Redox Properties of Cobalt Chelates with Delocalized Electronic Structure: Organometallic Derivatives

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Polarographic techniques are employed to investigate the electrode processes and to point out the influence of equatorial and axial ligands on the half-wave potentials of reversible electron transfers corresponding to formal redox couples $Co^{III} \longrightarrow Co^{II}$, $Co^{II} \longrightarrow Co^{I}$, and to one-electron oxidation, in some series of organometallic cobalt chelates. Free-energy relationships are found between the $E_{\frac{1}{2}}$ and the pK_a values of the hydrocarbon acid corresponding to the organic group in the axial position, showing that the effect is due to charge donation from the organic group, decreasing the electron affinity of the particle. The change of equatorial ligand has a parallel effect on $E_{\frac{1}{2}}$ of both reduction and oxidation waves.

THE role of the ligands on the relevant aspects of reactivity of naturally occurring transition-metal complexes includes the effect of the co-ordination sphere on the relative stability of different oxidation states and on the mechanisms of redox processes. Vitamin B_{12} group complexes offer important examples of redox processes involving a cobalt atom that can be coupled with chemical reactions at an axial co-ordination site. The effect of the equatorial macrocycle and of the *trans*-ligand on a given axial position was investigated in a series of cobalt chelates with several chelating agents which realize stepwise changes of the electronic situation in the co-ordination sphere going from one term to another in the series.[1]

Electrochemical investigation of the effects of the ligands offers the advantage that in a rapid reversible electron transfer the electron density in the molecule is changed without drastically altering the bonding scheme.[2] Moreover, the study of the effect of ligands on the redox process can be separated from that of chemical reactions of the products of electron transfer. This is particularly relevant in the organometallic derivatives when the

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[1] A. Bigotto, G. Costa, G. Mestroni, G. Pellizer, A. Puxeddu, E. Reisenhofer, L. Stefani, and G. Tauzher, *Inorg. Chim. Acta, Rev.*, 1970, **4**, 41.

[2] R. E. Dessy and L. Wieczorek, *J. Amer. Chem. Soc.*, 1969, **91**, 4963; R. E. Dessy, J. C. Charkoudian, T. P. Abeles, and A. L. Rheingold, *ibid.*, 1970, **92**, 3947.

reduction products undergo cleavage of the cobalt–carbon bond.

We pointed out [3] the effects of equatorial ligands on the redox couples cobalt(III)–cobalt(II) and cobalt(II)–cobalt(I) for complexes of the types $[Co^{III}(chel)L_2]^+$ and $[Co^{II}(chel)L_2]^0$ with different axial Lewis bases L, as well as a linear free energy relationship between the pK_a values of L and cobalt(III)–cobalt(II) redox potentials within several series of complexes with a given equatorial ligand (chel).*

We now report the effect of the equatorial ligand and of an organic group R as axial ligand on the reversible electron transfer in the complexes of the type $[R–Co(chel)L]^{0,+}$.†

EXPERIMENTAL

All the solutions were 0·5—1·5 × 10^{-3}M in *NN'*-dimethylformamide (DMF); supporting electrolyte: 0·2M-NEt_4ClO_4; all measurements were performed at 0 °C and in the dark.

Apparatus.—The polarographic curves were recorded with an Amel three-electrode controlled-potential polarograph Model 462 with self-balancing Recorder. Coulometric measurements were performed with the Potentiostat and Multipurpose Unit of the Amel Model 462 polarograph. Cyclic voltammetry was carried out with an operational amplifier-based three-electrode electronic polarograph, Amel Model 448. Current–time curves on the first drop (vertical capillary) were obtained with the oscillographic unit of the Amel Model 448 polarograph.

The characteristics of the dropping-mercury electrode in dimethylformamide–0·2M-NEt_4ClO_4 at 0 °C were m = 0·661 mg s^{-1} and t = 3·00 s for h = 81·0 cm (short-circuit with a calomel electrode S.C.E. Metrohm Model 390/F). The oxidation waves were recorded with a rotating platinum electrode (Metrohm Model EA 222) at 750 r.p.m.

