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RECENT DEVELOPMENTS IN THE FIELD OF ORGANOMETALLIC DERIVATIVES OF COBALT CHELATES

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Current interest in the last few years in cobalt chelates with macrocyclic ligands of the type shown in Fig. 1 is due to the unique and versatile chemical behaviour they exhibit either in the low spin d^6 Co^{III}, or the d^7 Co^{II} or d^8 Co^I formal oxidation state[1-3].

Two aspects of the chemistry of these complexes are especially relevant to biological problems, i.e. the reactions yielding stable organo-cobalt compounds[5-11] as in B_{12} coenzymes and the reversible oxygenation of Co^{II} representatives as in naturally occurring oxygen carriers[12-16].

The chelates* considered in the present paper are those shown in Fig. 2.

Owing to the very high stability of the coordination bonds in the equatorial plane occupied by the tetradentate or bis-bidentate ligand system, the reactive sites are essentially those in the axial position. Depending on the stability of the axial coordination bond, the preferred coordination number varies from six as in the octahedral complexes (Co^{III} or Co^{II}) to five as in square pyramidal structures of the organometallic bae and salen derivatives, and four in the square planar d^8 Co^I species[2,4].

The formation of relatively stable cobalt–carbon σ-bonds can be achieved (Fig. 3) either from Co^{III} complexes by the Grignard reaction or from the hydroxo-Co^{III} derivatives with organic compounds containing acidic hydrogen[2]. Organometallic derivatives can be obtained, together with XCo^{III} chel complexes, from Co^{II} chel by reaction with organic halides[17,18]. The latter easily undergo oxidative addition to the very nucleophilic cobalt atom of the Co^I species, again yielding a variety of organo-cobalt compounds.

The formation of a cobalt–carbon σ-bond is also implied in the various reaction paths of Co^{III} chelates with carbon monoxide[19-23]. In alcohol, the alkoxocarbonyls are obtained, probably by attack of RO^- on the intermediate carbonyl derivative Co(chel)(CO)L.

In the presence of water, the highly unstable Co(chel)(COOH) is easily decomposed to give Co^I species.

Essentially the same reaction paths were also observed for the chelating monoanion (DO)(DOH)pn (Fig. 2).

On the other hand, cleavage of the Co–C bond was observed in the homolytic thermal or photochemical reaction of the organo-cobalt chelates giving, in anaerobic conditions,

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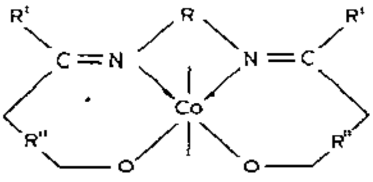
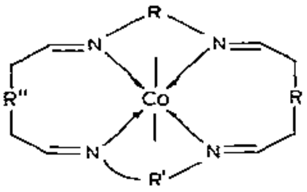
* The chelating dianions I–V will hereafter be indicated as "chel" except when it is necessary to specify the actual macrocycle.



I - IV



V -VI

Fig 1 Equatorial tetradentate chelating agents

the Co^{II} chel derivatives [19-21]

Rearrangement processes in biological systems in which the coenzyme B_{12} (5'-deoxyadenosylcobalamin) serves as intermediate hydrogen carrier were recently proposed to involve homolytic cleavage of the Co–C bond, e g as in the ethanolamine–ammonia lyase [24] and diol-dehydrase [25] reactions On the other hand, other reaction schemes assume heterolytic cleavage [26-28]

Reactions in which an enzyme-bound CH_3–Co derivative is a presumed intermediate are less well studied, but heterolytic cleavage of the Co–CH_3 bond is generally postulated

Notwithstanding the large amount of work completed, existing knowledge appears to be still inadequate to understand fully the detailed mechanism of Co–CH_3 bond fission and the underlying mechanistic concepts

In order to obtain a deeper insight into the mechanistic concepts underlying the formation and rupture of the Co–C bond under the conditions relevant to the function of the enzyme system, the coordination chemistry of the chelated cobalt atom must be considered

