Effect of Solvents on Electrode Processes of Cobalt Schiff Base Complexes and their Organometallic Derivatives

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The potentials corresponding to the redox processes $[Co^{II}L]^0 \rightleftharpoons [Co^{III}L]^+$ for cobalt chelates with tetradentate Schiff bases and $[Co^{III}L(R)]^0 \rightleftharpoons [Co^{IV}L(R)]^+$ for their organometallic derivatives (L = NN'-ethylenebis(salicylideneiminato) and NN'-ethylene(acetylacetonedi-iminato), R = Ph and Et) are measured in different donor solvents. The shift is linearly related with solvent donicities, in agreement with participation of the solvents in a coordination equilibrium in axial positions, coupled with the electron transfer.
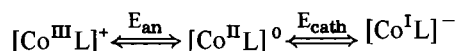
Introduction

A direct method for evaluating the effect of the ligands in a series of complexes is the determination of trends of electronic affinities by measurements of the redox potentials corresponding to the reversible electron transfers involving the same molecular orbitals. This is verified in several families of transition metal chelates with delocalized electronic structure, where it is also possible to measure the potentials in a sequence of one-electron transfers (redox series), corresponding to changes of formal oxidation state of the metal, coupled with changes of the preferred coordination number [1].

In cobalt chelates previously investigated, as model compounds for the study of the chemistry of vitamin B_{12}, the oxidation states are Co^{III}, Co^{II} and Co^{I}, while in their organometallic derivatives a Co^{IV} formal oxidation state is also accessible [2]. In dipolar aprotic solvents the cobalt(II)–Schiff base complexes of the type $[Co^{II}L]^0$ (†) [3] (where L is a chelating equatorial dianion as *salen*: NN'-ethylenebis-salicylideneiminato or *acen*: NN'-ethylenebis(acetilacetoneiminato) give a reversible one-electron reduction wave, which we have found [4] to be strongly influenced by the counter cations of the supporting electrolyte,

and a one-electron oxidation wave which is not affected by the counter cations, but seems to be influenced by the nature of the solvent.

The overall electrode processes can be schematized as:

$$[Co^{III}L]^+ \xrightarrow{\text{E}_{an}} [Co^{II}L]^0 \xrightarrow{\text{E}_{cath}} [Co^{I}L]^-$$

Analogous polarographic features are shown by the organometallic derivatives of the above complexes $[Co^{III}L(R)]^0$ (where R is a σ-bonded organic group in axial position; the solvent bonded in the other axial position is omitted in this formula: see preceeding footnote). In this case the overall electrode processes are represented by:

$$[Co^{IV}L(R)]^+ \xrightarrow{\text{E}_{an}} [Co^{III}L(R)]^0 \xrightarrow{\text{E}_{cath}} [Co^{II}L(R)]^-$$
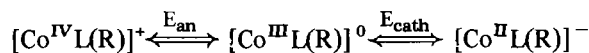
As in the non-organometallic parent chelates, again E_{cath} are influenced mainly by the supporting electrolyte counter cations and E_{an} mainly by the solvent, but to a lesser degree.

In a previous paper [4] we have determined to what extent the redox processes which lead to the lower Co^{II} and Co^{I} oxidation states are influenced by the nature of the supporting electrolyte, the stoicheiometry and the association constants of the ion pairs formed between cobalt chelate anions and the counter cations.

In this work we investigate, in several aprotic solvents, the one-electron oxidation processes for the non-organometallic $[Co^{II}salen]^0$ and $[Co^{II}acen]^0$ and their organometallic derivatives $[Co^{III}salen(R)]^0$ and $[Co^{III}acen(R)]^0$, where R is an organic group (Et or Ph). In the present paper we wish to report the results of investigations on the effect of the solvent on the electrode redox processes, in particular on the processes involving the Co^{III} and Co^{IV} oxidation states, and to attempt to rationalize them, correlating the redox potentials with a suitable solvent parameter, namely the 'donor number' as defined by Gutmann [5], which is a measure of the basicity of the solvent itself.

