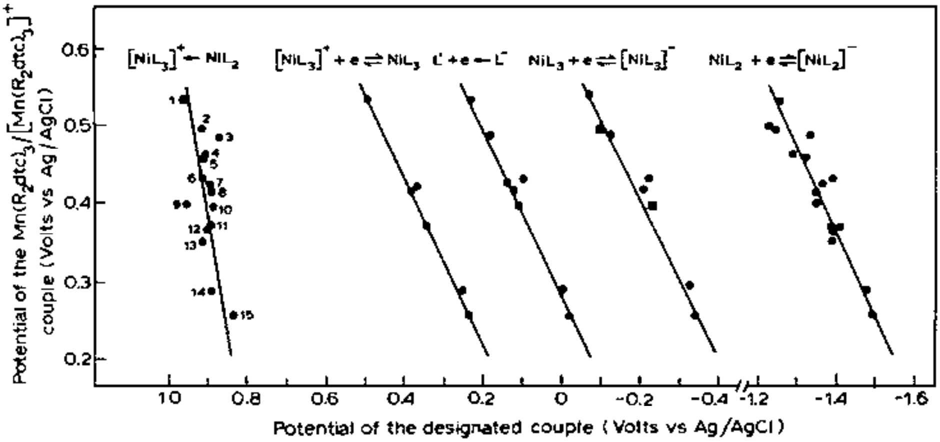


Fig. 15. Substituent effect on the designated couples compared with that of the corresponding substituent for the reversible $[Mn(R_2dtc)_3]^+/Mn(R_2dtc)_3$ couple. R_2 = 1, Bz_2; 2, Ph_2; 3, pyrr; 4, Ph, Me; 5, Ph, Et; 6, $(n\text{-}Bu)_2$; 7, Me_2; 8, Et_2; 9, 4-Mepip; 10, pip; 11, $(i\text{-}Bu)_2$; 12, 2-Mepip; 13, 2,6-Me_2pip; 14, $(i\text{-}Pr)_2$; 15, $(c\text{-}Hx)_2$. Reproduced by courtesy: Inorg. Chem., 14 (1975) 2980.

diagramatically the potentials of different electrode processes as a function of substituent. Clearly, the oxidation of $[R_2dtc]^-$ is a ligand-based step. The $Ni(R_2dtc)_2/[Ni(R_2dtc)_2]^-$ couple is metal-based as verified from ESR data presented earlier. $[Ni(R_2dtc)_3]^+$ has also been shown to be a nickel(IV) complex so that the redox couples relating the $[Ni(R_2dtc)_3]^{+,0,-}$ couples are also presumably metal-based. An important feature to emerge from Fig. 15 therefore is that differentiation between metal- and ligand-based electrode processes is not readily made from $E_{1/2}$ data obtained by varying substituents. The shifts in redox couple as shown in Fig. 15 are essentially parallel for all processes except for the oxidation of $Ni(R_2dtc)_2$ in eqn. 78 where the mechanism is uncertain and the significance of the substituent effects therefore not understood.

(vi) Electrochemistry of $Pd(R_2dtc)_2$, $[Pd(R_2dtc)_3]^+$, $Pt(R_2dtc)_2$ and $[Pt(R_2dtc)_3]^+$

The electrochemistry of palladium and platinum dithiocarbamates and their selenium analogues has been reported [150]. The oxidation of $Pd(R_2dtc)_2$ and $Pt(R_2dtc)_2$ occurs at considerably more positive potentials than that for $Ni(R_2dtc)_2$. With Pt the formation of $[Pt(R_2dtc)_3]^+$ is established by spectrophotometric monitoring of the electrolysis but a stoichiometric reaction (3 : 2) is not found as for the nickel(II) complex. It is likely that for Pt and Pd some of the intermediates presumably decompose before reaching the stage where $[Pt(R_2dtc)_3]^+$ or $[Pd(R_2dtc)_3]^+$ are formed.

Electrochemical reduction of $[Pt(R_2dtc)_3]^+$ and $[Pd(R_2dtc)_3]^+$ produces $Pt(R_2dtc)_2$ and $Pd(R_2dtc)_2$, respectively. With reduction of $[Ni(R_2dtc)_3]^+$, $Ni(R_2dtc)_3$ and $[Ni(R_2dtc)_3]^-$ are relatively stable intermediates on the electrochemical time-scale. With the corresponding Pt and Pd complexes a single two-electron reduction step is observed corresponding to the overall reaction

$$[Pt(R_2dtc)_3]^+ + 2\,e \rightarrow Pt(R_2dtc)_2 + [R_2dtc]^- \tag{86}$$

The mechanism for this reaction is unknown but the electrochemical behaviour is quite different from the nickel analogue, reflecting the different stability of the $M(R_2dtc)_3$ and $[M(R_2dtc)_3]^-$ intermediates for the triad.

The reduction of $Pd(R_2dtc)_2$ occurs in an analogous fashion to the nickel case [150]

$$Pd(R_2dtc)_2 \overset{\pm e}{\rightleftharpoons} [Pd(R_2dtc)_2]^- \tag{87}$$

although $[Pd(R_2dtc)_2]^-$ is not nearly as stable as $[Ni(R_2dtc)_2]^-$. With Pt no direct evidence exists, even on the electrochemical time-scale, for formation of $[Pt(R_2dtc)_2]^-$ although presumably it is formed as a transient intermediate. Reduction of the platinum complex occurs at very negative potentials and is accompanied by ligand loss. Other electrode processes associated with $Pt(R_2dtc)_2$ and $Pd(R_2dtc)_2$ redox chemistry have been reported but no details of products, etc. are available [150].

(vii) Electrochemistry of $Cu(R_2dtc)_2$

The reduction of $Cu(R_2dtc)_2$ at mercury electrodes has been reported in propylene carbonate [152]. At the dropping mercury electrode two well-defined one-electron reduction steps have been reported

$$Cu(R_2dtc)_2 \overset{\pm e}{\rightleftharpoons} [Cu(R_2dtc)_2]^- \overset{\pm e}{\rightleftharpoons} [Cu(R_2dtc)_2]^{2-} \tag{88}$$

$[Cu(R_2dtc)]^{2-}$ is unstable and the electrode processes are complicated by adsorption. In particular, interaction with mercury and mercury salts can occur

$$[Cu(R_2dtc)_2]^{2-} + Hg \rightleftharpoons Cu(Hg) + 2\,[R_2dtc]^- \tag{89}$$

$$Cu(R_2dtc)_2 + Hg(II) \rightleftharpoons Cu(II) + Hg(R_2dtc)_2 \tag{90}$$

and this needs to be included in the interpretation of electrochemical behaviour at mercury electrodes.

At platinum electrodes [11,12,54,153] well-defined reversible reduction and oxidation steps are observed.

$$[\mathrm{Cu}(\mathrm{R_2dtc})_2]^+ \overset{\pm e}{\rightleftharpoons} \mathrm{Cu}(\mathrm{R_2dtc})_2 \overset{\pm e}{\rightleftharpoons} [\mathrm{Cu}(\mathrm{R_2dtc})_2]^- \tag{91}$$

The data on $Cu(R_2dtc)_2$ again emphasize the remarkable ability of the $[R_2dtc]^-$ ligand to stabilize unusually high oxidation states, in this case Cu(III). Likewise the instability of $[Cu(R_2dtc)_2]^{2-}$ and many other lower oxidation state species of other metals, demonstrates that the high oxidation state stability is conferred at the expense of stability in the lower oxidation states.

(viii) Electrochemistry of some other dithiocarbamate complexes

The redox behaviour of a number of other dithiocarbamate complexes has been examined electrochemically. Of particular interest in this review is the oxidation of $M(R_2dtc)_2$ and $[M(R_2dtc)_3]^-$ ($M = Ba$, Zn, Cd and Hg) at platinum electrodes [154].

These complexes give rise to chemically irreversible oxidation processes. Since stable oxidation states such as Zn(III) or Cd(III) are extremely unlikely, it may be assumed that these are ligand-based processes leading to formation of thiuram disulphide, etc. (see eqn. 20). Unfortunately, these and many other irreversible oxidation electrode processes have not been sufficiently well characterized to confirm, unambiguously, this assumption. However, it does appear that, if no readily accessible higher oxidation state is available, the ligand, even when coordinated, will be oxidized to thiuram disulphide providing a sufficiently positive potential is applied. Consequently, virtually all dithiocarbamates are electroactive at a platinum electrode. Studies with chemical oxidants are consistent with this view [6].

At a mercury electrode, two reversible one-electron oxidation processes are observed in CH_2Cl_2 or acetone for a number of $Hg(R_2dtc)_2$ complexes [155]. Presumably elemental mercury from the electrode is involved in the redox process as is found for reduction (see Section B(i)). Oxidation of other dithiocarbamate complexes at a mercury electrode may involve exchange reactions [141] to form mercury complexes which leads to the observation that most metal dithiocarbamates can be oxidized at mercury. The mechanism of the electrode process in such cases will differ considerably from that at platinum and the high stability of $Hg(R_2dtc)_2$ generally makes the interpretation of polarographic data more complex.

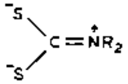
E. GENERAL CONCLUSIONS

(i) Stabilization of unusual oxidation states by dithiocarbamate ligands

The concept of an unusual oxidation state is rather ill-defined. However, by common practice it is usually regarded as an oxidation state which differs from that found when a metal is coordinated to simple σ-donor ligands such as water and other oxygen donors, etc. [156]. For example, with iron the usual oxidation states are (II) and (III) since $[Fe(H_2O)_6]^{3+}$ and $[Fe(H_2O)_6]^{2+}$ are stable in aqueous solutions. On this basis, the existence of an Fe(IV), Fe(I) or Fe(0) dithiocarbamate complex would be taken to imply that dithiocarbamate has an ability to stabilize iron in an unusual oxidation state.

With fluoride as a ligand, complexes such as $[FeF_6]^{2-}$, $[CuF_6]^{3-}$, $[NiF_6]^{3-}$ and $[NiF_6]^{2-}$ are well known [156]. These are iron(IV), copper(III), nickel(III) and nickel(IV) complexes, the high oxidation states being stabilized by the high electronegativity of fluorine. In this review it has been demonstrated that both chemical and electrochemical studies confirm that analogous complexes exist with dithiocarbamate as the ligand and X-ray crystal structures have established the existence of $[Fe(R_2dtc)_3]^+$, $[Cu(R_2dtc)_2]^+$ and $[Ni(R_2dtc)_3]^+$. Accordingly a distinct parallel exists with fluoride in regard to the complexes formed. However, dithiocarbamate does not possess the high electronegativity of fluorine and the question arises as to why it is effective in stabilizing high oxidation states.

According to Jørgensen [157] the position of diethyldithiocarbamate in the spectrochemical series lies between fluoride and water. Other spectral and ligand field parameters [158] are consistent with dithiocarbamate lying towards the fluoride end of the spectrochemical series so that the ability to stabilize high oxidation states should not be unexpected. The relevant feature of dithiocarbamate is the resonance form (**22**) which has a positive charge on



22

the nitrogen. The net effect of this π-electron flow from nitrogen to the sulphur atoms is a ligand with very strong electron σ-donor properties. This can transfer electron density to the metal and therefore stabilize a high oxidation state.

Russian workers [65,66,85,111,121,140,148,149], in their electrochemical reduction studies of transition metal dithiocarbamates, frequently refer to the instability of low oxidation state dithiocarbamate complexes. They also rationalize this in terms of dithiocarbamate being a ligand with strong σ-donor properties which does not favour formation of low oxidation states.