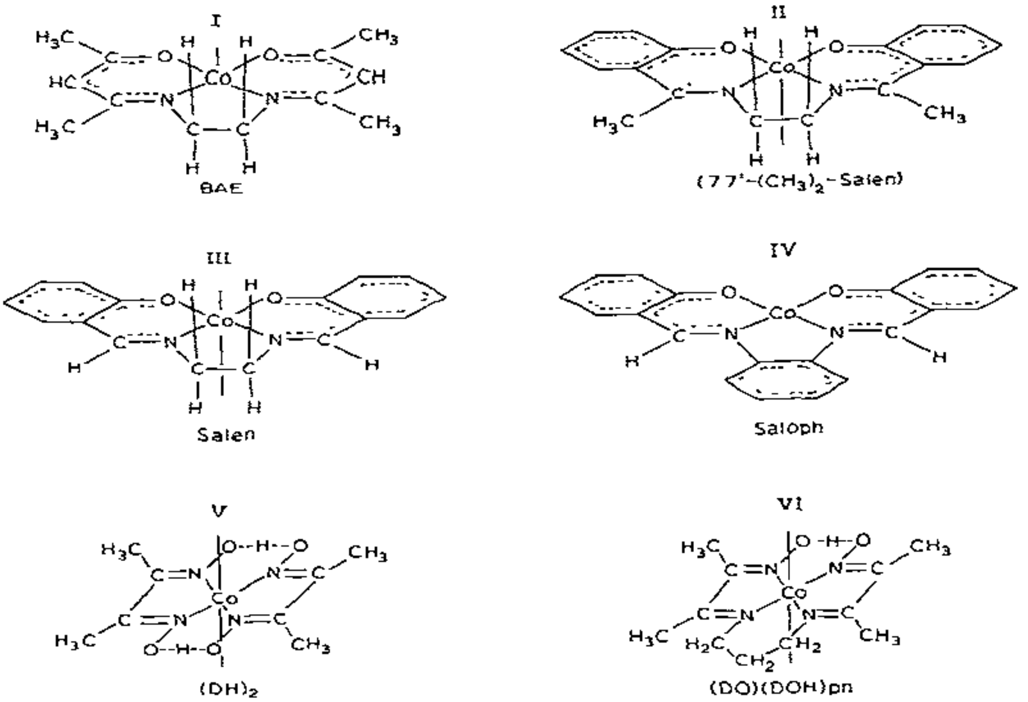
The molecular structure of the complexes obviously suggests two distinct main effects

(1) The effect of the axial ligands (a) on the *trans* position, and (b) on the equatorial ligand

(2) The effect of the equatorial ligand on the axial position.

Adopting this approach, the organic group can be considered as a ligand and the influence of the nature of the coordination sphere on the ground state properties as well as thermodynamic and kinetic aspects of the formation and rupture of the Co–C bond can be studied in reactions implying essentially the exchange of the organic group with another ligand in the axial position

(1) Evidence of the ground state *trans* influence of an axial ligand in the present series of chelates could be obtained from the increase in the chemical shift of the methyl hydro-



I BAE

II (7,7′-(CH$_3$)$_2$-Salen)

III Salen

IV Saloph

V (DH)$_2$

VI (DO)(DOH)pn

Fig. 2. I is *N*,*N*′-ethylenebis(acetylacetoneiminato), i.e. bae (dianion). II is *N*,*N*′-ethylenebis(7,7-dimethylsalicylideneiminato), i.e. 7,7′-(CH$_3$)$_2$-salen (dianion). III is *N*,*N*′-ethylenebis(salicylideneiminato), i.e. salen (dianion). IV is *o*-phenylene-bis(salicylideneiminato), i.e. saloph (dianion). V is bis-dimethylglyoximato, i.e. (DH)$_2$ (dianion). VI is diacetylmonoximeimino-diacetyl-monoximatoimino-propane-1,3, i.e. (DO)(DOH)pn (monoanion).

gens in $CH_3Co(bae)L$ (Table 1) complexes [29] or of the pyridine γ-hydrogens in $LCo(DH)_2py$ (ref. 30) (Table 2) with increasing basicity of the *trans* ligand L. The *cis* influence was shown from the increase of chemical shift of the methene bae hydrogens [29] (Table 3) and of the methyl hydrogens of the dimethylglyoxime in $(DH)_2$ derivatives with increasing basicity of the axial ligand [30] (Table 4).

