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Redox Behaviour of Mixed-ligand Five-coordinate Cobalt(I) Complexes with Isocyanides and Phosphines

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The oxidation mechanism of a series of mixed-ligand five-coordinate cobalt(I) complexes of the type $[Co(CNR)_3L_2]^+$ *(R =* C_6H_5, $4\text{-}CH_3C_6H_4$, $4\text{-}CH_3OC_6H_4$, $4\text{-}NO_2C_6H_4$, *and* $2,6\text{-}(CH_3)_2C_6H_3$; *L =* $P(OCH_3)_3$, *and* $P(C_6H_5)(OC_2H_5)_2$*) on mercury and platinum electrodes in dichloromethane is described. The primary reversible electron transfer between electrode and depolarizer is followed by a fast chemical reaction which brings about a change in configuration (and a dimerization). Correlations between redox properties of the species and their structural features are discussed.*

Introduction

The important role of low-spin cobalt complexes as homogeneous catalysts has been previously reported [1]. Isocyanide complexes are chemically related to cyanide and carbonyl derivatives and form important groups of compounds [2] useful for studying the relationships between structure and chemical properties within the same or similar series of complexes. The differences between the chemical properties of pentacyanocobaltate(II), which is a very efficient hydrogenation catalyst, and those of pentakis(alkylisocyanide)cobalt(II) have been explained in terms of important differences in their electronic and/or molecular structure [3].

For most low-spin cobalt(I) complexes the electronic structure and the unsaturated coordination favour oxidative-addition reactions, one of elemental steps of the overall mechanism by which these complexes behave as catalysts [4]. Therefore, from this point of view the knowledge of the redox properties seems to be very important.

Voltammetry is one of the most efficient tools to study the redox behaviour of coordination compounds, as shown in the case of isocyanide complexes [5–9]. Important relationships between standard redox potentials, nature of the central atom, and properties of isocyanide ligands can be obtained [7–10].

In a previous work some of us have described the synthesis and characterisation of a series of a mixed-ligand five-coordinated cobalt(I) complexes of the type $[Co(CNR)_3L_2]^+$ (R = C_6H_5, $2,6\text{-}(CH_3)_2C_6H_3$, $4\text{-}CH_3C_6H_4$, $4\text{-}CH_3OC_6H_4$, $4\text{-}NO_2C_6H_4$; L = $P(C_6H_5)(OC_2H_5)_2$, $P(OCH_3)_3$) [11]. In this paper we report the study of redox behaviour of the same compounds to correlate it to the structure of the species. Special attention is also paid to the possibility of using the information thus obtained to carry out electrosynthesis of new derivatives.

Experimental

Both cyclic voltammetric and polarographic tests were performed by using a multipurpose electrochemical apparatus previously described [12]. A X–Y recorder BAK 4T (Aritma, Prague) and a Tektronix 5103 N oscilloscope were used as recording devices. Special attention was paid to the compensation of R_u (uncompensated resistance) by a positive feedback technique [13] including a stabilisation circuit [14]. Bis(diphenyl)chromium iodide was used as inner reference to test our devices [16]. The estimated error of slope of polarographic wave was within ±5 mV.

The Kalousek commutator and the rotating disc electrode were made at the J. Heyrovsky Institute. Commutated polarographic experiments were performed with a LP7 type polarograph (Laboratorni pristroje, Prague) with a pen recorder EZ4 of 3.5×10^{-10} A/cm sensitivity. The iR drop in the electrolytic circuit was minimized by a Metrohm (Switzerland) electronic compensator.

The electrolyses on a large platinum electrode were carried out using a high voltage D.C. power supply BM 208 (Tesla, Brno, Czechoslovakia).

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TABLE I. Polarographic Data.

