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Electrochemistry of Metal Chelates in Non-aqueous Media

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A systematic account is given of experimental data on the electrochemical coordination reactions of compounds of metals with organic ligands in non-aqueous media. Attention is concentrated on the results of polarographic studies on the so-called inert chelate complexes. The influence of the nature of the metal and the ligand on the mechanism of the electrode reaction is discussed.
The bibliography includes 100 references

CONTENTS

I. Introduction 449
II. Electrochemical reduction of metal chelates with organic ligands in non-aqueous media 449
III. Anodic reactions of metal coordination compounds 457
IV. The role of the nature of the metal and the structure of the ligand in the mechanism of the electrochemical reduction of chelates 459

I. INTRODUCTION

Interest in the electrochemistry of coordination compounds in non-aqueous solutions is due to a number of causes. On the one hand, the vigorous development of inorganic chemistry and in the first place the chemistry of complex compounds requires tests on fundamental relations by various methods, including electrochemical methods. On the other hand, progress in electrochemistry, both theoretical (development of the theory of kinetic currents, mechanisms involving chemical reactions accompanied by charge transfer) and experimental (new apparatus permitting the recording of polarisation curves in solutions with a high ohmic resistance, new procedures for the detection of short-lived species at the electrode, etc.), has also stimulated the study of complexes in non-aqueous media by electrochemical methods. Many chelates are insoluble in aqueous media and the use of non-aqueous solvents therefore ensures suitable conditions for their investigation. From the practical point of view, studies in this field permit the solution of problems of electrocatalysis, electroplating, electrosynthesis of organometallic complexes (catalysts), and finally electroanalytical determination of metals.

Advances achieved hitherto in the polarography of organic compounds in aqueous and aqueous-organic media permit a more detailed examination of the effects accompanying the reduction of a complex species combined with an organic ligand. Virtually all organic substances are adsorbed to some extent on the surface of the mercury dropping electrode (m.d.e.), so that the shift of the half-wave potential ($E_{1/2}$) and the change in the slope of the reduction wave for the metal ion in solution in the presence of the organic ligand, on which conclusions concerning the stability of the complexes in solution and their composition are based, can be induced not only by complex formation but also by the inhibition of the reduction at the electrode, a change in the ψ' potential, etc. These effects are observed mainly when the region corresponding to the reduction of metal ions coincides with the region of the maximum adsorption of the organic ligand.

The study of complex formation processes by polarographic methods in non-aqueous media or in aqueous organic media with a high content of an organic solvent, where adsorption is considerably weakened and the above effects do not complicate the electrochemical reactions of complexes, is also promising in this connection. Furthermore, under these conditions, there is virtually no hydrolysis in solutions. The low dielectric constants of the majority of organic solvents have a significant influence on the behaviour of complexes at the electrode. Many metal ions, forming stable complexes in aqueous media, are highly solvated in organic solvents (for example, in ethylenediamine, formamides, acetonitrile, and dimethyl sulphoxide) and are characterised by high donor numbers. Problems of the solvation of metal cations have been reviewed recently in a collection of reports on non-aqueous electrochemistry[1]. The conditions governing the selection of a suitable solvent, supporting electrolyte, and reference electrode for the investigation of chelates are also discussed there.

Attention has been particularly concentrated recently on the use of aprotic solvents, for example, dimethylformamide (DMF). The usefulness of such solvents can be explained by the fact that the influence of protonation is weakened, the study of the mechanism of the electrode process is simplified, and it becomes possible to observe multistage electron transfer and the formation of complexes with the central atom in the lowest valence states, which are unstable under the usual conditions. Nor can one rule out the possibility of the selection on the basis of polarographic data of conditions for the electrochemical generation of these unstable species and the study of their chemical structure. Finally, in organic media it is possible to extend greatly the range of m.d.e. polarisation potentials.

In the present review an attempt is made to discuss the present state of electrochemical studies on metal chelates in non aqueous systems—to assess the fundamental achievements and prospects in this relatively new field.

II. ELECTROCHEMICAL REDUCTION OF METAL CHELATES WITH ORGANIC LIGANDS IN NON-AQUEOUS MEDIA

In order to elucidate the influence of the chemical structure of metal chelates on the mechanism of their electrochemical reduction, it is necessary to study a fairly wide range of coordination compounds with various types of chelate units, determined both by the nature of the central atom and by the properties of the donor atoms in the analytically useful functional groups and their steric disposition in the molecule of the organic reagent. The authors

realise that not all the series of coordination compounds have been considered in equal detail in this review, because a complete treatment of all chelating agents is impossible and is hardly desirable. Most attention has been devoted to the chelates of *d* elements with filled and unfilled *d* shells.

1. Electrochemical Reduction of Metal Dithiocarbamates at the Mercury Dropping Electrode

The polarographic reduction of dithiocarbamates (DTC) at the mercury electrode in DMF has been studied in a series of investigations[2-5]. Chelates having the general formula $(R_2NCS_2)_nM^{n+}$ $[(CH_2)_4ONCS_2]_nM^{n+}$ and $[(CH_2)_mNCS_2]_nM^{n+}$, where $M^{n+} = Zn^{2+}$, Cd^{2+}, Sn^{2+}, Tl^{+}, Pb^{2+}, Bi^{3+}, Cu^{2+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, or Ni^{2+}, R = CH_3, C_2H_5, n-C_3H_7, or n-C_4H_9, and m = 4, 5, or 6, were investigated. It was found that, in terms of their electrochemical behaviour, they can be divided into two groups. The first includes the dithiocarbamates of metals with filled *d* shells: Zn^{2+}, Cd^{2+}, Sn^{2+}, Hg^{2+}, Tl^{+}, Pb^{2+}, Bi^{3+}, and Cu^{2+}. They give rise to waves, corresponding to the reduction of the central ion to the metal, on polarograms obtained in DMF in the presence of $(C_2H_5)_4NClO_4$ as the supporting electrolyte; the values of their $E_{1/2}$ vary in the range from −0.6 to −1.5 V. The reduction is nearly reversible (except for the Cd^{2+} and Zn^{2+} chelates):

$$M^{n+}(R_2NCS_2)_n + n\,e + Hg \rightleftarrows M^0(Hg) + nR_2NCS_2^-.$$

The nature of the ligand is reflected in the polarographic properties of the chelates. The greater stability of complexes with ligands having a stronger electron-donating group is the cause of the displacement of $E_{1/2}$ towards cathodic potentials (in the range 0.05–0.07 V) as R is varied in a homologous series. The standard rate constants for charge transfer k_S (based on oscillopolarographic data) are in the range $(1.2–2.6) \times 10^{-2}$ cm s^{-1}. The form of the polarisation curves depends on the concentration of the complex, which is due to the adsorption activity of the DTC. The adsorbability is influenced by the nature of the solvent and R, which determine the solubility of the DTC. The reduction of this group of DTC takes place mainly in the range of E values close to the electrocapillary zero, where the adsorbability is manifested to the greatest extent.

Polarograms referring to the second group of complexes of the type $M^{n+}(R_2NCS_2)_n$, where $M^{n+} = Cr^{3+}$, Mn^{3+}, Fe^{3+}, Co^{3+}, or Ni^{2+}, consist of n plateaux corresponding to the successive transfer of n electrons. The reduction of Mn^{3+} chelates proceeds in two stages with the transfer of one and then two electrons. The product of the final irreversible stage is the metal on the mercury surface. The stepwise reduction of the DTC is complicated by the intervening dissociation of the intermediate complex species (the central atom in a low valence state) involving the formation of the $R_2NCS_2^-$ anion. The nature of the substituent at the nitrogen atom in the DTC molecule has some influence on the ease of reduction of complexes in DMF: an increase in the length of the aliphatic chain in the homologous series leads to a cathodic shift of $E_{1/2}$ for irreversible waves. The same shift occurs with increase in the size of the ring in heterocyclic derivatives. The lack of a simple correlation with the half-wave potentials of the one-electron reversible stage in the reduction of the dithiocarbamates of typical transition metals and the Taft constants of the substituents at the nitrogen atom can hardly be accounted for by the steric hindrance in the reduction reaction.

$E_{1/2}$ for the reversible one-electron process, characterising the energy of the lowest unoccupied molecular orbital, is apparently insensitive or only slightly sensitive to steric effects. The deviations of $E_{1/2}$ from the linear relation with the free energy are more likely to be due to a complex dependence of the adsorption of chelates on the nature of the groups involved and the influence of adsorbability on $E_{1/2}$.

Variation of the nature of the substituents R and R′ in the ligand fragment of iron(III) dialkyldithiocarbamates over a wide range made it possible to discover more refined factors influencing the reactivity of chelates of this type in the electrochemical reduction[6]. A study was made of the dependence of $E_{1/2}$ for the first reversible one-electron reduction stage on the energy difference between the ground and excited states. It was found that high-spin complexes are reduced more readily than low-spin complexes almost by 0.25 V. It was suggested[6] that the steric interaction with the sulphur atoms in low-spin complexes having bulky R and R′ groups leads to a non-planar structure of the fragment $[C_2N-CS_2]$ and the electron pair of the atoms can be delocalised only within the limits of the chelate unit; the ligand field is therefore strengthened. For small substituents R and R′, a planar mesomeric structure (mesoionic form) of the type $C_2N^{+} = CS_2$, with a shorter C–S bond, becomes preferable, so that the ligand field is weakened. To illustrate the influence of the steric effect of substituents on $E_{1/2}$, a comparison was made of the dithiocarbamates of the iron(III) complexes of pyrroline and 2,5-dimethylpyrroline[6].