Half-wave potentials were measured from polarograms recorded at 200 mV min^{-1} and a chart-speed of 2·5 cm min^{-1} (Amel Model 462) and 90 mV min^{-1} and 1·27 cm min^{-1} (Amel Model 448).

All the half-wave potentials are referred to S.C.E., which was separated by a fritted glass disc from a salt bridge containing the same solvent and supporting electrolyte as the examined solution. The latter was also separated from the salt bridge by a fritted glass disc. Polarographic cells were of conventional types. Controlled potential coulometry (c.p.r.) was carried out in a cell with a three-electrode system; a mercury pool of 12·5 cm^2 was used as working electrode.

Materials.—The complexes were prepared following procedures reported previously.[1,4] Dimethylformamide was purified over potassium carbonate and then distilled under reduced pressure before use. Other reagents were of analytical grade.

RESULTS

Polarograms of dimethylformamide solutions of complexes $[RCo^{III}(chel)H_2O]^0$ and $[RCo^{III}\{(DO)(DOH)pn\}H_2O]^+$ show the following redox steps (Figure 1).

Cobalt(III)–*Cobalt*(II) *Couples*.—A first well developed cathodic wave occurs in the range −0·7 to −2·0 V (see Table). The slopes of the plots of E against log $i/(i_d - i)$ fall in the range 0·050—0·054 V at 0 °C, in good agreement with the theoretical value for a monoelectronic reversible process. The cathodic currents have a diffusion character, as indicated by the experimental slope of the plot of log i against log t (0·16—0·20) and of log i against log h (0·5).

When the reduction products are sufficiently stable as in the case of phenyl derivatives, the monoelectronic process $[RCo^{III}(chel)]^0 + e \longrightarrow [RCo^{II}(chel)]^-$ could be proved also by coulometry of the exhaustive reduction to Co^{II} species at controlled potential. After successive electrochemical reoxidation the solution again gives the polarogram of the starting complex; this reoxidation process was also proved to be monoelectronic by coulometry at controlled potential.

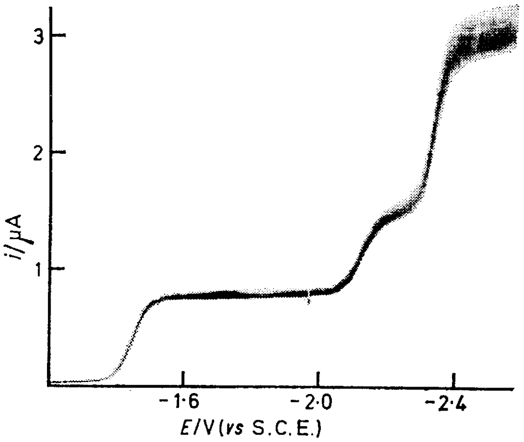

FIGURE 1 Polarogram of $[PhCo^{III}(salen)]^0$ (0·887 × 10^{-3}M) in dimethylformamide–0·2M-tetraethylammonium perchlorate; dropping mercury electrode *versus* S.C.E.

When the reduction product is unstable as in the case of methyl and ethyl derivatives, the number of electrons involved in the reduction was determined by cyclic voltammetry. The separation between the potential of the cathodic and anodic current peaks at high scan rate is found in the range 60—110 mV, consistent with a reversible monoelectronic process.

Decreasing the scan rate, the anodic current peak decreases and eventually disappears, showing that the reduction product is decomposed before the reoxidation potential is reached in the anodic sweep.