TABLE 1

Ground state *trans* influence. Dependence of chemical shifts of Co–CH$_3$ hydrogens on substituted pyridine as axial ligand in $CH_3Co(bae)$-pyrX

$\tau(CH_3)$	X
7.41	CN^-
7.43	H–
7.46	CH_3–

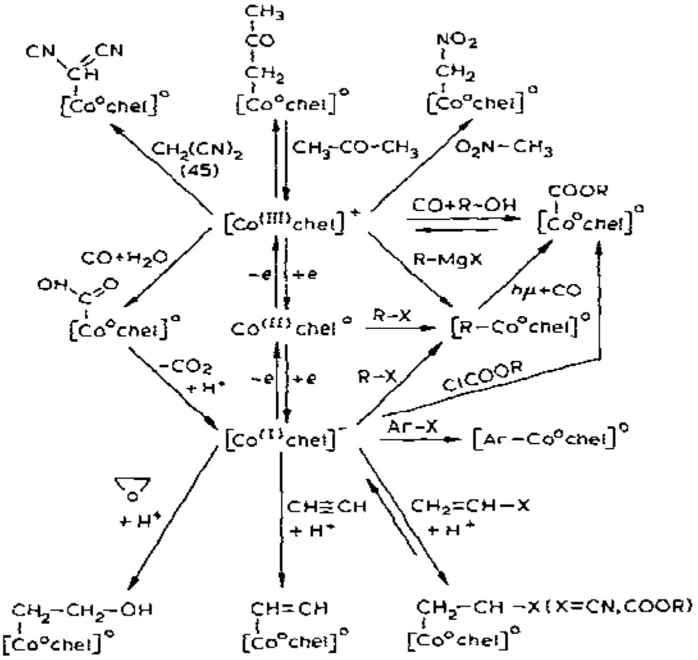


Fig 3 Reacting pattern of cobalt chelates in different oxidation states

If these chemical shifts reflect changes in electron density, these data together with changes in equatorial $H-C_{10}$ chemical shifts and axial CN stretching frequencies observed in cobalamins [11-13] can be interpreted assuming that the charge donation from the ligand to the metal is transmitted to equatorial and *trans* axial ligands [4] The same assumption can also explain the thermodynamic and kinetic aspects of reactivity at the axial position

The labilization of the axial Lewis base yielding square-pyramidal five-coordinate forms [33,34] increases with increasing donor power of an organic group [37] or a tertiary

TABLE 2

Ground state *trans* influence Dependence of chemical shifts of pyridine γ-hydrogens on R in $RCo(DH)_2Pyr$

R	τ(H-pyr)
CF_3-CH_2-	2.24
CH_3-	2.27
CH_3CH_2-	2.29
$n-C_3H_7-$	2.29
Free pyridine	2.37

TABLE 3
Ground state *cis* influence. Dependence of methene hydrogen chemical shifts on axial ligand R in RCo(bae)

R	τ(=CH–)
C_6H_5–	4 58
CH_2–CH–	4 76
CH_3–	4 88
CH_3–CH_2–	4 92

TABLE 4
Ground state *cis* influence Dependence of bae methyl hydrogen chemical shifts on axial ligand in XCo(DH_2)L

τ(CH_3)	X
7 79	CN^-
7 99	Cl^-
8 18	CH_3–
8 19	CH_3–CH_2–

phosphine in the *trans* position and can be attributed to the higher effective charge on the cobalt atom, closer to that characteristic of a lower oxidation and coordination number [4] (Tables 5 and 6).

The kinetic *trans* effect could be shown in a series of organometallic derivatives of the bis-diacetylmonoxime ligands VI from the trend of the dissociation rate of the limiting S_N 1 process, which increases with increasing donor power of the organic group [35] (Table 7)

Under suitable experimental conditions, the polarographic half-wave potential gives quantitative information concerning thermodynamic aspects of the interaction of the axial ligand with the rest of the molecule, owing to the fulfillment of the following conditions: (i) the electron exchange is fast and the electrode process is rigorously reversible and (ii) the chemical reactions, including release of Lewis base or the cleavage of the Co–C bond which follow the electron transfer, can be kept slow enough to be studied separately

Thus, a linear free energy relationship was found between the half-wave potential of the first reduction wave $E_{\frac{1}{2}}$ (I) corresponding to the process

$$[Co^{III}(chel)L_2]^+ \overset{e}{\rightleftharpoons} [Co^{II}(chel)L_2]^0$$

or

$$[Co^{III}\{(DO)(DOH)pn\}L_2]^{2+} \overset{e}{\rightleftharpoons} [Co^{II}\{(DO)(DOH)pn\}L_2]^+$$

