

POLAROGRAPHIC STUDY
OF SOME SCHIFF'S BASE AND
BISDIMETHYLGLYOXIMATO COBALT COMPLEXES:
AXIAL LIGAND EXCHANGE

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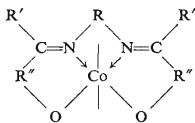
Dedicated to the 65th anniversary of the late Academician R. Brdička.

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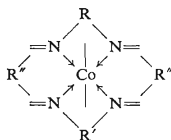
The examined models of vitamin B₁₂ group complexes undergo a rapid one-electron transfer and give a reversible electrode process at the dropping mercury electrode corresponding to the Co(III)—Co(II) formal oxidation states.

From the displacement of $E_{1/2}$ vs concentration of a Lewis base, behaving as axial ligand above and below the plane of the chelate, the axial ligand exchange equilibrium is studied and the trend of coordinating power to the axial position $BAE < 7,7'-(CH_3)_2 SALEN < SALEN < (DO) (DOH)pn$ is obtained. The trend is explained assuming that in the same order decreases the charge on the cobalt atom owing to decreasing donor power from the chelating agent. The behaviour of dimethylglyoximates is complicated by formation of binuclear complexes.

Transition metal complexes of chelating agents of the types I—VI are related to biologically relevant molecules such as porphyrins or vitamin B₁₂ coenzymes.



I, II, III, VI



IV, V

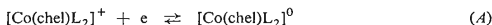
I, R = —CH₂—CH₂—; R' = CH₃; R'' = —CH=C—CH₃ N,N'-ethylenebis(acetylacetoniminato): BAE (dianion); II, R = —CH₂—CH₂—; R' = CH₃; R'' = *o*-C₆H₄ N,N'-ethylenebis(7,7'-dimethyl-salicylideneiminato): (7,7'-(CH₃)₂-SALEN) (dianion); III, R = —CH₂—CH₂— R' = H; R'' = *o*-C₆H₄— N,N'-ethylenebis(salicylideneiminato): SALEN (dianion); IV, R = —OH...O—; R' = —CH₂—CH₂—CH₂—; R'' = CH₃—C(=O)—C(=O)—CH₃ diacetylmonoximeimino-diacetylmonoximateoimino propane 1,3: (DO (DOH)pn (monoanion); V, R = R' = —OH...O—;

$R'' = \text{CH}_3 - \overset{\parallel}{\text{C}} - \overset{\parallel}{\text{C}} - \text{CH}_3$ bis-dimethylglyoximate: (DH)₂ (dianion); $VI R = o\text{-C}_6\text{H}_4-$; $R' = \text{H}$; $R'' = o\text{-C}_6\text{H}_4 - o\text{-phenylene-bis(salicylideneiminato)}$: SALOPH (dianion).

In our model approach to the study of coordination chemistry of vitamin B₁₂ group complexes¹⁻⁴ we considered the chelates of cobalt in the Co(I), Co(II), Co(III) formal oxidation states either in square planar or in five or six coordinated structure with one or two additional ligands above and below the equatorial plane formed by the *I-VI* tetradentate chelating agents.

Owing to the relevance of the axial coordination site and of the nature of cobalt-axial ligand bond in the biochemistry of vitamin B₁₂, the effect of the rest of the molecule to this site in the model compounds was specially studied. The influence of the equatorial ligand (*cis* effect)^{3,4} as well as that of *trans* axial ligand (*trans* effect)^{5,6} was separately examined.

It was previously suggested that the striking physico-chemical analogies between vitamin B₁₂ and model compounds as *e.g.* the characteristic relative stabilization of the Co(I) state could be extended to the electron transfer processes^{3,7}. We first used the electrochemical methods to investigate the effect of the chelating macrocycle and axial ligands on the *reversible* electrode reaction of the type



in which the electrode reaction proper consists in the acceptance of the electron in the redox orbital without extensive reorganization of the particle. The character of the redox orbital is assumed to be essentially d_{z^2} , centered on the cobalt atom.

Considering different chelates with the same axial ligand L we could show the effect of the chelating agent, or conversely changing the L's for a given equatorial situation we pointed out the effect of axial ligands on the electron affinity of the redox orbital (assuming that other factors influencing the standard free energy changes are approximately constant through the series). This amounts of course to understand to which extent the orbitals of the metal atom have lost their metal character on the formation of the complex⁸.

The results pointed out a) the dramatic effect of charge donation from equatorial and from axial ligands to the metal atom both on the Co(III) → Co(II) and Co(II) → Co(I) processes; b) the agreement of the trend of increasing electron affinity of the redox orbital in the order $\text{BAE} < 7,7'-(\text{CH}_3)_2\text{-SALEN} < \text{SALOPH} < \text{SALEN}$ with the trends of other properties related to the ground state effective charge of metal atom.