Although in certain cases the reduction of chelates is in fact complicated by adsorption effects, the ease of reduction of dithiocarbamates of both groups at the m.d.e. is largely determined by the nature of the central atom, which is consistent with the "metallic" nature of the metal–ligand bond. However, the ease of reduction is apparently influenced in certain cases by the contribution of the mesomeric form of the ligand.

The results of a study of the electrochemical reduction of nickel dithiocarbamates by chronopotentiometry were published recently[7]. A study was made of the complexes with aliphatic straight-chain, branched, and alicyclic groups in DMF in the presence of 0.1 M $NaClO_4$ as the supporting electrolyte and platinum and stationary mercury electrodes. In all cases the authors[7] observed a single reduction wave, and not two, because the range of the possible polarisations of the electrodes in the presence of sodium perchlorate was insufficiently broad, i.e. the authors studied only the first stage of the reduction of the nickel chelates. It was found that the complexes are reduced irreversibly (with rare exceptions) and that the product $i\tau^{1/2}$ [where i is the current density and τ the duration of the arrest on the chronopotentiometric $E = f(t)$ curve] is independent of the current density. Consequently preceding dissociation of the complexes was not observed under the experimental conditions. It follows from these data[7] that the greater the stability of the chelates, the lower the charge-transfer rate constant. Having noted that in the series of complexes investigated the orbital to which an electron is transferred is mainly "metallic", the authors[7] believe that in certain cases there is a possibility of a shift of the location of the transferred electron from the metal to the ligand, for example, on passing from the dibenzyl derivative to the dicyclohexyl derivative. Comparison of the results of Budnikov and coworkers[3-5] and Ahmed and Magee[7] shows that the replacement of mercury by platinum leads to a significant change in the nature of the one-electron stage in the reduction of nickel

dithiocarbamates. The absence of a clear dependence of the ease of reduction at the platinum microelectrode on the structure of the ligand (with a large scatter of the peak potentials E_p along the potential axis) and the low rate of charge transfer apparently indicate a significant influence of the adsorption and kinetic contributions on the electrode process under these conditions[7].

In connection with the problem of the elucidation of the biological role of metals in enzymes, the oxidation-reduction properties of certain molybdenum and vanadium complexes of a number of sulphur-containing ligands, which form the inner coordination sphere, including dithiocarbamates, were investigated by electrochemical methods[8,9]. These complexes were regarded as models of metalloenzymes. The formation of dinuclear dimers, which determine the mechanism of the behaviour at the electrode, is characteristic of molybdenum(V) dithiocarbamate chelate complexes. Dinuclear complexes with DTC were not observed for vanadium in different oxidation states[9]. The transfer of the first electron to $V(R_2NCS_2)_3$ at the platinum electrode is reversible. The reduction of $VO(R_2NCS_2)$ proceeds in a complex manner and involves the formation at one of the stages of a certain amount of the $V(R_2NCS_2)_3$ species apart from the main product V_2O_3. The reduction of $VO(R_2NCS_2)_3$ results in the formation of $VO(R_2NCS_2)_2$ and the ligand anion. In the molybdenum complexes the DTC ligands give rise to a more "electron saturated" environment around the central ion than other ligands, for example 8-hydroxyquinoline[8].

2. Mixed-Ligand Metal Complexes with Dithiocarbamates in Electrochemical Reactions

When complexes are formed with variable-valence transition metal ions, those with metals in a high oxidation state (Cr^{3+}, Mn^{3+}, Fe^{3+}, and Co^{3+}) are as a rule stabilised. The introduction into the chelate molecule of ligands exhibiting π-acceptor properties [2,2′-bipyridyl(Bipy) and 1,10-phenanthroline(Phen)] promotes the stabilisation of the low oxidation state of the central atom. An example is provided by manganese(II) and iron(II) complexes $M(R_2NCS_2)_2Bipy$ or $M(R_2NCS_2)_2Phen$.[10] When they are reduced in DMF at the m.d.e., the polarograms show four plateaux corresponding to one-electron transfers in accordance with the mechanism $M^{2+} \rightleftharpoons M^{+}$ and $M^{+} \rightleftharpoons M$ and the reduction of Bipy or Phen. Similar heteroligand complexes are also formed by Zn^{2+}. In contrast to simple zinc(II) dithiocarbamates, they are reduced in stages with formation of an intermediate species in which the central atom has a formally low valence state. The unpaired electron in the product of the reversible electron transfer to $Zn(R_2NCS_2)_2Bipy$ is delocalised over the Bipy ligand and occupies an antibonding π^* orbital. In the electrolysis of a solution of this complex at the potential of the limiting current of the first one-electron wave, the $Bipy^{-}$ radical-anion was detected by EPR.[11,12]

Nickel(II) dithiocarbamates do not form heteroligand complexes with Bipy. However, in the presence of Bipy or Phen an increase in the limiting current of the first reversible one-electron wave at the expense of the second and an anodic shift of both branches are observed. Similar phenomena are also observed for the chromium(III) and cobalt(III) dithiocarbamates when the above π-acceptors are added to the polarographed solution. The increased current is due to the kinetic contribution. The results indicate a chemical reaction of π-acceptors with the one-electron transfer product (ECE mechanism):

$$M^{(n+1)}(R_2NCS_2)_n + e \rightleftarrows [M^{n+}(R_2NCS_2)_n]^-$$

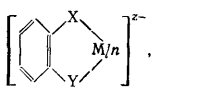
$$[M^{n+}(R_2NCS_2)_n]^- + \text{Bipy(Phen)} \xrightarrow{k} [M^{(n-1)}(R_2NCS_2)_{n-1}]\text{Bipy(Phen)} + R_2NCS_2^- .$$

The intermediates formed at the electrode in acetonitrile are more stable. The electrolysis of a solution of the chromium(III) complex at the potential of the limiting current of the first wave in the presence of Bipy exhibits a distinct spectrum of paramagnetic species containing lines due to splitting by the four nitrogen atoms. According to polarographic data, the heteroligand complex $Cr^{+}[(C_2H_5)_2NCS_2]Bipy$ is formed under these conditions. Since Cr^{3+}, having the d^5 electronic configuration, can form octahedral complexes, it follows that under the electrolysis conditions there is a possibility of the addition of yet another molecule and the formation of the complex species $Cr^{+}(C_2H_5)_2NCS_2(Bipy)_2$, whose signal is observed in EPR spectra[13].

Among other heteroligand complexes containing DTC, studies were made on compounds having the composition $[(Cp)_2VR_2NCS_2]^{+}$, where R = CH_3, C_2H_5, n-C_4H_9, or iso-C_3H_7, and Cp = cyclopentadienyl[14]. They are reduced in acetone in the presence of $(C_2H_5)_4NClO_4$ as the supporting electrolyte in two one-electron stages. The first reduction wave is fully reversible, while the second is irreversible. It is suggested that the reversible wave corresponds to the transfer of one electron to a non-bonding orbital of the vanadium atom with formation of a neutral vanadium(III) complex, tending to split off a free $R_2NCS_2^-$ anion. It was established by a.c. polarography that the dissociation is facilitated in the presence of oxygen. The free anion can oxidise metallic mercury to Hg^{+} at a potential more negative that $E_{1/2}$ for the first cathodic wave. The mechanism of the electrode process corresponding to the first wave has been described by an EC_1EC_2 scheme and is regarded as a special case of the ECE mechanism.

3. Dithiolates and Related Chelates

Dithiolate complexes, i.e. compounds with the chelate unit , where M is a transition metal, have been the subject of numerous polarographic studies. The first investigations in this field are examined in two reviews[15,16]. The polarograms of complexes in this group have several waves, the first of which is as a rule reversible. The stepwise nature of the reduction process has been observed in a series of inner complexes in which the structure of the coordination shell is[17]



where M = Cu, Ni, Co, Pd, or Pt for $n = 2$ and V, Cr, Mo, or W for $n = 3$, with formation of species where $z = 1$ or 2 ($n = 2$) and $z = 1$, 2, or 3 ($n = 3$).

In methylene chloride the intermediate species are fairly stable. The influence of the donor atoms X and Y on the ease of transfer of the first electron was examined qualitatively in relation to nickel bis-complexes[18]. It was established that $E_{1/2}$ for the nickel chelates undergoes a "cathodic" shift in the following series of coordination cells:

$$[NiN_4] < [NiN_2S_2] < [NiS_4] \leqslant [NiO_2S_2].$$

In a subsequent study [19], these results were refined and in addition to the influence of the donor atoms in the chelate unit on $E_{1/2}$ was discussed in relation to the zinc, copper, palladium, and cobalt inner complexes with *o*-mercaptophenol, 1-mercapto-2-naphthol, and 1-hydroxy-2-pyridinethione.

Together with polarography, the EPR method was used in the studies under consideration [15-19]. The fact that the transfer of the first electron to the dithiolate is reversible with formation of a stable paramagnetic product in a suitable solvent permits the use of this electrode reaction for the electrochemical generation of such a product. Interest in the electrochemical generation of species of this kind is due primarily to the ease with which it can be followed. Application of the EPR method not only established the formation of paramagnetic species, but also yielded valuable information about the nature of these species, about the nature of the metal–ligand bond, etc.

