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Vitamin B_{12} Model Compounds - Cobalt Chelates of Bis(Diacetylmonoxime -Imino)Propane 1-3

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The preparation and properties of a new series of Vit. B_{12} model compounds, — cobalt chelates of bis-(diacetylmonoximeimino)propane1,3 are reported. The synthesis of organometallic derivatives as model molecules of alkylcobalamins is discussed. Rationalization of the coordination chemistry of cobalt atom in these and other previously reported model molecules is attempted by consideration of the influence of equatorial ligands on the axial position and the trans effect between axial ligands.

Introduction

The chelating agents previously proposed in this laboratory[1-6] and the bis(dimethylglyoximato)dianion used by Schrauzer[7] to prepare model complexes of Vit. B_{12}, form essentially planar tetradentate conjugate macrocycles including the cobalt atom, in octahedral or square-pyramidal complexes.[6]

As a common feature with corrins all these ligands strongly stabilize either metal-carbon σ-bond on axial position and low oxidation states of the cobalt atom.

The relevant aspects of chemical analogies with Vit. B_{12} compounds resides in the reactivity of the axial position.

To determine the steric and/or electronic requirements responsible for the coordination chemistry characteristic of Vit. B_{12} it is necessary to dispose of several representatives of model molecules showing gradual changes in the relevant aspects of the physico-chemical properties.

The axial position in the complexes being considered, this amounts study the cis effect of different planar macrocycles on the same axial ligand and the trans effect of several axial ligands to a fixed one for the same equatorial system.

Comparison of ground state properties, thermodynamic and kinetic aspects of reactivity should lead to a description of the oxidation state of the cobalt atom, of the nature of axial bonds and of reaction mechanisms as determined by the planar chelating agent.

All the tetradentate ligands till now used were dianions. The situation in the corrinoids is somewhat different as the planar tetradentate ligand is a monoanion, the charge on the macrocycle including the cobalt atom and the overall electronic density on the equatorial plane being then presumably different.

It was thus highly interesting to search for a ligand which more closely simulates the Vit. B_{12} situation as far as the effects on the cobalt are concerned.

The present paper is devoted to the examination of the consequencies of the monoanion character of the tetradentate ligand 1-diacetylmonoxime-imino-3-diacetylmonoximato-imino-propane and the comparison with other chelating agents as far as the analogies between the model complexes and the corrinoids are concerned.

Results

The chelating agents bis(diacetylmonoxime-imino)-propane 1-3: $(DOH)_2$pn, and bis(diacetylmonoxime-imino)ethano 1.2:$(DOH)_2$en, were synthesized using the procedure of Uhlig and Friedrich.[9]

The nickel complexes 1(diacetylmonoximato-imino-3-(diacetylmonoxime-imino)propane nickel perchlorate $[Ni(II)\{(DO)(DOH)pn\}]ClO_4$ and 1(diacetylmonoximato-imino)-2-(diacetylmonoxime-imino)ethane nickel perchlorate $[Ni(II)\{(DO)(DOH)en\}]ClO_4$ were prepared by the above Authors. (DO) and (DOH) are used for the (hydrogen bonded) diacetylmonoximato-imino and diacethylmonoxime-imino groups respectively. The assumed structures are square-planar with ionically bound ClO_4^-. The corresponding complexes with I^- or SCN^- are assumed to be square-pyramidal. The former complex containing one six-membered ring between two five-membered rings is more stable than the latter one containing three adjacent five-membered rings.

By reaction of $(DOH)_2$pn with CoX_2 (X = Cl, Br, I) in ethanol-water or acetone-water at room temperature followed by air oxidation, we prepared the crystalline green diamagnetic complexes $[Co(III)X_2\{(DO)(DOH)pn\}]^\circ$ (**I**). The complexes are insoluble in water. The solubility in acetone, methylene chlo-

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[1] G. Costa, G. Mestroni, G. Tauzher, and L. Stefani, *J. Organomet. Chem. 6*, 181 (1966).
[2] G. Costa, G. Mestroni, and L. Stefani, *J. Organomet. Chem. 7*, 493 (1967).
[3] G. Costa and G. Mestroni, *J. Organomet. Chem. 11*, 325 (1968).
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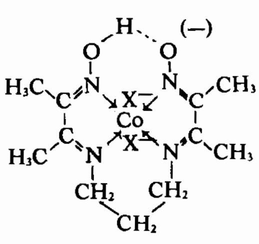
[6] G. Costa and G. Mestroni, *Tetrahedron Letters, 1967*, 4005.
[7] G. N. Schrauzer, *Accounts of Chemical Research, 1*, 97 (1968).
[8] S. Brückner, M. Calligaris, G. Nardin, and L. Randaccio, private communication.
[9] E. Uhlig and M. Friedrich, *Zeitsch. für Anorg. und Allgem. Chemie 343*, 299 (1966).