Thermodynamic aspects of the effect of ligands on the reactive axial sites of the present models are by no means less important than ground state properties in the understanding of the mechanism which determines the features of the chemical behaviour and biological reactivity of vitamin B₁₂.

The replacement of a ligand by another molecule (another ligand or a solvent molecule) is one of the fundamental reaction of metal ions in solutions and often an important feature of biological systems.

We devoted the present paper to the informations given on this topic by the polarographic behaviour of the above complexes in connection with the axial ligand exchange equilibria.

TABLE I
 Characteristics of the Polarographic Waves of $[\text{Co(III)(DH)}_2(\text{PBu}_3)_2]^0$, $[\text{Co(III)(DH)}_2(\text{PBu}_3)_2]^+$ $[\text{Co(III)(DH)}_2\text{Cl}_2]^-$ and Related Complexes
 25.00 \pm 0.01°C; s.c.e. (aq.).

Supporting electrolyte and compound	Co(III)-Co(II)		Co(III)-Co(II)		Reduction of the ligand and catalytic wave ^e	
	$E_{1/2}, \text{V}$	$\frac{i_d}{Cm^{2/3}t^{1/6}}$	$E_{1/2}, \text{V}$	$\frac{i_d}{Cm^{2/3}t^{1/6}}$	$E_{1/2}, \text{V}$	$\frac{i_d}{Cm^{2/3}t^{1/6}}$
0.2N-HCl in (70% H ₂ O + 30% EtOH)						
$[\text{Co(DH)}_2\text{Cl}_2]^-$ $[\text{Co(DH)}_2(\text{PBu}_3)_2]^+$	-J	0.6	-0.59	0.65	-1.0	-
$[\text{Co(DH)}_2(\text{DH})\text{Cl}_2]^0$	-J	1.35	-	-	-0.6 ^d	-
$[\text{Co(DH)}_2(\text{PBu}_3)_2]^+ \text{Cl}^-$	-	-	-0.59	1.4	-1.0	-
$[\text{Co(DH)}_2(\text{PBu}_3)_2]^0$	-	1.36	-0.42	1.3	-1.0	-
0.25N-LiCl in 95% EtOH						
$[\text{Co(DH)}_2\text{Cl}_2]^-$ $[\text{Co(DH)}_2(\text{PBu}_3)_2]^+$	-J	0.52	-	-	-0.8	1.5 ^h
$[\text{Co(DH)}_2(\text{DH})\text{Cl}_2]^0$	-J	1.08	-	-	-0.8	-
$[\text{Co(DH)}_2(\text{PBu}_3)_2]^+ \text{Cl}^-$	-	-	-	-	-0.78	2.1 ^b
$[\text{Co(DH)}_2(\text{PBu}_3)_2]^0$	-0.63	1.04	-0.8	1.14	-	-

^a Determined from $i_d/Cm^{2/3}t^{1/6}$ as compared with all other chelates of the type studied in the present work. ^b Determined by C.P.R. ^c The final reduction product was identified as 2,3 diamino butane from the complete reduction of the ligand dimethylglyoxime.^{1,3} ^d Followed by an ill defined wave at -0.8 V vs s.c.e. ^e Catalytic wave. ^f Corresponds to the reduction of the aquated anion ($\frac{1}{4}$ equivalent of the salt formula). ^g Corresponds to the reduction of the cation ($\frac{1}{4}$ equiv. of the salt formula). ^h Corresponds to the reduction of the anion from Co(II) to Co(I) formal oxidation state together with the reduction of the cation from Co(III) to Co(I). ⁱ The polarographic reduction of complexes having very strong donors as axial ligands in neutral or alkaline solution (including thus OH^- as strong axial ligand) give polarographic waves at relatively negative values corresponding to an overall bielectronic process Co(III)-Co(I). This process is not discussed in the present paper. ^j Wave masked by chloride ions.

EXPERIMENTAL

Apparatus. The polarographic curves were recorded with Amel three-electrodes controlled potential polarograph Mod. 462 with self-balancing Recorder.

Coulometric and potentiometric measurements were performed using the Potentiostat and Multipurpose Unit of the Amel Mod. 462 polarograph. The temperature was kept constant at $25.00 \pm 0.01^\circ\text{C}$ for all the measurements.

The characteristics of the dropping mercury electrode (D.M.E.) used in alcohol 95%-LiNO₃ 0.25M were: $m = 1.043 \text{ mg s}^{-1}$ and $t = 3.00 \text{ s}$ (obtained with a knocker) for $h = 75 \text{ cm}$.