Compound	$E_{1/2}$[a]	Slope[b]	i_d/c[c]	νCN[d]
$[Co(C_6H_5NC)_3L_2]^+$ [e]	+0.080	89	1.92	2069
	+0.380			
$[Co(2,6\text{-}(CH_3)_2C_6H_3NC)_3L_2]^+$	+0.445	60	1.69	2060
$[Co(4\text{-}CH_3OC_6H_4NC)_3L_2]^+$	+0.405	71	1.76	2079
$[Co(4\text{-}CH_3C_6H_4NC)_3L_2]^+$	+0.360	79	1.74	2073
$[Co(4\text{-}NO_2C_6H_4NC)_3L_2]^+$	+0.455	52	1.67	2050
$[Co(C_6H_5NC)_3L'_2]^+$	+0.410	58	1.50	2078
$[Co(2,6\text{-}(CH_3)_2C_6H_3NC)_3L'_2]^+$	+0.460	50	2.0	2066

[a] In V *vs.* SCE. [b] In mV. [c] In A/mmol; i_d/c for reference compound bis(diphenyl)chromium iodide is in the 1.4–1.8 range. [d] In cm^{-1} from ref. 11. [e] $L = P(C_6H_5)(OC_2H_5)_2$, $L' = P(OCH_3)_3$.

Analog integrator (Amel Mod. 558, Italy) was used to measure the spent charge.

Voltammetric and electrochemical measurements were made in an universal modular electrolytic vessel [17], using a three electrode system at room temperature. An hammer kept the dropping time of the mercury electrode constant at 3.17 s. The mercury flow rate was m = 0.275 mg/s with a mercury column height of 30 cm. All the potential values are referred to a saturated calomel electrode (SCE) (by Radelkis, Hungary), which was connected to the solution via thin ceramic tip. A platinum plate was used as auxiliary electrode. Stationary mercury electrode of Kemula type, stationary platinum electrode (0.5 mm O.D. platinum wire sealed into a glass tube) and rotating platinum electrode (2 mm O.D. platinum rode in a teflon rode) were used as working electrodes.

IR and electronic spectra were recorded on a Perkin-Elmer or Unicam SP800 spectrophotometers. E.s.r. spectra were measured using a Varian E4 spectrometer; the active species was generated by electrolysis on a platinum electrode at a constant potential set up according to the voltammetric measurements.

All manipulation and voltammetric measurements on the solutions were carried out using Schenk type glassware technique under argon [18].

Chemicals

The $[Co(CNR)_3L_2]^+$ perchlorate complexes were synthesized according to the method previously described [11]. The investigation of the complexes was carried out in dichloromethane (DCM) (Uvasol by Merck, Darmstadt, Germany). DCM was stored over anhydrous K_2CO_3 and distilled over P_2O_5 immediately before use. Unfortunately some of the studied complexes are not stable in dimethylformamide and acetonitrile. The supporting electrolyte tetrabutylammonium perchlorate (TBAP) was prepared from tetrabutylammonium hydroxide and perchloric acid. The salt was recrystallised three times, dried under vacuum for five days at 50 °C, and then stored over P_2O_5.

Results

Polarography

The half-wave potentials reported in Table I, indicate that all the studied compounds in DCM (0.1 *M* TBAP) exhibit one polarographic oxidation wave except the $[Co(CNC_6H_5)_3(P(C_6H_5)(OC_2H_5)_2)_2]^+$ complex which gives two oxidation waves.

In the whole available range of potentials two reduction steps of $E_{1/2} = -1.11$ and -1.70 V were observed only for the complex $[Co(4\text{-}NO_2C_6H_4\text{-}NC)_3(P(C_6H_5)(OC_2H_5)_2)_2]^+$. The study to elucidate the mechanism of this process is in progress. The dependence of the limiting currents of oxidation waves on the square root of the height of the mercury column was strictly linear crossing the origin axes in agreement with diffusion controlled electrode processes. Limiting diffusion current resulted linearly dependent on the concentration of depolariser in the concentration range 1×10^{-4}–1×10^{-2} M. Values of diffusion current constants are reported in Table I. For the $[Co(CNC_6H_5)_3(P(C_6H_5)(OC_2H_5)_2)_2]^+$ derivative the i_d/c value is referred to the current sum of both waves (see discussion) and their limiting currents are equal. A comparison of the diffusion current constant with the value obtained for the reference compound suggests a transfer of one electron in the oxidation. This result agrees with the values of the oxidation polarographic slopes obtained from their logarithmic analyses (Table I) indicating that the oxidation process seems to be polarographically reversible or quasi-reversible.