Addition of π-acceptor ligands such as bipyridine to electrochemically reduced solutions of $M(R_2dtc)_n$ complexes leads to isolation of stable mixed dithiocarbamate complexes, π-acceptor ligands being well-known for their ability to stabilize low oxidation states. In the Russian work the electrochemical and other data establish that low oxidation state dithiocarbamate complexes do exist as precursors to the final product containing the π-acceptor ligand. Thus it is clear that dithiocarbamate complexes in unusually low oxidation states do exist, but they are unstable relative to their higher oxidation state analogues.

With dithiophosphinate complexes [8], π-electron flow can occur from sulphur to the empty *d* orbitals of the phosphorus atom thereby stabilizing a low oxidation state of a transition metal (see **23a** and **23b**). Thus polarographic reduction of mercury dithiocarbamate and mercury dithiophosphinate complexes to elemental mercury, and the free ligand [24] demonstrates how much more difficult it is to break the mercury–sulphur bond in the case of the dithiocarbamate complex.

(a) (b)

23

Electrochemical data for dithiocarbamate complexes are therefore consistent with the concept of strong σ-donor properties dominant over weak π-back donation thereby producing complexes that are relatively easy to oxidize and conversely hard to reduce. Other 1,1-dithiolates are not expected to have such strong electron donor properties unless they can readily form the resonance stabilized dianionic form.

Having reached the above conclusion, it should be emphasized that dithiocarbamate complexes are not confined to high oxidation states. They exist in a wide range of oxidation states including those which can be described as unusually low oxidation state complexes. Thus the nickel(I) species $[Ni(R_2dtc)_2]^-$ has been well-characterized by ESR experiment [151] and a copper(I) species $[Cu(R_2dtc)_2]^-$ certainly appears to exist. What the electrochemical data demonstrate unambiguously is that the low oxidation state complexes are reactive species and therefore not readily isolable as stable solids.

(ii) Origins of irreversible electrode processes in electrochemical studies of dithiocarbamate complexes

In all instances where data have been carefully examined, the standard rate of electron transfer, k_s, at E^0 has been found to be rapid for oxidation or reduction of transition metal dithiocarbamates [159–161]. From the electron transfer point of view, electrode processes are therefore reversible or close to reversible, and this applies whether the complexes are kinetically labile or not. For example, both $Fe(R_2dtc)_3$ in which rapid ligand exchange is present (see Fig. 5) and $Co(R_2dtc)_3$ complexes in which no ligand exchange occurs [162] give reversible electron transfer processes. With many sulphur chelates heterogeneous electron transfer rates tend to be considerably faster at mercury than at platinum electrodes [163,164]. This also appears to be true for dithiocarbamate complexes, although strong adsorption frequently complicates studies at mercury electrodes.

Departure from reversibility frequently has its origin in a structural rearrangement in dithiochelate electrochemistry. Irreversibility associated with oxidation has been found in some cases to involve an increased coordination number. For example, with six-coordinate $Os(R_2dtc)_3$ and $Ru(R_2dtc)_3$ complexes in acetonitrile, electrochemical oxidation leads to the seven-coordinate complexes $[Os(R_2dtc)_3(CH_3CN)]^+$ and $[Ru(R_2dtc)_3(CH_3CN)]^+$, respectively. Similarly, in the presence of adventitious water, the electrochemical oxidation of $V(R_2dtc)_3$ is also chemically irreversible because of the reaction in eqn. 62

$$[V(R_2dtc)_3]^+ + H_2O \rightarrow [V(R_2dtc)_3(H_2O)]^+$$

which follows the charge transfer step. Dimer–monomer equilibria involving formation of a seven-coordinate species may also accompany the oxidation step (eqn. 59)

$$2\,[Os(R_2dtc)_3]^+ \rightleftharpoons [Os_2(R_2dtc)_6]^{2+}$$

Oxidation of four-coordinate $Ni(R_2dtc)_2$ leads to formation of the six-coordinate complex $[Ni(R_2dtc)_3]^+$, although in this instance the mechanism for the reaction is unclear.

Most high oxidation state dithiocarbamates are electrochemically generated at a potential more positive than that for oxidation of the free ligand to thiuram disulphide. Thermodynamically, this is consistent with the observation that reactions of the kind (eqn. 36)

$$2\,[Fe(R_2dtc)_3]^+ + 2\,[R_2dtc]^- \rightarrow 2\,Fe(R_2dtc)_3 + R_4tds$$

occur spontaneously. Irreversible oxidation processes therefore frequently have their origin in the formation of thiuram disulphide. Oxidation of $Hg(R_2dtc)_2$, $Cd(R_2dtc)_2$ and $Zn(R_2dtc)_2$ at a platinum electrode probably occurs with formation of R_4dts and Hg(II), Cd(II) or Zn(II), respectively and clearly is ligand based.

Many other irreversible oxidation processes also show evidence of formation of oxidized ligand species (eqns. 18–20). For example, oxidation of $Co(R_2dtc)_3$ or $Ru(R_2dtc)_3$ in acetone or dichloromethane at a platinum electrode leads to isolation of the dimers $[M_2(R_2dtc)_5]^+$ (M = Co, Ru) and oxidized ligand. Dimers of this stoichiometry are also encountered in chemical oxidation based on aerobic BF_3. However, the same chemical reaction with the more easily oxidized $Fe(R_2dtc)_3$ or $Mn(R_2dtc)_3$ leads to $[Fe(R_2dtc)_3]^+$ or $[Mn(R_2dtc)_3]^+$, respectively. Generation of $[M(R_2dtc)_3]^+$ in an initial step can readily lead to formation of $[M_2(R_2dtc)_5]^+$ via subsequent reaction of $[M_2(R_2dtc)_3]^+$ and $M(R_2dtc)_3$ and an internal redox reaction as in reaction scheme (92)

$$M(R_2dtc)_3 \overset{\pm e}{\rightleftharpoons} [M(R_2dtc)_3]^+$$

$$[M(R_2dtc)_3]^+ + M(R_2dtc)_3 \rightleftharpoons [M_2(R_2dtc)_6]^+$$

$$[M_2(R_2dtc)_6]^+ \rightarrow [M_2(R_2dtc)_5]^+ + R_2dtc\cdot$$

$$2R_2dtc\cdot \rightarrow R_4tds$$

$$R_4tds \rightarrow [bitt]^{2+} + S + 2\,e \qquad (92)$$

Alternatively, the initially generated cation may undergo an intramolecular electron transfer reaction to produce a coordinatively unsaturated species which can react with the starting material (reaction scheme 93),

$$[M(R_2dtc)_3]^+ \rightarrow [M(R_2dtc)_2]^+ + \tfrac{1}{2}R_4dts$$

$$[M(R_2dtc)_2]^+ + M(R_2dtc)_3 \rightarrow [M_2(R_2dtc)_5]^+ \qquad (93)$$

Although the mechanism for this binuclear complex formation is unknown, it is clear that when the E^0 value for the $[M(R_2dtc)_3]^+/M(R_2dtc)_3$ couple is significantly more positive than that for oxidation of the ligand at a platinum electrode, the formation of the binuclear complex, R_4tds and/or $[bitt]^{2+}$ is to be expected. Thermodynamically, this is the favoured reaction pathway.

On the other hand, the most common reason for an irreversible reduction process appears to be loss of $[R_2dtc]^-$ and the concomitant formation of a metal complex of a lower coordination number. Thus in dichloromethane, the irreversible processes given in eqns. 68 and 75 result in loss of ligand

$$M(R_2dtc)_3 \overset{\pm e}{\rightleftharpoons} [M(R_2dtc)_3]^- \rightarrow M(R_2dtc)_2 + [R_2dtc]^-$$

$$M(R_2dtc)_2 + 2\,e \rightarrow M + 2\,[R_2dtc]^-$$

where M = Cr or Co.

The lower oxidation state anionic dithiocarbamate complexes are kinetically labile and loss of ligand frequently occurs on the electrochemical time-scale. Dithiocarbamate complexes, whilst generally easy to oxidize are frequently very difficult to reduce, and therefore very air-sensitive. Consequently, whilst electrochemical data indicate that anionic complexes such as $[Fe(R_2dtc)_3]^-$, $[Ni(R_2dtc)_2]^-$, $[Cu(R_2dtc)_2]^-$, $[Mn(R_2dtc)_3]^-$, etc. should be stable, they have rarely been well-characterized because of air sensitivity and kinetic lability. In the solid state, the neutral species such as $Fe(R_2dtc)_2$, $Co(R_2dtc)_2$ and CuR_2dtc have been characterized by X-ray structural analysis and are frequently dimeric, tetrameric, hexameric, or even higher oligomers.

Metal-based reduction of a complex leads to additional electron density in the metal. The electron donor properties of $[R_2dtc]^-$ are substantial so that ligand loss provides an obvious route to lowering the electron density associated with the metal. Oligomer formation is also an energetically favourable process assisting ligand loss and minimizing the degree of coordination unsaturation. Electrochemical data provide no evidence that $[R_2dtc]^-$ itself can be reduced within accessible potential ranges so that ligand- rather than metal-based reduction does not appear to be energetically favoured.

(iii) Comparison of electrochemical behaviour of dithiocarbamate(1,1), dithiolene(1,2) and dithioacetylacetonate(1,3) complexes

From an electrochemical point of view, it can be demonstrated that the redox processes of both "odd" π-ligand systems such as 1,1-dithiocarbamates and 1,3-dithioacetylacetonates (SacSac) and "even" systems such as the 1,2-dithiolenes are governed by the kinetics, thermodynamics and structural factors related to the ligands. These can be far more important than the electron configuration of the ligand. Figure 16 shows a cyclic voltammogram for reduction and oxidation of $Ni(SacSac)_2$. A chemically reversible reduction step (eqn. 94) occurs and clearly this reaction is similar to the reversible

$$Ni(SacSac)_2 \overset{\pm e}{\rightleftharpoons} [Ni(SacSac)_2]^- \tag{94}$$

reduction of the $Ni(R_2dtc)_2$ complex (eqn. 76). However, $Ni(SacSac)_2$ is generated at much more negative potentials and the electrochemistry of the free $[SacSac]^-$ ligand, as noted in the Introduction, provides evidence for the existence of a $[Ph{-}Sac\ Ph{-}Sac]^{2-}$ dianion at accessible potentials. Consequently, with $[SacSac]^-$ as a ligand, lowering of charge via transfer of electron density onto the ligand can provide stabilization. With $[R_2dtc]^-$ this pathway is apparently less accessible and ligand loss occurs to achieve the same goal. Reduction of dithioacetylacetonate complexes on some occasions may therefore be ligand-based [15]. However, some examples where the reduction is clearly metal based are also available [165].

$$M(SacSac)_3 \overset{\pm e}{\rightleftharpoons} [M(SacSac)_3]^- \quad (M = Fe, Ru, Os) \tag{95}$$

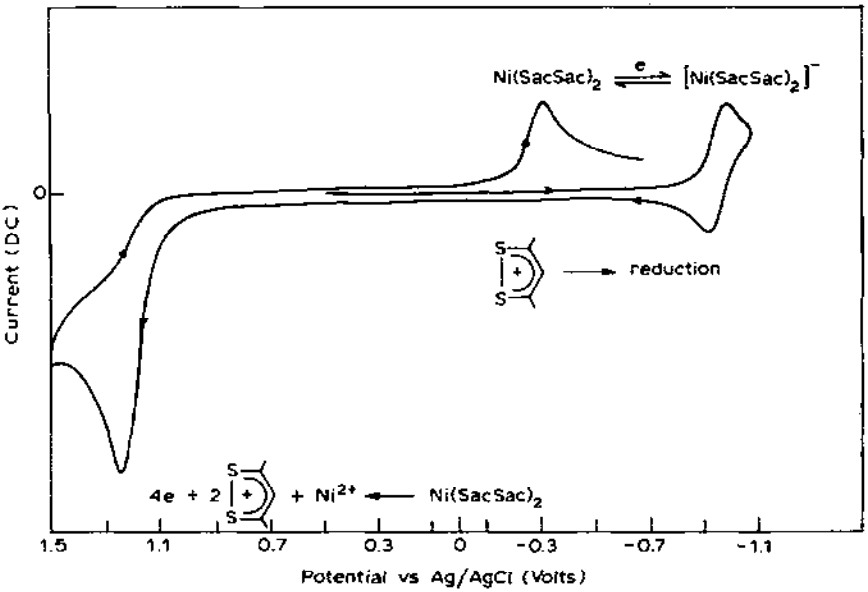


Fig. 16. Cyclic voltammogram of Ni(SacSac)$_2$ in acetone (0.1 M Et_4NClO_4). Reference electrode is Ag/AgCl (acetone, 0.1 M LiCl). Reproduced by courtesy: Inorg. Chem., 14 (1976) 1118.