The half-wave potentials were measured from polarograms recorded at a rate of 50 mV/min and chart speed of 2 cm/min.

The reference s.c.e. was separated by a fritted disk glass 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 disk glass.

Polarographic cells were of conventional types.

Controlled potential coulometry was carried out in a cell with three-electrodes system; a mercury pool of 12.5 cm² was used as working electrode.

Materials. The complexes were prepared following procedures reported in our previous papers^{3,4}. Aniline was purified by refluxing over iron powder and then distilled under vacuum, and controlled by refraction index. Other reagents were of analytical grade.

RESULTS AND DISCUSSION

The investigation of unsymmetrically substituted dimethylglyoximates [Co(III). (DH)₂L'X]⁰ (X = anion) is complicated by the existence of coordination isomer salts [Co(III)(DH)₂L₂]⁺ [Co(III)(DH)₂X₂]⁻ (ref.⁹), especially when L' is a very strong donor. We investigated the particular case of L' = PBu₃ with the following results.

The product of the Tschugaeff's reaction of CoCl₂.6 H₂O with dimethylglyoxime in ethanol, followed by air-oxidation and addition of PBu₃ in 1 : 1 molar ratio was found to be not the uncharged complex [Co(DH)₂PBu₃Cl]⁰ as previously reported¹⁰, but the salt [Co(DH)₂(PBu₃)₂]⁺ [Co(DH)₂Cl₂]⁻ (ref.^{11,12}). The anion is easily aquated in aqueous solution giving [Co(DH)₂(H₂O)₂]⁺. The complex [Co(DH)₂. (PBu₃)Cl]⁰ can be prepared indeed from [Co(DH₂)Cl.H₂O]⁰ by addition of PBu₃ in less than stoichiometric amount.^{11,12}

The polarographic behaviour of the salt is different from that of the uncharged complex [Co(DH)₂PBu₃Cl]⁰. The first and second irreversible waves in the polarograms are in fact due to the Co(III) → Co(II) reduction of the aquated complex anion and of the cation respectively, in agreement with the behaviour of separately obtained and examined [Co(DH₂)(DH)Cl₂]⁰ and [Co(DH)₂(PBu₃)₂]⁺Cl⁻, as illustrated in the Table I.

The formation of the salt can be explained^{11,12} by the strong trans-labilizing power of the tributylphosphine in the course of the Tschugaeff's reaction (less strong donors as triphenylphosphine give regularly [Co(III)(DH)₂PPh₃Cl]⁰). It could be also considered the higher stability of [Co(DH)₂(PBu₃)₂]⁺ relative to [Co(DH)₂.

.PBU₃Cl]⁰ and/or the insolubility of the salt [Co(DH)₂(PBU₃)₂]⁺ [Co(DH)₂.Cl₂]⁻ which is precipitated when PBU₃ (added in 1 : 1 molar ratio) is completely used for the formation of the cation.

In order to compare the effect of the equatorial chelating agent in a possibly simple axial ligand exchange mechanism, we decided to consider the exchange in weakly

TABLE II

Characteristics of the Process Co(III)–Co(II) in 95% C₂H₅OH, 0.25M-LiNO₃
+ *i*_d for Co(III), – *i*_d for Co(II) Complexes; V vs s.c.e.

Complex	C · 10 ³ mol/l	E ^o ^b V	E _{1/2} V	<i>i</i> _d /C μA/mM	$\frac{\Delta E}{\Delta \log [i/(i_d - i)]}$ mV
[Co(III)(DO)(DOH)pn(H ₂ O) ₂] ²⁺ . (ClO ₄) ₂ ⁻	1.0	—	+0.194	+1.29	62
[Co(II)(DO)(DOH)pn(H ₂ O) ₂] ⁺ . (PF ₆) ⁻	0.6	—	+0.188	-1.20	64
[Co(II)BAE] ^{0(a)}	1.30	+0.092	+0.092	-1.39	60
[Co(II)(7,7'-(CH ₃) ₂ -SALEN)] ⁰ (^a)	1.46	—	+0.092	-1.40	64
[Co(II)SALEN] ^{0(a)}	1.30	+0.158	+0.160	-1.60	64

^a *n* = 1 (C.P.O.); ^b Values obtained with Pt electrode at various stages of the controlled potential oxidation of the Co(II) chelate.

TABLE III

Characteristics of the First Wave Co(III)–Co(II) in Aniline
Supporting electrolyte: 0.2M-N(C₂H₅)₄ClO₄.