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†The species in solution which undergo the redox processes are pseudo-octahedral six coordinated, with the donor solvents in axial positions; in the lower oxidation state the preferred coordination number decreases. In all the formulae of $[Co^{II}L]^0$ the solvent is omitted as axial ligand.

Experimental

All cyclic voltammetric measurements were made with an operational amplifier-based three-electrode electronic PAR model 170 Electrochemistry System.

A palladium wire stationary electrode was used as indicator; the potentials are referred to the saturated calomel electrode (s.c.e.), which was separated by a fritted glass disc from a salt bridge containing the same solvent and supporting electrolyte as for the examined solution; the latter was also separated from the salt bridge by a fritted glass disc. Owing to the high cell resistences in the aprotic solvents, the potential drop was always compensated with the application of an amount of feedback just below that required for oscillation of the system (monitored on an oscilloscope).

All the measurements were made at 20 °C and, for the photolabile organometallic derivatives, in the dark. The concentration of the supporting electrolyte was 0.1 mol dm^{-3}, that of the examined complexes $1 \times 10^{-4}-1 \times 10^{-3}$ mol dm^{-3}, according to their solubility.

As we wish to compare potential values obtained in different solvents using the same reference electrode through the experiments, the liquid junction potential phenomena are not negligible; we overcome this problem referring the potential values to a typically reversible system such as the ferrocene—ferrocinium redox couple, assumed as a standard [6].

Materials

The cobalt chelates were prepared following previously reported procedures [7]. The solvents used were nitromethane (NM), acetonitrile (AN), dimethylsulfoxide (DMSO) and pyridine (Py), dried and purified for electrochemical use [8]. The tetra-ethylammonium perchlorate (TEAP) used as supporting electrolyte was dried before use.

Results and Discussion

Oxidation of the Non-organometallic Chelates

[Co^{II}salen]^0 and [Co^{II}acen]^0 give in nitromethane, acetonitrile and dimethylsulfoxide, at stationary noble electrodes, cyclic voltammetric curves as in Fig. 1, corresponding to the electrode process [Co^{III}L]$^+$ $\overset{\pm\epsilon}{\Longleftrightarrow}$ [Co^{II}L]^0; the reversibility of this process can be tested from separation of the anodic—cathodic peak potentials at increasing scan rates (generally from 50 mV s^{-1} to 10 V s^{-1}). In pyridine, the following values at scan rate of 50 mV s^{-1} were found:

[Co^{II}salen]^0: $(E_p)_a = -0.290, (E_p)_c = -0.475$

[Co^{II}acen]^0: $(E_p)_a = -0.425, (E_p)_c = -0.685$
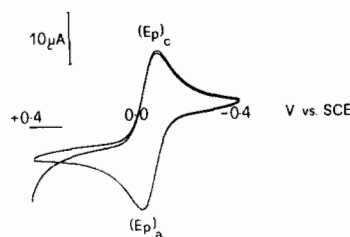
Fig. 1. Cyclic voltammetric curve of [Co^{II}acen]^0 (1×10^{-4} mol dm^{-3}) in 0.1 mol dm^{-3} TEAP in DMSO, at a palladium wire electrode; the scan rate is 50 mV s^{-1}. The peak potential values, $(E_p)_a = -0.023$ and $(E_p)_c = -0.093$, are uncorrected for liquid-junction potential.

showing that the process is irreversible in this solvent; these data are not correlable with the data obtained in NM, AN and DMSO, where the redox processes are reversible.

