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REDOX PROPERTIES OF SOME CHELATES OF RHODIUM(I) AND IRIDIUM(I) CONTAINING π-BONDING LIGANDS

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Summary

The voltammetric behaviour of chelates of the type [M(chel)L]$^+$ (M = Rh, Ir; chel = 2,2'-bipyridine (bipy); 1,10-phenanthroline (phen); L = *cis,cis*-cycloocta-1,5-diene; norbornadiene and [Rh(chel)$_2$L]$^+$ (chel = bipy; phen; L = fumaronitrile; acrylonitrile) has been studied in acetonitrile. The reduction proceeds in two reversible one-electron steps. Only for [Rh(phen)$_2$L]$^+$ was a slow electrode reaction found. Stepwise reduction of these cationic complexes leads to anionic complexes with formal oxidation number (—1) through the stable oxidation state (0). The phenanthroline chelates interact strongly with the electrode material.

All the complexes, with exception of [Rh(chel)cod]$^+$, undergo oxidation at the mercury electrode. Detailed study of the mechanism suggests that the main products of the electrooxidation are complexes containing Hg-metal bonds.

Introduction

Coordinative and redox addition reactions play an important role in homogeneous reactions of d^8 square-planar complexes and are significant steps in catalytic processes promoted by these compounds [1]. Recently new series of d^8 square-planar complexes of rhodium and iridium containing bidentate ligands and π-bonding ligands were synthesized [2—4], and found to give easily coordinative and redox addition with small molecules. To throw light on the mechanism of these reactions, we have studied the redox properties of some of the aforementioned cationic compounds with metal oxidation state I and present the results in this paper.

Electrochemical techniques have been useful to investigate the redox properties of coordination [5], and organometallic compounds [6] including π-ligand—metal complexes [7]. Such studies, which for many years centered on the relations between redox properties and structure, now also include the preparation of new species with central metal atoms in low oxidation states, and the study of their reactions.

Results

Electroreduction

(a) Rhodium(I) complexes of the type [Rh(chel)L]$^+$. The electrochemical reduction at the dropping mercury electrode (DME) of [Rh(bipy)L]$^+$ (10^{-3} *M*, in acetonitrile * 0.1 *M* in tetraethylammonium perchlorate) shows four polarographic waves (Fig. 1, waves II—V) **.

The limiting currents of waves II and III are in a 1/1 ratio and depend linearly on the concentration of the depolarizer in the range 1×10^{-4} to 2×10^{-3} *M*. The wave height varies with the square root of the height of the mercury column, indicating a diffusion-controlled process. A comparison of the limiting diffusion currents with a reference substance ($[Cr(C_{12}H_{10})_2]I$), which gives a reversible one-electron reduction step at the same concentration and under the same conditions [8], shows an exchange of one electron at each step. The theoretical equation of the curve $\log i/(i_d - i) = f(E)$ for reversible systems was verified for both reduction steps. Both cyclic voltammetry and use of the Kalousek commutator confirmed the reversibility of the electrode processes (see Fig. 2).

Therefore it is possible to conclude that the reduction of cationic complexes proceeds in two one-electron steps with change of the formal oxidation number of the central atom from I to —I, through a stable 0 state.

Values of the half-wave potentials are listed in Table 1. The polarographic behaviour of the reduction steps IV and V (Fig. 1) suggested that chemical side reactions complicate the sequence of redox steps. Verification of electrochemical relations is, however, rather difficult at such negative potentials and the difficulties are increased by the high sensitivity of this system to proton donors. While the presence of water in the system has little influence on the polarographic waves I—III, it is a determining factor for the pattern of waves IV and V. Therefore its concentration had to be kept at very low levels. The slope of the logarithmic analysis curve for waves IV and V corresponds to reversible electrode processes. The limiting current is not linearly dependent on the concentration of depolarizer and $E_{1/2}$ depends on the drop time and temperature. The occurrence of a diffusion-controlled electrodic process suggests that a very rapid chemical reaction follows the redox change.