Complex	C · 10 ³ mol/l	E _{1/2} V	<i>i</i> _d /C μA/mM	$\frac{\Delta E}{\Delta \log [i/(i_d - i)]}$ mV
[Co(III)BAE(C ₆ H ₅ NH ₂) ₂] ⁺ (ClO ₄) ⁻	1.95	-0.474	0.42	59
[Co(III)7,7'-(CH ₃) ₂ SALEN(C ₆ H ₅ NH ₂) ₂] ⁺ (ClO ₄) ⁻	1.41	-0.404	0.61	58
[Co(II)SALEN(C ₆ H ₅ NH ₂) ₂] ⁺ (ClO ₄) ⁻	0.92	-0.324	0.63	61
[Co(II)SALOPH(C ₆ H ₅ NH ₂) ₂] ⁺ (ClO ₄) ⁻	1.23	-0.334	0.58	60
[Co(III)(DH) ₂ (C ₆ H ₅ NH ₂) ₂] ⁺ (ClO ₄) ⁻	1.17	-0.328	0.69	59
[Co(III)(DO)(DOH)pn(C ₆ H ₅ NH ₂) ₂] ²⁺ (ClO ₄) ₂ ⁻	0.62	-0.106	0.73	58

coordinating solvent from complexes of the type $[\text{Co(III)(chel)L}_2]^+$ symmetrically substituted in the axial positions.

All representatives of the present chelates of general formulae $[\text{Co(III)(chel)L}_2]^+$ appear to undergo an overall irreversible monoelectronic process at the D.M.E., the first wave corresponding to the formal reduction $\text{Co(III)} \rightarrow \text{Co(II)}$. These results agree with the very few and sparse data on some Co(III) -dimethylglyoximates which were reported to give irreversible^{10,14} $\text{Co(III)} \rightarrow \text{Co(II)}$ polarographic waves.

It can be pointed out that with stronger Lewis bases only the slope of the logarithmic analysis deviates from the theoretical value for a reversible monoelectronic process while with weaker bases it is also splitted into two waves¹⁸.

On the other hand, we found that when it is possible to examine solutions containing excess axial ligand and when chemical reactions do not precede or follow

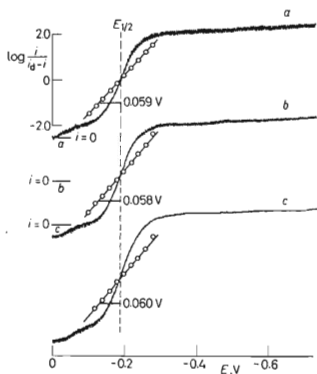


FIG. 1

Polarograms of $[\text{Co(III)(SALEN)(C}_6\text{H}_5\text{NH}_2)_2]^+$

$C = 1 \cdot 10^{-3} \text{ M}$ in $\text{C}_2\text{H}_5\text{OH}$, 0.25 M LiNO_3 , 0.2 M aniline. *a* before; *b* at about 50% C.P.R.; *c* after complete reduction to $[\text{Co(II)(SALEN)(C}_6\text{H}_5\text{NH}_2)_2]^0$. Together with the polarograms the respective log plot and $\Delta E/\Delta \log [i/(i_d - i)]$ values are also drawn. C.P.R. at -0.60 V indicate a one-electron reduction ($n = 0.94$). S.C.E.

TABLE IV
Equilibrium Constants (Eq. (2))

Complex	log <i>K</i>
$[\text{Co(III)BAE(C}_6\text{H}_5\text{NH}_2)_2]^+(\text{ClO}_4)^-$	9.59
$[\text{Co(III)7,7'-(CH}_3)_2\text{SALEN(C}_6\text{H}_5\text{NH}_2)_2]^+(\text{ClO}_4)^-$	8.41
$[\text{Co(III)SALEN(C}_6\text{H}_5\text{NH}_2)_2]^+(\text{ClO}_4)^-$	8.20
$[\text{Co(III)(DO)(DOH)pn(C}_6\text{H}_5\text{NH}_2)_2]^{2+}(\text{ClO}_4)_2^-$	5.07

the electron transfer, well defined reversible waves are obtained. The reversible waves obtained in anhydrous alcohol solution of $[\text{Co(II)chel}]^0$ are due to the redox process $\text{Co(III)} \rightleftharpoons \text{Co(II)}$ of the complexes $[\text{Co(chel)}(\text{C}_2\text{H}_5\text{OH})_2]^+$ (Table II). This was confirmed also by controlled potential oxidation of $[\text{Co(II)chel}]^0$.

Reversible waves were also obtained in anhydrous pyridine³ or aniline (Table III) or even in alcohol solution in the presence of excess pyridine³ or aniline (Table IV, Fig. 1).

The difference between the characteristics of the polarographic wave in the absence and in the presence of excess axial ligand shows that in the former case the wave is distorted because of the axial ligand exchange with even weakly coordinating solvent molecules. With strong donors L or in the presence of excess L the ligand exchange equilibrium is sufficiently displaced as to maintain the $[\text{Co(chel)L}_2]^+$ as the predominant electroactive species.