Table I.

		C%		H%		N%		X%	
		Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
(I)	$[Co(III)\{(DO)(DOH)pn\}Cl_2]$	35.82	35.80	5.18	5.19	14.95	15.18	19.06	19.22
(II)	$[(Co(III)\{(DO)(DOH)pn\}Br_2$	28.91	28.85	4.32	4.18	12.08	12.25	34.73	34.90
(III)	$[Co(III)\{(DO)(DOH)pn\}I_2]$	24.04	23.93	3.58	3.47	9.98	10.00	46.11	45.98
(IV)	$[Co(III)\{(DO)(DOH)pn\}(NH_3)_2]Br_2$	26.85	27.08	5.12	5.05	16.88	17.08		
(V)	$[Co(III)\{(DO)(DOH)pn\}(NH_3)_2]I_2$	22.37	22.54	4.45	4.30	14.42	14.34	43.28	43.31
(VI)	$[Co(III)\{(DO)(DOH)pn\}(NH_3)_2](ClO_4)_2$	25.79	24.37	4.76	4.33	15.00	16.12		
(VII)	$[Co(III)\{(DO)(DOH)pn\}(C_4H_6N_2)_2](ClO_4)_2$	34.63	34.51	4.64	4.73	17.13	16.95		
(VIII)	$[Co(DOpn)_2]ClO_4 . H_2O$	34.60	34.40	6.22	6.18	17.33	17.20		
(IX)	$[Co(DOen)_2]ClO_4$	32.18	32.55	5.44	5.45	18.92	18.98		
(X)	$[CH_3Co\{(DO)(DOH)pn\}H_2O]ClO_4$	33.31	33.46	5.85	5.62	12.81	13.01	8.26	8.23
(XI)	$[C_2H_5Co\{(DO)(DOH)pn\}H_2O]ClO_4$	35.11	35.10	5.99	5.89	12.61	12.60	7.85	7.97
(XII)	$[C_3H_7Co\{(DO)(DOH)pn\}H_2O]ClO_4$	42.65	42.65	5.59	5.57	11.12	11.06		
(XIII)	$[CH_3Co\{(DO)(DOH)pn\}H_2O]B(C_6H_5)_4$	66.24	66.47	7.05	6.82	8.80	8.61		
(XIV)	$[C_2H_5Co\{(DO)(DOH)pn\}H_2O]B(C_6H_5)_4$	66.40	66.87	7.23	6.97	7.95	8.43		
(XV)	$[CH_3Co\{(DO)(DOH)pn\}(C_3H_4N_2)]B(C_6H_5)_4$	66.84	66.86	6.89	6.61	11.94	11.99		
(XVI)	$[CH_3Co\{(DO)(DOH)pn\}(C_3H_4N_2)]PF_6$	33.76	34.23	4.75	4.98	15.76	15.97		
(XVII)	$[C_2H_5Co\{(DO)(DOH)pn\}(C_3H_4N_2)]B(C_6H_5)_4$	67.16	67.23	6.88	6.77	12.21	11.76		
(XVIII)	$[C_2H_5Co\{(DO)(DOH)pn\}(C_3H_4N_2)]PF_6$	35.42	35.57	5.20	5.22	15.55	15.56		
(XIX)	$[C_3H_7Co\{(DO)(DOH)pn\}(C_3H_4N_2)]B(C_6H_5)_4$	67.12	67.49	6.86	7.04	11.48	11.52		
(XX)	$[C_7H_7Co\{(DO)(DOH)pn\}(C_3H_4N_2)]ClO_4$	45.18	45.29	5.29	5.43	15.04	15.09		
(XXI)	$[CH_3Co\{(DO)(DOH)pn\}(C_4H_6N_2)]ClO_4$	38.74	38.84	5.71	5.70	17.17	16.99		
(XXII)	$[C_2H_5Co\{(DO)(DOH)pn\}(C_4H_6N_2)]ClO_4$	40.25	40.12	5.87	5.94	16.61	16.52		
(XXIII)	$[C_7H_7Co\{(DO)(DOH)pn\}(C_4H_6N_2)]ClO_4$	46.55	46.28	5.79	5.65	14.71	14.72		
(XXIV)	$[CH_3Co\{(DO)(DOH)pn\}(C_7H_6N_2)]ClO_4$	43.07	42.98	5.64	5.31	15.54	15.83		
(XXV)	$[CH_3Co\{(DO)(DOH)pn\}(NH_3)]B(C_6H_5)_4$	65.96	66.57	7.13	6.98	10.58	10.78		
(XXVI)	$[CH_3Co\{(DO)(DOH)pn\}I]$	33.01	32.74	5.20	5.15	12.74	12.73		
(XXVII)	$[CH_3Co\{(DO)(DOH)pn\}SCN]$	42.11	42.03	5.97	5.97	18.80	18.86		
(XXVIII)	$[C_6H_5Co\{(DO)(DOH)pn\}Br]$	45.07	44.84	5.33	5.31	12.44	12.31		
(XXIX)	$[C_6H_5Co\{(DO)(DOH)pn\}H_2O]ClO_4$	41.56	41.35	5.30	5.30	11.07	11.35		
(XXX)	$[C_6H_5Co\{(DO)(DOH)pn\}I$	40.40	40.65	4.60	4.82	11.33	11.16		
(XXXI)	$[Co(II)\{(DO)(DOH)pn\}(H_2O)_2]B(C_6H_5)_4$	66.39	66.10	7.32	7.00	12.07	12.17		
(XXXII)	$[Co(I)\{(DO)(DOH)pn\}P(C_6H_5)_3]$	62.17	62.14	6.10	6.12	10.00	9.96		