Oxidation of the Organometallic Chelates

[Co^{II}salen(R)]^0 and [Co^{III}acen(R)]^0, give in the investigated aprotic solvents cyclic voltammetric curves as in Fig. 2. At more anodic potentials we observe the anodic—cathodic peaks $(E_p)_a'$ and $(E_p)_c'$, corresponding to a reversible one-electron redox process [Co^{III}L(R)]^0 $\overset{\pm\epsilon}{\Longleftrightarrow}$ [Co^{IV}L(R)]$^+$. The ratio $(i_p)_c/(i_p)_a$, which depends on the stability of the cobalt(IV)—carbon bond, increases towards unity as the scan rate increases. At more cathodic potentials we observe the anodic—cathodic peaks $(E_p)_a''$ and $(E_p)_c''$ at the same potentials as the redox couple of the relative non-organometallic product [Co^{II}L]^0 $\overset{\pm\epsilon}{\Longleftrightarrow}$ [Co^{III}L]$^+$. These voltammograms suggest an irreversible reaction following the reversible charge transfer process, as depicted by the scheme:
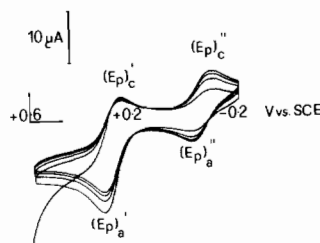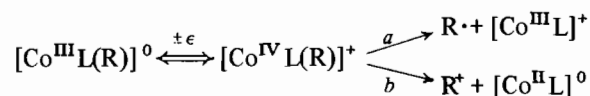
$$[Co^{III}L(R)]^0 \overset{\pm\epsilon}{\Longleftrightarrow} [Co^{IV}L(R)]^+ \overset{a}{\underset{b}{\Big\langle}} \begin{matrix} R^{\cdot} + [Co^{III}L]^+ \\ R^+ + [Co^{II}L]^0 \end{matrix}$$

Fig. 2. Cyclic voltammetric curve of [Co^{III}acen(Et)]^0 (1×10^{-4} mol dm^{-3}) in 0.1 mol dm^{-3} TEAP in DMSO, at a palladium wire electrode; the scan rate is 50 mV s^{-1}. $(E_p)_a' = +0.325$ and $(E_p)_c' = +0.256$ are uncorrected for liquid junction potential; $(E_p)_a''$ and $(E_p)_c''$ values are the same as in Fig. 1.

where *a* and *b* are two alternative mechanisms for the cobalt—carbon cleavage reaction following the primary oxidation at the electrode [9].

The solvent strongly influences the ratio $(i_p)_c/(i_p)_a$ at a fixed scan rate for the process $[Co^{III}L(R)]^0 \Longleftrightarrow [Co^{IV}L(R)]^+$, as is shown in Fig. 3. The observed voltammetric behaviour corresponds to a reversible charge transfer followed by an irreversible chemical reaction:

$$R \overset{\pm e}{\Longleftrightarrow} O$$

$$O \overset{K_f}{\longrightarrow} Z$$
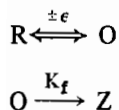
The rate constants K_f, that can be evaluated from cyclic voltammograms by Nicholson's procedure [10], for the experiments related in Fig. 3 were found in the order: $Py(>1.5 \text{ s}^{-1}) > DMSO(0.80 \text{ s}^{-1}) > NM(0.25 \text{ s}^{-1}) > AN(0.06 \text{ s}^{-1})$.

With regard to the role played by the equatorial ligand, we can observe that $[Co^{IV}acen(Et)]^+$ reacts slower than $[Co^{IV}salen(Et)]^+$, in all the examined solvents. In the experiments reported in Fig. 4,

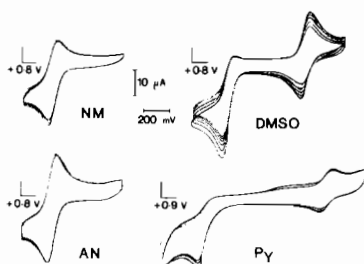Fig. 3. Cyclic voltammetric curves of $[Co^{III}salen(Et)]^0$ (2×10^{-4} mol dm^{-3}) in 0.1 mol dm^{-3} TEAP, in nitromethane, acetonitrile, dimethylsulfoxide and pyridine, at a palladium wire electrode; the scan rate is 200 mV s^{-1}; the potential values are uncorrected for liquid-junction potentials.
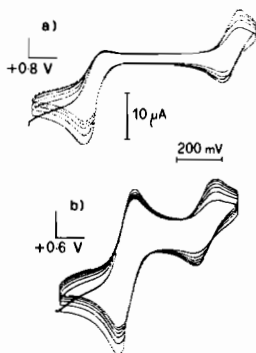