Cobalt(II)–*Cobalt*(I) *Couples*.—A second well developed wave can be observed in all complexes examined (except $[EtCo(bae)]^0$) from *ca.* −0·9 V to the limit of the explorable range (see Table). Even this reduction process is monoelectronic and reversible as indicated by the logarithmic

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* (chel) Stands for the following dianions: salen = *NN'*-ethylenebis(salicylideneaminato); saloph = *NN'*-*o*-phenylenebis(salicylideneaminato); 7,7'-Me_2salen = *NN'*-ethylenebis-(7,7'-dimethylsalicylideneaminato); bae = *NN'*-ethylenebis(acetylacetoneiminato),[3] and for the monoanion (DO)(DOH)pn = 1,3-diacetylmonoxime-imino-diacetylmonoximato-iminopropane.[4]

† The actual complexes prepared were the aquo-derivatives $[R–Co(chel)H_2O]^{0,+}$. Dimethylformamide solutions of these complexes are likely to contain pseudo-octahedral six-co-ordinated species with the solvent donor in axial position. In the lower oxidation states the axial bond with the donor molecule is weaker.[5] From all the formulae dimethylformamide is omitted as axial ligand.

[3] G. Costa, G. Mestroni, A. Puxeddu, and E. Reisenhofer, *J. Chem. Soc.* (*A*), 1970, 2870.

[4] G. Costa, G. Mestroni, and E. de Savorgnani, *Inorg. Chim. Acta*, 1969, **3**, 323.

[5] G. Costa, A. Puxeddu, and E. Reisenhofer, *Coll. Czech. Chem. Comm.*, 1971, **36**, 1065.

analysis of the polarographic curves showing that the slope of the graph of E against $\log i/(i_d - i)$ is 0·050—0·054 V at 0 °C. In the case of $[EtCo\{(DO)(DOH)pn\}]^{+}$, $[MeCo\{(DO)(DOH)pn\}]^{+}$, and $[Ph{\cdot}CH_2Co\{(DO)(DOH)pn\}]^{+}$, giving unstable reduction products, the low value of i_d is due to the reaction of the reduction products.

The electrode processes revealed by the first and second polarographic waves are thus (1) for the chelating dianions and (2) for the {(DO)(DOH)pn} monoanion.

$$[RCo^{III}(chel)]^{0} \xrightarrow{+e} [RCo^{II}(chel)]^{-} \xrightarrow{+e} [RCo^{I}(chel)]^{2-} \quad (1)$$

$$[RCo^{III}\{(DO)(DOH)pn\}]^{+} \xrightarrow{+e} [RCo^{II}\{(DO)(DOH)pn\}]^{0} \xrightarrow{+e} [RCo^{I}\{(DO)(DOH)pn\}]^{-} \quad (2)$$

A third wave is observed for several of the examined compounds at very negative potentials and was not further studied.

Chemical Reactions involving the Products of the Electron Transfer.[6]—In the case of $[RCo(salen)]^{0}$ ($R = Me$ or Et), exhaustive reduction at controlled potential corresponding to the first reduction step yields a green solution containing the $[Co^{I}(salen)]^{-}$ species which can be identified by the voltammetric curve, visible spectrum, and oxidative addition reaction with organic halides (RX) yielding again stable organometallic Co^{III} derivatives $[RCo^{III}(salen)]^{0}$. These results are consistent with the processes (3) at the electrode.

$$[MeCo^{III}(salen)]^{0} \xrightarrow{+e} [MeCo^{II}(salen)]^{-} \longrightarrow Me{\cdot} + [Co^{I}(salen)]^{-} \quad (3)$$

The reduction of the corresponding $[MeCo^{III}\{(DO)(DOH)pn\}]^{+}ClO_4^{-}$ exhibits a more complicated chemical behaviour, involving reaction of the two-electron reduction product with the starting complex and dismutation of the product of the one-electrode reduction, as shown in the Scheme. The investigation of the reaction involving the reduction products was reported elsewhere.[6]

Oxidation Wave.—All the complexes examined give a well defined anodic wave in this range (Figure 2 and Table). The plots of E against $\log i/(i_d - i)$ show again the characteristic of a reversible monoelectronic process and the same conclusion can be inferred by comparison of i_d with that of the cathodic wave corresponding to the Co^{III}–Co^{II} reduction step.