Additionally, with Co(SacSac)$_3$ the cobalt(II) species is produced with loss of ligand [166].

$$\mathrm{Co(SacSac)_3} \overset{\pm e}{\rightleftharpoons} [\mathrm{Co(SacSac)_3}]^- \rightarrow \mathrm{Co(SacSac)_2} + [\mathrm{SacSac}]^- \qquad (96)$$

This is a characteristic expected in the dithiocarbamate electrochemistry where the reduction is metal-based. Hence, whether the reduction step

$$\mathrm{Co(SacSac)_2} \overset{\pm e}{\rightleftharpoons} [\mathrm{Co(SacSac)_2}]^- \qquad (97)$$

is metal or ligand based has yet to be ascertained.

In Fig. 16 the oxidation of Ni(SacSac)$_2$ is clearly irreversible and very different from the oxidation of Ni(R$_2$dtc)$_2$. This is a four-electron oxidation resulting in formation of the dithiolium and nickel(II) cations [167].

$$\mathrm{Ni(SacSac)_2} \rightarrow \mathrm{Ni^{2+}} + 2\,[\mathrm{C_5H_7S_2}]^+ + 4\,\mathrm{e} \qquad (98)$$

Many oxidation steps for SacSac complexes result in the formation of the dithiolium cation [168] and indeed this species invariably produces the major peak in mass spectrometry [9,168–170], reflecting the high stability of the resonance-stabilized cation.

The frequent generation of the dithiolium cation on electrochemical

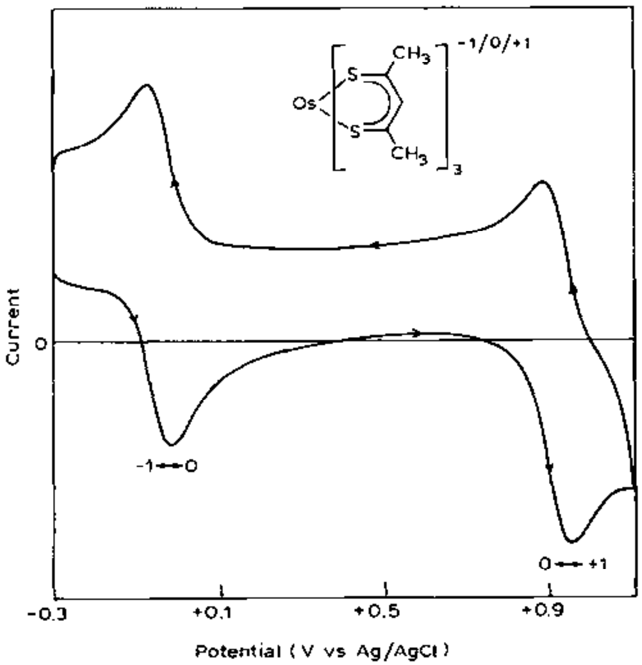


Fig. 17. Cyclic voltammogram for reduction and oxidation of $Os(SacSac)_3$ in acetone (0.1 M Et_4NClO_4) at a scan rate of 50 mV s^{-1}. Reference electrode as for Fig. 16. Reproduced by courtesy from ref. 171.

oxidation of 1,3-dithio complexes does not necessarily mean that 1,3-ligands are unable to stabilize unusually high oxidation states nor does it mean that oxidation steps are necessarily ligand based. Data now available indicate that formation of the dithiolium cation is kinetically very fast and probably occurs via oxidation at relatively negative potentials. Resonance stabilization associated with the cyclized cation occurs as the preferred pathway to dimerization of the kind associated with the generation of thiuram disulphide. It is the very high stability of the dithiolium cation which mitigates against isolation of unusually high oxidation state thioacetylacetonate complexes and not any other unusual characteristic associated with its electronic configuration. Thus Fig. 17 demonstrates that provided the thiophilic osmium is used, electrochemical and chemical reversible oxidation and reduction can be observed [171]

$$[\mathrm{Os(SacSac)_3}]^+ \overset{\pm e}{\rightleftharpoons} \mathrm{Os(SacSac)_3} \overset{\pm e}{\rightleftharpoons} [\mathrm{Os(SacSac)_3}]^- \tag{99}$$

Furthermore, with $Pt(SacSac)_2$ the electrochemically reversible oxidation is

$$\mathrm{Pt(SacSac)_2} \overset{\pm e}{\rightleftharpoons} [\mathrm{Pt(SacSac)_2}]^+ \tag{100}$$

also observed under conditions of cyclic voltammetry [15]. This high formal oxidation state complexes of dithioacetylacetone can be produced provided that either the internal redox process generating a dithiolium cation can be suppressed with a thiophilic metal or by employing a short time-scale electrochemical measurement method.

From the above it can be seen that the question of whether electron transfer steps are metal or ligand based is not governed solely by whether ligand steps such as

$$L^{2+} \overset{\pm e}{\rightleftharpoons} L^{+} \overset{\pm e}{\rightleftharpoons} L^{0} \overset{\pm e}{\rightleftharpoons} L^{-} \overset{\pm e}{\rightleftharpoons} L^{2-} \qquad (101)$$

exist, where L^{2+}, L^{+}, L^{0}, L^{-} and L^{2-} are isostructural. In the same way as oligomerization of a metal complex such as $[Cu(R_2dtc)]_4$ enhances the stability of the copper(I) oxidation state, so dimerization

$$2[R_2dtc]^{-} \rightarrow R_4tds + 2\,e$$

or cyclization

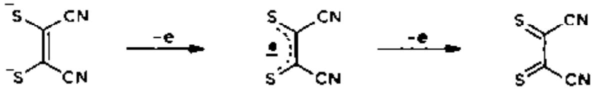
$$[SacSac]^{-} \rightarrow [C_5H_7S_2]^{+} + 2\,e$$

can lead to ligand oxidation as an alternative to the stabilization of unusually high oxidation states.

With 1,2-dithiolene complexes, extended electron transfer reactions can be observed. For example, when mnt (mnt = maleonitriledithiolate i.e. **6** with R = CN) is used as the ligand it is possible (Fig. 18) to produce a reversible reduction step [172]

$$[M(mnt)_2]^{2-} \overset{\pm e}{\rightleftharpoons} [M(mnt)_2]^{3-} \quad (M = Ni, Pd, Pt) \qquad (102)$$

in addition to ligand-based oxidation steps



(103)

The reduction step occurs at a very negative potential and has been shown by ESR to be metal based [172–174] as is the case for reduced $Ni(R_2dtc)_2$. On oxidation, a series of reversible steps is observed

$$[M(mnt)_2]^{2-} \overset{\pm e}{\rightleftharpoons} [M(mnt)_2]^{-} \overset{\pm e}{\rightleftharpoons} M(mnt)_2 \qquad (104)$$

which have been shown to be ligand-based (see eqn. 103). With the dithiolene complexes dimerization (e.g. dithiocarbamates) or cyclization (e.g. dithioacetylacetonates) is not observed. However, when the ligand is coordinated valence isomerization can transfer electron density from the metal to the ligand as is the case with some macrocycles [175] so that any one of the

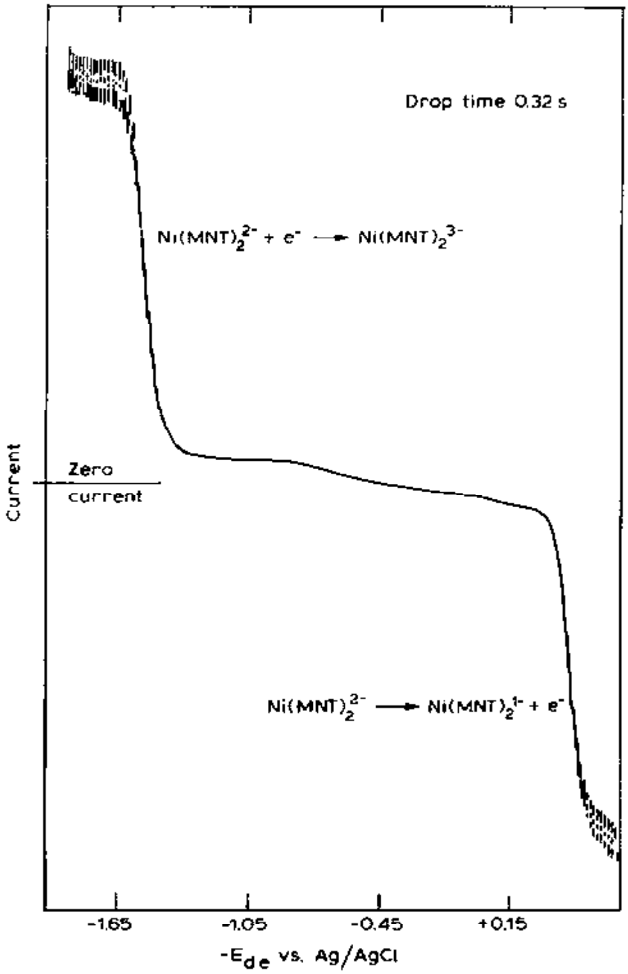
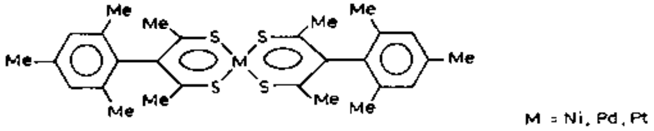


Fig. 18. Polarographic reduction and oxidation of $[Ni(mnt)_2]^{2-}$ at the dropping mercury electrode (drop time = 0.32 s) in acetone (0.1 M Et_4NClO_4). Reference electrode as for Fig. 16. Reproduced by courtesy from ref. 172.

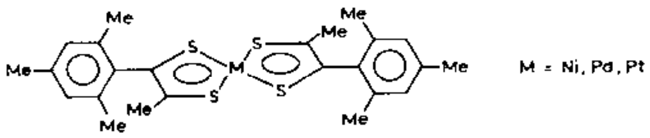
forms mnt$^+$, mnt and mnt$^-$ may be regarded as being coordinated to the metal. This intraligand redox capacity has been recognized for many years and is best exemplified by the classical quinone–semiquinone–hydroquinone series. If such organic compounds are effective ligands, then extended electron transfer reactions are expected in their metal complexes.

Complexes of 1,1-, 1,2- or 1,3-dithioligands therefore, exhibit redox behaviour which is readily rationalized from a structural point of view. However, the "odd" versus "even" classification of ligands, whilst being useful, can lead to difficulties if it is pursued too far.