Two studies have been published, in which cyclic voltamperometry was used to investigate the mechanism of the one-electron transfer reactions involving cobalt [20] and nickel [21] maleonitriledithiolate (mnt) complexes. The method made it possible to study in detail the $[Co(mnt)_2]^{z-}$ (z = 0, 1, or 2) system in the absence and presence of pyridine (Py), to calculate the rate constant for the formation of heteroligand cobalt complexes with mnt and Py having the composition $[Co(mnt)_2Py]^-$ and $[Co(mnt)_2Py_2]^-$, and to propose a mechanism for the electrode process [20]. The triply charged anionic nickel complex with this ligand can be obtained by the reduction of the corresponding dianion at the electrode in acetonitrile or dimethoxyethane [21]. In the presence of traces of atmospheric oxygen this process takes place almost instantaneously. Analysis of the EPR spectra showed that the unpaired electron in the $[Ni(mnt)_2]^{3-}$ species is largely localised at the metal.

Polarography together with other methods has been used in the study of the dithiolene complexes of zirconium(IV), titanium(IV), and molybdenum in different valence states with toluene-3,4-dithiol in acetonitrile and methylene chloride [22]. Electrode transfer to the depolariser is irreversible in these processes.

4. Metal Diketonates in Electrochemical Reduction Reactions

The electrochemical behaviour of transition metal chelates with acetylacetone and certain dithiodiketones containing stable five-membered rings in their structure has been discussed in a review [23]. This section deals with studies carried out in recent years which are not included in the above review [23]. Thus interesting results were obtained in the investigation of the influence of substituents in the chelate ring in the series of trisdiketonate ruthenium(II) and ruthenium(III) complexes on the ease of reduction in DMF at a rotating platinum microelectrode [24]. Ruthenium complexes of this type, in both oxidation states, proved to be kinetically stable under the experimental conditions. The stage involving electron transfer to the ruthenium(III) chelate is reversible and uncomplicated by accompanying chemical reactions:

$$Ru(R_1COCHCOR_3)_3 + e \rightleftarrows Ru(R_1COCHCOR_3)_3^-.$$

$E_{1/2}$ varies over an unusually wide range (approximately 1.84 in DMF) as R_1 and R_2 are altered. The analogous range of variation of E was found to be at most 1.5 V in an earlier study [15] for a series of substituted chelates with a delocalised electronic structure of the type $M(S_2C_2R_2)_n$, where M is a transition metal (but not ruthenium). Electrochemical data for ruthenium(III) chelates of the type under consideration made it possible to employ the principle of the linearity of free energy in order to describe their reactivities in the one-electron transfer reaction. It has been stated [24] that cobalt(III) dithiocarbamate, for example, $Co[(C_2H_5)_2NCS_2]_3$, is reduced irreversibly in DMF at a platinum electrode with transfer of one electron. This finding is consistent with data for the reduction of nickel(II) dithiocarbamate under analogous conditions, discussed above [7].

The reduction of chromium(III) tris-β-diketonates was studied in dimethyl sulphoxide and 85% aqueous dioxan [25]. In the pure solvent the chelates CrL_3 (here HL = $R_1COCHR_2COR_3$; R_2 = H, R_1 = R_3 = H, CH_3, CF_3, or C_6H_5; R_1 = H, R_3 = CH_3, t-C_4H_9, or C_6H_5; R_1 = CH_3, R_3 = CF_3 or C_6H_5; R_1 = CF_3, R_3 = C_6H_5 or t-C_4H_9; R_1 = R_3 = CH_3, R_2 = CH_3, C_2H_5, or C_4H_9; R_1 = C_6H_5, R_3 = CH_3, R_2 = CH_3, C_2H_5, or C_4H_9; R_1 = R_3 = C_6H_5, R_2 = CH_3, C_2H_5, or C_4H_9) gave rise to one-electron waves, the first of which is associated with the reversible reduction

$$CrL_3 + e \rightleftarrows CrL_3^-.$$

On the other hand, in a mixed solvent the process is less reversible and the polarograms show one wave. The values of $E_{1/2}$ are in the range from −0.4 to −1.8 V, depending on the nature of R_1, R_2, and R_3. The effects of substituents are additive and are determined by their polarity. There is no correlation between $E_{1/2}$ and the usual parameters characterising the ligand field, while the spherical potential of the ligand field varies in parallel with the ease of reduction of the chelate. It is suggested [25] that the dependence of $E_{1/2}$ on the nature of R_1, R_2, and R_3 is associated with changes in electron density at the oxygen atoms of the pseudoaromatic chelate ring.

Vanadyl acetylacetonate in acetonitrile is reduced at the mercury electrode via a complex mechanism involving two electrons. In the presence of a diketone the process is complicated by intervening chemical reactions of the intermediates in the reduction process with acetylacetone [26]. Nickel(II) bis-β-dithiodiketonate complexes are reduced with electron transfer in stages involving the formation of intermediate charged complex species [27].

A comparative study of the influence of the nature of the oxygen and sulphur donor atoms on the ease of reduction in the general case led to the same conclusions as for the similar nickel complexes with a five-membered chelate unit [18,19], i.e. the replacement of O by S facilitates the reduction. The greater the number of sulphur atoms in the coordination unit of nickel β-diketonate, the less negative are the potentials at which the reduction takes place and the higher the charge transfer rate constants. In terms of the ease of reduction, these chelates can be arranged in the sequence $NiS_4 > NiS_2O_2 > NiO_4$. The same series is in essence retained for the values of k_S: $NiS_4 \simeq NiS_2O_2 > NiO_4$. [27] As for ruthenium β-diketonates [24], the values of $E_{1/2}$ for the first stage in the reduction of nickel(II) bis-β-dithiodiketonates in acetone cover a fairly wide range [28]. However, the dependence of $E_{1/2}$ on $\Sigma\sigma^*$ is not linear, despite the fact that the reduction at this stage leads to the formation of a thermodynamically stable oxidation-reduction pair.

Palladium(II) acetylacetonate is reduced irreversibly in DMF with consumption of two electrons (to form the metal amalgam) [29], which agrees with data for alcohol–benzene solutions [30].

5. Complexes with Schiff Bases

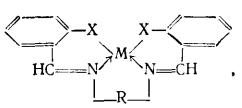
One of the first studies on chelates of this type concerned cobalt complexes with ligands which are structural analogues of one of the fragments of vitamin B_{12}.[31,32] An electrochemical model of the reduction processes involving the cleavage of the cobalt–carbon bond was studied in relation to the reduction of cobalt complexes of the type RCo^{2+}, where R = C_6H_5 or CH_3, with N,N′-ethylenebis(salicylideneamine) (H_2A) and 1,3-bisdiacetylmonoximeiminopropane (HB) in DMF. The C_6H_5–CoA chelate gives rise to three one-electron waves on the polarograms. The first two are of a diffusional and reversible type. According to data derived from cyclic voltamperograms and electrolysis at a controlled potential, the product of the one-electron transfer $[C_6H_5–CoA]^-$ is fairly stable. The dianion $[C_6H_5–CoA]^{2-}$, formed in the second reduction stage, is unstable under these conditions. The chelate CH_3–CoA is reduced in the first stage to $[CH_3–CoA]^-$, decomposing at the electrode with formation of a number of products: Co, CoA^-, and CH_3^-.

The second and third stages are poorly reflected in the curves. The chelate $[C_6H_5–CoB]^+$ gives rise to two reversible one-electron plateaux on the polarograms; the product of the two-electron transfer is fairly stable and can be isolated after electrolysis at a controlled potential. The electrochemical reduction of the $[CH_3–CoB]^+$ species proceeds via the mechanism

$$[CH_3–CoB]^+ + e \rightleftarrows CH_3–CoB,$$
$$CH_3–CoB + e \rightleftarrows [CH_3–CoB]^-.$$

The neutral species disproportionates with formation of $(CH_3)_2CoB$ and CoB. The same products are formed as a result of the interaction of the initial species and the monoanion. The different types of electrochemical behaviour of the chelates $[C_6H_5–Co]^{2+}$ and $[CH_3–Co]^{2+}$ with the above ligands are due to weaker electron-donating properties of phenyl compared with methyl. The electrode reactions of these coordination compounds simulate to some extent the biochemical action of vitamin B_{12}.[32]

The redox properties of complexes having the structure[33]



where M = Co, Ni, or Cu, X = O or NH, and R = $CH_2–CH_2$, $(CH_2)_3$, or $CH(CH_3)CH_2$, were investigated at a platinum electrode in methylene chloride. The low-valence state of the central atom in the bis-complexes of the same metals with the Schiff bases obtained from acetylacetone and salicylaldehyde and amines is stabilised at the m.d.e. on reduction via the process $M^{2+} \rightleftarrows M^+$; the stabilisation can be explained by the square-planar structure of the initial ligands[34].