$$\begin{tikzcd}
{[MeCo^{III}\{(DO)(DOH)pn\}]^{+}} \arrow[r, phantom, "\rightleftharpoons"] & {[MeCo^{II}\{(DO)(DOH)pn\}]^{0}} \arrow[r, phantom, "\rightleftharpoons"] \arrow[d] & {[MeCo^{I}\{(DO)(DOH)pn\}]^{-}} \arrow[dd, "+(A)"] \\
(A) & {\tfrac{1}{2}[Me_2Co^{III}\{(DO)(DOH)pn\}]^{0}\ (B) + \tfrac{1}{2}[Co^{I}\{(DO)(DOH)pn\}]^{0}\ (C)} & \\
 & & (B) + (C)
\end{tikzcd}$$

SCHEME

Cyclic voltammetry at high sweep rate (40 V s⁻¹) with a stationary platinum electrode in the potential range of the oxidation wave of $[MeCo^{III}(salen)]^{0}$ shows that the process $[MeCo(salen)]^{0} - e \longrightarrow [MeCo(salen)]^{+}$ is rapid and reversible and that the oxidation product is unstable.

Half-wave potentials (in V *vs.* S.C.E.) and i_d/c (μA/mmol) of $Co^{III} \longrightarrow Co^{II}$, $E_{\frac{1}{2}}$(I) and $Co^{II} \longrightarrow Co^{I}$, $E_{\frac{1}{2}}$(II) redox couples from polarograms at dropping mercury electrode, and half-wave potentials (in V *vs.* S.C.E.) of the oxidation wave, $E_{\frac{1}{2}}$(ox) from polarograms at rotating platinum electrode for $[RCo^{III}(chel)]^{0}$ and $[RCo^{III}\{(DO)(DOH)pn\}]^{+}ClO_4^{-}$ (0·5—1·5 × 10^{-3}M) in dimethylformamide–0·2M-tetraethylammonium perchlorate

		salen					{(DO)(DOH)pn}			
Axial ligand	pK_a	$E_{\frac{1}{2}}$(I)	i_d/c	$E_{\frac{1}{2}}$(II)	i_d/c	$E_{\frac{1}{2}}$(ox)	$E_{\frac{1}{2}}$(I)	i_d/c	$E_{\frac{1}{2}}$(II)	i_d/c
Et	40·5	−1·71	0·75	−2·17	0·65	+0·57	−0·93	0·65		
Me	39	−1·57	0·8	−2·17	0·8	+0·62	−0·86	0·6	−1·44	(0·3)
Ph	37	−1·42	0·8	−2·11	0·8	+0·81	−0·83	0·6	−0·93	0·6
$PhCH_2$	35	−1·25	0·8	−2·08	0·8		−0·74	0·5	−1·44	(0·25)
Equatorial ligand		Et					Ph			
{(DO)(DOH)pn}		−0·93	0·65	−1·4			−0·83	0·6	−0·93	0·6
Saloph		−1·54	0·65	−1·97	0·5	+0·74	−1·33	0·8	−1·83	
Salen		−1·71	0·75	−2·17	0·65	+0·57	−1·42	0·8	−2·11	0·8
α-Me-salen		−1·80	0·6	−2·24	0·8	+0·48	−1·46	0·8	−2·27	
bae		−1·97	0·7			+0·35	1·88	0·7		

Influence of the Ligands.—Increasing donor power of the axial ligands displaces the half-wave potentials of the first cathodic wave toward more negative values. Linear dependence is found with the pK_a values of the hydrocarbon acid corresponding to the organic group axial ligand, independently from the nature of equatorial ligand (Figure 3).

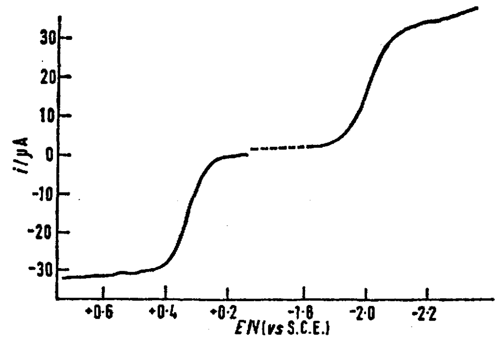

FIGURE 2 Polarogram of $[EtCo^{III}(bae)]^{0}$ (1·5 × 10^{-3}M) in dimethylformamide–0·2M-tetraethylammonium perchlorate; rotating platinum electrode *versus* S.C.E.