The extent of electron delocalization in transition metal complexes has been widely discussed in many other areas of chemistry. Redox properties provide only an indirect guide and this has caused many difficulties in deciding whether an electron transfer reaction is ligand or metal based or whether there are fundamental differences between "odd" and "even" π-ligand systems. Musso and co-workers [176] have developed a semi-quantitative probe to examine cyclic electron delocalization. The basis for this technique is the NMR chemical shift difference $\Delta\delta$ with the *o*- and *p*-methyl groups of a methyl substituent attached to a ring system. Delocalized π-systems have values of $\Delta\delta > 0.30$ p.p.m. and localized π-systems have $\Delta\delta$ values < 0.30 p.p.m. Nazzal and Mueller-Westerhoff [177] have applied this technique to the 1,3-dithioacetylacetonate and 1,2-dithiolene complexes shown in structures **24** and **25**. As stated in the Introduction the dithioacetylacetonates, **24**, are examples of "odd" and the dithiolenes, **25**, of "even" complexes. It has been postulated by Schrauzer [4,10] that all the "even" ligand complexes should be fully delocalized. On the other hand, Musso and co-workers have shown [178,179] that in the "odd" ligand acetylacetonates of different transition and non-transition metals, only delocalization within the ligand anion exists and no cyclic electron delocalization extends to the metal. In this respect the parent M(SacSac)$_2$ species of the dithioacetylacetonato complexes [180] differ greatly from the acetylacetonates. Using the same NMR technique to examine the aromaticity of a range of components led the authors [179] to conclude that all complexes, "even" or "odd", with sulphur-containing conjugated ligands will show a considerable degree of cyclic electron delocalization. NMR data on **24** and **25** support this conclusion. All of the SacSac derivatives show the same $\Delta\delta$ of ca. 0.32 p.p.m., which, according to the criteria developed by Musso and co-workers [178,179], places them in the category of "aromatic" species. In the dithiolene series the nickel complex stands out as being strongly delocalized ($\Delta\delta = 0.40$ p.p.m.) while the Pd and Pt congeners with $\Delta\delta$ of 0.31 and 0.34 p.p.m., are similar in



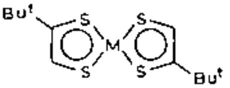
24



25

the amount of delocalization to their SacSac analogues. In view of Schrauzer's arguments [4,10] referred to in the Introduction, this result is surprising because, seeing that the nickel complex approaches benzene ($\Delta\delta = 0.46$ p.p.m.) in its aromaticity, all dithiolene complexes [2] would be expected to be much more delocalized than their "odd" ligand SacSac analogues. Clearly, this is not the case.

A comparison of proton NMR spectra [177] of $M(SacSac)_2$ (M = Ni, Pd, Pt) with those of the t-butyl substituted dithiolenes (**26**) also reveals that the



26

NMR shifts are dominated by charge distribution rather than by cyclic electron delocalization.

The conclusion to be drawn from these NMR results is that the merit of the "even"/"odd" distinction, as originally proposed by Schrauzer [4,10], lies in the clear and correct topological differentiation between these two types of complexes, but that these differences manifest themselves only in properties which directly depend on the symmetry characteristics of the entire molecule. Stability and cyclic electron delocalization evidently do not fall into this category [177].

The NMR data have profound implications for electrochemistry. Numerous papers have described the electrochemistry of mixed 1,1- and 1,2-; 1,1- and 1,3-; and 1,2- and 1,3-complexes. In each case the measured parameters are very close to the average value for the two different ligands, i.e. the "even" versus "odd" characteristics are averaged over the metal complex. Data on the $[Ni(SacSac)(mnt)]^-$ species [167] strongly support this suggestion. Mixed 1,1- and 1,2-complexes [11,12] also exhibit averaged behaviour for a large range of properties including electrochemical data.

(iv) Substituent effects

The data available strongly support the hypothesis that redox properties of dithiochelates are closely allied to charge distribution associated with the metal–ligand system. However, extrapolation from the NMR data referred to above suggests that electrochemical properties are unlikely to enable distinctions to be made as to the extent of the cyclic electron delocalization over the metal–ligand system. Nevertheless, the charge distribution is of great importance and a large E^0 dependence can be expected on the R group of the ligand, irrespective of whether the redox process is metal- or ligand-based or on the extent of electron delocalization. It is well established that substituent effects observed in electrochemistry depend directly on the electron withdrawing or electron donating effect of the substituent [181]. The same dependence is found in the electrochemistry of 1,1-, 1,2- or 1,3-dithio transition metal complexes because the charge distributions between metal and ligand are altered in a similar manner. Thus, the dependence of redox potential on substituent provides no evidence on whether the oxidation or reduction is ligand- or metal-based (cf. Fig. 15).

Figures 6, 15 and 19–22 provide examples of the substituent effect for several "even" and "odd" systems. For a given class of compound, large electrode potential ranges are available by varying the R group. Note that the magnitude of the substituent effects for dithiocarbamate complexes are similar, being essentially independent of the metal.

References 9 and 54 summarize the dithiocarbamate and dithioacetylacetonate $E_{1/2}$ data, respectively, for a range of metals bound to the same ligand. For both the 1,1- and 1,3-dithiochelates the considerable influence of the metal is noted and this is also true for the 1,2-chelates. Clearly both the R group (organic) and metal group influence the $E_{1/2}$ value. Figure 23

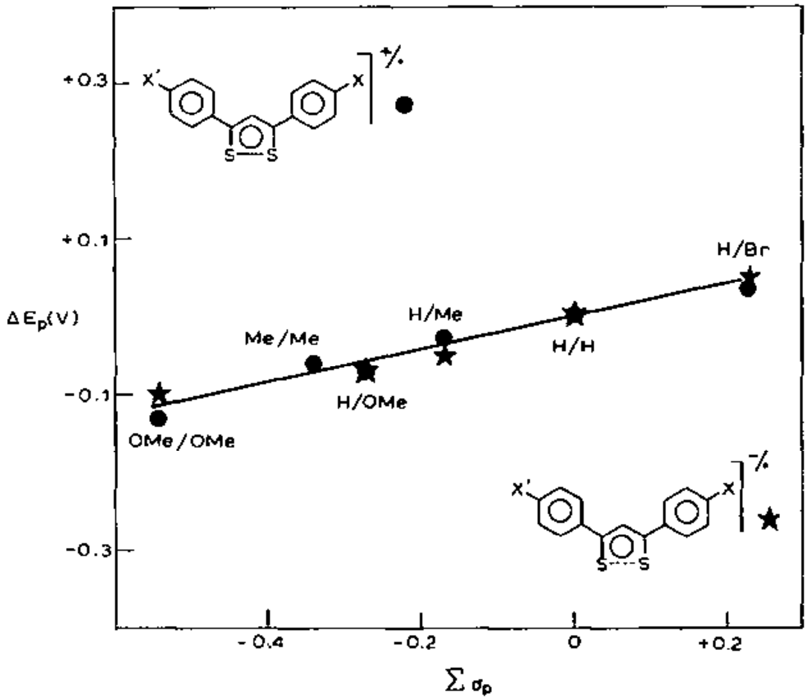


Fig. 19. Substituent dependence of the reduction potentials of aryl-substituted dithio-β-diketonate anions. $\Delta E_p = E_{1/2}$ referred to that of phenyl-substituted derivative ($X = X' = H$ as zero, σ_p = substituent coefficient from ref. 181). ΔE_p values calculated from data in ref. 45. Reproduced by courtesy from ref. 171.

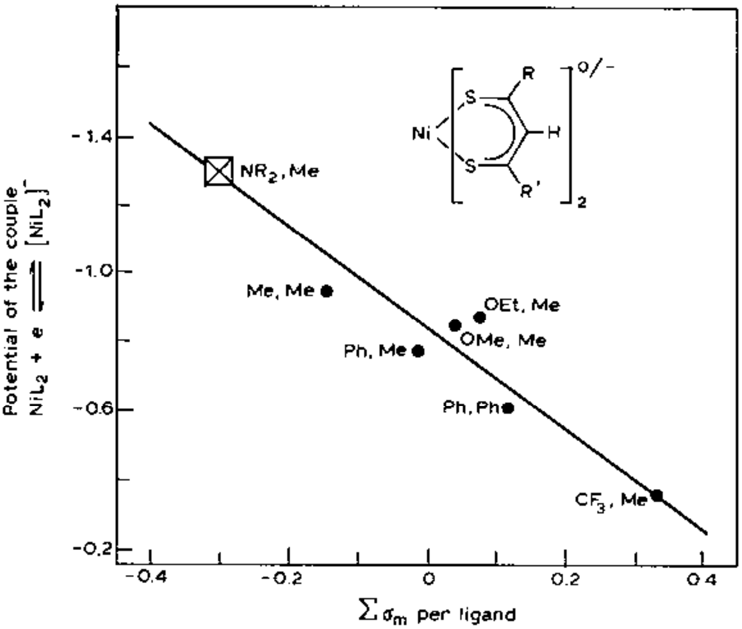


Fig. 20. Correlation between substituent effects (approximated by the Taft parameter $\Sigma\sigma_m$) and the reduction potentials of Ni(R–Sac R′–Sac)$_2$. Reproduced by courtesy: Inorg. Chem., 15 (1976) 1118.

demonstrates that in many respects the $E_{1/2}$ values for the dithiocarbamate complexes follow the expected pattern for a metal-based system. However, analogous plots can be generated for dithioacetylacetonate complexes where some of these redox processes are partially ligand-based. The question therefore arises as to whether electrochemical data may be used to distinguish between metal- and ligand-based redox behaviour or between "odd" and "even" ligand systems. This question has led to substantial ambiguities and difficulties, the extent of which was alluded to in the Introduction. Two specific examples discussed in further detail below highlight the extent of the problems that have arisen.

In the first example Saji and Aoyagui [182] have suggested that a linear relationship between half-wave potential for the reduction of a transition metal complex and its free ligand is indicative that the electrochemical reduction occurs via a molecular orbital mainly composed of the ligand π^* orbital. They then argue that this holds for three particular ligands when coordinated to Fe, Ru and Os. Unfortunately, the alternative interpretation (i.e., a metal-based redox step) has not been shown by them to disobey the same relationship. Indeed, if the oxidation potentials of the dithiocarbamate ligand are plotted against the metal-based redox processes of the same

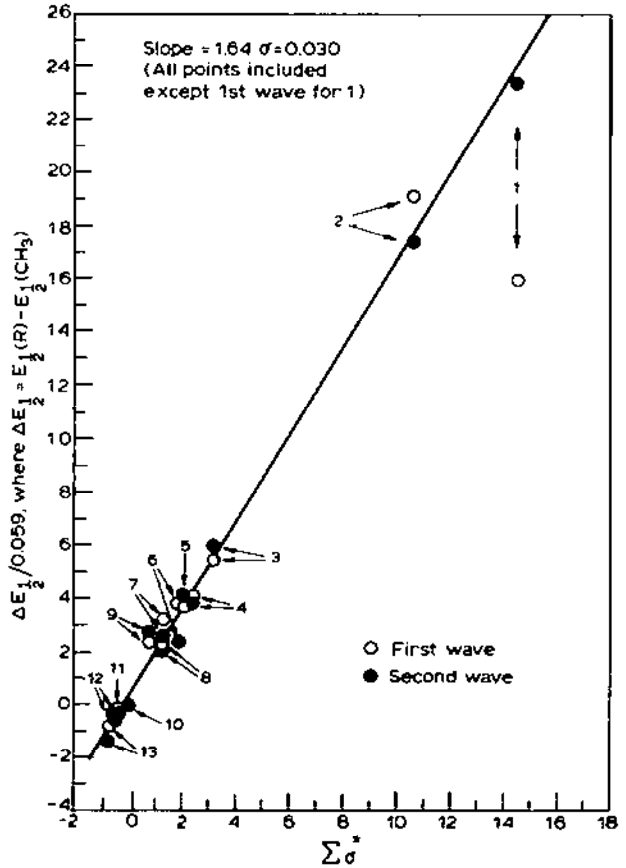


Fig. 21. Plot of $\Delta E_{1/2}$ (0.059) vs. Taft's substituent constant weighted for number of R groups present for $Ni(S_4C_4R_4)$ complexes. R = 1, CN; 2, CF_3; 3, p-C_6H_4Cl; 4, C_6H_5; 5, $NiS_4C_4Ph_2H_2$; 6, H; 7, p-$C_6H_4CH_3$; 8, $NiS_4C_4(CH_3)_2Ph_2$; 9, p-$C_6H_4OCH_3$; 10, CH_3; 11, C_2H_5; 12, n-C_3H_7; 13, i-C_3H_7. Reproduced by courtesy: Transition Met. Chem., 4 (1968) 299.

ligands, the linear correlation shown in Fig. 15 is obtained, confirming that plots of this type do not illuminate the mechanism of reduction or oxidation processes.