The cyclic voltammogram in a single scan (Fig. 2) shows two redox couples only, corresponding to the polarographic waves II and III (Fig. 1). When a multiscan was applied, further current peaks corresponding to the waves IV and V ap-

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* Acetonitrile was chosen as solvent because of its favourable potential range for both reduction and oxidation processes and because of the stability of the complexes in its solutions.

** Abbreviations used: an = acrylonitrile; bipy = bipyridine; cod = cyclooctadiene; dmso = dimethylsulphoxide; DPE = 1,2-bis(diphenylphosphinoethane); fun = fumaronitrile; nbd = norbornadiene; phen = 1,10-phenanthroline; TEAP = tetraethylammonium perchlorate.

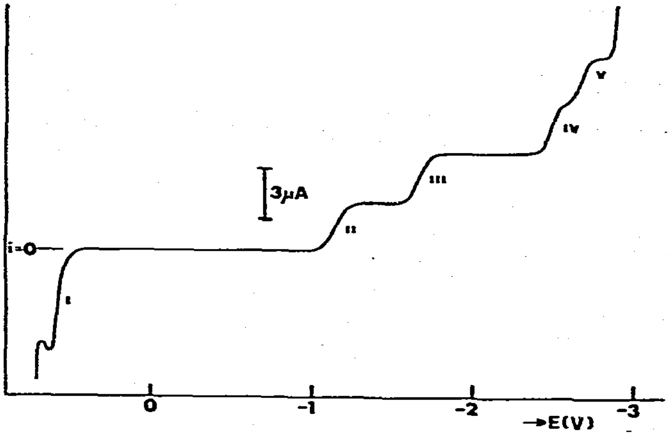

Fig. 1. Polarogram of [Rh(bipy)nbd]$^+$ in acetonitrile (10^{-3} *M*; 0.1 *M* TEAP as supporting electrolyte).

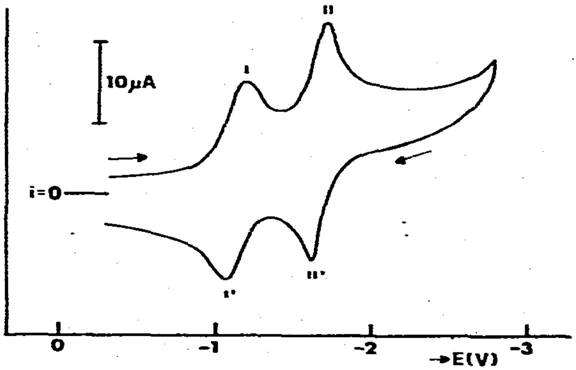

Fig. 2. Cyclic voltammogram (single) [Rh(bipy)nbd]$^+$ in acetonitrile (2×10^{-3} *M*; 0.1 *M* TEAP as supporting electrolyte) at a stationary mercury electrode.

TABLE 1

HALF-WAVE POTENTIALS (V vs. SCE) FOR THE COMPLEXES [M(chel)$_x$L]$^+$

Compound	Oxidation wave	Reduction wave	
		1st step	2nd step
[Rh(bipy)nbd]$^+$	+0.59	−1.175	−1.670
[Rh(bipy)cod]$^+$	—	−1.165	−1.660
[Rh(phen)nbd]$^+$	+0.56	−1.185	−1.675
[Rh(phen)cod]$^+$	—	−1.175	−1.665
[Ir(bipy)nbd]$^+$	+0.42	−0.955	−1.445
[Ir(bipy)cod]$^+$	+0.47	−0.950	−1.445
[Ir(phen)nbd]$^+$	+0.15	−0.960	−1.450
[Ir(phen)cod]$^+$	+0.43	−0.955	−1.445
[Rh(bipy)$_2$an]$^+$	+0.48	−1.43	−1.64
[Rh(bipy)fun]$^+$	+0.54	−1.34	−1.55
[Rh(phen)$_2$an]$^+$	+0.48	−1.42	−1.63
[Rh(phen)$_2$fun]$^+$	+0.45	−1.28	−1.53

peared. Simultaneously a deep blue colour appeared around the stationary electrode surface. A comparison with the voltammetric behaviour of the free ligands showed that steps IV and V are due to a reduction of free bipy generated by the decay of the electrode reaction product. The electroreduction mechanism of a bipy complex, e.g. $[\mathrm{Rh(bipy)nbd}]^+$, can thus be described schematically as in eq. 1.