When H_2O is the axial ligand in the $[\text{Co(chel)}(\text{H}_2\text{O})_2]^+$ complexes the acid dissociation of the ligated water should also be considered. The pK' 's for the equilibria



were determined in water solution:

chel	7,7'-(CH_3) ₂ SALEN	SALEN	SALOPH	(DH) ₂	(DO)(DOH)pn
pK'	7.06	6.86	6.73	5.14	4.17

The corresponding Co(II) complexes have much higher pK' 's for the ligated H_2O . The potentiometric titration of $[\text{Co}(\text{DH})_2(\text{H}_2\text{O})_2]^0$ does not show any dissociation of coordinated H_2O until pH 11.

In acid solution the Co(II) species are unstable as can be seen from the formation constant in water-methanol solution¹⁵ ($\log k = 17.7$). These results show that H_2O is much more firmly bound in the Co(III) than in Co(II) chelates of the present types, in agreement with the generally higher lability of the Co(II) as compared with Co(III) complexes^{3,11}.

In alkaline solution the $E_{1/2}$ of Co(III) dimethylglyoximates is displaced towards more negative value giving an overall bielectronic reduction $\text{Co(III)} \rightarrow \text{Co(I)}$ (see footnote (i) to the Table I).

We thus limited further experiments to the following cap.

Axial Ligand Exchange Equilibria in Symmetrical Complexes of the Type $[\text{Co(chel)L}_2]^+$ in the Presence of Excess $L(\text{C}_2\text{H}_5\text{OH}, \text{C}_6\text{H}_5\text{NH}_2, \text{C}_5\text{H}_5\text{N})$

When the electrode process (A) takes place in solution of pure coordinating solvent L, no ligand exchange needs to be considered as influencing the characteristics

of the polarographic wave. The electron transfer proper is rapid and the electrode process is reversible as confirmed by the logarithmic plot of the cathodic, mixed and anodic waves obtained before, at an intermediate stage and at the end of the controlled potential reduction (C.P.R.) (Fig. 1).

If the potential at the D. M. E. is expressed by the equation

$$(E_{D.M.E.})_L = E_L^0 - RT \ln \frac{[\text{Co(II)(chel)L}_2]_0^0}{[\text{Co(III)(chel)L}_2]_0^+}, \quad (1)$$

TABLE V

Characteristics of the First Wave Co(III)-Co(II) in 95% C₂H₅OH, 0.25M-LiNO₃ with Different Amounts of Free Aniline (calculated from the p*K* of aniline in ethanol)²¹.

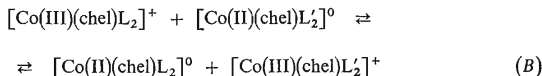
Complex (conc. 1 · 10 ⁻³ mol/l)	Aniline mol/l	E _{1/2} V	i _d /C μA/mM	$\frac{\Delta E}{\Delta \log [i/(i_d - i)]}$ mV
[Co(III)BAE(C ₆ H ₅ NH ₂) ₂] ⁺ (ClO ₄) ⁻	0.01	-0.158	1.25	—
	0.02	-0.181	1.30	62
	0.03	-0.200	1.27	—
	0.05	-0.221	1.32	61
	0.07	-0.240	1.32	62
	0.10	-0.261	1.28	—
	0.20	-0.294	1.26	60
	0.30	-0.315	1.23	63
	0.40	-0.323	1.26	62
	1.00	-0.372	1.27	60
	2.00	-0.397	1.22	59
4.00	-0.420			
[Co(III)(7,7'-(CH ₃) ₂ SALEN)(C ₆ H ₅ NH ₂) ₂] ⁺ (ClO ₄) ⁻	0.03	-0.150	1.04	57
	0.10	-0.211	1.14	60
	0.30	-0.264	1.27	58
	1.00	-0.288	1.25	63
[Co(III)SALEN(C ₆ H ₅ NH ₂) ₂] ⁺ (ClO ₄) ⁻	0.10	-0.159	1.22	64
	0.20	-0.188	1.20	59
	0.30	-0.201	1.23	62
	0.50	-0.220	1.24	
	1.00	-0.245	1.18	63
	2.00	-0.266	1.18	60
5.00	-0.283	1.12	60	

TABLE V
(Continued)