The electrochemical reduction of cobalt chelates having the general formula RCoLX,[35] where R = C_6H_5, CH_3, C_2H_5, or $CH{=}CH_2$, L = the monoanion of 1-diacetyl monoximatoimino-3-diacetylmonoximeiminopropane or a tetradentate dianion [*N*,*N*′-ethylenebis(salicylideneaminate), *N*,*N*′-ethylenebis-(7,7-dimethylsalicylideneaminate), or *N*,*N*′-ethylenebis(acetylacetoneiminate)] and X is the solvent, was investigated by polarography at the m.d.e. in DMF, pyridine, and dimethyl sulphoxide. The nature of the group R and the solvent X influences the stability of the one-electron transfer product. The complex of the first ligand gives rise to two one-electron plateaux on the polarogram, the second of which corresponds to the formation of a species in which the degree of oxidation of the central atom is +1. The complex $[C_6H_5–Co]^-$, obtained as a result of electrolysis at a controlled potential E, was identified spectrophotometrically. The species $[RCoL]^-$, derived from chelates with R = CH_3 or C_2H_5, reacts in the course of electrolysis with the initial depolariser, forming bis-complexes. The values of $E_{1/2}$ for the first plateaux are satisfactorily correlated with the pKa of acids of the type RH.

In another study[36] the same workers described the polarographic behaviour of cobalt complexes having the composition $[Co^{3+}YL_2]^+$ and $[Co^{2+}Y_2]^0$, where Y is an equatorial ligand—the dianion of an imine of the same type as in earlier investigations[35] and L is an axial ligand: methylamine, n-propylamine, benzylamine, aniline, pyridine, and similar amines. The complexes are reduced in 95% ethanol via two reversible one-electron stages corresponding to a formal change in the degree of oxidation of cobalt:

$$[Co^{3+}YL_2]^+ + e \rightleftarrows Co^{2+}YL_2 \text{ and}$$
$$Co^{2+}YL_2 + e \rightleftarrows [Co^{+}YL_2]^- ,$$

but only in the presence of an excess of the amine L. In the absence of the amine, the first reduction stage is irreversible, which was explained by the subsequent chemical stage in which L is split off. At a platinum microelectrode under the same conditions[36] oxidation takes place with the reversible transfer of one electron via the formal mechanism:

$$Co^{2+} - e \rightleftarrows Co^{3+}.$$

The values of $E_{1/2}$ for the first reduction stage of these chelates with various Y reflect the influence of the electronic structure of the tetradentate ligand. An increase in the degree of conjugation in the structure of Y causes an "anodic" shift of $E_{1/2}$. The observed correlation between $E_{1/2}$ for the first stage and the pKa of the amines indicates a transfer of electron density from L to Y. This correlation occurs only for ligands with the same electronic and steric configurations of the nitrogen donor atom. The small change of $E_{1/2}$ for the second stage as a function of the nature of L shows that the interaction of the amine with cobalt is only slight. The authors[36] suggest that $E_{1/2}$ for the first stage characterises the energy of the unoccupied molecular orbital.

The electrochemical reduction of 37 mononuclear and dinuclear copper(II) complexes with imino-ligands L (L = substituted β-ketoamines, β-iminoamines, or pyrrole-2-aldimines) in DMF in the presence of tetra-n-propylammonium perchlorate as the supporting electrolyte was investigated by electrochemical methods and ultraviolet spectroscopy[37]. The mononuclear complexes are reduced with consumption of one electron. The dinuclear chelates are reduced with transfer of two electrons in one of two consecutive stages as a function of the nature of L with formation of the corresponding copper(I) chelates. Complexes of this type, which have a non-planar structure, are reduced more readily than planar chelates. The ease of their reduction increases in the sequence rigid tetradentate (with N_4 units) < bidentate (with N_2O_2 units) < bidentate (with N_2S_2 units) ligands.

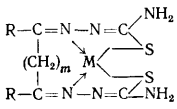
6. The Behaviour of Thio- and Seleno-semicarbazone Metal Complexes at the Mercury Dropping Electrode in DMF

The ligand in complexes of thio- and seleno-semicarbazones is in many cases the protonated form of the initial organic reagent. For this reason they exhibit different types of behaviour at the electrode[38-42]. Metal complexes with the thiosemicarbazones of acetone (Hthac), benzaldehyde (Hthbz), anthranilic aldehyde (Hthan), salicylaldehyde (Hthsa), and their selenium analogues give rise to different numbers of waves on polarograms in DMF in the presence of $(C_2H_5)_4NClO_4$ as the supporting electrolyte. The polarograms of copper(I) chelates with Hthac and Hthbz contain two waves. Their first one-electron waves are nearly reversible:

$$\underset{(L = \text{ligand})}{CuL} + e + Hg \rightleftarrows Cu(Hg) + L^- \ .$$

The second waves, at negative potentials, are due to the ligand liberated in the first stage. They are of the kinetic type and differ from the waves of the initial Hthac and Hthbz by their parameters owing to the deprotonation of the reactants on complex formation. The copper(II) chelate complex of H_2thsa gives rise to one two-electron wave on polarograms. The thio- and seleno-semicarbazones of anthranilic aldehyde react with Cu^{2+} to form complexes $Cu(HL)Cl_2$, i.e. without the displacement of hydrogen ions. They give rise to an extended irreversible wave on polarograms, corresponding to the reduction of the central ion, and a wave due to the reduction of the ligand with $E_{1/2}$ close to that of the initial Hthan or Hsesan.

The mechanism of the reduction of copper(II) complexes of bisthiosemicarbazones under the conditions corresponding to the first wave is probably analogous to the mechanism of the reduction of copper(I) chelate complexes of Hthac and Hthbz. The constant k_S for this stage is $(0.50 \pm 0.16) \times 10^{-2}$ cm s^{-1}. $E_{1/2}$ diminishes with increase of the number of methylene groups in the ligand fragment of the chelate. The structures of copper(II) complexes of bisthiosemicarbazones have in general three chelate rings[39]:



For $m = 0$ or 1, the middle ring is five- or six-membered, i.e. is the most stable, and this factor is responsible for the maximum chelating effect. With increase of m to three, the middle ring expands and makes no contribution to the stabilisation of the chelate structure. The possibility of forming complexes of this type promotes the stabilisation of the central atom in the +2 oxidation state. For $m = 4$, this does not happen: the bisthiosemicarbazone behaves similarly to Hthac or Hthbz, i.e. copper(II) is reduced to copper(I) with formation of the corresponding complex. The thiosemicarbazones of salicylaldehyde and anthranilic aldehyde (H_2thsa and Hthan) and their selenium analogues form the cobalt complexes $[Co(HL)_2]X$, in which the metal is in the +3 oxidation state. Their polarograms contain two waves. The first extended, irreversible wave (with $E_{1/2} \simeq -1.1$ V) formally corresponds to the reduction of the metal ion in the complex and the second at $E \simeq -1.5$–-2.0 V corresponds to the electrochemical reaction of the ligand anion.

The cathodic shift of $E_{1/2}$ on passing from cationic complexes of the type $[Co(Hthsa)_2]Cl$ to the anionic complexes $NH_4[Co(thsa)_2]$ can apparently be accounted for not only by the formation of a more stable complex in the latter case, but also by the sign of the charge of the species being reduced. The results of the investigation showed that $E_{1/2}$ is independent of or depends little on the nature of outer-sphere ion X.[41] Nickel ions react with reagents of this type to form complexes of two kinds: with and without substitution of the hydrogen atoms in the ligand. The complexes $[Ni(HL)_2]Cl_2$ give rise to two irreversible waves on the polarograms. The first diffusional stage formally corresponds to the process $Ni^{2+} \rightarrow Ni^0$, while the second is due to the ligand.

For nickel chelate complexes of bisthiosemicarbazones, the stepwise transfer of two electrons is observed. The stepwise mechanism of the reduction indicates the formation of intermediate complex species with a formally low-valence state of the central atom[42]:

$$NiL + e \rightleftarrows [NiL]^- + e \rightleftarrows [NiL]^{2-} \ .$$

The electrochemical behaviour of cadmium, lead, and nickel complexes with reagents of the above type has been described[40].

Comparison of the polarographic behaviour of metal chelate complexes (having structures of the same type) of various thiosemicarbazones reveals the following regularity. If the metal does not form an amalgam with mercury or its solubility in mercury is low, then the product of the two-electron transfer exists for a time at the electrode, which is the reason for the reversibility of the process (nickel chelates having the structure of the inner complex type). Subsequent electron transfer to the chelate dianion formed should apparently occur at very much higher negative potentials E, so that there are no waves due to the ligands. On the other hand, if the metal is readily soluble in mercury (for example, lead and cadmium), then the formation of an amalgam promotes the deactivation of the two-electron transfer product with formation of species differing from the initial thiosemicarbazone and being reduced at more "cathodic" potentials E. The difference between them can be explained by the fact that the ligand in the inner complex structure is a deprotonated thiol form of the thiosemicarbazone. In those cases where complex formation proceeds without the elimination of protons, the ligand and the initial thiosemicarbazone give rise to virtually identical waves on the polarograms.

7. Metal Chelate Complexes of Certain Hydroxyazo-Compounds in DMF

In terms of their electrochemical behaviour, these complexes like the metal complexes of dithiocarbamates and thiosemicarbazones can be divided into two groups, depending on the electronic configuration of the central atom[43-45]. Cadmium(II), lead(II), tin(II), and copper(II) complexes are reduced in DMF at the m.d.e. in two stages. The first stage corresponds to the transfer of two electrons and formally involves the electrochemical reduction of the central ion in the chelate. The second wave is due to the ligand L, liberated when the complex is reduced in the first stage. The parameters of the two waves differ from those of the initial azo-compounds.