In the second example, Patterson and Holm [17] expressed surprise both at the ease and the reversibility of reduction of the Ru(III)/Ru(II) couple for some substituted M(III) acetylacetonates and related complexes. They also determined the influence of substituents by comparing the polarographic behaviour of a range of Ru(III) compounds. Linear correlations of $E_{1/2}$ and substituent parameters (Hammett or Taft functions) were reported (Fig. 22) and $E_{1/2}$ values encompassing a range of almost 2.0 V were found.

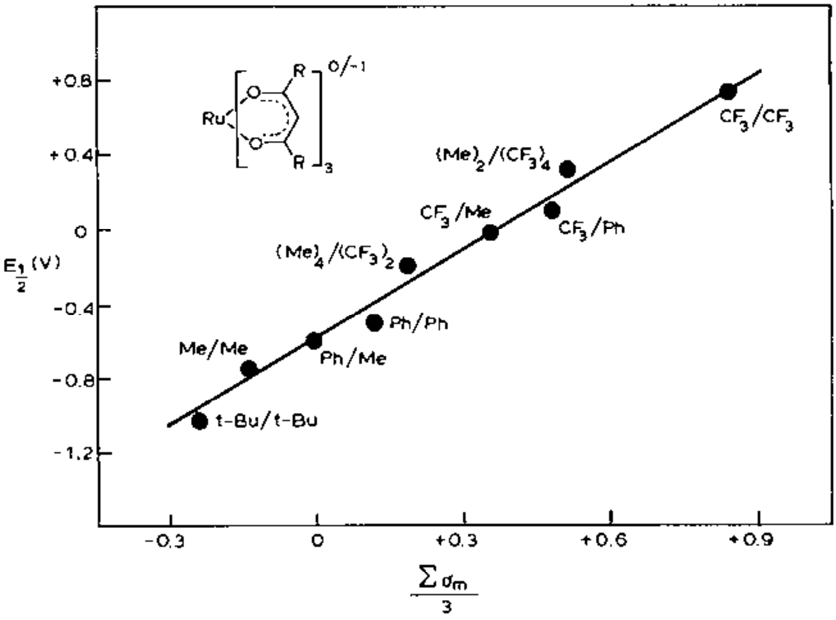


Fig. 22. Substituent dependence of $E_{1/2}$ for ruthenium tris (β-diketonato) complexes. σ_m values from ref. 181, $E_{1/2}$ values from ref. 17. Reproduced by courtesy from ref. 171.

The most electron-withdrawing substituents gave the most readily reduced species, i.e. the most positive $E_{1/2}$ values. Presumably their surprise arose because the electrochemical behaviour observed with oxygen donor ligands and an "odd" π-electron system was remarkably similar to that found in dithiolene chemistry and this was not anticipated, i.e. reversible electrochemistry with large substituent effects. It has been erroneously assumed in the past that a close relationship between substituent effects and free energy ($E_{1/2}$ values) when found for organometallic complexes implies that the reducing electrons are added to an orbital possessing substantial ligand character. For purely organic systems the effect of a substituent on $E_{1/2}$ can be derived on sound theoretical grounds, but the extension to inorganic complexes requires careful consideration as linear relationships are observed independently of whether the redox process is metal- or ligand-based.

In summary it should be noted that: (1) regardless of the "even" or "odd" nature of the system, most dithio chelates exhibit to some extent a series of one-electron redox steps. Hence the absence or presence of a series of redox steps is not a reliable criterion for distinguishing "odd" and "even" systems; (2) chemical and electrochemical reversibility or irreversibility is observed with all classes of dithio chelates. The reversibility of an electrode process is determined primarily by k_s and the presence or absence of coupled chemical

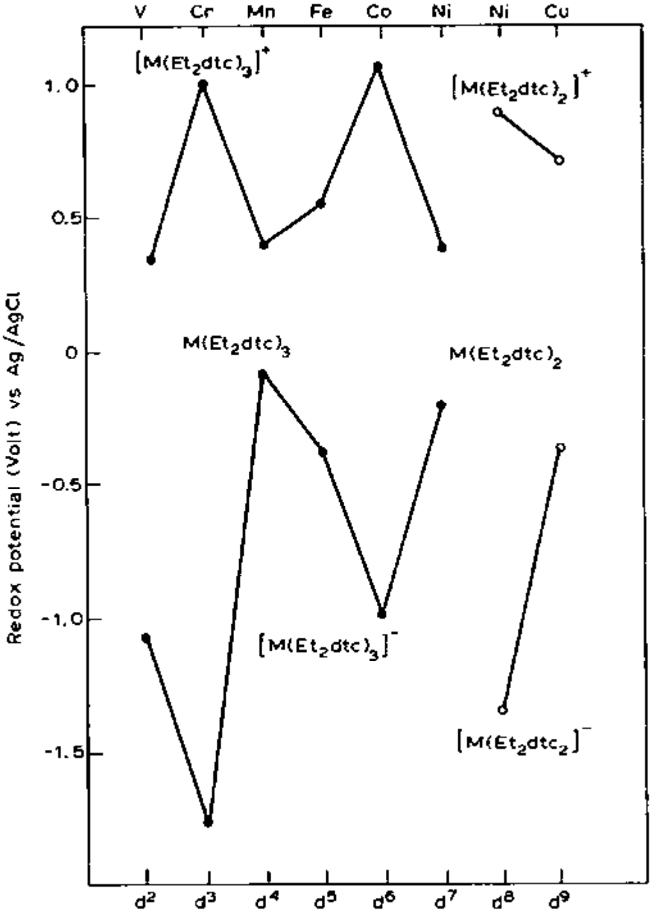


Fig. 23. Correlation diagram of redox potential with 3*d* orbital population.

reactions and their rates as noted earlier. These considerations are unique for each redox system and arise irrespective of whether the redox process is metal- or ligand-based; (3) substituent effects on the redox potential of related couples are observed for each class of ligand, e.g. the 1,2-dithio couple, $[Ni(S_2C_2R_2)_2]^- \overset{\pm e}{\rightleftharpoons} [Ni(S_2C_2R_2)_2]^{2-}$ and the 1,1-dithio couple, $Mn(R_2dtc)_3 \overset{\pm e}{\rightleftharpoons} [Mn(R_2dtc)_3]^-$ are representative despite the fact that the redox couples are effectively ligand- and metal-based, respectively. Thus the observation of a large substituent effect does not enable an assignment of the metal- or ligand-based nature of the electrode process to be made; (4) charge effects are very important and contribute significantly to the $E_{1/2}$ value independently of whether the electrode process is metal- or ligand-based.

The observation of reversible electrochemical behaviour only requires that two species A and B exist (assuming the stoichiometry of eqn. 6) related by transfer of an electron and that the reaction is in equilibrium at all potentials. The presence of low-lying metal or ligand orbitals is not relevant to the argument of whether or not reversible electrochemical behaviour should be observed. The polarographic $E_{1/2}$ value is closely related to E^0. Using the well-known relationship

$$-\Delta G^0 = nFE^0 = RT \ln K \tag{105}$$

where K describes the equilibrium under consideration leads to the conclusion that $E_{1/2}$ is a measure of a free energy or an equilibrium term, i.e. $E_{1/2}$ under reversible conditions has thermodynamic significance. Thus

$$E_{1/2} = \text{constant} + \frac{RT}{nF} \ln \frac{[\mathrm{A}]}{[\mathrm{B}]} \tag{106}$$

where the constant includes terms derived from the reference electrode. The value of $E_{1/2}$ is simply determined by the equilibrium position or the relative stability of the two species A and B involved in the half cell. Any variable influencing the thermodynamics of A differently to B will alter the equilibrium constant and therefore $E_{1/2}$. Hence for a difference in $E_{1/2}$ to be observed as a result of changing an R group for example, the R group must influence to a differing degree the stabilities of the two species, A and B. It is not sufficient to consider only the influence of the substituent group on species A, but also its influence on B. This factor is readily overlooked.

(a) Metal based redox reaction

Using the above approach the substituent effect can be examined from a thermodynamic viewpoint. For the redox couple M(III)/M(II)

$$E = E^0_{\mathrm{M(III)/M(II)}} - \frac{RT}{nF} \ln \frac{[\mathrm{M(II)}]}{[\mathrm{M(III)}]} \tag{107}$$

where solvation terms have been deleted from all equations for clarity. The formation of complexes of these cations occurs via reactions of the type

$$\mathrm{M}^{3+} + 3\,\mathrm{L}^- \overset{\beta_{\mathrm{III}}}{\rightleftharpoons} \mathrm{ML}_3$$

$$\mathrm{M}^{2+} + 3\,\mathrm{L}^- \overset{\beta_{\mathrm{II}}}{\rightleftharpoons} [\mathrm{ML}_3]^-$$

where β_{III} and β_{II} are the stability constants. That is

$$\beta_{\mathrm{III}} = \frac{[\mathrm{ML}_3]}{[\mathrm{M}^{3+}][\mathrm{L}^-]^3}$$

and

$$\beta_{\mathrm{II}} = \frac{[\mathrm{ML}_3^-]}{[\mathrm{M}^{2+}][\mathrm{L}^-]^3}$$

Substitution for [M(II)] and [M(III)], yields the result

$$E = E^0_{\mathrm{M(III)/M(II)}} - \frac{RT}{nF}\ln\frac{\beta_{\mathrm{III}}}{\beta_{\mathrm{II}}} - \frac{RT}{nF}\ln\frac{[\mathrm{ML}_3^-]}{[\mathrm{ML}_3]} \tag{108}$$

If equal diffusion coefficients for all species and a diffusion-controlled electrode process are assumed, then for the $\mathrm{ML}_3/[\mathrm{ML}_3]^-$ couple

$$E_{1/2} = E^0_{\mathrm{M(III)/M(II)}} - \frac{RT}{nF}\ln\frac{\beta_{\mathrm{III}}}{\beta_{\mathrm{II}}} \tag{109}$$

Thus, when a change in metal ion oxidation state occurs, the $E_{1/2}$ value is determined by both the E^0 value of the (solvated) metal ion couple and the relative stabilities of the complexed ion in the two oxidation states.

For many of the sulphur ligands under consideration the observed trends in redox potential with substituent are adequately rationalized by assuming a simple electrostatic approach. The ligands are negatively charged and hence (neglecting entropy considerations) to a first approximation a change in oxidation state of the chelated metal ion will result in a greater stability of the complex in the higher oxidation state. For M(III) and M(II) this implies that β_{III} will be greater than β_{II} which means that the $E_{1/2}$ value for the couple $\mathrm{ML}_3/[\mathrm{ML}_3]^-$ should be more negative than the solvated metal ion couple. This argument assumes, of course, that the covalent contribution of π back-bonding or steric interactions do not dominate the thermodynamics.

In the case where the charge distribution over the ligand is influenced by the substituents, either by resonance or inductive effects, this will be important in determining the effective negative charge at the donor atoms. For example, if a full negative charge resides on each of the sulphur atoms then $\beta_{\mathrm{III}} \gg \beta_{\mathrm{II}}$ and the redox potential for the $\mathrm{ML}_3/[\mathrm{ML}_3]^-$ couple will be substantially more negative than that for the (solvated) metal ions. However, if R is a strong electron-withdrawing group the effective charge on the ligating atoms will be reduced, the ratio $\beta_{\mathrm{III}}/\beta_{\mathrm{II}}$ decreased and the redox couple shifted to a more positive potential.