Complex (conc. $1 \cdot 10^{-3}$ mol/l)	Aniline mol/l	$E_{1/2}$ V	i_d/C $\mu\text{A}/\text{mM}$	$\frac{\Delta E}{\Delta \log [i/(i_d - i)]}$ mV
[Co(III)(DH) ₂ (C ₆ H ₅ NH ₂) ₂] ⁺ (ClO ₄) ⁻	0.010	-0.288	1.02	— ^b
	0.020	-0.301	1.05	— ^b
	0.030	-0.305	1.04	— ^b
	0.050	-0.319	1.04	— ^b
	0.100	-0.340	1.08	— ^b
	0.200	-0.340	1.15	— ^b
	0.400	-0.352	1.08	— ^b
	1.000	-0.354	1.12	56
	2.000	-0.360	1.20	62
5.000	-0.370	1.04	60	
[Co(III)(DO)(DOH)pnC ₆ H ₅ NH ₂] ₂ ²⁺ (ClO ₄) ₂ ⁻	0.00	+0.194	1.29	62
	0.003	+0.015	1.23	61
	0.010	-0.048	1.24	64
	0.030	-0.093	1.26	61
	0.100	-0.130	1.14	62
	0.305	-0.146	^a	63
	1.000	-0.162	^a	60

^a Saturated solution; ^b quasi reversible.

(symbol \square_0 refers to concentration at the electrode surface) and $(E_{1/2})_L \approx E_L^0$ for the reversible process, assuming very similar values for the diffusion coefficients, thus for the equilibrium

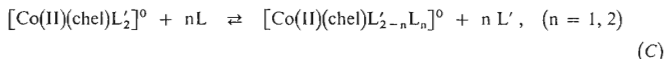


where $L = \text{C}_2\text{H}_5\text{OH}$ and $L' = \text{C}_6\text{H}_5\text{NH}_2$ and the couples $\text{Co(II)}-\text{Co(III)}-(\text{chel})\text{L}_2$ and $\text{Co(II)}-\text{Co(III)}-(\text{chel})\text{L}'_2$ are considered in pure L and L' respectively, the equilibrium constant is obtained (Table IV) from the data of Table II and III:

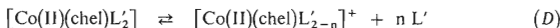
$$(E_{1/2})_L - (E_{1/2})_{L'} = \frac{RT}{F} \ln \frac{[\text{Co(II)(chel)L}_2]^0 [\text{Co(III)(chel)L}'_2]^+}{[\text{Co(III)(chel)L}_2]^+ [\text{Co(II)(chel)L}'_2]^0}_{\text{equil.}} = 0.059 \log K. \quad (2)$$

$(E_{1/2})_L$ in pure aniline is different from the limiting value of $(E_{1/2})_L$ in alcohol in the presence of excess aniline owing to the liquid junction potential.

On the other hand the equilibrium



with equilibrium quotient $\beta_n = [\text{Co(II)(chel)L}'_2]/[\text{Co(II)(chel)L}'_{2-n}L_n][L']^n$, can be investigated when complexes of the type $[\text{Co(III)(chel)L}'_2]^+$ are reduced at the D.M.E. in a solution of a relatively weakly coordinating solvent L and when the electrode reaction proper is followed, and $E_{1/2}$ influenced, by the axial ligand exchange. Alternatively the equilibrium



could be considered, but the expression for the equilibrium constant does not change as L in Eq. (C) represents the weakly coordinating solvent.

Aniline was chosen as L' because it is of suitable strength to allow the ligand exchange equilibrium to be observed. Ethanol was used as L instead of water owing to the low solubility of the compounds in H₂O and in order to minimize acid-base equilibria.

If the electroactive species which is reduced at the D.M.E. is $[\text{Co(III)(chel)L}'_2]^+$ the electrode potential is given by Eq. (1) (expressed in terms of L') and when equilibrium (C) or (D) is taken into account

$$E_{D.M.E.} = E_{L'}^0 - \frac{RT}{F} \ln \frac{[\text{Co(II)(chel)L}'_{2-n}L_n]_0^0}{[\text{Co(III)(chel)L}'_2]_0^+} - \frac{RT}{F} \ln \beta_n - \frac{RT}{F} \ln [L']^n.$$

Assuming that the predominant species electroactive at the electrode surface are $[\text{Co(II)(chel)L}'_{2-n}L_n]^0$ and $[\text{Co(III)(chel)L}'_2]^+$, neglecting the activity coefficients, the differences of the diffusion coefficients of the Co(II) and Co(III) species, and considering that the only species present in the bulk of the solution is $[\text{Co(III)(chel)L}'_2]^+$, the half wave potential is given by

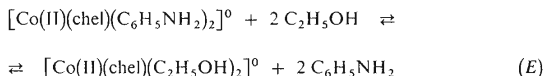
$$E_{1/2} = E_{L'}^0 - \frac{RT}{F} \ln \beta_n - n \frac{RT}{F} \ln [L'], \quad (3)$$

where $[L']$ is the concentration of the free ligand.