The nature of the ligand is reflected in the polarographic properties of the chelates. The greater stability of complexes with ligands forming an additional coordinate bond due to the lone electron pair of the nitrogen atom in the heterocycle is the cause of the shift of $E_{1/2}$ towards more "cathodic" values. The introduction of a sulphur atom into the heterocycle reduces the electron-donating

properties of nitrogen in this ring and diminishes the strength of the M–L bond, which is reflected in the value of $E_{1/2}$.

The irreversibility of the second stage in the reduction of chelates in this group and its kinetic nature are evidently due to the decomposition of negatively charged complex species formed in the first stage, as in the reduction of chelate complexes of thio- and seleno-semicarbazones:

$$ML_n + 2e \rightleftarrows [ML_n]^{2-} + Hg \xrightarrow{k'} M^0(Hg) + nL^{(3-n)-};$$
$$n = 1, 2.$$

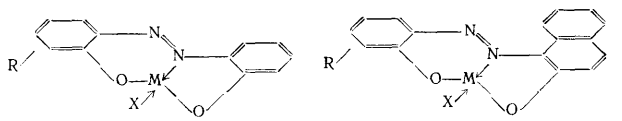
Manganese(II), nickel(II), and zinc(II) complexes, which constitute a second group of compounds, are reduced, in contrast to the previous compounds, via two irreversible one-electron stages, which are followed by a third irreversible wave. Comparison of the EPR spectra of the products of the one-electron reduction of nickel(II) and zinc(II) complexes with the EPR spectra of the products of the reduction of the initial azo-compound shows that the spin density of the transferred electron is localised at the ligand[46]. Taking into account the fact that the values of $E_{1/2}$ for chelates of this type with different metals differ insignificantly, presumably in this case the M–L bond is of the ligand type. Compared with the complexes of *o*-hydroxyazo-compounds, the chelate complexes of *o*,*o*'-dihydroxyazo-compounds are reduced at more negative potentials, since they form a more stable structure with metal ions, in which two pseudoaromatic rings are generated.

The limiting current of the first reduction wave of the nickel(II) and zinc(II) complexes of *o*,*o*'-dihydroxyazo-compounds exceeds the current of the second wave and the one-electron level. This is caused by the disproportionation of the products formed in the first stage. The disproportionation constants are in the range $(1-20) \times 10^4$ litre $mole^{-1}s^{-1}$. For certain rates of polarisation of the electrode, it is possible to eliminate almost completely the influence of the subsequent reactions and the electrode process can be regarded as reversible. For this range of rates, the equation of the linear relation between the free energy and the Hammett substituent constants can be put in the form

$$\Delta E_p' = \rho_\pi \sigma_R,$$

where $\Delta E_p'$ is the shift of the E peak on the oscillopolarograms under the influence of the substituents. This makes it possible to estimate the influence of substituents on the ease of the electrochemical reduction of the complexes, whose reduction under the conditions of classical polarography is complicated by the subsequent chemical reactions of the primary products of the reversible charge transfer[47].

The introduction of *m*- and *p*-substituents into the benzene ring of the ligand in chelates of the type



(where M = Ni, Zn, or Mn in the +2 oxidation state, X is the solvent, and R = *p*-NH_2, *p*-OH, *m*-Cl, *m*-Br, or *m*-I) alters E_p, but hardly influences other process parameters. The sensitivity of the reaction centre to the influence of substituents for zinc(II) complexes is somewhat smaller than for the analogous nickel(II) and manganese(II) chelates. The increase of $\rho_\pi(\rho_\pi^*)$ for chelates of the latter type can be accounted for by the increase of the electron density at the reaction centre owing to the involvement of the *d* electrons of the metals in the conjugation system. Owing to the characteristics of its electronic structure, the possibility of $p_\pi - d_\pi$ binding involving Zn^{2+} is smaller than for transition *d* elements, which is reflected in the sensitivity of the reaction centre to the influence of substituents[47].

8. Metal Complexes of 2,2'-Bipyridyl and 2,2',2''-Terpyridyl in Electrochemical Reactions

Extensive studies on the polarographic behaviour of the chelates of typical transition metals have been carried out by Japanese investigators. Their earlier publications and those of other workers are discussed in a review[23]. Among the later studies on the polarography of bis-complexes, mention should be made of those concerning cobalt(II) and manganese(II) chelate complexes of bis-2,6-(2'-quinolinyl)pyridine[48], dicyanobispyridyl complexes of cobalt(III),[49] dichlorobispyridyl complexes of chromium(III),[50] and tungsten(V) and tungsten(IV) hexachloride complexes with Bipy in acetonitrile[51]. When the heteroligand complex $[Co(CN)_2(Bipy)_2]^+$ is reduced at the m.d.e. in dimethyl sulphoxide[48], three diffusion waves are observed. Each corresponds to the transfer of one electron, as for the cobalt(III) cyanide and bipyridyl complexes:

$$[Co(CN)_2(Bipy)_2]^+ + e \rightarrow Co(CN)_2(Bipy)_2 + e \rightarrow [Co(CN)_2(Bipy)_2]^- + e \rightarrow [Co(CN)_2(Bipy)_2]^{2-}.$$

In the concluding stage of the process, metallic cobalt is partly deposited, since the last complex is unstable under the experimental conditions. The formation of species with the central atom in the zero oxidation state has been confirmed oscillopolarographically.

In the presence of water, the one-electron reduction is accompanied by rapid disproportionation of the ligand and substitution by water molecules, which leads to the formation of an equimolar mixture of $[Co(CN)_4(Bipy)_2]^{2-}$ and $[Co(Bipy)_2(H_2O)_2]^{2+}$. The polarographic characteristics of the bipyridyl complexes in DMF can be found for ruthenium(III) in the paper of Patterson and Holm[37] and for osmium(IV) and iron in the paper of Misono et al.[52] Chelates with ligands of this type have been studied by electrically generated luminescence[53]. Its intensity depends on the stability of the intermediate species, which is determined in its turn by the nature of the ligand.

In the electrochemical studies examined above the metal in the initial depolariser was in the usual oxidation state, equal to two or three. Species with the central atom in a lower oxidation state arose at the electrode during electrochemical reduction; in certain cases they could be identified on the basis of their spectra.

For example, the absorption spectra of electrochemically generated unstable species were obtained in the reduction of bipyridyl complexes of cobalt(II) at a silver electrode in propylene carbonate[54].

There has been recently a renewed increase of interest in the study of electrode reactions of complexes of metals in a low oxidation state and in the determination of factors stabilising these complexes. The reversible one-electron reduction of heteroligand nitrosylbipyridylruthenium complexes having the overall formula $[Ru(Bipy)_2(NO)X]^{3+}$, where $X = Cl^-$, N_3^-, NO_2^-, NH_3, Py, or acetonitrile, was investigated by cyclic oscillopolarographic methods using a platinum electrode in acetonitrile[55]. It has been shown by EPR and infrared spectroscopy that the transfer of electrons is localised at the nitrosyl group.

Using the same methods as in the above study[55] and in addition the coulometric procedure, it has been shown[56] that the two consecutive one-electron stages in the reduction of diphenylbisbipyridylchromium(III) in acetonitrile and dimethyl sulphoxide occur at $E_{1/2} = 1.21$ and 1.64 V (relative to the saturated calomel electrode), regardless of the nature of the solvent and the material of the electrode, via the mechanism

$$[(C_6H_5)_2\,Cr\,(Bipy)_2]^+ + e \rightleftarrows [(C_6H_5)_2\,Cr\,(Bipy)_2]^0 + e \rightleftarrows [(C_6H_5)_2\,Cr\,(Bipy)_2]^-.$$

The higher degree of solvation of the depolariser in dimethyl sulphoxide compared with that observed in acetonitrile is reflected in the diffusion coefficient: 2.0×10^{-6} and 1.5×10^{-5} $cm^2 s^{-1}$ respectively.

A series of studies[57-62] devoted to the polarographic properties of transition metal complexes with different (ranging from +2 to −1) oxidation states of the central atom in the initial depolariser and also to the investigation of the kinetics of electron transfer in the corresponding oxidation-reduction pairs of the type $[M(Bipy)_3]^{n+}/[M(Bipy)_3]^{(n-1)+}$ arising at the electrode, have been published recently. The potentials $E_{1/2}$ of the first reversible one-electron stages in the reduction of Bipy, 4-methyl-2,2′-bipyridyl, 5-methyl-2,2′-bipyridyl and the corresponding iron(II), ruthenium(II), and osmium(II) complexes[67] in DMF have been compared. If it is assumed that the reduction of a chelate involves only the coordinated ligand, then there should be a linear relation between the electron affinity of the complex and that of the free ligand in the series of chelates of the same metal. Such a relation has been observed experimentally for iron, ruthenium, and osmium complexes with ligands of the same type:

$$E^{red}_{1/2,c} = E^{red}_{1/2,L} + C,$$

where the subscripts c and L refer to the $E_{1/2}$ of the complex and the free ligand and C is a constant. Since $E_{1/2}$ for complexes of metals M in the same oxidation state with any one ligand L varies by not more than 80 mV, for metals in the iron–ruthenium–osmium series, an electron is transferred to a molecular orbital of the π^*-ligand type.