TABLE 5
Thermodynamic *trans* influence of axial ligands on the equilibrium quotient for the reaction[a]

$$\text{R–Co(bae)L} \underset{(30^\circ\text{C})}{\overset{K}{\rightleftharpoons}} \text{R–Co(bae)} + \text{L}$$

L	pK	R			
		C_2H_6–	CH_3–	CH_2=CH–	C_6H_5–
p-$ClC_6H_4NH_2$	3.98	1.14	0.26	0.19	0.17
$C_6H_5NH_2$	4.58	0.87	0.20	0.18	0.12
p-$CH_3C_6H_4NH_2$	5.12	0.68	0.14	0.11	0.08
C_5H_5N	5.23	0.24	0.02	0.02	0.05
4-$CH_3C_6H_4N$	6.02	0.21	0.12	0.02	0.19

[a] G. Costa and L. Stefani, unpublished results.

TABLE 6
Thermodynamic *trans* influence of tertiary phosphines on the equilibrium quotient for the reaction

$$[\text{Co(chel)PR}_3]^+ + \text{NO}_2^- \overset{K}{\rightleftharpoons} [\text{Co(chel)(PR}_3\text{)(NO}_2\text{)}]^0$$

PR_3	σ^*	(bae)	(salen)
PPh_3	+ 1.80	4.69	5.57
PPh_2Et	+ 1.10	3.54	3.88
PBu_3	– 0.39	2.87	3.09

TABLE 7
Kinetic *trans* effect of organic groups as axial ligands

$$[\text{R–Co}\{\text{(DO)(DOH)pn}\}\text{H}_2\text{O}]^+ + \text{Y} \rightarrow [\text{R–Co}\{\text{(DO)(DOH)pn}\}\text{Y}]^+ + \text{H}_2\text{O}$$

$$\text{M–H}_2\text{O} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{M} + \text{H}_2\text{O}$$

(Y = imidazole)

R	k_1 (sec^{-1})
C_6H_5–	3.6 ± 0.3
CH_3–	24.8 ± 5.6
$C_6H_5CH_2$–	226 ± 28
C_2H_5–	251 ± 23
n-C_3H_7–	602 ± 139

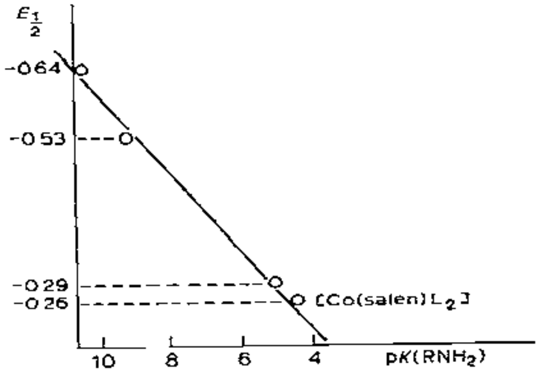


Fig 4

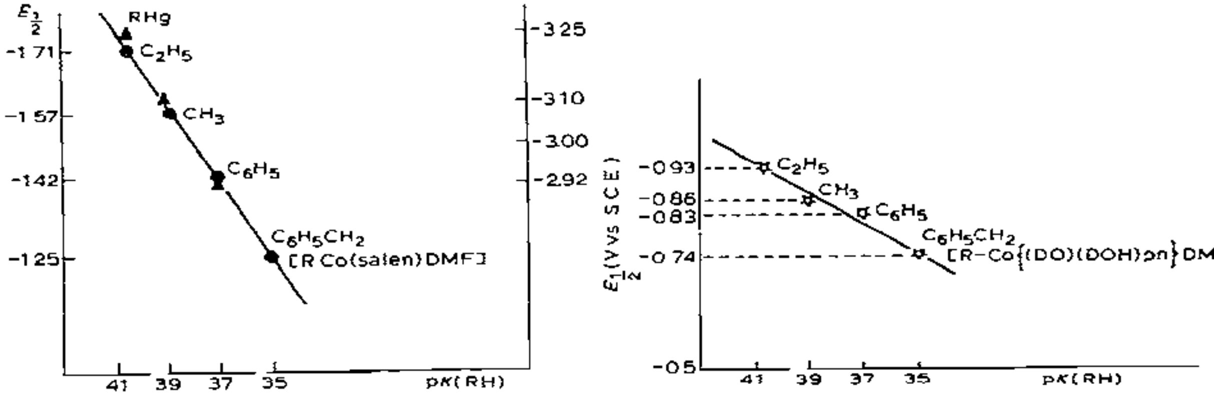


Fig 5

and the protonation constant of the Lewis base L [36,37] (Fig. 4)