ride, benzene, methanol, tetrahydrofurane (THF) increased from the chloro to the iodo derivatives.



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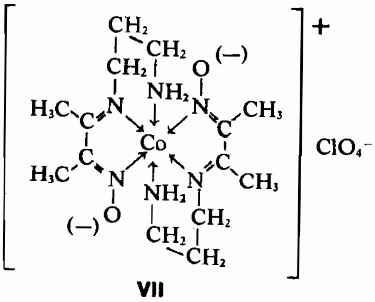

VII

Attempting the preparation of $[Co\{(DO)(DOH)pn\}(H_2O)_2]^{2+}$ by reaction of cobalt acetate in ethanol with $(DOH)_2pn$ followed by addition of $NaClO_4$, the complex $[Co(DOpn)_2]^+ClO_4 . H_2O$ was obtained instead. With the ligand $(DOH)_2en$ exactly analogous results are obtained (1:1 electrolyte, I.R. spectrum $\nu_{NH} = 3100, 3200\ cm^{-1}$).

(DOpn) and (DOen) are used for the 1-amino-3-diacetylmonoximato-iminopropane and 1-amino-2-diacetylmonoximato-imino-ethane respectively.

Water soluble 1:2 electrolytes of the type $[Co\{(DO)(DOH)pn\}L_2]^{2+}2X^-$ ($X = Br, I, ClO_4$; $L = NH_3$, Nmethyl-imidazole) are obtained by treatment of $[Co\{(DO)(DOH)pn\}X_2]$ with L.

The organometallic derivatives were obtained by treatment of $[Co\{(DO)(DOH)pn\}Br_2]$ with Grignard reagents in THF followed by hydrolysis of the reaction mixture and addition of $NaClO_4$. The resulting compounds are orange-red crystalline solids, soluble in water, 1:1 electrolytes of the type $[R–Co\{(DO)(DOH)pn\}H_2O]^+ClO_4^-$ ($R = CH_3, C_2H_5, C_6H_5, C_7H_7$; ($R = CH_3$) = 86 ohm^{-1} cm^2).