[6] G. Costa, A. Puxeddu, and E. Reisenhofer, *Experientia Suppl.*, 1971, **18**, 235.

Moreover, the slopes of the linear relationships for complexes of the type $[\text{RCo}^{\text{III}}(\text{salen})]^0$ are almost exactly the same as those of the RHg^{I} subvalent species and not very different from that of the complexes $[\text{RCo}^{\text{III}}\{(\text{DO})(\text{DOH})\text{pn}\}]^+$ or even $[\text{Co}^{\text{III}}(\text{salen})(\text{RNH}_2)_2]^+$.[3] The effect of the axial ligand on the second cathodic wave corresponding to the formal reduction Co^{II}–Co^{I} is much weaker (see Table). The influence of the nature of the equatorial ligand on both reduction steps as well as on the oxidation waves can be clearly seen in Figure 4.

The differences between the half-wave potentials of successive steps for all the equatorial ligands and a given R are almost constant, *i.e.*, $E_{\frac{1}{2}}(\text{II}) - E_{\frac{1}{2}}(\text{I}) = -0{\cdot}44$ V and $E_{\frac{1}{2}}(\text{I}) - E_{\frac{1}{2}}(\text{ox}) = -2{\cdot}28$ V. This implies that the $E_{\frac{1}{2}}$ values can be plotted against an empirical parameter x of the equatorial chelating ligand such as to yield almost exactly parallel straight lines for all the three polarographic values.

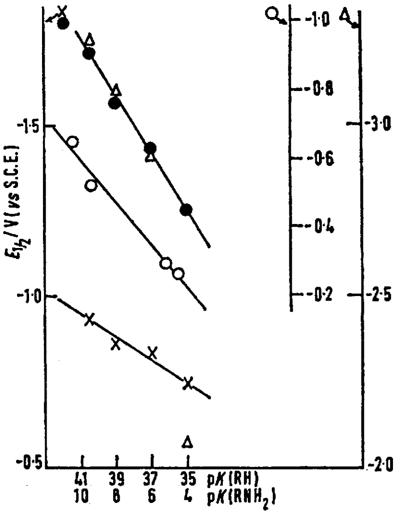

FIGURE 3 Correlation of $E_{\frac{1}{2}}$ for the redox couple $\text{Co}^{\text{III}} \longrightarrow \text{Co}^{\text{II}}$ with $\text{p}K_a$ for axial ligands (R = Et, Me, Ph, and Ph·CH$_2$). $[\text{RCo}^{\text{III}}(\text{salen})]^0$, (●); $[\text{RCo}^{\text{III}}\{(\text{DO})(\text{DOH})\text{pn}\}]^+\text{ClO}_4^-$, (×); RHg, (△); $[\text{Co}^{\text{III}}(\text{salen})(\text{RNH}_2)_2]^+\text{ClO}_4^-$, (○)

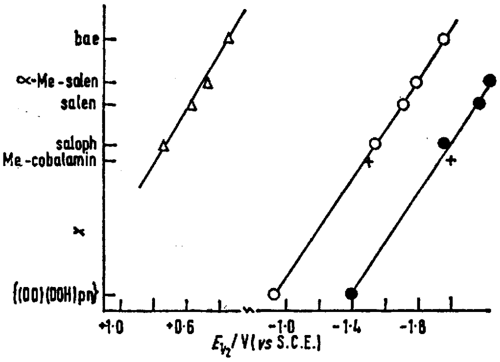

FIGURE 4 Plot of the empirical parameter x against $E_{\frac{1}{2}}$ for $[\text{EtCo}^{\text{III}}(\text{chel})]^{+,0}$ complexes: $E_{\frac{1}{2}}(\text{ox})$, (△); $E_{\frac{1}{2}}(\text{I})$, (○); $E_{\frac{1}{2}}(\text{II})$, (●). Reported values for methylcobalamin: $E_{\frac{1}{2}}(\text{I})$, $E_{\frac{1}{2}}(\text{II})$, (+)