The tris-complexes of chromium(I), chromium(0), vanadium(0), titanium(0), and molybdenum(0) have been studied by polarographic and cyclic voltamperometric methods[58] in DMF and tetrahydrofuran. Multiplateau waves are observed on the polarograms of these complexes in both the cathodic and anodic potential ranges, corresponding to multistage electron transfer. The half-wave potentials for reversible oxidation-reduction systems arising at the electrode have been determined. An empirical rule has been derived for the assessment of the nature of the orbital occupied by the electron transferred in the electrochemical reaction on the basis of $E_{1/2}$ for the complex with a methyl group introduced into the Bipy molecule. Thus, the transferred electron occupies an antibonding ligand orbital in the reduced forms of the redox pairs VL_3^-/VL_3^{2-}, CrL_3/CrL_3^-, CrL_3^-/CrL_3^{2-}, and CrL_3^{2-}/CrL_3^{3-}, where L = Bipy. In the corresponding VL_3^{2+}/VL_3^+ and VL_3^+/VL_3 complexes it occupies the t_{2g} orbital, which is of a metallic type. The difference between the energy levels of the orbitals of the complexes has been discussed quantitatively on the basis of the shift of their $E_{1/2}$ in relation to the $E_{1/2}$ of the free ligands. In the series of complexes $V(Bipy)_3^-$, $Cr(Bipy)_3$, and $Fe(Bipy)_3^{2+}$ the energy of the lowest unoccupied molecular π^* orbital is increased[58].

The values of k_S for trisbipyridyl chromium complexes have been determined by the method of the double galvanostatic pulse[59] at the m.d.e. and for analogous iron, ruthenium, osmium, chromium, titanium, vanadium, and molybdenum chelates[58] at a platinum electrode in DMF. In a series of these complexes k_S is independent (or depends little) of the oxidation-reduction potential of the corresponding redox pair, which varies from +1.03 to −1.54 V, of the degree of oxidation of the central atom in the oxidised form of the complex, of the nature of the solvent, and of the type of the electrode. This shows that the rate of charge transfer in the reduction of the complexes is largely determined by the electronic configuration of the reacting species. For species where the transferred electron is localised in the molecular orbital of the ligand π^* type, the values of k_S lie in the range 0.1 to 0.3 cm s^{-1}. For complexes in the reduction of which an electron is transferred to a molecular orbital of the metallic t_{2g} type, the values of k_S are in the range 0.8–1.3 cm s^{-1}. The constant k_S for the Bipy/Bipy$^-$ system is virtually the same as the value for the first group of the complexes investigated (~ 0.15 cm s^{-1}). On the basis of this finding, it has been suggested[58] that the contribution of the energy of reorganisation of the solvent† to the change in k_S is not as large as might have been expected. It is noteworthy that the values of k_S for the $[Fe(Bipy)_3]^{2+}/[Fe(Bipy)_2]^+$, $[Fe(Bipy)_3]^{3+}/[Fe(Bipy)_3]^{2+}$, and $[Cr(Bipy)_3]^+/[Cr(Bipy)_3]^0$ systems are close to the k_S for the Bipy/Bipy$^-$ redox system[58]. This difference can be accounted for by the fact that, in the oxidation of the $[Fe(Bipy)_3]^+$ species, an electron leaves a ligand π^* orbital, whereas in the reduction of the corresponding $[Fe(Bipy)_3]^{2+}$ species, an electron passes to a metallic t_{2g} orbital.

Information about the formation of bipyridyl complexes with a metal in a low oxidation state can be found for zerovalent vanadium[61], for Co$^-$,[63] for ruthenium in heteroligand nitrosoarene complexes with Bipy[64], and for manganese and chromium in complexes with certain aromatic tridentate ligands[65].

The overall mechanism of the reduction of metal bis-complexes with terpyridyl (Terpy) is similar to the mechanisms quoted above for reduction with stepwise electron transfer, for example, for chromium(III) chelates[65]:

$$[Cr(Terpy)_2]^{3+} + e \rightleftarrows [Cr(Terpy)_2]^{2+} + e \rightleftarrows [Cr(Terpy)_2]^+.$$

Manganese(II), cobalt(II), nickel(II), and europium(III) chelates of terpyridyl in acetonitrile have been investigated by different versions of the polarographic method[66]. Reversible electron transfer is observed for the first two stages in the reduction of manganese and cobalt complexes, but anions of the type $[Co(Terpy)_2]^-$ have not been detected. The reduction of the complex $[Eu(Terpy)_2]^{3+}$ involves the initial formation of $[Eu(Terpy)_2]^{2+}$. This species reacts further at the electrode with consumption of two electrons and the formation of zerovalent europium. The standard rate constant for this stage is 6.7×10^{-4} cm s^{-1}, which shows that it is clearly irreversible. The subsequent waves at the edge of the range of negative potentials are due to the reduction of the Terpy species. It has been concluded[66] that the d elements in the zero oxidation state exhibit a greater tendency towards complex formation than the f elements.

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† In reactions of the complexes one distinguishes processes involving the reorganisation of the inner and outer coordination spheres. The latter includes also the reorganisation of the solvent in which the complex is dissolved.

Like bipyridyl, another heterocyclic ligand—1,10-phenanthroline—is capable of stabilising the low oxidation states of transition metals[67]. The electrochemical reactions of these complexes resemble processes with participation of bipyridyl analogues[67,68]. It has been suggested[69] that the significant involvement of the π binding of the metal in the lowest oxidation state to the ligand as well as the ability of phenanthroline and its alkyl-substituted derivatives to delocalise the charge on the central atom even in the presence of a tetrahedral environment (in bis-complexes) are factors stabilising the intermediate electrode products. The polarograms of the tris-complex of iron(II) of 4,7-diphenyl-1,10-phenanthroline contain six reversible one-electron plateaux, each of which corresponds to a successive stage in the oxidation state of the metal from 2+ to 4−, i.e. the final species obtained in the reduction of the tris-chelate has six electrons in excess of the number characteristic of the usual oxidation state[67]. This quantity Δ (in the given case Δ_6) is the maximum attained electrochemically for low-spin metal complexes.

9. Metal Complexes of Phosphines in Electrochemical Reduction Reactions

The metal complexes with substituted phosphines as one of the ligands have become much investigated by electrochemical methods in recent times. Interest in these compounds is because they can be extremely active homogeneous catalysts of reactions of unsaturated organic compounds. Furthermore, such complexes, with the central atom in a low oxidation state, can be used to bind carbon monoxide as well as nitrogen in an active form.

Using mainly classical polarography and cyclic voltamperometry, a group of Italian investigators carried out a series of studies on the electrochemistry of coordination compounds of this type in non-aqueous media[70-75]. Under an argon atmosphere, in a 50% mixture of toluene and acetonitrile containing a certain amount of triphenylphosphine, a study was made of *trans*-chlorocarbonyl-bis(triphenylphosphine)rhodium(I) $RhCl(CO)[P(C_6H_5)_3]_2$. Its reduction takes place with addition of two electrons in one stage and the formation of a complex anion with the metal in the formal 1-oxidation state. The anion reacts further with the depolariser, which leads to a species in which rhodium is in the zero oxidation state[70]. Rhodium(I) and iridium(I) complexes of bisdiphenylphosphinoethane $(C_6H_5)_2P-CH_2-CH_2-P(C_6H_5)_2$, another π-acceptor, have the composition ML_2Cl and the polarograms also exhibit a single two-electron reversible diffusion wave in acetonitrile[71]. The addition of water leads to the disappearance of anodic peaks from the cyclic curve. During electrolysis at a controlled potential in solutions of the complexes, the colour of the solution changes and precipitates are formed. Apart from bands characteristic of the ligand in L, bands corresponding to rhodium and iridium hydrides were identified in the infrared spectra of the electrolysis products. The authors[71] suggest the following mechanism of the reduction at the m.d.e. in the presence of proton donors:

$$(ML)_2^+ \overset{2e}{\rightleftarrows} (ML)_2^- \xrightarrow{\text{proton donors}} MHL_2.$$

Data for the oxidation-reduction behaviour of these compounds have been compared with the reactivities of the anionic complexes in which the metal is in the 1-oxidation state and which have the d^{10} configuration[71].

In contrast to rhodium and iridium complexes[71], the cobalt complexes of bisdiphenylphosphinylethane having the general formula CoL_2ClO_4 are reduced with the reversible transfer of two electrons in stages[73]. The product of electrolysis at a controlled potential E, corresponding to the limiting current of the first wave and isolated in the form of red crystals, was identified as CoL_2 in which the central atom is in the zero oxidation state. At the potential of the second wave the unstable species $[CoL_2]^-$ is formed at the electrode and reacts with the solvent, which leads to the formation of $CoHL_2$. Thus the stabilisation of low valence states of the metals in electrochemical reduction reactions can be attributed to the high π^*-acceptor capacity of ligands of the given type.