Fig. 4. Cyclic voltammetric curves of $[Co^{III}salen(Et)]^0$ (5×10^{-4} mol dm^{-3}) (*a*) and of $[Co^{III}acen(Et)]^0$ (6.5 $\times$ 10^{-4} mol dm^{-3}) (*b*) in dimethylsulfoxide; the scan rate is 200 mV s^{-1}.

where the solvent was DMSO, we found the following values: $K_f = 0.17$ and 0.80 s^{-1} for $[Co^{IV}salen(Et)]^+$ and for $[Co^{IV}acen(Et)]^+$ respectively.

The oxidation at controlled potential of the phenyl-derivatives in acetonitrile yields quantitatively biphenyl; these experiments suggest that in this solvent and for the phenyl—cobalt derivatives considered, the oxidative cleavage of the cobalt(IV)—carbon bond follows the reaction path *a* of the scheme; further investigations on the role played by the solvents on this cleavage are in progress.

Dependence of the Oxidation Potentials on the Donicity of the Solvent.

We have hereafter considered only the voltammetric responses corresponding to reversible charge transfers. Even when a chemical reaction follows the electron transfer proper as in the organometallic derivatives, the electrode response approaches reversible behaviour in all present cases.

The anodic peak potentials relative to the redox processes $[Co^{II}L]^0 \Longleftrightarrow [Co^{III}L]^+$ for the non-organometallic, and $[Co^{III}L(R)]^0 \Longleftrightarrow [Co^{IV}L(R)]^+$ for the organometallic chelates respectively, corrected for liquid-junction potentials, were plotted *versus* a solvent parameter which measures the relative donor abilities of the various solvents, *i.e.* the 'donor number'. These plots show that the reversible oxidation potentials of our complexes are a linear function of the donicity of the considered solvents, as seen in Fig. 5. We can observe that the oxidation peak potentials, for both $[Co^{II}L]^0$ and $[Co^{III}L(R)]^0$ complexes, while shifting linearly with the solvent donicity, are not directly correlated with the dielectric con-
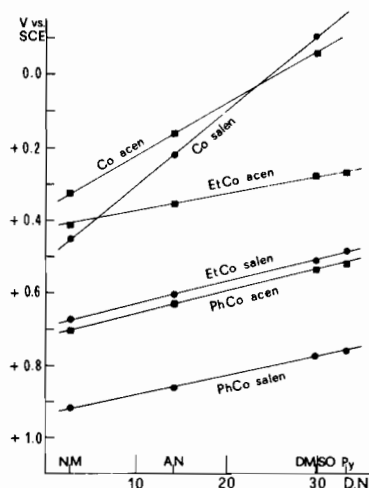

Fig. 5. Oxidation peak potentials as a function of the donor number of the solvents; the values for AN are the same as in the experiments; the other values (for NM, DMSO and Py) are corrected for liquid-junction potentials, by referring them to the ferrocene—ferrocinium redox couple (see Experimental).

stants of the solvents [11]; this suggests that the solvents are directly involved in the overall electrode process. Indeed, the shift of the oxidation peak potentials towards more cathodic values as the donicity of the solvent increases, is in agreement with the increase of the electronic density on the chelated metal as an effect of the coordination of the solvent in axial positions; the increase is larger for $[Co^{II}$-salen]^0, which seems therefore more sensitive to the solvent effect than $[Co^{II}acen]^0$.