For the sake of comparison a similar plot is reported in Figure 5 for the complexes of the type $[\text{Co}^{\text{III}}(\text{chel})\text{L}_2]^+$ having Lewis bases as axial ligands (L = pyridine,[3] aniline,[5] PPh_2Et[7]). Notwithstanding the different solvents, the plot of $E_{\frac{1}{2}}(\text{II})$ yields nearly parallel lines for the above types of axial ligand L; in this case the effect of changing the equatorial ligand is much weaker on the first wave $\text{Co}^{\text{III}} \longrightarrow \text{Co}^{\text{II}}$ than in the second wave $\text{Co}^{\text{II}} \longrightarrow \text{Co}^{\text{I}}$ and the differences $E_{\frac{1}{2}}(\text{II}) - E_{\frac{1}{2}}(\text{I})$ are no more constant.

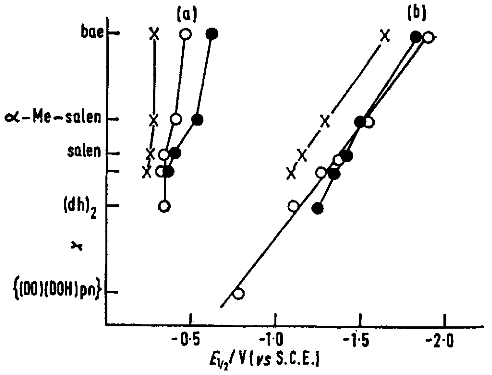

FIGURE 5 Plot of the empirical parameter x against E for the complexes: $[\text{Co}^{\text{III}}(\text{chel})(\text{PPh}_2\text{Et})_2]^+\text{ClO}_4^-$, (×); $[\text{Co}^{\text{III}}(\text{chel})(\text{PhNH}_2)_2]^+\text{ClO}_4^-$, (○); $[\text{Co}^{\text{III}}(\text{chel})(\text{py})_2]^+\text{ClO}_4^-$, (●). The redox couple is (a) $\text{Co}^{\text{III}} \longrightarrow \text{Co}^{\text{II}}$, (b) $\text{Co}^{\text{II}} \longrightarrow \text{Co}^{\text{I}}$

DISCUSSION

In the organometallic complexes as well as in the previously examined cobalt chelates $[\text{Co}^{\text{III}}(\text{chel})\text{L}_2]^+$ electron transfer is generally rapid and no appreciable structural or electronic reorganization appears to be required before the electrode reaction proper.

The acceptance or removal of the electron(s) is helped by a drift of charge both in the π-electron system and in the σ-framework. The reversibility of the electrode process makes it possible to attach thermodynamic significance to the polarographic half-wave potential which can be thus correlated with the electron affinity of the orbital accepting the electron (redox orbital).

$E_{\frac{1}{2}}$ values for the complexes $[\text{RCo}^{\text{III}}(\text{chel})]^0$ are *more cathodic* than those of $[\text{Co}^{\text{III}}(\text{chel})\text{L}_2]^+$, and *much more cathodic* than those of conventional cobalt complexes, but strikingly *less cathodic* than those corresponding to the process $\text{RHg} + \text{e} \longrightarrow \text{R}^- + \text{Hg}$.[8]

This can be explained by assuming that the redox orbital in the present complex $[\text{RCo}^{\text{III}}(\text{chel})]^0$ is formed by mixing the σ-carbon orbital and a cobalt orbital, which is strongly influenced by chelation. The organometallic chelates exhibit intermediate electron affinity between the $[\text{Co}^{\text{III}}(\text{chel})\text{L}_2]^+$ and RHg complexes, where the orbitals accepting the electron are assumed to be essentially localized on the cobalt and on the carbon atom respectively.