A parallelism between the results of kinetic measurements and polarographic data has been observed[74] in the study of the following platinum(II) complexes: in 1,2-dimethoxyethane at the m.d.e (L = piperidine): *trans*-$\{Pt[P(C_2H_5)_3]_2Cl_2\}$, *trans*-$\{PtL[P(C_2H_5)_3]Cl_2\}$, and *trans*-$[PtL_2Cl_2]$. The ease of reduction diminishes in the series of these compounds, i.e. the phosphine complex is reduced more readily than, for example, a heteroligand complex with piperidine. The authors suggest that the rate of nucleophilic S_N^2 substitution of the phosphine-complex is sensitive to changes in the nature of the entering group.

An irreversible two-electron diffusion wave is observed in the reduction of a tetrakis(triphenyl phosphite) complex of rhodium(I) at the m.d.e. It is suggested that it is highly solvated in acetonitrile[75]. The product of the addition of two electrons $[RhL_4]^-$, where L is triphenyl phosphite, was identified after electrolysis at a controlled potential. Platinum complexes of triphenylphosphine in DMF at the m.d.e are reduced with the consumption of two electrons and the formation of the corresponding zerovalent platinum complex[76]. In the presence of water the product of the two-electron reduction is converted into a hydride complex having the composition $Pt[(C_6H_5)_3P]_2H(Cl)$. Comparison of the values of $E_{1/2}$ for the above compound and the initial depolariser shows that the introduction of a hydride ion into the inner coordination sphere of this complex causes a marked hindrance of the charge-transfer process.

III. ANODIC REACTIONS OF METAL COORDINATION COMPOUNDS

Much less attention has been devoted to anodic processes in the electrochemistry of metal complexes with organic ligands than to reduction processes. The main reason for this is that in the case of the m.d.e. a comparatively limited range of polarisation potentials is available. On the other hand, the use of solid electrodes for these purposes began quite recently. There has been a growth of interest in recent times in the investigation of the anodic process involving a wide variety of complexes in organic and mixed solvents, including electrochemical oxidation at solid electrodes, particularly for compounds in which the central atom is in a low oxidation state.

In the anodic oxidation of metal complexes an electron may be abstracted both from the orbitals of the central atom and from molecular orbitals of the ligand type. The products exhibit different stabilities. Useful information about the structure of these species can be obtained by EPR. The dependence of the oxidation potentials on the ionisation potentials is frequently linear. This finding confirms the validity of the idea that the primary stage in

the oxidation of the complex involves the abstraction of an electron from the highest occupied molecular orbital.

The oxidation-reduction properties of typical transition metal dithiocarbamates have been studied for the first time comparatively recently at a platinum electrode in acetone as a function of the nature of the complex-forming ion and substituents R and R′ in the ligand fragment of the chelate[77]. Judging from the results, the majority of the electron transfer reactions are rapid. The products of one-electron oxidation of many dithiocarbamates in acetone have comparatively short lifetimes (determined from cyclic voltamperometric data). The nature of the substituents R and R′ affects the ease of oxidation of the metal dithiocarbamates. However, a simple Taft correlation between $E_{1/2}^{ox}$ and the sum of the Taft substituent constants was not found. According to the authors[77], this is associated with the steric effects of the alkyl groups in the one-electron transfer reactions. In the series investigated the complexes of all the metals with *N*,*N*-dicyclohexyldithiocarbamate are oxidised most readily, while the chelates with *N*,*N*-dibenzyldithiocarbamate are oxidised with the greatest difficulty. Diethyldithiocarbamate derivatives occupy an intermediate position. The opposite relation has been observed for the reduction of the same compounds. In the series of the metal dithiocarbamates investigated the values of $E_{1/2} = E_{1/2}^{ox} - E_{1/2}^{red}$ depend significantly on the nature of the metal atom:

M	Cr	Mn	Fe	Co	Ni	Cu
$E_{1/2}$, V	2.58	0.48	0.92	2.02	2.34	1.07

This demonstrates the predominantly metallic nature of the molecular orbital in which the electron transferred in the electrochemical step is localised.

The oxidation of nickel(II) diethyldithiocarbamate has been investigated in no less detail at a platinum electrode than in acetonitrile[78]. Like the corresponding copper and iron chelates[79,80], the nickel(II) compounds are oxidised electrochemically comparatively readily and this can serve as a basis of the synthesis of metal dithiocarbamates with a high oxidation state of the central atom. The first stage in the oxidation of nickel(II) dithiocarbamates is reversible abstraction of one electron. Coulometric measurements at the limiting one-electron oxidation current yield $n = 1.3$. In the presence of $(C_2H_5)_4NBF_4$ electrolysis at a controlled potential leads to two products: $Ni^{4+}[(C_2H_5)_2NCS_2]_3BF_4$, in which the formal oxidation state of the metal is 4+, and $Ni^{2+}(BF_4)_2$ with an oxidation state of 2+. Nickel(IV) chelates have been isolated and identified.

In the anodic reactions of chromium, molybdenum, and tungsten complexes having the composition $L_2M(CO)_2$, where L = bis(diphenylphosphino)methane, the stepwise abstraction of two electrons is accompanied by the isomerisation of the *cis*-cation in the complex to the *trans*-cation; the *trans*-isomers of complexes with this ligand L are oxidised more readily than the similar complexes with bis(diphenylphosphino)ethane[81]. Using cyclic voltamperometry, electrolysis at a controlled potential, EPR, the oxidation of cobalt(III) and rhodium(III) chelate complexes with derivatives of dimethylglyoxime and salicylideneaniline has been investigated[82,83] at a platinum electrode in acetonitrile, methylene chloride, and a mixture of the latter with toluene. The supporting electrolyte was a 0.1 M $(C_2H_5)_4NBF_4$ solution.

Previously unknown complexes with formally quadrivalent cobalt and rhodium, in which the metal–carbon σ bond is retained, were observed in the reversible one-electron oxidation of chelates of the type $RCoL_2Py$ (R = CH_3, C_2H_5, or $C_6H_5CH_2$; L = bisdimethylglyoximate dianion), RCoL [R = CH_3, C_2H_5, iso-C_3H_7, or n-C_4H_9; L = bis(salicylidenato)ethylenediamine dianion], and RRhLPy [R = CH_3, n-C_3H_7, or iso-C_3H_7; L = bis(salicylidenato)ethylenediamine dianion]. The lifetime of these species has been estimated as amounting to several minutes. The stability of the complex species with the metal in the 4+ oxidation state and the ease of the oxidation of the initial chelates increase as R is varied in the sequence $CH_3 < C_2H_5 <$ n-$C_3H_7 <$ n-$C_4H_9 <$ iso-C_3H_7. On the basis of these data, it is suggested that during oxidation at the electrode an electron is abstracted from the central atom or from the group R and not from the chelating ligand. The product of the oxidation of the complexes is an analogue of the carbonium ion R^+.[82]

It is fairly interesting to compare the oxidation potentials of the complexes and the frequencies of the charge-transfer bands in the ultraviolet spectra. Such a correlation has been drawn for the trisbipyridyl complexes of iron, osmium, ruthenium, cobalt, and chromium, in which the metal is in the 2+ oxidation stage[83]. It is known that the minimum energy corresponding to the frequency of the charge-transfer band can be represented by the difference $\nu = I_C - A_L^C$, where I_C is the vertical ionisation potential of the t_{2g} orbital in the metal complex and A_L^C is the electron affinity of the lowest antibonding π^* orbital in the coordinated ligand. It is suggested that, during the oxidation of the complex, an electron leaves the t_{2g} orbital. Furthermore, it is believed that there is a linear relation between the electron affinities of the coordinated ligand and the organic compound not bound in the complex, in a series of chelates of the same metal with different ligands, which is expressed by the following relation:

$$E_{1/2,C}^{ox} - E_{1/2,L}^{red} = \nu + C,$$

where C is a constant. A simple correlation between $E_{1/2,C}$ and ν has not been observed for the complexes $[FeL_3]^{2+}$, $[RuL_3]^{2+}$, $[OsL_3]^{2+}$, $[CrL_3]^{2+}$, and $[CoL_3]^{+}$.[84] However, if one uses the difference $E_{1/2,C}^{ox} - E_{1/2,L}^{red}$ instead of $E_{1/2,C}^{ox}$, then the former is linearly correlated with the energy corresponding to the frequency of the charge-transfer band.

Thus there is a linear relation between this energy characteristic and the oxidation potentials of the complexes corrected for the electron affinity of the π-acceptor ligand. If an electron leaves the t_{2g} orbital during oxidation, then $E_{1/2}^{ox}$ for the tris-complex of a transition metal with bipyridyl undergoes a cathodic shift in the following sequence when a methyl group is introduced into the ligand: Bipy < 5,5′-CH_3-Bipy < 4,4′-CH_3-Bipy. The empirical rule concerning the influence of substitution on $E_{1/2}$ is used as a criterion in the determination of the configurations of transition metal complexes of bipyridyl on the basis of electrochemical data[84].

Data have been published[27] on the oxidisability of nickel(II) chelates formed with dihydric *o*-phenols and their mono- and di-thio-analogues in acetone at a platinum electrode. In terms of the ease of their oxidation, these chelates can be arranged in the following sequence: $NiS_4 > NiO_2S_2 > NiO_4$. The irreversible one-electron oxidation in methylene chloride of complexes of the type $Ir(CO)XL_2$, where X = halide anion and L = tertiary phosphine, terminates with the formation of a dimer having a metal–metal bond, in which iridium is in the 2+ oxidation state[85].