(b) Ligand based redox reaction

Examination of the theory for the case where a ligand orbital is used in the charge transfer step actually permits, in the ideal case, a possible electrochemical distinction to the previous case where a change in formal oxidation state of the metal occurs. The dithiolene (L) electrochemistry is determined by the possibility of intraligand redox behaviour between L, L^-

and L^{2-} (cf. eqn. 101). Thus reduction of the complex can involve the ligand L accepting an electron to become L^*, i.e. either $L + e \rightarrow L^-$ or $L^- + e \rightarrow L^{2-}$ (where L^* is the reduced form of L with the charges omitted for clarity). The metal $M(X)$ shall be regarded as remaining in the same overall oxidation state (X) during the charge transfer process so that

$$M(X)L_p \overset{\pm e}{\rightleftharpoons} M(X)L_p^* \tag{110}$$

For the free ligand process

$$L \overset{\pm e}{\rightleftharpoons} L^* \tag{111}$$

$$E = E^0_{L/L^*} + \frac{RT}{nF} \ln \frac{[L]}{[L^*]} \tag{112}$$

Now the formation constants are

$$\beta_L = \frac{[M(X)L_p]}{[M(X)][L]^p}$$

$$\beta_{L^*} = \frac{[M(X)L_p^*]}{[M(X)][L^*]^p}$$

with substitution giving

$$E = E^0_{L/L^*} + \frac{RT}{pnF} \ln\left(\frac{\beta_{L^*}}{\beta_L}\right) + \frac{RT}{pnF} \ln \frac{[M(X)L_p]}{[M(X)L_p^*]} \tag{113}$$

Again assuming equal diffusion coefficients and diffusion-controlled conditions for the $M(X)L_p/M(X)L_p^*$ couple

$$E_{1/2} = E^0_{L/L^*} + \frac{RT}{pnF} \ln \frac{\beta_{L^*}}{\beta_L} \tag{114}$$

In contrast to the previously described case where a change in metal ion oxidation state occurs, the present $E_{1/2}$ value is governed not by the E^0 of the metal ion couple but by the E^0 of the ligand system, i.e. the redox couple in eqn. 111.

Clearly, E^0_{L/L^*} will be dependent on the substituent R and hence $E_{1/2}$ will be also dependent upon this substituent. The redox behaviour of such systems should be largely influenced by the charge of a particular metal ion involved. Herein lies the real difference in the electrochemical behaviour of ligand and metal based systems and differences should not be couched in terms of reversibility or substituent effects, etc.

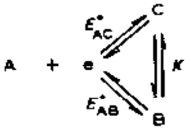
Geiger and co-workers [15] have effectively employed arguments consistent with this idea in their definitive work. Thus they have noted that $E_{1/2}$

values for reduction of Ni(SacSac)$_2$, Pd(SacSac)$_2$ and Pt(SacSac)$_2$ are almost independent of the metal. In contrast the dithiocarbamate analogues have very metal-dependent $E_{1/2}$ values. The implication of this result is that the M(SacSac)$_2 \overset{\pm e}{\rightleftharpoons}$ [M(SacSac)$_2$]$^-$ (M = Ni, Pd, Pt) processes are predominantly ligand-based, whereas the M(R$_2$dtc)$_2 \overset{\pm e}{\rightleftharpoons}$ [M(R$_2$dtc)$_2$]$^-$ couples are predominantly metal-based. Spectroscopic evidence is consistent with this assignment. Electrochemical data which compare the well established ligand- and metal-based electrochemical steps for the reduction of M(mnt)$_2$ (M = Ni, Pd, Pt) also clearly show this kind of distinction between metal- and ligand-based steps. It is clear that X-ray structures or ESR data are more definitive than electrochemical measurements in assigning the nature of the redox process and such data should be collected wherever possible.

(v) Redox Properties of Dithio Chelate Systems in Spin Equilibrium

As noted above, electrochemical measurements have established that the oxidation and reduction potentials for dithiocarbamates of Cr(III), Mn(III), Fe(III) and Co(III) display an almost identical dependence upon the R$_1$ and R$_2$ substituents. This is consistent with the hypothesis that the redox potentials of the complexes are dominated by electron density at the metal centre rather than by differences in electronic configuration of the metal ion. This view is reinforced by the absence of detectable trends in the redox potentials of iron(III) dithiocarbamates which contain different proportions of low-spin and high-spin isomers [27]. For example the oxidation potentials of the low-spin complexes Fe(i-Pr$_2$dtc)$_3$ and Fe(Ph$_2$dtc)$_3$ differ by ca. 300 mV but with the latter compound being oxidized at about the same potential as the high-spin complex Fe(pyrrdtc)$_3$. This insensitivity of redox potential to spin state is at first sight surprising, but can be rationalized providing the time scale of the spin interconversion is extremely fast. Indeed, Mossbauer and NMR spectra of iron(III) dithiocarbamates demonstrate [69] that the relaxation times are certainly very much shorter than 10^{-7} s.

Consider the reversible reduction of a compound A to give two electroactive products, B and C, which differ in spin but exhibit a very rapid interconversion with an equilibrium constant K.



$$K = [C]/[B] \qquad (115)$$

From the Nernst equation, the redox potential for the reduction can be expressed in terms of the concentration of either C or B

$$E_{\mathrm{AC}} = E^0_{\mathrm{AC}} - \frac{RT}{nF}\ln\frac{[\mathrm{C}]}{[\mathrm{A}]} \tag{116}$$

$$E_{\mathrm{AB}} = E^0_{\mathrm{AB}} - \frac{RT}{nF}\ln\frac{[\mathrm{B}]}{[\mathrm{A}]} \tag{117}$$

where E_{AC} and E_{AB} are the measured potentials. If the degree of reduction of A is represented by α, the equilibrium concentrations of the reduced species are $[\mathrm{B}] = \alpha/(1+K)$ and $[\mathrm{C}] = [K/(1+K)]\alpha$. Accordingly, the measured potential can be expressed as

$$\begin{aligned} E_{1/2}(\mathrm{measd}) &= E^0_{\mathrm{AC}} - \frac{RT}{nF}\ln\left(\frac{K}{1+K}\right) \\ &= E^0_{\mathrm{AB}} - \frac{RT}{nF}\ln\left(\frac{1}{1+K}\right) \end{aligned} \tag{118}$$

where the logarithmic term in α vanishes when $\alpha = 1/2$ to give $E_{1/2}$(measured) and the standard reduction potentials are correlated by the equation

$$E^0_{\mathrm{AB}} = E^0_{\mathrm{AC}} - \frac{RT}{nF}\ln K \tag{119}$$

In the specific case of ${}^6A_1$–${}^2T_2$ spin equilibrium of iron(III) dithiocarbamates [158], in eqn. 115 $\mathrm{A} \equiv \mathrm{Fe}^{\mathrm{IV}}$, $\mathrm{B} \equiv \mathrm{Fe}^{\mathrm{III}}_{\mathrm{ls}}$ and $\mathrm{C} \equiv \mathrm{Fe}^{\mathrm{III}}_{\mathrm{hs}}$. Since the kinetics of establishing the spin equilibrium are very fast, they do not perturb the measured potential and

$$E_{1/2}(\mathrm{measured}) = E^0(\mathrm{Fe}^{\mathrm{IV}}\text{–}\mathrm{Fe}^{\mathrm{III}}_{\mathrm{hs}}) - \frac{RT}{F}\ln\frac{K}{1+K}$$

The variation of $E_{1/2}$(measd) with K is illustrated in Fig. 24 and can be considered in the two regions $K > 1$ and $K < 1$ which correspond to high-spin and low-spin ground states, respectively. The measured potential $E_{1/2}$(measured) asymptotes to E^0_{AC} as $K \to \infty$ or to E^0_{AB} as $K \to 0$, but at intermediate values of K the reduction potential is displaced to more positive values by the spin equilibrium. The maximum deviation of the measured potential from the standard $[E_{1/2}(\mathrm{measured}) - E^0_{\mathrm{AC}}]$ or $[E^0_{1/2}(\mathrm{measured}) - E^0_{\mathrm{AB}}]$ is $(RT/F)\ln 2$ or 17.8 mV (cf. Fig. 24).

Since the Fe(IV)/Fe(III) redox potentials (see Fig. 6) fall in the range $+0.67 \geq E_{1/2}(\mathrm{measured}) \geq +0.41$ V, it is not surprising that the small perturbations (i.e. ≤ 18 mV) arising from different proportions of low-spin and high-spin isomers do not emerge. Hence it can be concluded that the measured potential should not vary significantly from the redox potential of the ground-state spin form of the ferric complexes.

As noted earlier, the definitive relationship between substituent and redox

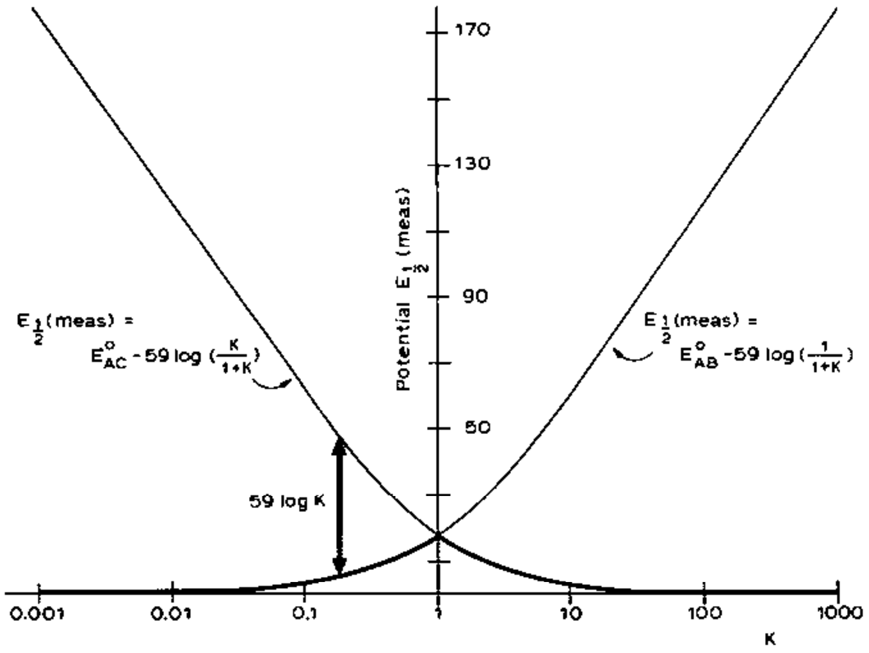


Fig. 24. Graphical plots of the relationships (in mV) $E_{1/2}$(measured) = $E^0_{AC} - 59 \log[K/(1+K)]$ and $E_{1/2}$(measured) = $E^0_{AB} - 59 \log[1/(1+K)]$. It should be noted that each curve refers to a different reference potential, viz. E^0_{AC} and E^0_{AB}, respectively. Reproduced by courtesy: Inorg. Chem., 14 (1975) 1894.

potential observed for other metal dithiocarbamates holds equally well for iron. With the exception of pyrrolidyl, all of the derivatives studied so far possess the low-spin ground state, i.e. $E_{1/2}$(measured) refers to the region $0 \leq K \leq 1$, so that it is not surprising that this relationship is preserved. However, it is significant that $E_{1/2}$(measured) for high-spin Fe(pyrrdtc)$_3$, where $K \gg 1$, also conforms to the simple expectations establishing unambiguously that the reduction and oxidation potentials of iron(III) dithiocarbamates do not reflect the intrinsic low-spin $\rightleftharpoons$ high-spin equilibrium but display the same substituent dependence as is found for other tervalent transition metals from the first row.