The influence of the nature of Lewis bases L shows that free-energy relationships hold between $E_{\frac{1}{2}}(\text{I})$, reflecting the electron affinity of the particle, and the protonation constants of either Lewis bases L or carbanions R^- as

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[7] G. Tauzher, G. Mestroni, A. Puxeddu, R. Costanzo, and G. Costa, *J. Chem. Soc.* (*A*), 1971, 2504.

[8] R. E. Dessy, W. Kitching, T. Psarras, R. Salinger, and T. Chiven, *J. Amer. Chem. Soc.*, 1960, **88**, 460.

axial ligands. This suggests that in the examined series the main effect of the axial ligand consists of charge donation from the ligand to the metal *via* the σ-bond.

The product resulting from the electron transfer can be represented as a carbanion co-ordinated to the Co^{II} species $Co^{II}–R^-$, except in the cases of very strong donor groups where the Co–C bond could be described as $Co^I–R$. This interpretation is consistent with the chemical evidence showing, *e.g.*, that $[PhCo^{II}(salen)]^-$ is relatively stable while $[MeCo^{II}(salen)]^-$ decomposes giving $[Co^I(salen)]^-$.[6]

It is noteworthy that the influence of the nature of the organic group is still parallel in $[RCo^{III}(chel)]^0$ complexes and in RHg^I species notwithstanding the irreversibility of the polarographic process in the latter.

The influence of the equatorial chelating agent is even more remarkable. In spite of the difference in the nature of the axial ligand, the effect of the chelating dianions shows the same trend in both series $[Co^{III}(chel)L_2]^+ClO_4^-$ and $[EtCo^{III}(chel)]^0$. Further, this trend (bae > α-methylsalen > salen > saloph) parallels other trends of ground-state and thermodynamic properties of different series of cobalt chelates,[1] suggesting that it qualitatively reflects the decreasing overall donor power of the equatorial ligand.

In contrast the displacement of $E_{\frac{1}{2}}$ values due to the change of equatorial ligand in the couple $[Co^{III}(chel)L_2]^+–[Co^{II}(chel)L_2]^0$ is much less than that in the couple $[Co^{II}(chel)L_2]^+–[Co^I(chel)L_2]^-$. This suggests that in the organometallic derivatives the influence of the equatorial and axial ligand is comparable in Co^{III} and Co^{II} species, while in the $[Co^{II}(chel)L_2]^0$ complexes $E_{\frac{1}{2}}$ of the $Co^{II}–Co^I$ couple appears to be mainly determined by the equatorial ligand, owing to the decreased interaction of the axial Lewis base in the lower oxidation state of the metal.[5]

Recently [9] it was found that the transmethylation reaction Me–[Co] + [Co]′ ⟶ Me–[Co]′ + [Co] (where [ ] stands for one of the present equatorial ligands, and the metal remains in the formal Co^{III} oxidation state) shows that the methyl donor power decreases in the order $[(Me_2Co\{(DO)(DOH)pn\}] > [MeCo(bae)] > [MeCo(salen)] > [MeCo(saloph)] >$ methylcobalamin $> [MeCo\{(DO)(DOH)pn\}]$.

The displacement of the oxidation potentials toward less positive values parallels the ease of displacement of the axial organic group as a carbanion, showing that the transfer occurs from the less electrophilic cobalt to the more electrophilic one. Both trends thus appear to be determined by the overall donor power of the equatorial ligand. In $[Me_2Co\{(DO)(DOH)pn\}]$, the relatively low donor power of the equatorial ligand is supplemented by the very strong labilization caused by the *trans*-effect of one methyl group upon the other.

On the other hand, the electron transfer from the electrode to the organometallic complex can be considered as a model for charge donation from the axial ligand to the cobalt atom, which results in chemical activation by increasing negative charge on the cobalt–carbon bond and induces carbanionic reactivity of the organic group.

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[1/1007 *Received*, 18*th June*, 1971]

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[9] G. Costa, G. Mestroni, and C. Cocevar, *Tetrahedron Letters*, 1971, **21**, 1869.