When the values of $E_{\frac{1}{2}}$ (I) for the organometallic derivatives

$$[\mathrm{RCo(salen)DMF}]^0 \overset{e}{\rightleftarrows} [\mathrm{RCo(salen)DMF}]^-$$

$$[\mathrm{RCo\{(DO)(DOH)pn\}DMF}]^+ \overset{e}{\rightleftarrows} [\mathrm{RCo\{(DO)(DOH)pn\}DMF}]^0$$

are plotted against the pK_a of the corresponding hydrocarbon acid, a linear free energy relationship is obtained For RCo(salen) chelates the slope is almost coincident with that of the subvalent RHg compounds, though the latter are reduced at much more negative potentials [38] (Fig 5).

As the enthalpy and entropy differences involved in the redox processes are low and can be assumed constant along each series of chelates with the same equatorial ligand, $H_{\frac{1}{2}}$ (I) is a measure of the electron affinity of the particle, mainly representing the electron affinity of the molecular orbital accepting the electron (redox orbital)

The displacement of $E_{\frac{1}{2}}(\mathrm{I})$ values of organo-cobalt chelates relative to the organomercury RHg species can be explained assuming that in the former complexes delocalization of the charge donated by the organic group in the redox orbital is mainly centred on the cobalt atom Within a series with a given chelating agent the $E_{\frac{1}{2}}(\mathrm{I})$ values are determined by the protonation constant of the organic group R^-

(2) The effect of the equatorial ligand is obviously the most important factor determining the physico-chemical properties and the reactivity at the axial position as, for instance, in the vit B_{12} group complexes and oxygen carriers

The possibility of expressing this effect in quantitative terms comes from examination of the series of chelates I -VI which show a stepwise variation of the electronic situation around the metal atom Evidence of the effect on a ground state property is given by the decrease of the carbonyl stretching frequency in the series of acyl- and alkoxo-carbonyl derivatives This trend parallels the increase of the pK_a values of the diaquo derivatives with the same equatorial ligand (Table 8) and presumably also the stabilization of the five-coordinate $CH_3Co(chel)$ species which are obtained under vacuum at 80°C for chel = bae but only at 150°C when chel = salen

All the trends can be explained by the increase of the effective charge on the cobalt atom in going from (DO)(DOH)pn to bae chelates, assuming that this charge is transmitted to the axial ligand As a consequence, in the acyl derivatives the bond order of the carbonyl group decreases and in the aquo complexes the acid strength of the coordinated water decreases through weakening of the Co–O bond

Here again, the results of electrochemical investigation provide quantitative data expressing the overall effect of the equatorial ligand on the electron affinity of a molecular orbital which appears to influence the coordination bond in the axial positions [37-40]

In fact, the half-wave potential $E_{\frac{1}{2}}(\mathrm{II})$ of the second reduction step $Co^{II}-Co^{I}$ is influenced to almost the same extent in both the organometallic and $[Co(chel)L_2]^+$ complexes (Fig 6)

TABLE 8

Ligand	$\nu_{C=O}$ (cm^{-1}) for $\mathrm{CH_3\underset{\underset{O}{\|}}{C}-Co(chel)C_4H_6N_2}$	pK_1 for $\mathrm{\overset{OH_2}{\underset{OH_2}{Co(chel)}} \xrightleftharpoons{-H^+} \overset{OH}{\underset{OH_2}{Co(chel)}}}$	Electrochemical potential vs S C E for $[R-Co(chel)]^{n+} + e \rightarrow [R-Co(chel)]^{(n-1)+}$
bae	1670		−1 97
7,7′-$(CH_3)_2$salen	1675	7 06	−1 80
salen	1687	6 86	−1 71
saloph	1690	6 73	−1 54
$(DH)_2$	1690	5 14	
(DO)(DOH)pn	1694	4 17	−0 93