TABLE II. Voltammetric Data.

Compound	$E_{1/2}$[a]	$(E_p)_A$[b]	$(E_p)_C$	ΔE_p	Slope[c]
$[Co(C_6H_5NC)_3L_2]^+$	+0.515	+0.850	+0.300	0.260	152
	+0.759	+0.560			86
$[Co(2,6\text{-}(CH_3)_2C_6H_3NC)_3L_2]^+$	+0.495	+0.600	+0.300	0.300	132
$[Co(4\text{-}CH_3OC_6H_4NC)_3L_2]^+$	+0.442	+0.492	+0.280	0.212	143
$[Co(4\text{-}CH_3C_6H_4NC)_3L_2]^+$	+0.383	+0.470	+0.200	0.270	107
$[Co(4\text{-}NO_2C_6H_4NC)_3L_2]^+$	+0.525	+0.570	+0.420	0.150	139
$[Co(C_6H_5NC)_3L'_2]^+$	+0.525	+0.800	+0.200	0.600	105
$[Co(2,6\text{-}(CH_3)_2C_6H_3NC)_3L'_2]^+$	+0.505	+0.700	+0.280	0.420	101

[a] In V *vs.* SCE. Measured at a rotating platinum disc electrode. [b] In V *vs.* SCE. Scan rate of 0.196 V/s. [c] In mV. [d] L = $P(C_6H_5)(OC_2H_5)_2$; L' = $P(OCH_3)_3$.

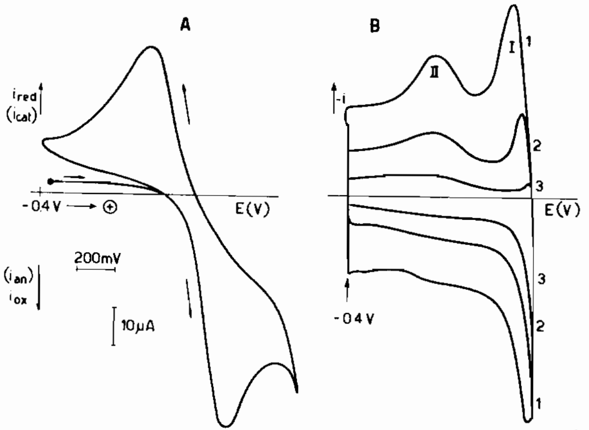

Fig. 1. Cyclic voltammogram of $[Co(4\text{-}CH_3OC_6H_4NC)_3L_2]^+$ in DCM (0.1 *M* TBAP) at a stationary platinum electrode. A) The reverse potential is 300 mV behind the peak. Scan rate 0.485 V/s. B) The reverse potential is at one third of the peak. Scan rate 1–889 V/s, 2–454 V/s, 3–186 V/s; registered by sample and hold circuit.

Voltammetry at a Rotating Platinum Electrode

In DCM (0.1 *M* TBAP) the oxidation of all compounds on a rotating platinum electrode resulted analogous to their polarographic behaviour. They are oxidised in one step with the exception of the $[Co(CNC_6H_5)_3(P(C_6H_5)OC_2H_5)_2)_2]^+$ complex which shows two oxidation waves. Half-wave potentials are listed in Table II. The linear dependence of limiting current on the square root of the disc angular velocity follows the Levich equation and indicates that the electrode process is mass transfer controlled. The same linear dependence but with negative slope is observed by measuring the current at potentials different from those of the limiting current, suggesting a slow electron transfer reaction. The slope values of voltammetric curves obtained from their logarithmic analysis confirm this observation.

Cyclic Voltammetry

Cyclic voltammetry was carried out both on mercury and platinum electrodes. Unfortunately the oxidation of the complexes on mercury electrodes takes place at positive potentials, and the anodic peak can be clearly distinguished from the mercury discharge only by using an hanging mercury electrode. On the contrary, on a platinum wire electrode it is possible to carry out quantitative measurements in similar experimental conditions.