These conclusions based on thermodynamic considerations should be general and suggest that proposals for biological pathways involving spin-state-dependent redox potentials are unlikely to effect a thermodynamically related potential shift of any appreciable magnitude. On the other hand, kinetic terms such as the apparent rate of electron transfer could be influenced substantially by spin changes accompanying the redox process.

ACKNOWLEDGEMENT

The authors gratefully acknowledge valuable discussions with A.R. Hendrickson during the preparation of this paper.

REFERENCES

1 A.M. Bond, Modern Polarographic Techniques in Analytical Chemistry, Marcel Dekker, New York, 1980, and references cited therein.

2 H.B. Gray, Transition Met. Chem., 1 (1965) 239.

3 J.A. McCleverty, Prog. Inorg. Chem., 10 (1968) 49.

4 G.N. Schrauzer, Transition Met. Chem., 4 (1968) 299.

5 J.A. McCleverty, in N.S. Hush (Ed.), Reactions of Molecules at Electrodes, Wiley/Interscience, London, 1971, pp. 403–492.

6 D. Coucouvanis, Prog. Inorg. Chem., 11 (1970) 233; 26 (1979) 301.

7 R. Eisenberg, Prog. Inorg. Chem., 12 (1970) 295.

8 J. Willemse, J.A. Crass, J.J. Steggerda and C.P. Keijzers, Struct. Bonding (Berlin), 28 (1976) 83.

9 T.N. Lockyer and R.L. Martin, Prog. Inorg. Chem., 27 (1980) 223.

10 G.N. Schrauzer, Acc. Chem. Res., 2 (1969) 72.

11 J.G.M. van der Linden and H.G.J. van der Roer, Inorg. Chim. Acta, 5 (1971) 254.

12 J.G.M. van der Linden, J. Inorg. Nucl. Chem., 34 (1972) 1645.

13 A. Furuhashi, S. Kawai, Y. Hayakawa and A. Ouchi, Bull. Chem. Soc. Jpn., 43 (1970) 553.

14 A.M. Bond, G.A. Heath and R.L. Martin, Inorg. Chem., 10 (1971) 2026.

15 W.L. Bowden, J.D.L. Holloway and W.E. Geiger, Jr., Inorg. Chem., 17 (1978) 256.

16 D.C. Olson, V.P. Mayweg and G.N. Schrauzer, J. Am. Chem. Soc., 88 (1966) 4876.

17 G.S. Patterson and R.H. Holm, Inorg. Chem., 11 (1972) 2285.

18 V.T. Solomatin, S.P. Rzhavichev and T.N. Artemova, Zh. Anal. Khim., 32 (1977) 1077; Russ. J. Anal. Chem., 32 (1977) 847, and references cited therein.

19 D. de Montauzon, R. Poilblanc, P. Lemoine and M. Gross, Electrochim. Acta, 23 (1978) 1247, and references cited therein.

20 Y. Mugnier, C. Moise, J. Tirouflet and E. Laviron, J. Organomet. Chem., 186 (1980) C49, and references cited therein.

21 A.M. Bond, J.R. Thackeray and A.T. Casey, Inorg. Chem., 12 (1973) 887.

22 A.M. Bond, J.R. Thackeray and A.T. Casey, J. Chem. Soc., Dalton Trans., (1974) 773.

23 A.M. Bond, J.R. Thackeray and A.T. Casey, Inorg. Chem., 13 (1974) 84.

24 A.M. Bond, A.T. Casey and J.R. Thackeray, J. Electrochem. Soc., 120 (1973) 1502.

25 A.M. Bond, A.T. Casey and J.R. Thackeray, J. Electroanal. Chem., 48 (1973) 71.

26 A.R. Hendrickson, R.L. Martin and N.M. Rohde, Inorg. Chem., 13 (1974) 1933.

27 R. Chant, A.R. Hendrickson, R.L. Martin and N.M. Rohde, Inorg. Chem., 14 (1975) 1894.

28 W. Stricks and S.K. Chakravarti, Anal. Chem., 34 (1962) 508.

29 D.J. Halls, A. Townshend and P. Zuman, Anal. Chim. Acta, 40 (1968) 459; 41 (1968) 51, and references cited therein.

30 S.J. Joris, K.I. Aspila and C.L. Chakrabarti, Anal. Chem., 41 (1969) 1441.

31 T.H. Randle, T.J. Cardwell and R.J. Magee, Aust. J. Chem., 28 (1975) 21.

32 K.I. Aspila, S.J. Joris and C.L. Chakrabarti, J. Phys. Chem., 74 (1970) 3625.

33 K.I. Aspila, C.L. Chakrabarti and V.S. Sastri, Anal. Chem., 45 (1973) 363, and references cited therein.
34 S.G. Salamy and J.C. Nixon, Recent Developments in Mineral Dressing, Institute of Mining and Metallurgy, London, 1953, p. 503, and references cited therein.
35 S. Sun and R.T. Holzmann, Anal. Chem., 29 (1957) 1298.
36 M. Marijosuma and T. Yamaiki, Sci. Rep. Res. Inst. Tohoku Univ. Ser. A, (1969) 33.
37 A.M. Bond, A.R. Hendrickson and R.L. Martin, J. Electrochem. Soc., 119 (1972) 1325.
38 R.L. Martin and A.F. Masters, Inorg. Chem., 14 (1975) 885.
39 G. Cauquis and D. Lachenal, J. Electroanal. Chem., 43 (1973) 205.
40 C. Scrimager and L.J. Dehayes, Inorg. Nucl. Chem. Lett., 14 (1978) 125.
41 H. Monien and R. Bovenkerk, Z. Anal. Chem., 300 (1980) 33.
42 L.H. Cutler, U.S. Pat. 4,032,416 (S1. 204-79; C25B3/02), 28 June 1977, Appl. 665,550, 10 March 1976.
43 R. Woods, J. Phys. Chem., 75 (1971) 354, and references cited therein.
44 R. Woods, Aust. J. Chem., 25 (1972) 2329.
45 K. Bechgaard, V.D. Parker and C.Th. Pederson, J. Am. Chem. Soc., 95 (1973) 4373.
46 C.Th. Pederson and V.D. Parker, Tetrahedron Lett., (1972) 767.
47 A.M. Bond, A.R. Hendrickson and R.L. Martin, J. Am. Chem. Soc., 95 (1973) 1449.
48 G.A. Heath, R.L. Martin and I.M. Stewart, Aust. J. Chem., 22 (1969) 83.
49 A. Furahashi, K. Watanuki and A. Ouchi, Bull. Chem. Soc. Jpn., 42 (1969) 260.
50 D.C. Olson, V.P. Mayweg and G.N. Schrauzer, J. Am. Chem. Soc., 87 (1965) 1483, 3585; 88 (1966) 3235, and references cited therein.
51 H.E. Simmons, D.C. Blomstrom and R.D. Vest, J. Am. Chem. Soc., 84 (1962) 4756, 4772, 4782.
52 C.G. Krespan, J. Am. Chem. Soc., 83 (1961) 3434.
53 J.A. McCleverty, D.G. Orchard and K. Smith, J. Chem. Soc. A, (1971) 707.
54 R. Chant, A.R. Hendrickson, R.L. Martin and N.M. Rohde, Aust. J. Chem., 26 (1973) 2533.
55 L. Cambi and A. Cagnasso, Atti. Accad. Naz. Lincei, 14 (1931) 71; Chem. Abstr., 26 (1932) 2172.
56 C.P. Prabhakaran and C.C. Patel, Indian J. Chem., 7 (1969) 1257.
57 R.M. Golding, P. Healy, P. Newman, E. Sinn, W.C. Tennant and A.H. White, J. Chem. Phys., 52 (1970) 3105.
58 G. Aravamudan, D.H. Brown and D. Venkappayya, J. Chem. Soc. A, (1971) 2744.
59 D.G. Holah and C.N. Murphy, Can. J. Chem., 49 (1971) 2726.
60 P.C. Healy and A.H. White, J. Chem. Soc., Dalton Trans., (1972) 1883.
61 E.A. Pasek and D.K. Straub, Inorg. Chem., 11 (1972) 259.
62 R.Y. Saleh and D.K. Straub, Inorg. Chem., 13 (1974) 3017.
63 R.M. Golding, C.M. Harris, K.J. Jessop and W.C. Tennant, Aust. J. Chem., 25 (1972) 2567.
64 K.L. Brown, R.M. Golding, P.C. Healey, K.J. Jessop and W.C. Tennant, Aust. J. Chem., 27 (1974) 2075.
65 V.F. Toropova, G.K. Budnikov and N.A. Ulakhovich, Zh. Obshch. Khim., 45 (1975) 380; Russ. J. Gen. Chem., 45 (1975) 368.
66 V.F. Toropova, R.G.K. Budnikov and N.A. Ulakhovich, Talanta, 25 (1978) 263.
67 O.A. Ileperuma and R.D. Feltham, Inorg. Chem., 14 (1975) 3042.
68 J.L.K.F. de Vries, J.M. Trooster and E. de Boer, Inorg. Chem., 12 (1973) 2730.
69 R.L. Martin and A.H. White, Transition Met. Chem., 4 (1968) 113.
70 B.F. Hoskins and B.P. Kelly, Chem. Commun., (1968) 1517.