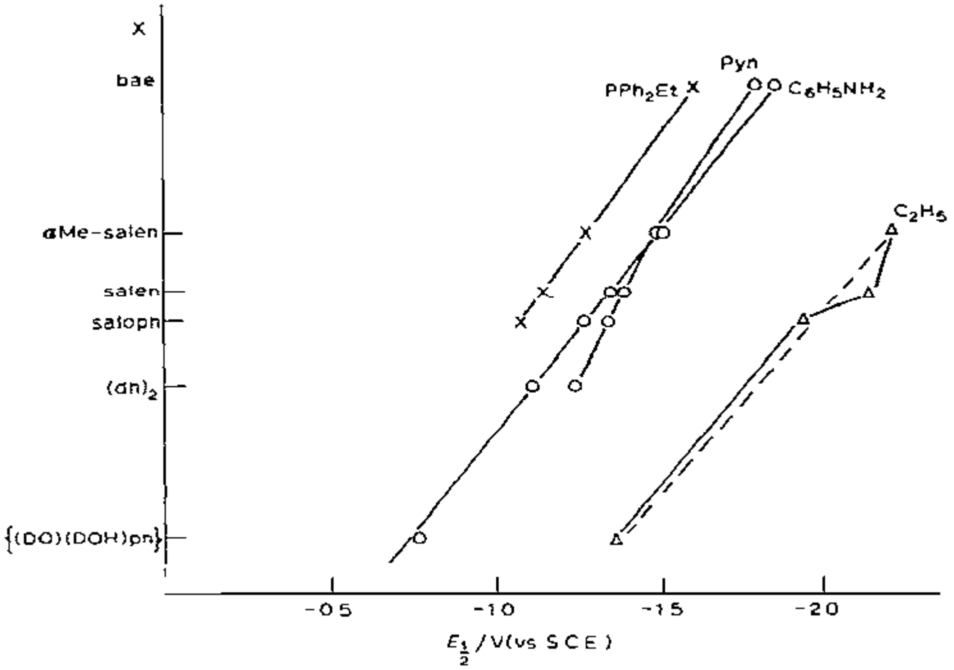


Fig. 6

$$[\mathrm{RCo(chel)L}]^+ \underset{-e}{\overset{+e}{\rightleftarrows}} [\mathrm{RCo(chel)L}]^0 \underset{-e}{\overset{+e}{\rightleftarrows}} [\mathrm{RCo(chel)L}]^- \underset{-e}{\overset{+e}{\rightleftarrows}} [\mathrm{RCo(chel)L}]^{2-}$$

$$E_{\frac12}(\mathrm{ox}) \qquad\qquad E_{\frac12}(\mathrm{I}) \qquad\qquad E_{\frac12}(\mathrm{II})$$

$$[\mathrm{Co(chel)L_2}]^+ \underset{-e}{\overset{+e}{\rightleftarrows}} [\mathrm{Co(chel)L_2}]^0 \underset{-e}{\overset{+e}{\rightleftarrows}} [\mathrm{RCo(chel)L_2}]^-$$

$$E_{\frac12}(\mathrm{I}) \qquad\qquad E_{\frac12}(\mathrm{II})$$

(The chemical reactions following the electron transfer are not considered.)

The dependence can be expressed by a linear relationship of the type

$$E_{\frac12} = ax + c$$

where x is a parameter related to the nature of the chelating agent. The relation holds only approximately and the slope is slightly different for different axial ligands but it is much more precisely obeyed, and the slope is almost the same, when the three redox potentials $E_{\frac12}(\mathrm{ox})$, $E_{\frac12}(\mathrm{I})$ and $E_{\frac12}(\mathrm{II})$ for the organometallic complexes are considered (Fig. 7). If we compare these results with the trends of other effects of equatorial ligand previously dis-