$$\begin{array}{l} [\mathrm{Rh(bipy)nbd}]^+ \overset{e}{\rightleftharpoons} [\mathrm{Rh(bipy)nbd}]^0 \overset{e}{\rightleftharpoons} [\mathrm{Rh(bipy)nbd}]^{1-} \\ \hphantom{[\mathrm{Rh(bipy)nbd}]^+ \rightleftharpoons [\mathrm{Rh(bipy)nbd}]^0 \rightleftharpoons [\mathrm{Rh(b}} \Downarrow \\ \hphantom{[\mathrm{Rh(bipy)nbd}]^+ \rightleftharpoons [\mathrm{Rh(bipy)nbd}]^0 \rightleftharpoons{}} [\mathrm{Rhnbd}]^{1-} + \mathrm{bipy} \end{array} \qquad (1)$$

The product of the chemical decomposition reaction of the rhodium(—I) species was not studied in detail.

Compounds of the type $[\mathrm{Rh(phen)L}]^+$ also reduce through two reversible one-electron steps, but no chemical side reaction of the rhodium(—I) species occurs. However, a dramatic difference in the behaviour of the system was found on using DME vs. stationary electrodes, owing to a strong reaction between the reduction products and the electrode itself.

At a platinum electrode the reduction of the complexes proceeds by the same mechanism. In this case, however, the values of $E_{1/2}$ are more negative (Table 2), and the logarithmic analyses of the voltammetric curves give higher slopes, corresponding to a quasi-reversible electrode process.

(b) Iridium(I) complexes of the type [Ir(chel)L]$^+$. The electrochemical behaviour of this group of compounds in acetonitrile at a DME vs. stationary mercury and platinum electrodes (0.1 *M* TEAP as supporting electrolyte) is similar to that of rhodium(I) complexes. All the compounds under study are reduced at a DME in two reversible one-electron steps (Fig. 3).

The values of the corresponding half-wave potentials are collected in Table 1. The reduction proceeds according to eq. 2.

$$\mathrm{Ir^I} \overset{e}{\rightleftharpoons} \mathrm{Ir^0} \overset{e}{\rightleftharpoons} \mathrm{Ir^{-I}} \qquad (2)$$

The reaction between the electrode reduction products and the electrode itself was also observed for the iridium derivatives, when chel = phen. Fig. 4 shows a typical cyclic voltammogram.

The increase in the cathodic peak II of the second redox couple and of the anodic peak I' of the first redox couple, is apparent. A test using the criteria of Wopschall and Shain [9] confirmed the presence of typical adsorption processes. A detailed study of these processes is in progress.

TABLE 2

HALF-WAVE POTENTIALS (V vs. SCE) AND SLOPES OF THE VOLTAMMETRIC CURVES FOR THE 1st and 2nd REDUCTION STEP OF THE COMPLEXES $[\mathrm{Rh(chel)L}]^+$ OBTAINED AT THE PLATINUM ROTATING ELECTRODE IN ACETONITRILE (0.1 *M* TEAP), *T* 297 K

Compound	$E_{1/2}$ (I)	Slope (mV)	$E_{1/2}$ (II)	Slope (mV)
$[\mathrm{Rh(bipy)nbd}]^+$	−1.18	70	−1.69	74
$[\mathrm{Rh(bipy)cod}]^+$	−1.18	80	−1.68	78
$[\mathrm{Rh(phen)cod}]^+$	−1.20	78	−1.72	76
$[\mathrm{Rh(phen)nbd}]^+$	−1.20	70	−1.71	77