Eq. (3) represents the linear relationship between $E_{1/2}$ and the log of the concentration of the free ligand L' with slope n and intercept $E_{L'}^0 - (RT/F) \ln \beta_n$ (ref.¹⁶⁻¹⁸).

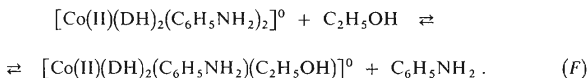
The graph of $E_{1/2}$ vs. $\log [L']$ (see Table V and Fig. 2) suggests that the above

assumptions are justified and Eq. (2) holds with $n = 2$ for all chelating agents in a given range of free ligand concentration except for $(DH)_2$ for which $n = 1$ in about the same range of $\log [L']$. A gradual increase of the slope from $n = 2$ towards $n = 0$ is observed at increasing values of $[L']$, but linear dependence is not found with $n = 1$ in any range of $[L']$. The stability constants β_2 ($\beta_n; n = 2$) of Eq. (3) referring to the equilibria:



were calculated from E_L^0 (Table III) and from the intercepts $E_L^0 - (RT/F) \ln \beta_2$ of the straight lines with slope $n = 2$ of Fig. 2 (Table VI).

The corresponding β constant for dimethylglyoximate-cobalt aniline complex refers to the equilibrium



In all cases the limiting slope $n = 0$ corresponds to the complete displacement of equilibria (E) or (F) to the left. In the intermediate range between $n = 2$ and $n = 1$ the species $[\text{Co(II)}(\text{chel})(\text{C}_6\text{H}_5\text{NH}_2)(\text{C}_2\text{H}_5\text{OH})]^0$ cannot be neglected in the axial ligand exchange equilibria.

The reduction mechanism of dimethylglyoximate-cobalt complexes appears to be complicated by at least two factors: a) the dissociation of the $\text{O}-\text{H}\cdots\text{O}$ hydrogen in the equatorial plane, which depends on the strength of the axial ligand²⁰. It represents an inverse *cis* effect of the axial ligand donor power upon the electronic structure of the equatorial plane. When aniline is the axial ligand the pK of the dissociation

TABLE VI
Stability Constants β_2 (Eq. (3))

Complex	$\log \beta_2$
$[\text{Co(III)}\text{BAE}(\text{C}_6\text{H}_5\text{NH}_2)_2]^+(\text{ClO}_4)^-$	-1.76
$[\text{Co(III)}(7,7'-(\text{CH}_3)_2\text{SALEN}(\text{C}_6\text{H}_5\text{NH}_2)_2)^+(\text{ClO}_4)^-$	-1.42
$[\text{Co(III)}\text{SALEN}(\text{C}_6\text{H}_5\text{NH}_2)_2]^+(\text{ClO}_4)^-$	-0.91
$[\text{Co(III)}(\text{DO})(\text{DOH})\text{pn}(\text{C}_6\text{H}_5\text{NH}_2)_2]^{2+}(\text{ClO}_4)_2^-$	2.70

of the hydrogen bonded hydrogen is sufficiently high to minimize the influence of this equilibrium on the overall reduction mechanism.

b) The reactivity of the first formed Co(II) species. The slope of the plot of $E_{1/2}$ vs $\log [L']$ indicates that only one ligand is rapidly displaced in the reversible reaction following the electron transfer proper. It cannot be proved that the ligand L' is substituted by a solvent (ethanol) molecule but there are indications that the reversible displacement is followed by a slow chemical reaction.

From $[\text{Co(III)}(\text{DH})_2(\text{PPh}_3)\text{Cl}]$ we prepared in fact the dimer $[\text{Co(II)}(\text{DH})_2\text{PR}_3]_2$ by electroreparative reduction in water methanol. In pure aniline the first reversible monoelectronic cathodic wave at -0.7 V disappears by C.P.R. with consumption of about 1 F per g mol and formation of an anodic wave at the same potential and the same intensity of the cathodic wave before C.P.R. The height of the anodic wave decreases *slowly* with time to about a half of its original value. The same results were obtained in pure pyridine.

By oxidation of the solution at this stage (at controlled potential: -0.2 V) and consumption of about 1 F per mol a cathodic wave is reobtained, but it shows again about half the height of the cathodic wave of the parent compound.

On the other hand, in ethanol-aniline 0.1M solution the monoelectronic reversible cathodic wave disappears by C.P.R. at -0.6 V with consumption of about 0.5 F per mol and formation of an anodic wave at the same potential but also of an ill defined cathodic wave at more negative potentials and preceding the Co(II) reduction (at -0.95 V) C.P.R. at -0.8 V occurs instead regularly with consumption of about 1 F. Even in these cases the anodic wave decreases with time.