71 P.C. Healy and A.H. White, Chem. Commun., (1971) 1446.
72 P.C. Healy and A.H. White, J. Chem. Soc., Dalton Trans. (1972) 1163.
73 J.G. Leipoldt and P. Coppens, Inorg. Chem., 12 (1973) 2269.
74 R.L. Martin, N.M. Rohde, G.B. Robertson and D. Taylor, J. Am. Chem. Soc., 96 (1974) 3647.
75 G. Cauquis and D. Lachenal, Inorg. Nucl. Chem. Lett., 9 (1973) 1095.
76 J. Willemse and J.J. Steggerda, Chem. Commun., (1969) 1123.
77 P.T. Beurskens, W.P.J.H. Bosman and J.A. Cras, J. Cryst. Mol. Struct., 2 (1972) 183.
78 B.M. Mattson and L.H. Pignolet, Inorg. Chem., 16 (1977) 488.
79 G.L. Meissler, E. Zoebisch and L.H. Pignolet, Inorg. Chem., (1978) 3636.
80 J.A. McCleverty, S. McLuckie, N.J. Morrison, N.A. Bailey and N.W. Walker, J. Chem. Soc., Dalton Trans., (1977) 359.
81 R.M. Golding, K. Lehtonen and B.J. Ralph, J. Inorg. Nucl. Chem., 36 (1974) 2047.
82 R.M. Golding and K. Lehtonen, Aust. J. Chem., 27 (1974) 2083.
83 R.M. Golding, L.L. Kok, K. Lehtonen and R.K. Nigam, Aust. J. Chem., 28 (1975) 1915.
84 L.H. Pignolet, G.S. Patterson, J.F. Weiher and R.H. Holm, Inorg. Chem., 13 (1974) 1263.
85 V.F. Toropova, G.K. Budnikov, N.A. Ulakhovich and I.P. Viter, Zh. Obshch. Khim., 45 (1975) 1359; Russ. J. Gen. Chem., 45 (1975) 1329.
86 A.H. Ewald, R.L. Martin, E. Sinn and A.H. White, Inorg. Chem., 8 (1969) 1837.
87 W. Kemula, A. Hulanicki and W. Nawrot, Rocz. Chem., 36 (1962) 1717; 38 (1964) 1065.
88 A. Domenicano, A. Vaciago, L. Zambonelli, P.L. Loader and L.M. Venanzi, Chem. Commun., (1966) 476.
89 L.H. Pignolet, Inorg. Chem., 13 (1974) 2051.
90 C.L. Raston and A.H. White, J. Chem. Soc., Dalton Trans., (1975) 2405, 2410, 2418.
91 B.M. Mattson, J.R. Heiman and L.H. Pignolet, Inorg. Chem., 15 (1976) 564.
92 K.W. Given, B.M. Mattson and L.H. Pignolet, Inorg. Chem., 15 (1976) 3152.
93 G.L. Miessler and L.H. Pignolet, Inorg. Chem., 18 (1979) 210.
94 L. Cambi and L. Malatesta, Ber. Dtsch. Chem. Ges., 70 (1937) 2067.
95 L. Malatesta, Gazz. Chim. Ital., 68 (1938) 195.
96 L.R. Gahan and M.J. O'Connor, Chem. Commun., (1974) 68.
97 A.R. Hendrickson, J.M. Hope and R.L. Martin, J. Chem. Soc., Dalton Trans., (1976) 2032.
98 S.H. Wheeler, B.M. Mattson, G.L. Miessler and L.H. Pignolet, Inorg. Chem., 17 (1978) 340.
99 K.W. Given, B.M. Mattson, M.F. McGuiggan, G.L. Miessler and L.H. Pignolet, J. Am. Chem. Soc., 99 (1977) 4855.
100 D.J. Cole-Hamilton and T.A. Stephenson, J. Chem. Soc., Dalton Trans., (1974) 739.
101 M. Ahmed and R.J. Magee, Proc. Indian Acad. Sci., Sect. A, 88 (1979) 401.
102 A.R. Hendrickson, R.L. Martin and D. Taylor, Aust. J. Chem., 29 (1976) 269.
103 R.S. Nicholson and I. Shain, Anal. Chem., 36 (1964) 706.
104 R.A. Bozis, Diss. Abstr. Int. B, 32 (1972) 6268; Chem. Abstr., 77 (1972) 108887y.
105 A.H. Dix, J.W. Diesveld and J.G.M. Van Der Linden, Inorg. Chim. Acta, 24 (1977) L51.
106 K.W. Given, S.H. Wheeler, B.S. Jick, L.J. Maheu and L.H. Pignolet, Inorg. Chem., 18 (1979) 1261.
107 L.J. Maheu and L.H. Pignolet, Inorg. Chem., 18 (1979) 3626.
108 P.B. Critchlow and S.D. Robinson, J. Chem. Soc., Dalton Trans., (1975) 1367.
109 D.J. Cole-Hamilton and T.A. Stephenson, J. Chem. Soc., Dalton Trans., (1976) 2396.
110 S.H. Wheeler and L.H. Pignolet, Inorg. Chem., 19 (1980) 972.
111 L.F. Serebritskaya and F.M. Tulyupa, Zh. Neorg. Khim., 21 (1976) 1394; Russ. J. Inorg. Chem., 21 (1976) 762.

112 T.L. Riechl, L.J. De Hayes and D.T. Sawyer, Inorg. Chem., 15 (1976) 1900.
113 P. Vella and J. Zubieta, J. Inorg. Nucl. Chem., 40 (1978) 613.
114 B. Kastening and L. Holleck, Z. Elektrochem., 63 (1959) 166.
115 R.S. Nicholson and I. Shain, Anal. Chem., 36 (1964) 706.
116 R.S. Nicholson, J.M. Wilson and M.L. Olmstead, Anal. Chem., 38 (1966) 542.
117 B. Kastening, Anal. Chem., 41 (1969) 1142.
118 L. Nadjo and J.M. Savéant, J. Electroanal. Chem., 33 (1971) 419.
119 C.P. Andrieux and J.M. Savéant, J. Electroanal. Chem., 33 (1971) 453.
120 C.P. Andrieux, L. Nadjo and J.M. Savéant, J. Electroanal. Chem., 42 (1973) 223.
121 G. K. Budnikov, A.V. Il'yasov, V.I. Morozov and N.A. Ulakhovich, Zh. Neorg. Khim., 21 (1976) 473; Russ, J. Inorg. Chem., 21 (1976) 255.
122 D.C. Bradley and M.H. Chisholm, J. Chem. Soc. A, (1971) 2741.
123 T.M. Brown and J.H. Smith, J. Chem. Soc., Dalton Trans., (1972) 1614.
124 J.F. Rowbottom and G. Wilkinson, Inorg. Nucl. Chem. Lett., 9 (1973) 675.
125 A. Nieupoort, J.H.E. Moonen and J.A. Cras, Rec. Trav. Chim. Pays-Bas, 92 (1973) 1086.
126 A. Nieupoort, Proc. Conf. Chemistry and Uses of Molybdenum, Univ. Reading, 1975; Climax Molybdenum Co., 1974, p. 143.
127 Z.B. Varadi and A. Nieuwpoort, Inorg. Nucl. Chem. Lett., 10 (1974) 801.
128 A. Nieuwpoort, J. Less-Common Met., 36 (1974) 271.
129 C.A. McAuliffe and B.J. Sayle, Inorg. Chim. Acta, 12 (1974) L7.
130 A. Nieuwpoort, H.M. Claessen and J.G.M. van der Linden, Inorg. Nucl. Chem. Lett., 11 (1975) 869.
131 A. Nieuwpoort and J.J. Steggerda, Rec. Trav. Chim. Pays-Bas, 95 (1976) 250.
132 A. Nieuwpoort and J.J. Steggerda, Rec. J. R. Neth. Chem. Soc., 95 (1976) 289.
133 J. Hyde and J. Zubieta, J. Inorg. Nucl. Chem., 39 (1977) 289.
134 P.C.H. Mitchell and R.O. Scale, J. Chem. Soc., Dalton Trans., (1975) 110.
135 L.J. De Hayes, H.C. Faulkner, W.H. Doub, Jr. and D.T. Sawyer, Inorg. Chem., 14 (1975) 2110.
136 P. Vella and J. Zubieta, J. Inorg. Nucl. Chem., 40 (1978) 477.
137 J. Hyde, K. Venkatasubramanian and J. Zubieta, Inorg. Chem., 17 (1978) 414.
138 F.A. Schultz, V.R. Ott, D.L. Relison, D.C. Bravard, J.W. McDonald and W.E. Newton, Inorg. Chem., 17 (1978) 1758.
139 J.R. Bradbury, A.F. Masters, A.C. McDonnell, A.A. Brunette, A.M. Bond and A.G. Wedd, J. Am. Chem. Soc., 103 (1981) 1959.
140 G.K. Budnikov, V.F. Toropova and N.A. Ulakhovich, Zh. Obshch. Khim., 44 (1974) 492; Russ. J. Gen. Chem., 44 (1974) 473.
141 A.M. Bond, A.R. Hendrickson, R.L. Martin, J.E. Moir and D.R. Page, Inorg. Chem., in press, and references cited therein.
142 A.R. Hendrickson and R.L. Martin, J. Chem. Soc., Chem. Commun., (1974) 873.
143 A.R. Hendrickson, R.L. Martin and D. Taylor, J. Chem. Soc., Dalton Trans., (1975) 2182.
144 D. Lachenal, Inorg. Nucl. Chem. Lett., 11 (1975) 101.
145 A.R. Hendrickson, R.L. Martin and N.M. Rohde, Inorg. Chem., 14 (1975) 2980.
146 M. Ahmed and R.J. Magee, Anal. Chim. Acta, 75 (1975) 431.
147 T.H. Randle, T.J. Cardwell and R.J. Magee, Aust. J. Chem., 29 (1976) 1191.
148 G.K. Budnikov and N.A. Ulakhovich, Zh. Obshch. Khim., 46 (1976) 1129; Russ. J. Gen. Chem., 46 (1976) 1117.
149 G.K. Budnikov, N.A. Ulakhovich, O.Yu. Kargina and L.G. Fomina, Zh. Obshch. Khim., 48 (1978) 1667; Russ. J. Gen. Chem., 48 (1978) 1527.

150 J.G.M. van der Linden and A.H. Dix, Inorg. Chim. Acta, 35 (1979) 65.
151 G.A. Bowmaker, P.D.W. Boyd, G.K. Campbell, J.M. Hope and R.L. Martin, Inorg. Chem., 21 (1982) 1152.
152 T.H. Randle, T.J. Cardwell and R.J. Magee, Aust. J. Chem., 29 (1976) 85.
153 A.R. Hendrickson, R.L. Martin and N.M. Rohde, Inorg. Chem., 15 (1976) 2115.
154 A. Nieuwpoort, A.H. Dix, P.A.T.W. Porskamp and J.G.M. van der Linden, Inorg. Chim. Acta, 35 (1979) 221.
155 A.M. Bond, R. Colton, M. Dillon, J.E. Moir and D.E. Page, Inorg. Chem., in press.
156 R.S. Nyholm and M.L. Tobe, Adv. Inorg. Chem. Radiochem., 5 (1963) 1.
157 C.J. Jørgensen, J. Inorg. Nucl. Chem., 24 (1962) 1571.
158 A.H. Ewald, R.L. Martin, I.G. Ross and A.H. White, Proc. R. Soc. London, Ser. A, 280 (1964) 235.
159 A.M. Bond, R.J. O'Halloran, I. Ruzic and D.E. Smith, Anal. Chem., 48 (1976) 872.
160 Y. Yasuda, K. Suga and S. Aoyagui, J. Electroanal. Chem., 86 (1978) 259.
161 A.H. Dix, F.H.M. Schut, P.P.J. Schlebos and J.G.M. van der Linden, J. Electroanal. Chem., 111 (1980) 71.
162 M.C. Palazzotto, D.J. Duffy, B.L. Edgar, L. Que Jr. and L.H. Pignolet, J. Am. Chem. Soc., 95 (1973) 4537.
163 A.M. Bond, R.L. Martin and A.F. Masters, Inorg. Chem., 14 (1975) 1432.
164 A.M. Bond, R.L. Martin and A.F. Masters, J. Electroanal. Chem., 72 (1976) 187.
165 A.M. Bond, G.A. Heath and R.L. Martin, J. Electrochem. Soc., 117 (1970) 1362.
166 A.M. Bond, G.A. Heath and R.L. Martin, Inorg. Chem., 10 (1971) 2026.
167 A.R. Hendrickson, J.M. Hope and R.L. Martin, Inorg. Chem., 15 (1976) 1118.
168 G.A. Heath, R.L. Martin and I.M. Stewart, Aust. J. Chem., 22 (1967) 83.
169 R.L. Martin and I.M. Stewart, Nature (London), 210 (1966) 522.
170 A.R. Hendrickson and R.L. Martin, Aust. J. Chem., 25 (1972) 257.
171 A.F. Masters, Ph.D. Thesis, Australian National University, Canberra, Australia, 1975.
172 A.R. Hendrickson, Ph.D. Thesis, University of Melbourne, Australia, 1972.
173 T.E. Mines and W.E. Geiger, Jr., Inorg. Chem., 12 (1973) 1189.
174 W.E. Geiger, Jr., T.E. Mines and F.C. Senftleber, Inorg. Chem., 14 (1975) 2141.
175 R.R. Gagne and D.M. Ingle, J. Am. Chem. Soc., 102 (1980) 1444.
176 B. Bock, M. Kuhr and H. Musso, Chem. Ber., 109 (1976) 1184.
177 A. Nazzal and U.T. Mueller-Westerhoff, Transition Met. Chem., 5 (1980) 318.
178 M. Kuhr, B. Bock and H. Musso, Chem. Ber., 109 (1976) 1195.
179 G. Bill and H. Musso, Justus Liebigs Ann. Chem., (1979) 803.
180 U.T. Mueller-Westerhoff and A. Alscher, Angew. Chem. Int. Ed. Engl., 19 (1980) 638.
181 P. Zuman, Substituent Effects in Organic Polarography, Plenum Press, New York, NY, 1967.
182 T. Saji and S. Aoyagui, J. Electroanal. Chem., 108 (1980) 223, and references cited therein.