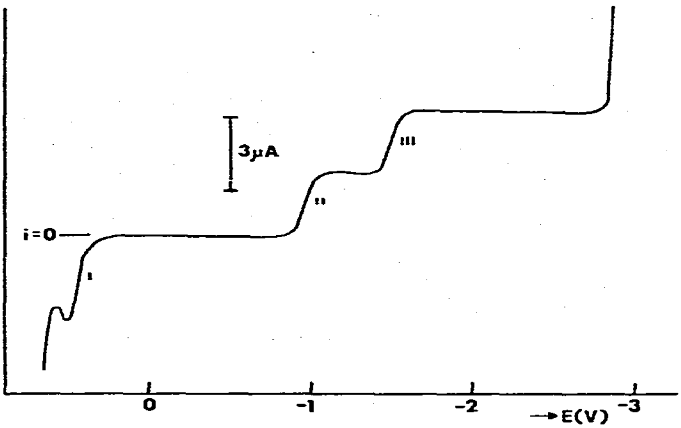

Fig. 3. Polarogram of [Ir(bipy)nbd]$^+$ in acetonitrile (10^{-3} *M*; 0.1 *M* TEAP as supporting electrolyte).

(c) Complexes of the type [Rh(chel)$_2$L]$^+$. The electrochemical reduction of this group of complexes shows a general pattern similar to that described above. When chel = bipy the electrode process is characterized by two reversible one-electron steps, whereas, when chel = phen, the reduction process is totally irreversible. A great instability of the species with a low oxidation state of the metal is suggested by further polarographic waves corresponding to the reduction of free ligands chel and L. The values of $E_{1/2}$ are summarized in Table 1.

Electrooxidation

All the complexes under study, except [Rh(chel)cod]$^+$, undergo oxidation at the DME in acetonitrile (0.1 *M* TEAP as supporting electrolyte). $E_{1/2}$ values are listed in Table 1. Since the electrooxidation proceeds only at a mercury electrode the material of the electrode itself must play an important role in the process. The electrode process is diffusion-controlled or very nearly to that ([Rh(chel)nbd]$^+$). The limiting currents depend linearly on the concentration of depolarizer in the range 1×10^{-4} to 2×10^{-3} *M*. Their heights correspond to the

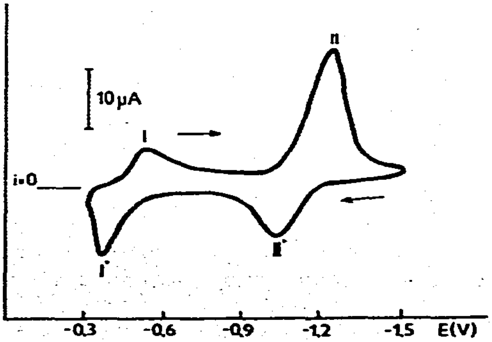

Fig. 4. Cyclic voltammogram of [Ir(phen)cod]$^+$ in acetonitrile (10^{-3} *M*; 0.1 *M* TEAP as supporting electrolyte) at DME. Scan rate *v* 95 V/sec. IR drop is not fully compensated.

TABLE 3

HALF-WAVE POTENTIALS (V vs. SCE) OF OXIDATION WAVES OF THE COMPLEX ($E_{1/2}$(I)) AND REDUCTION WAVES OF THE PRODUCTS OF THIS OXIDATION ($E_{1/2}$ (I))

Compound	$E_{1/2}$ (I)	$E_{1/2}$ (II)
$[Rh(bipy)nbd]^+$	+0.59	+0.33
$[Rh(phen)nbd]^+$	+0.56	+0.56; +0.30
$[Ir(bipy)nbd]^+$	+0.42	−0.17
$[Ir(bipy)cod]^+$	+0.47	−0.15
$[Ir(phen)nbd]^+$	+0.15	−0.10
$[Ir(phen)cod]^+$	+0.43	+0.43; +0.05
$[Rh(bipy)_2an]^+$	+0.48	−0.30
$[Rh(bipy)_2fun]^+$	+0.54	−0.18
$[Rh(phen)_2an]^+$	+0.48	−0.38
$[Rh(phen)_2fun]^+$	+0.45	−0.25

exchange of 0.5—2 electrons, as resulting from comparison with a typical one-electron reduction wave (Fig. 1, wave II). In all cases the oxidation wave exhibits a characteristic current maximum (Fig. 1, wave I), which does not allow satisfactory analyses of the polarographic curve. The electroactivity of the products of the electrooxidation was proved with the aid of the Kalousek commutator. The $E_{1/2}$ reduction values of the oxidation products are given in Table 3.