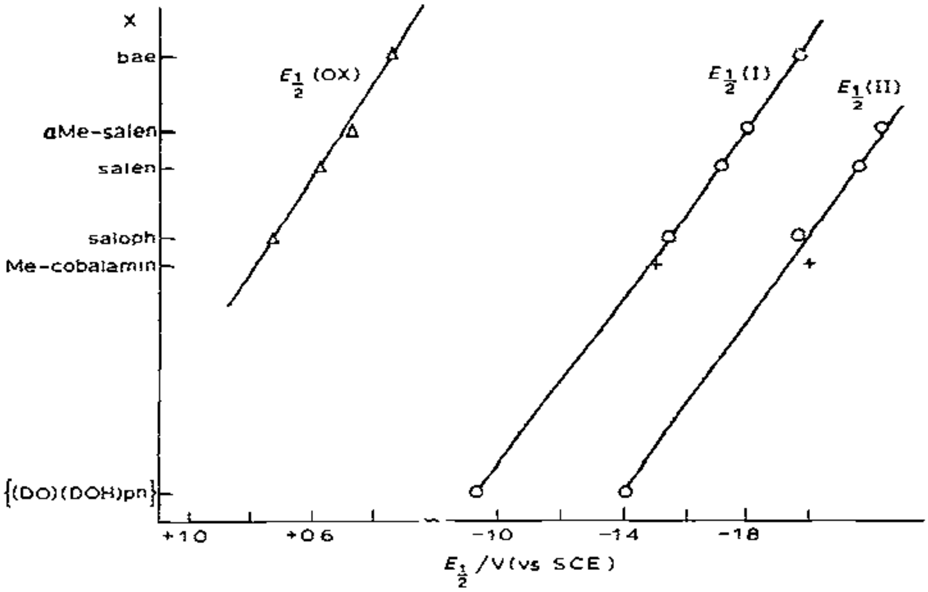


Fig 7

cussed, it follows that the increase of electron affinity as given by displacement of $E_{\frac{1}{2}}$ towards less negative potentials is in agreement with the assumption of an increase of effective charge on the cobalt atom going from (DO)(DOH)pn to bae chelates This suggests that this is also the trend of the overall donor power of the equatorial ligand

We shall now try to consider, in the light of the above results, the simplest reactions involving formation and rupture of the Co–C bond, i e alkyl exchange reaction between two differently chelated cobalt atoms[40-42]

$$[CH_3Co(chel)H_2O]^0 + [Co(chel')(H_2O)_2]^+$$
$$\rightleftharpoons [Co(chel)(H_2O)_2]^+ + [CH_3Co(chel')(H_2O)]^0$$

Thus the methyl group is transfered from the methyl-cobalt bae to the $[Co(salen)(H_2O)_2]^+$ and not vice versa, but the reaction $[CH_3Co(salen)H_2O]$ + $[Co(saloph)(H_2O)_2]$ comes to equilibrium The methyl derivatives of any of the bae, salen, saloph chelates act as methyl donor towards the aquo derivatives of the chelates V and VI and aquocobalamin, viz

$$[CH_3Co(chel)H_2O]^0 + [Co\{(DO)(DOH)pn\}(H_2O)_2]^{2+}$$
$$\rightleftharpoons [Co(chel)(H_2O)_2]^+ + [CH_3Co\{(DO)(DOH)pn\}H_2O]^+$$

$$[CH_3Co(chel)H_2O] + \text{aquocobalamin} \rightleftharpoons \text{methylcobalamin} + [Co(chel)(H_2O)_2]^+$$

On the other hand, (DO)(DOH)pn appears to be a better acceptor than aquocobalamin, the reaction

$$\begin{aligned}&\text{methylcobalamin} + [Co(DO)(DOH)pn(H_2O)_2]^{2+}\\&\qquad\rightarrow \text{aquocobalamin} + [CH_3Co(DO)(DOH)pn(H_2O)]^+\end{aligned}$$

being observed

The (DO)(DOH)pn chelate containing two methyl groups in the axial position turns out to be an even better donor of methyl groups than all other monomethyl chelates examined until now From experimental data on the direction of the methyl group transfer we can now propose the following order for the "methyl donor" power

$$\begin{aligned}&[(CH_3)_2Co\{(DO)(DOH)pn\}]^0 > \underset{E_{\frac{1}{2}}(I) = -1\ 97}{[CH_3Co(bae)H_2O]^0} > \underset{E_{\frac{1}{2}}(I) = -1\ 71}{[CH_3Co(salen)H_2O]^0}\\&> \underset{E_{\frac{1}{2}}(I) = -1\ 54}{[CH_3Co(saloph)H_2O]^0} > \underset{E_{\frac{1}{2}}(I) = -1.4}{\text{methyl cobalamin}} > \underset{E_{\frac{1}{2}}(I) = -0\ 93}{[CH_3Co\{(DO)(DOH)pn\}H_2O]}\end{aligned}$$

Examination of this trend leads to some important observations

(1) The order is parallel to the displacement of $E_{\frac{1}{2}}(I)$ towards less cathodic values (the actual values given are those of the corresponding C_2H_5 derivatives).