In the corresponding organometallic derivatives $[Co^{III}L(R)]^0$, the potentials are again linearly dependent on the solvent donicity, but the slope of E *vs.* DN is lower and less influenced by the nature of the equatorial ligand. This difference of the solvent effect between the non-organometallic $[Co^{II}L]^0$ and the organometallic $[Co^{III}L(R)]^0$ species, is in agreement with the *trans* influence of the organic axial group, which lowers the equilibrium constants of the solvent coordination on the free axial position.

The formally cobalt(IV) derivatives $[CoL(R)]^+$, produced by chemical reaction, or electrogenerated by oxidation at noble electrode as in our case, were reported [12] to react as carbonium ions with nucleophiles or to decompose homolytically. With the exception of acetonitrile as solvent, the rate constants of the chemical reaction of $[Co^{IV}L(R)]^+$ in the different solvents follows the same order as the redox potential for the process $[Co^{III}L(R)]^0 \longleftrightarrow [Co^{IV}$-$L(R)]^+$, which suggests that the cobalt–carbon cleavage is influenced by the charge on cobalt in the same way as the oxidation potential.

Together with the data previously reported on the effect of the cations of the supporting electrolyte, the present results on the solvent effect point out that electronic intermolecular effects can be transferred to the metal, directly or through the equatorial ligand, and the effect on the electronic affinity can be of the same order, or even higher than the effect due to the variation of the nature of the equatorial ligand itself. Moreover, the observed solvent effects

on the relative stability of the cobalt–carbon bond in the organometallic derivatives considered can be useful to interpret reactions catalyzed by metalloenzymes, where, as in our model compounds, the reactive position of the metal can be strongly influenced by variations in the coordination at the *trans* position. More specifically, the understanding of the cleavage mechanisms of the cobalt–carbon bond should take into account also the role of the solvent together with that of the nucleophilic substrate.

References

1 G. Costa, *Pure and Applied Chem.*, *30*, 335 (1972).
2 G. Costa, G. Mestroni, A. Puxeddu and E. Reisenhofer, *J. Chem. Soc. A*, 2870 (1970); G. Costa, A. Puxeddu and E. Reisenhofer, *J. C. S. Dalton*, 1519 (1972); *ibid.*, 2034 (1973).
3 G. Costa, A. Puxeddu and E. Reisenhofer, *Collection Czechoslov. Chem. Commun.*, *36*, 1065 (1971); D. R. Crow, 'Polarography of Metal Complexes', Academic Press, London (1969).
4 E. Reisenhofer and G. Costa, *J. C. S. Dalton*, 521 (1976).
5 V. Gutmann, *Coord. Chem. Rev.*, *18*, 225 (1976); 'Coordination Chemistry in Non-Aqueous Solvents', Springer, New York (1968).
6 H. M. Koepp, H. Wendt and H. Strehlow, *E. Elektrochem.*, *64*, 483 (1960).
7 A. Bigotto, G. Costa, G. Mestroni, G. Pellizer, A. Puxeddu, E. Reisenhofer, L. Stefani and G. Tauzher, *Inorg. Chim. Acta Rev.*, *4*, 41 (1970).
8 C. K. Mann, in 'Electroanalytical Chemistry', ed. by A. J. Bard, Marcel Dekker, New York, vol. 3, p. 57 (1969).
9 G. Costa, A. Puxeddu and E. Reisenhofer, *Experientia Suppl.*, *18*, 235 (1971).
10 R. S. Nicholson and I. Shain, *Anal. Chem.*, *36*, 706 (1964).
11 M. E. Peover, in 'Electroanalytical Chemistry', ed. by A. J. Bard, Marcel Dekker, New York, vol. 2, p. 11 (1967).
12 P. Abley, E. R. Dockal and J. Halpern, *J. Am. Chem. Soc.*, *94*, 659 (1972); D. Dodd and M. D. Johnson, *J. Chem. Soc., Chem. Commun.*, 571 (1971); I. Y. Levitin, A. L. Sigan and M. E. Vol'pin, *J. Chem. Soc., Chem., Commun.*, 685 (1972).