These values indicate that oxidation is a totally irreversible electrode process for all the compounds, except for $[Rh(phen)nbd]^+$ and $[Ir(phen)cod]^+$ complexes, for which there are both reversible and irreversible steps. On the other hand we have found that all complexes giving an oxidation wave react with the Hg^{2+} cation. A change of colour is observed after mixing the Hg^{2+} * solution with that of the complex. Increasing the Hg^{2+} concentration a decrease in the polarographic wave I (Fig. 1) is observed, while a new reduction wave appears and grows. The $E_{1/2}$ of the first reduction wave of the product of the homogeneous reaction between the complex and Hg^{2+} is identical with that of the product of electrooxidation ($E_{1/2}$ (II) in Table 3). The overall stoichiometry of the reaction, as determined by polarometric titrations, shows that one Hg^{2+} ion reacts with three molecules of the complex (two in the case of $[Rh(bipy)_2fun]^+$).

Discussion

The results show that the reduction of d^8 complexes of rhodium and iridium proceeds in two one-electron steps, leading to final d^{10} anionic species according to eq. 3.

$$\underset{d^8}{M^I} \overset{e}{\rightleftharpoons} \underset{d^9}{M^0} \overset{e}{\rightleftharpoons} \underset{d^{10}}{M^{-1}} \tag{3}$$

The species with the electron configuration d^9 are stable intermediates owing to the high π-acceptor capacity of the ligands, which promotes a delocalisation

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* $[Hg(dmso)_6](ClO_4)_2$ was used as soluble mercuric salt.

of the electron density. In agreement with this hypothesis, d^8 complexes with a ligand of weak acceptor capacity, as for example $[IrX(CO)L_2]$ (X = Cl, Br, I: L = substituted phosphines) [10] or $[M(DPE)]^+$ (M = Rh, Ir) [11], are reduced in a single two-electron step.

The increase in the electron density on the central atom weakens the metal—ligand σ-bond and strenghtens the π-bond. As a consequence the complexes $[Rh(bipy)L]^{1-}$ loose bipy rather than the ligand L. The entropy effect and the higher degree of conjugation lead to greater thermodynamic stability for the phen derivatives.

The values of $E_{1/2}$ for the reversible reduction waves of $[M(chel)L]^+$ do not change significantly with the nature of the ligand field, especially for the iridium complexes. This indicates that the redox changes are localized mainly on the redox orbital of the central atom and not on the molecular orbital deriving mainly from π^*-orbitals, as for example in the case of bipyridine transitional metal complexes [12]. Unfortunately this conclusion is limited to few series of compounds.

In contrast, a dramatic difference exists between the half-wave potentials of rhodium(I) and iridium(I) complexes as can be seen from Table 1. Rhodium(I) compounds are reversibly reduced at more negative potentials than iridium(I) complexes and this is in agreement with the fact that the latter are stronger Lewis acids than the corresponding rhodium(I) derivatives. In fact iridium(I) compounds more easily coordinate both anionic ligands and unsaturated substrates [3,4].

In the case of complexes $[Rh(chel)_2L]^+$ the mechanism of the electroreduction depends strongly upon the nature of the ligand chel. In acetonitrile all the complexes of this group show a significant thermodynamic instability, which increases with decrease in the oxidation state of the metal. The reason may lie in the change of atomic configuration induced by the change in the electronic configuration.

For the mechanism of electrooxidation at a DME the experimental results suggest the interpretation shown in eq. 4a, 4b.

$$Hg \rightarrow Hg^{2+} + 2e \qquad (4a)$$

$$Hg^{2+} + n[M(chel)_x L]^+ \rightarrow \{Hg[M(chel)_x L]_n\}^{(n+2)+} \qquad (4b)$$

($n = 3$; 2 in the case of $[Rh(bipy)_2fun]^+$).

According to eq. 4, the electrooxidation first requires oxidation of the mercury metal, a process which is favoured by the reaction with the complex. Such a mechanism, which implies a redox addition reaction between a Lewis base (complex) and a Lewis acid (Hg^{2+}), was previously found for the electrooxidation of organometallic compounds [13] and Vaska's complexes [14] and for the oxidation of $[Co(CN)_5]^{3-}$ in aqueous solutions [15].