(2) The methyl donor power is determined by both the equatorial and the axial ligand, i.e it is sensitive to both the *cis* and *trans* effect

Both conclusions show that the release of the organic group is favoured by an increase of the electronic charge on the cobalt atom The effect should be noted of one methyl group in $[(CH_3)_2Co\{(DO)(DOH)pn\}]$, acting by charge donation to the cobalt atom and strongly enhancing the release of the *trans* methyl group relative to $[CH_3Co\{(DO)(DOH)pn\}H_2O]$

The transfer of the CH_3 group requiring higher electron affinity in the acceptor than in the donor complex can be considered formally as involving a coordinated carbanion. A binuclear intermediate could be assumed, the methyl transfer taking place from the less electrophilic metal atom to the more electrophilic one The cleavage of the Co—C bond from the donor cobalt atom probably occurs via electrophilic attack of the acceptor Co atom to the saturated carbon atom This is believed to occur in the removal of organo-ligands assisted by Ag^+ or Hg^{++}, recently reported as a substitution of coordinated carbanion [43] and in the dealkylation of alkylcobalamins with mercuric acetate, which probably occurs via an S_E2 mechanism [44] This mechanism is also implied in the conversion of inorganic mercury to methylmercury compounds by methylcobalamin and is probably also operating in the formation of highly toxic organomercurials in living systems [46]

The formation of the Co–C bond instead involves the nucleophilic attack of the carbanion to the Co–OH_2 bond of the acceptor complex as in the carbanion nucleophilic substitution of activated methylene groups leading to formation of Co^{III}-alkyl compounds [45], viz

$$[Co^{III}(salen)OR]^0 + R'CH_2R'' \rightarrow [Co^{III}(salen)CHR'R'']^0 + ROH$$

The evidence discussed in the present paper shows how changes in the nature of the equatorial and *trans*-axial ligand can help the cleavage of the Co–C bond in the CH_3^- group transfer, by increasing the electronic charge on the cobalt atom For a given acceptor atom, the driving force of the reaction parallels the decrease of the electron affinity, which can be expressed by $E_{\frac{1}{2}}$ values The opposite trend should be expected for the reaction involving the transfer of a potential CH_3^+ group This type of reaction can take place by the attack of a nucleophilic Co^I chelate to the carbon atom of an organic halide The cleavage of the Co–C bond, yielding Co^I vit B_{12s}, was proposed for the vit B_{12}-dependent methionine biosynthesis In this case the formation of the Co–C bond is said to occur by oxidative addition to Co^I while the fission of the bond yielding the Co^I species is a reductive demethylation As a special case, the formation of the dimethyl derivative $[(CH_3)_2Co\{(DO)(DOH)pn\}]^0$, by chemical or electrochemical reduction of $[CH_3Co\{(DO)(DOH)pn\}H_2O]^+$, can be explained either by transfer of CH_3^- from Co^I to CO^{III} complex or as a transfer of CH_3^+ from CO^{III} to Co^I species Another most interesting type of transmethylation reaction requires coupling with a redox process

Methyl-vitamin B_{12} was shown to be demethylated by a Pt^{II}–Pt^{IV} system A mechanism involving attack on Pt^{II} was proposed [47], viz.

$$Pt^{II} + CH_3B_{12} \rightarrow Pt^{II}CH_3B_{12} \xrightarrow{Pt^{IV}} Pt^{II} + Pt^{IV}CH_3 + B_{12a}$$

In this case probably the Pt^{II} atom of the $Pt^{II}CH_3B_{12}$ intermediate has to be oxidized in order to help the cleavage of the Me–Co bond In the biological methyl transfer a coupled redox process is likely, involving the Co atom

Further studies on model systems should show how coupled redox processes or changes in the coordination sphere leading to changes in electronic charge on the cobalt atom can promote Co–C bond formation and fission

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