The above results could be tentatively explained by the formation of binuclear complexes. In pure aniline the binuclear compound is slowly formed after complete reduction of the original complex to Co(II) species.

In ethanol-aniline solution the Co(II) species should react more rapidly with not yet reduced Co(III) species yielding possibly binuclear complexes corresponding to a reduction of only a half of the cobalt atoms. Binuclear complexes with total

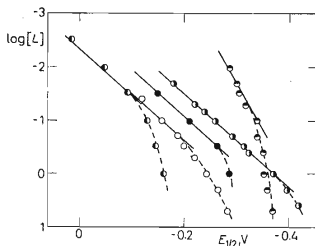


FIG. 2

$E_{1/2}$ vs s.c.e. for the process Co(III)–Co(II) for the complexes $[\text{Co(III)}(\text{chel})(\text{C}_6\text{H}_5\text{.NH}_2)_2]^+$ plotted vs $\log [L]$

$L = \text{C}_6\text{H}_5\text{NH}_2$. Roman numerals refer to the scheme in the introduction. ● I, ● II, ○ III, ● IV, ● V.

charge of +5 on two cobalt atoms connected by bridging groups such as $[(\text{NH}_3)_4 \cdot \text{Co}(\text{NH}_2)(\text{H}_2\text{O})_2\text{Co}(\text{NH}_3)_4]^{5+}$ are not new¹⁹.

CONCLUSIONS

The main conclusions concern the general effect of chelation on the mechanism of electrode reduction and the trend of coordinating power of cobalt atom in the axial sites relative to different equatorial tetradentate chelating agents.

For all present chelates it can be concluded that electron transfer and subsequent axial ligand exchange are sufficiently rapid to give reversible electrode reaction. The cobalt complexes of present chelates belong thus to the group including cobalt complexes of dipyriddy, *o*-phenanthroline and vitamin B_{12a} which Konrad and Vlček recognized as having a rapid and reversible electron transfer and electrode reaction^{19,20}. Furthermore it can be pointed out the lability of axial ligands in the Co(II) chelates relative to the Co(III) complexes of the same type.

The K and β_2 values are not true thermodynamic constants as activity coefficient and liquid junction potential are unknown. On the other hand, the experimental conditions were kept constant through all the complexes examined and the trends obtained are thus quite valid for the comparison of the behaviour of different chelating agents.

The redox potential difference between Co(III)-Co(II) couples in ethanol and pyridine is higher the stronger the difference between the donor power of L' and L and decreases in the order BAE > 7,7'-(CH₃)₂-SALEN > SALEN.

Moreover from the β_2 values of all chelates except (DH)₂ one obtains directly the trend of coordinating power of the chelating agent: increasing in the order BAE < 7,7'-(CH₃)₂-SALEN < SALEN < (DO)(DOH)pn.

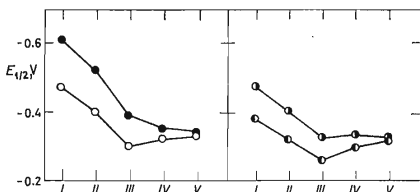


FIG. 3

$E_{1/2}$ vs S.C.E. of $[\text{Co(III)(chel)L}_2]^+$

● L = pyridine, determined in anhydrous pyridine; ○ L = pyridine in C₂H₅OH, 0.5M pyridine; ◐ L = C₆H₅NH₂ in aniline; ◑ L = C₆H₅NH₂ in C₂H₅OH, 0.5M aniline. Roman numerals refer to the scheme in the introduction.

The same information is given also by the difference between $E_{1/2}$ in pure aniline and $E_{1/2}$ in alcohol with a given excess of aniline (Fig. 3).

From Fig. 2 it can also be seen that the higher the coordinating power of the Co(II) species toward the stronger base L' the lower the value of $\log [L']$ at which the slope of the plot of $E_{1/2}$ vs. $\log [L']$ starts to deviate from the value $n = 2$. At higher value of $\log [L']$ the species $[\text{Co(II)(chel)L'L}]^0$ become important over $[\text{Co(II).(chel)L}_2]^0$ going finally toward increasing stability of $[\text{Co(II)(chel)L}_2]^0$.

The trend of decreasing β_2 can be interpreted as the order of *cis* effect that is of labilizing power of equatorial ligands to the axial position. It increases by increasing negative charge donated in the cobalt atom by the equatorial chelating system. This evidence is in agreement with that of other properties as electron affinity of Co(II) species or nucleophilicity of Co(I) species, which are similarly influenced by the charge on the cobalt atom^{3,7}.

The behaviour of Co(II) dimethylglyoximates is different: the coordinating power to axial position is high but it is apparently complicated by the tendency to form binuclear species.

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