The $E_{1/2}$ oxidation values may give a qualitative indication of the reactivity of our complexes, the most positive $E_{1/2}$ potentials (e.g. L = cod derivatives) or the absence of oxidation wave indicating low reactivity. The less positive $E_{1/2}$ values o of iridium(I) derivatives in comparison with those of rhodium(I) reflect the general behaviour of these complexes [16] and are in agreement with their reactivities towards small molecules [4].

The fact that the electrode material determines the electrode process suggests that complexes with Hg—M bonds could be prepared electrosynthetically, and this will be the subject of future work.

Experimental

Instruments and equipments

Polarographic measurements were made on a LP 7 type polarograph (Laboratorní přístroje, Prague) with a pen recorder EZ 4 of a sensitivity of 3.5×10^{-10} A/cm. The IR drop in the electrolytic circuit was eliminated by an electronic compensator based on operating amplifiers.

The Kalousek commutator used for the study of the products of the electrode process and the rotating disk electrode were constructed in the workshop at the Heyrovský Institute.

Cyclic voltammograms were recorded with the aid of a multipurposal electrochemical apparatus. The potentiostat circuit, constructed in the polarographic laboratory, was a modified version of that described by Lauer and Osteryoung [17], while, in the function generator, a modification of the circuit of Pospíšil [18] was used. Details will be published elsewhere [19]. The cyclic voltammograms were recorded on a BAK 4T X-Y recorder (Aritma, Prague) and on an Orion EMG oscilloscope Model TR-4401 using a symmetrical preamplifier Model TR-4706 (Hungary).

Voltammetric measurements were made in a universal modular electrolytic vessel [20] by using a three-electrode system. The dropping mercury electrode had a drop time t_1 = 4.8 sec for a height of the mercury column of 50 cm and a potential of —0.5 V vs. saturated calomel electrode in 0.1 *M* TEAP in acetonitrile; the rate of flow of mercury was m = 0.73 mg · sec^{-1}. All the potential values are referred to a saturated calomel electrode (SCE), connected to the solution by a salt bridge having a fritted glass disc on its tip. The bridge was filled with a solution of 0.1 *M* TEAP in acetonitrile.

A twisted platinum wire (length 10 cm and diameter 0.05 cm) was used as auxiliary electrode. Stationary mercury electrode of Kemula type and stationary platinum electrode (platinum wire of 0.05 cm diameter sealed into a glass tube) were used as working electrodes.

All manipulations and measurements of the compounds were carried out using the Schlenk tube technique under nitrogen [21].

Chemicals

As the protogenic species greatly influence the voltammetric behaviour at the most negative potentials, the water content in all the chemicals used must be very low.

The complexes $[M(chel)L]PF_6$ (M = Rh, Ir; chel = bipy, phen; L = cod, ndb) and $[Rh(chel)_2L]PF_6$ (chel = bipy, phen; L = fun, an) were synthesized by published methods [2—4].

$[Hg(dmso)_6](ClO_4)_2$ was synthesized according to Carlin et al. [22].

The measurements were carried out on acetonitrile solutions. Of the several methods which have been suggested to prepare pure and anhydrous acetonitrile for electrochemical purposes [23] the following procedure was chosen, owing to the high content of acrylonitrile in the available acetonitrile: 10 ml of aqueous 10% potassium hydroxide were added to 1000 ml of acetonitrile and the solution was refluxed for 5 h. 20 g of Al_2O_3 were then added and the heating was continued for a further 3 h. Fractional distillation gave acetonitrile, the purity of which was tested both polarographically and spectrophotometrically (λ 200 nm). Before use, the acetonitrile was refluxed for two hours over phosphorus pentoxide and distilled under nitrogen.

The supporting electrolyte, TEAP, was prepared from perchloric acid and tetraethylammonium hydroxide (Lachema, 20% in water). The solution was cooled and the white crystals of perchlorate was filtered off. The salt was recrystallized three times from water, dried under vacuum for five days at 70°C, and stored over phosphorus pentoxide under an inert gas.

All other chemicals were of reagent grade.

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