IV. THE ROLE OF THE NATURE OF THE METAL AND THE STRUCTURE OF THE LIGAND IN THE MECHANISM OF THE ELECTROCHEMICAL REDUCTION OF CHELATES

The results of the electrochemical study of the coordination compounds of *d* elements with organic ligands in non-aqueous solvents make it possible to put forward general considerations concerning the influence of the nature of the central atom and the ligand on the nature of the electrode reactions. Depending on the electronic configuration of the complex-forming ion and the type of ligand, chelates are reduced in one or several stages. In terms of the nature of the first stage, electrochemical processes can be conventionally divided into two large groups. The metal chelates of the first group, which are of the inner complex type, undergo reversible reduction at the m.d.e. A slow electron transfer in the electrochemical stage proper is more characteristic of the second group. The conventional nature of this subdivision is due to the fact that in many instances, for example, with increased concentration of the depolariser, the process is complicated by the adsorption of the latter on the m.d.e. and becomes irreversible. For certain inner complexes, charge transfer is complicated by the subsequent chemical deactivation of the primary electron transfer product. The chelates of the second group are reduced irreversibly regardless of the duration of electrolysis in the course of the recording of the polarisation curve.

Among the electrochemical reactions of chelates in the first group, reversible one-electron processes, which can be regarded as purely electron transfer reactions, are of greatest interest. With rare exceptions, they are characteristic of metal chelates (including inner complexes), with unfilled *d* shells. In multistage reduction, with the transfer of one electron in each stage, intermediates are formed in which the central atom is in a formally low oxidation state. In such cases the electrochemical process can be represented as electron transfer to the lowest unoccupied molecular orbital; $E_{1/2}$ is a thermodynamic quantity and reflects the energy level of this orbital of the complex. The reaction centre to which an electron is transferred is delocalised and embraces a group of atoms with a common unoccupied molecular orbital, including the metal atom. When the electron occupies the lowest vacant molecular orbital, the activation barrier is apparently comparatively low[86].

In those cases where a rigorous correlation is observed between the half-wave potential and the $\Sigma\sigma$ of the substituents (the Hammett or Taft constants), the latter must be regarded as a consequence of the different sensitivities of the lowest unoccupied molecular orbital to the influence of substituents. The deviation of the values of $E_{1/2}$ from those predicted by the regression equation can have different causes: adsorbability of the components of the electrochemical reaction on the electrode surface, the influence of the subsequent chemical reaction, for example, with the solvent or impurities in the latter, etc. In this case the half-wave potential loses its rigorous thermodynamic significance, because it reflects not only the energy level of the lowest unoccupied molecular orbital of the complex, but also the influence of the subsequent chemical stage. The contribution of adsorption to the electrode process, which complicates the correlations, is particularly notable for complexes of sulphur-containing ligands.

The values of $E_{1/2}$ for reversible uncomplicated stages can be correlated with photoelectron spectroscopic data characterising the electron binding energies. Such correlations make it possible to predict the properties of hitherto unknown complexes.

The problem of the oxidation state of the central atom in the intermediate species formed is fairly complex. Quantum-chemical calculations of the populations of the atomic orbitals and of the degree of their overlap, which make it possible to discover the composition of the orbital to which an electron is transferred in the electrochemical stage proper as well as the most probable distribution of electron density in the one-electron transfer product, might be very useful. Such calculations have been made for certain types of coordination compounds. They showed, for example, that the molecular orbital to which an electron is transferred in the reduction of ruthenium(III) tris-β-diketonates is of the ligand type. This result implies that the contribution of the metallic t_{2g} (or e_a) orbital is much smaller than the contribution of the $\pi(\sigma+\pi)$ orbitals of the ligand to the common unoccupied molecular orbital of the complex. This is consistent with the considerable influence of the nature of the substituents on the ease of reduction[24]. However, for the majority of metal coordination compounds with different donor atoms, quantum-chemical data are not as yet available.

The unpaired electron in the one-electron reduction product can occupy one of the vacant *d* orbitals of the metal, so that the oxidation state of the latter is determined by the charge of the complex species. Its stability depends to a large extent on the π-acceptor properties of the ligand. π-Acceptor ligands are known to decrease the energy of the orbitals localised predominantly at the central atom and to increase the strength of the metal–ligand bond via the reverse dative bonding mechanism. This explains the fairly high stability of transition metal complexes of bipyridyl and terpyridyl with the central atom in a low oxidation state, which are formed in electrochemical reduction in non-aqueous media.

Analysis of literature data shows that the stabilisation of complexes with metals in low oxidation states depends on the nature of the ligands, the nature of their donor atoms, the number of rings formed, and the nature of the metal. In addition, account must be taken of the aromatic properties of the chelate rings formed. The formation of species with the metal in the 1+ oxidation state in the reduction of tris-complexes of iron(II) with aliphatic di-imines of the type $H_3C-N=C(R)-C(R)=N-CH_3$, where R = H or CH_3,[86] can be explained by the fact that the chelate units in these complexes and in the bipyridyl complexes are similar.

It is of interest that the apparent standard electron transfer rate constants lie in the narrow range of values $1\times10^{-2} - 2.5\times10^{-2}$ cm s^{-1} for a large group of metal chelates (thio- and bisthio-semicarbazones, dithiocarbamates, and complexes with *o*,*o'*-dihydroxyazo-compounds). The probable cause of this may be the similarity of the transition states in the charge-transfer reaction and of the factors which determine the magnitude of the energy barrier[87]. The dependence of k_S on the electronic configuration of the reacting species has been discussed[61-63]. If the metal orbital, for example t_{2g}, delocalised over the molecule and involved in the formation of an $M \rightarrow L\,\pi$ bond (in chelates with bipyridyl, terpyridyl[57,62], and the di-imines mentioned above[86]) makes the main contributions to the molecular orbital to which an electron is transferred, then the change in the geometry of the species formed as a result of the latter process can prove to be insignificant compared with the change in the geometry of the initial depolariser molecule. In other words, if the electrolysis product differs from the depolariser by not more than one electron, then the molecules with the metal in both oxidation states can have approximately the same configuration.

In this case the rate of electron transfer is fairly high, and, conversely, the activation energy for the reverse process is relatively small. An electron may be transferred to a molecular orbital made up of atomic orbitals of another type, for example, e_g, involved in the formation of an M–Lσ bond; under these conditions, electron transfer leads to appreciable changes of the length of the M–L bonds, and hence in the geometry of the molecules of the reduction products. Such a process requires a greater activation energy and the rate of charge transfer is therefore comparatively low. In general, k_S, determined experimentally by relaxation electrochemical methods, is frequently much lower than the theoretical value[62]. Apart from the factors mentioned above, k_S can be influenced by the range of potentials in which the complexes are reduced and by the charge of the complex species. Thus it has been concluded[88] that the formal charge has a significant influence on the rate of electron transfer (the heterogeneity of the process) and that the reorganisation of the solvent can play an important role. We may recall the Vlček rule, according to which the reduction potential is more negative the greater the degree of localisation of the orbital to which the first electron is transferred[89]. This is consistent with the data for bipyridyl complexes[62,90]. However, it is still unknown whether this conclusion is valid for metal chelates with sulphur-containing ligands[27].

Slow charge transfer in the electrochemical stage proper is characteristic of coordination compounds of cobalt, nickel, and copper and certain other metals with thio- and seleno-semicarbazones, formed without substitution of hydrogen atoms (the second group of complexes). They have the structure of chelates but the latter does not include cyclic $(pd)\pi$ systems, typical for inner complexes, which ensure the delocalisation of electrons via a d-orbital centre. Since chelates in this group are charged, they are highly solvated in DMF and similar solvents. Part of the coordination capacity of the metal can be consumed in the interaction with the solvent, particularly when the ligands have polar groups. The formation of a solvation shell hinders electron transfer to the depolariser, i.e. gives rise to an overvoltage. Thus, on passing to solvents with high donor numbers and high dielectric constants, the reversibility of the reduction diminishes[3] and $E_{1/2}$ undergoes a cathodic shift[91].

This review describes the results of some of the studies on the coordination compounds of metals and similar systems by modern electrochemical methods, which are being prosecuted at the present time[92-94]. Presumably the conclusions and generalisations concerning electrochemical properties of metal chelates with organic ligands having comparatively simple structures will in future prove useful in the study of complexes with more complex ligands, whose oxidation-reduction reactions simulate the biological functions of natural products (vitamins, enzymes, etc.) belonging to the class of coordination compounds. The electrochemical processes involving many organic physiologically active compounds are known to occur at fairly high potentials, which are not attainable in biological systems. It is logical to suppose that the physiological activity of many of these compounds may be due to complexes of the compound with microelements in living tissues and not to the initial compound itself. The redox properties of such complexes can differ significantly from those of the organic compound and their oxidation-reduction potentials are usually much lower and are within the scale of potentials characteristic of the living cell[95]. Finally, the study of the properties of chelates makes it possible to select conditions for the electrosynthesis of compounds with valuable properties, including catalytic activity in homogeneous processes[96,97]. This should be encouraged by the development of research into the reactions of chelates at electrodes made of materials of different types[98,100] and a deeper investigation into the essential features of the processes involving coordination compounds, which is impossible without further comprehensive study of their structures by various methods, including electrochemical methods.

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