At the platinum stationary electrode only one redox couple was observed (Fig. 1A). In the case of $[Co(CNC_6H_5)_3(P(C_6H_5)(OC_2H_5)_2)_2]^+$ two anodic and one associated cathodic peak were obtained. These results are similar to those found at the rotating platinum electrode and agree with the Randles–Sevcik equation (i_p – $v^{1/2}$, i_p – c). The anodic to cathodic peak current ratio is equal to one and is independent of the scan rate.

Rather great ΔE_p values, increasing with scan rate, indicate a slow electrode reaction or quite irreversible overall process (Table II).

There are no significant differences between cyclic voltammograms obtained using platinum or mercury stationary electrodes and between single or multi-scanning program. On mercury electrodes the difference between peak potentials exceeds 200 mV.

The polarographic reversibility (or quasi-reversibility) of the oxidation process is in contrast with the idea of a slow electron transfer reaction suggesting some chemical complication. Therefore one can suppose that a reversible one electron transfer followed by a fast chemical reaction takes place. No reversible cathodic peaks were observed by increasing the scan rate up to 2000 V/s or by reversing the voltage to about 0.1 V more positive than the peak potential. Due to the experimental limitations the reverse potential was taken at the bottom of oxidation peak. E_λ was set up at one third of the peak current and kept constant, while the backward scan rate was

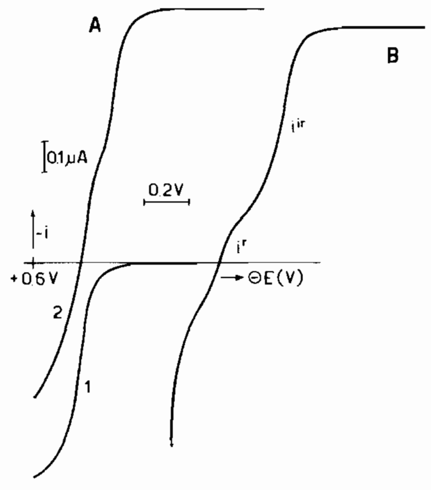

Fig. 2. Kalousek commutator polarogram of $[Co(4\text{-}CH_3OC_6H_4NC)_3L_2]^+$ in DCM (0.1 *M* TBAP) at 23 °C. A1) Normal polarographic oxidation wave. A2) Commutated polarographic wave. B) The same as in A1 at −5 °C. i^r, Reversible part; i^{ir}, Irreversible part of the cathodic wave.

increased from 100V/s up to 1000 V/s. Cyclic voltammograms were recorded on X–Y recording instrument equipped with circuit sample and hold. The voltammograms reported in Fig. 1B (curves 1, 2 and 3 recorded at scan rates greater than 150 V/s) show two associated reduction peaks. While peaks I are reversible, peaks II correspond to the reduction peak observed on previously recorded voltammogram in Fig. 1A.

Kalousek Commutator Technique

The reversible character of the electrode process was tested by using a Kalousek commutator. A commutated polarographic wave is shown in Fig. 2. The height of cathodic current is in agreement with one electron transfer in the oxidation step and the wave is constituted of two waves which are nearly undistinguishable (Fig. 2A). The frequency change, in the 1–25 Hz range does not influence this picture, while the decrease of temperature causes a better differentiation of both steps (Fig. 2B). The first cathodic step (i^r), whose half-wave potential is identical with that of the oxidation step, corresponds to the reversible reduction of the primary product of the electrooxidation. The second step (i^{ir}) corresponds to the reduction of the species which underwent a chemical change.

A shift to more negative values of the second step half-wave is observed by decreasing the temperature. This means that a higher degree of irreversibility takes place by decreasing the temperature. A variation of the commutation frequency changes the ratio of limiting currents of both reduction waves, while the i^r/i^{ir} ratio increases with frequency.