The substitution of H_2O with other Lewis bases (*e.g.* $L = NH_3$, imidazole, Nmethyl-imidazole, benzimidazole) was afforded with excess of L. The cationic nature of the complex $[CH_3Co\{(DO)(DOH)pn\}H_2O]^+$ was confirmed by electrophoretic measurements. By treatment with $NaB(C_6H_5)_4$ the insoluble tetraphenylborate is obtained. Uncharged complexes of the type $[CH_3Co\{(DO)(DOH)pn\}X]^\circ$ are obtained with KI or KSCN.

The presence of the hydrogen bond was confirmed from the n.m.r. spectra.[10] Finally the proposed structure is definitely confirmed by X-rays diffraction data.[11]

The organometallic derivatives $[R–Co\{(DO)(DOH)pn\}H_2O]^+X^-$ can be obtained also by reduction under nitrogen atmosphere of $[Co\{(DO)(DOH)pn\}Br_2]$ in methanol-water with $NaBH_4$ in the presence of the alkyl halide with increasing yield in the order $R = C_2H_5 < CH_3 < C_6H_5–CH_2$.

This method was unsuccesful using $C_6H_5–Br$ or $nC_3H_7–Br$ which were apparently unreactive toward reduced complex.

If the same procedure is followed in alkaline medium and in the presence of Lewis base (L = imidazole, Nmethyl-imidazole) the alkyl derivatives

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(10) H. A. O. Hill, G. Pellizer, *et al.* unpublished results.

(11) S. Brückner, M. Calligaris, G. Nardin, and L. Randaccio, to be published.

Table II.

	Frequencies (cm^{-1} $.10^{-3}$) and log ε_{max} (in brackets)										Solvent
$[CH_3Co\{(DO)(DOH)pn\}(H_2O)]ClO_4$			35.8	[3.67]	31.8 (sh)	[3.41]	24.6	[3.20]	21.4	[3.33]	H_2O
$[CH_3Co\{(DO)(DOH)pn\}(C_4H_6N_2)]ClO_4$			35.8	[3.74]	32.8 (sh)	[3.53]	24.8	[3.27]	21.6	[3.25]	H_2O
$[C_2H_5Co\{(DO)(DOH)pn\}H_2O]ClO_4$			35.8	[3.72]	32.4 (sh)	[3.56]	24.2	[3.21]	20.8	[3.35]	H_2O
$[C_2H_5Co\{(DO)(DOH)pn\}(C_4H_6N_2)]ClO_4$			35.7	[3.69]	32.6 (sh)	[3.52]	24.3	[3.24]	21.0	[3.30]	H_2O
$[C_7H_7Co\{(DO)(DOH)pn\}(H_2O)]ClO_4$			34.7	[4.05]	obs		26.8	[3.64]	20.2	[3.06]	H_2O
$[C_7H_7Co\{(DO)(DOH)pn\}(C_4H_6N_2)]ClO_4$			34.5	[4.12]	obs		25.1	[3.66]	20.4	[3.10]	H_2O
$[C_6H_5Co\{(DO)(DOH)pn\}H_2O]ClO_4$			35.8 (sh)	[3.80]	30.7	[3.56]	26.6 (sh)	[3.15]	21.8	[3.04]	H_2O
$[Co(DO)(DOH)pn(NH_3)](ClO_4)_2$			obs		32.4	[3.65]	27.0 (sh)	[8.90]			H_2O
$[CH_3Co(DO)(DOH)pnH_2O]ClO_4$			34.4	[3.77]	29.5 (sh)	[3.48]	25.2 (sh)	[3.26]	21.1	[3.34]	$CHCl_3$
$[CH_3Co(DO)(DOH)pnH_2O]ClO_4$			34.5	[3.75]	29.6 (sh)	[3.44]	24.8	[3.23]	21.2	[3.41]	CH_3OH
$[CH_3Co(DO)(DOH)pn(C_4H_6N_2)]ClO_4$			34.5	[3.79]	29.5 (sh)	[3.45]	24.6	[3.33]	22.2 (sh)	[3.24]	CH_3OH
$[Co(DO)(DOH)pn]Cl_2$			39.05	[4.39]	31.6 (sh)	[3.71]					CH_3OH
$[Co(DO)(DOH)pn]Br_2$			33.3	[4.26]			25.2 (sh)	[3.31]			CH_3OH
$[Co(DO)(DOH)pn]I_2$					29.05	[4.23]			21.4	[3.92]	CH_3OH
$[Co(DO)(DOH)pnP(C_6H_5)_3]$	39.4	[4.35]	32.8 (sh)	[3.86]	obs		25.8	[3.64]	23.0	[3.66]	15.4 3.86 C_2H_5OH

$[R\text{–}Co\{(DO)(DOH)pn\}L]^+$ are obtained in high yield.