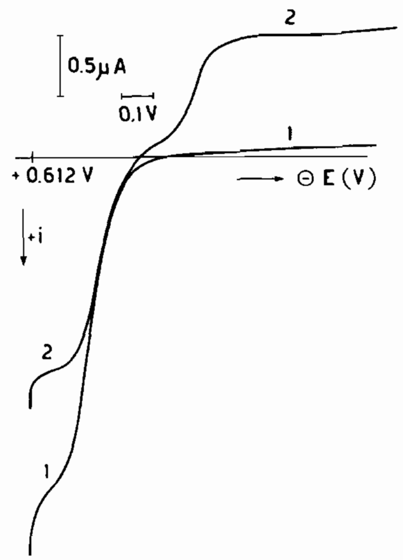

Fig. 3. Electrolysis of $[Co(4\text{-}CH_3OC_6H_4NC)_3L_2]^+$ in DCM (0.1 *M* TBAP) at a platinum working electrode. 1) Polarogram carried out before electrolysis. 2) Polarogram carried out on the partially electrolyzed solution.

Electrolysis at the Platinum Electrode

During the controlled potential (+0.6 V) electrolysis at the platinum electrode a decrease of the oxidation wave limiting current was observed and a new reduction wave appeared and grew (Fig. 3). The sum of the cathodic and anodic currents is constant. By controlled potential coulometry the consumption of one electron per molecule has been found. The half-wave potential of the cathodic wave is more negative than those of the primary product and of the final product. Therefore, one can conclude that the final product generated by electrolysis is different from that obtained by voltammetry. The final product is stable in solution under normal laboratory conditions. To identify this compound chemical oxidation of acetone solution of the starting complexes was carried out by adding stoichiometric amount of silver perchlorate in acetone. A color change of the solution with formation of black silver metal is observed. The solvent was evaporated under reduced pressure and the product dissolved in DCM. The polarogram of this solution was identical to that of the partially electrolyzed solution of the complex. This fact suggests that the electrochemical oxidation product is very similar to that obtained by chemical oxidation of the complex.

Discussion

The obtained results indicate that the electrooxidation of the $[Co(CNR)_3L_2]^+$ complexes proceeds via a complicated mechanism, which is the same on mercury and platinum electrodes. The first step seems

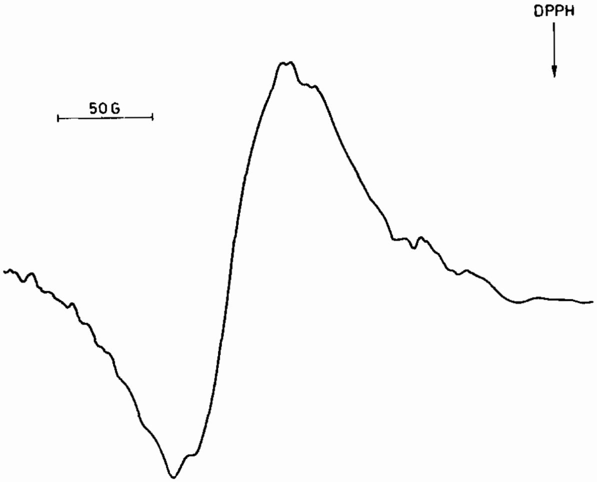

Fig. 4. E.s.r. spectrum of the $[Co(4\text{-}CH_3OC_6H_4NC)_3L_2]^+$ solution after electrolysis at a platinum electrode in the e.s.r. cell.

to be a fast reversible one electron transfer between the electrode and the depolarizer. This step causes a change of the electronic configuration of the compound while its structure is maintained

$$[Co(CNR)_3L_2]^+ \overset{e}{\rightleftharpoons} [Co(CNR)_3L_2]^{2+} + e^-$$

In a previous paper [11] it has been shown that complexes of the type $[Co(CNR)_3L_2]^+$ have trigonal bipyramidal structures with the three isocyanide ligands in equatorial positions. Therefore, we can assume the *trans*-configuration for the primary electrode product. The peculiar voltammetric behaviour of the complex with R = C_6H_5 can be explained in terms of a mixture of two different configurations. Differences between half-wave potentials for *cis* and *trans* isomers have already been described [25, 26].

Both cyclic voltammetry and Kalousek commutator technique indicate that the first charge transfer step is followed by a fast chemical reaction. In fact the product of this chemical change is still a Co(II) species as indicated by its e.s.r. spectrum shown in Fig. 4 ($g = 2.11$). The e.s.r. signal does not change when the electrochemical production of the oxidized product, in the e.s.r. cell, is interrupted. This seems to indicate that the e.s.r. signal is due to the final product. Since it has not been possible to observe any immediate decomposition or changes in the coordination, as would have been by color change of the Co(II) species, it seems reasonable to suggest for the final compound a structural configuration different from that of the primary product.

It is well known [19] that low energy is required when a D_{3h} trigonal bypiramid is transformed in a C_{2v} square pyramid. Therefore, one can suppose that the oxidation to a $3d^7$ configuration favors the formation of a species with a C_{2v} symmetry. The same structure has been previously observed for the $[Co(CNR)_5]^{2+}$ and the $[Co(CN)_5]^{3-}$ ions [3]. While both Co(I) and Co(II) cyanide derivatives have the same geometrical structure, a fast rearrangement takes place when the pentakis(isocyanide)-cobalt(I) complex is oxidized to the corresponding cobalt(II) species.

$$\underset{D_{3h}}{Co(I)} \underset{+e}{\overset{-e}{\rightleftharpoons}} \underset{D_{3h}}{Co(II)} \xrightarrow{\text{fast}} \underset{C_{2v}}{Co(II)} \xrightarrow{\text{slow}} \text{Final Product}$$

In our case any attempt to isolate in a pure form the final product was unsuccessful due to the instability of this compound which decomposes in the solid state. The disappearance of the e.s.r. signal can be observed in solution after the oxidation to the final product suggesting that a spin-pairing process such as dimerisation or oligomerisation may occur, as observed also in the case of the pentakis(methylisocyanide)cobalt(II) derivative [20].

The half wave potentials of the complexes reported in Tables I and II depend on the nature of both the isocyanide and phosphine ligands. While one case is reported [7] in which no relationship between $E_{1/2}$ and the nature of the isocyanide R substituent has been found, some examples are known in which a good linear dependence of the $E_{1/2}$ on the Hammett's σ [5, 6, 10] or on the HOMO energy [21] are observed. In our case a good linear dependence is observed between the $E_{1/2}$ and the νCN of the coordinated isocyanide ligands of the starting complexes. On the other hand, although the electrode process is not a pure reversible charge transfer step the main conditions for a qualitative relationship between the $E_{1/2}$ and the Hammett's σ constant for *p*-substituent in the phenylisocyanide group seems to be fulfilled [22]; *i.e.* the reaction center is the central metal atom and the substituent on the benzene ring can influence the electron density on the cobalt atom through the conjugated system. Half-wave potentials become more anodic in the order R = $4\text{-}CH_3C_6H_4 < C_6H_5 < 4\text{-}CH_3OC_6H_4 < 4\text{-}NO_2C_6H_4$ which is the increasing order of electron withdrawing ability of the group; this increases the half-wave potential and makes the oxidation of the complexes more difficult.

The influence of the phosphine ligands on the redox properties is also significant. The $P(C_6H_5)(OC_2H_5)_2$ derivatives are more easily oxidized than those containing the $P(OCH_3)_3$ ligand. This is probably related to the stronger π-acceptor ability of the trimethylphosphite compared to the diethylphenylphosphonite, than to the lower steric hindrance of the first.

The steric hindrance seems to play an important role in the oxidation electrode process of the $2,6\text{-}(CH_3)_2C_6H_3NC$ complexes; in fact their rather positive half-wave potentials support this idea.

Finally, the direct electrosyntheses of $[CoL_2(CNR)_3]^{2+}$ complexes is quite difficult because the first oxidation step is immediately followed by fast chemical reactions producing different final cobalt(II) species.

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