Contrasting with the corresponding derivatives of BAE and salen[12] (dianionic chelating ligands from bis(acetylacetone)-ethylendiamine and bis(salicylaldehyde)ethylendiamine, respectively) the organometallic derivatives $[R\text{–}Co\{(DO)(DOH)pn\}L]^+$ do not react with RMgBr, in the same experimental conditions.

The reduction of $[Co\{(DO)(DOH)pn\}Br_2]$ with $NaBH_4$ gives a transient blue colour which is characteristic of Co^I species. The reduced intermediates are stable in the presence of Lewis bases in alkaline medium and can be isolated using tertiary prosphines. Under nitrogen atmosphere the five coordinate blue diamagnetic solid $[Co(I)\{(DO)(DOH)pn\}P(C_6H_5)_3]$ was isolated.

By treatment of this complex with $C_6H_5\text{–}CH_2Cl$ in benzene an orange-yellow solution is obtained. After evaporation of the solvent, addition of aqueous imidazole and $NaClO_4$, the complex $[C_6H_5\text{–}CH_2Co\{(DO)(DOH)pn\}(imidazole)]ClO_4$ was isolated.

When $[Co\{(DO)(DOH)pn\}Br_2]$ is reduced by $NaBH_4$ in methanol-water in the absence of a Lewis base and R–X, the transient blue colour turns rapidly to red violet. The Co^{II} derivative $[Co\{(DO)(DOH)pn\}(H_2O)_2]BPh_4$ was precipitated from the solution by addition of $NaBPh_4$.

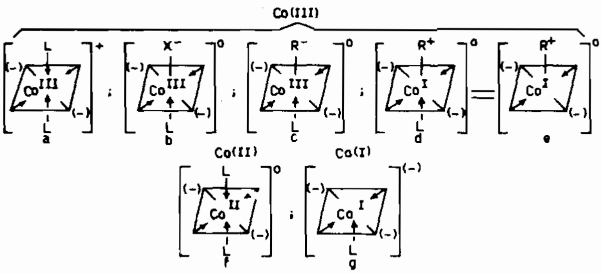
In alkaline medium in the presence of Nmethylimidazole and $C_6H_5CH_2\text{–}Cl$ the organometallic derivative is formed, likely by disproportion of the Co^{II} species.

U.V. and visible spectra of organometallic derivatives and $[Co(I)\{(DO)(DOH)pn\}P(C_6H_5)_3]$ are reported in Table II.

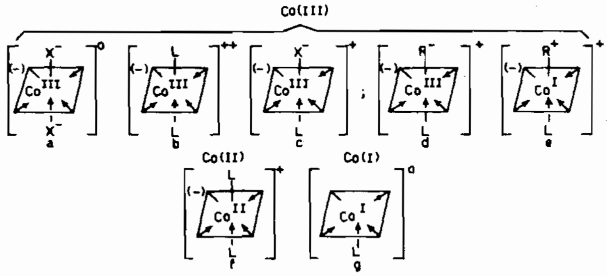
Discussion

In order to rationalize the coordination chemistry of cobalt atom in the model molecules of Vit. B_{12} it is important to understand the mutual influence of ligands, especially that of the equatorial ligand on the axial positions (*cis-effect*) and the trans-effect between axial ligands.

For chelating agents acting as dianions and monoanions the overall charge of the complexes in the different formal oxidation states of cobalt and the formal charge distributions in the different complexes can be summarized as follows:



Scheme I



Scheme II

The transmission of the dative electronic effects from the « upper » ligand R to L (structures c, d, scheme I), labilizes the dative L→Co bond. By varying the nature of R the equilibrium

$$R\text{–}Co(chel)L \rightleftharpoons R\text{–}Co(chel)+L \qquad (1)$$

is displaced toward the five-coordinated species (structure e) owing to charge donation (mainly via σ bond) from R to cobalt[13]. This was observed in the [R–Co(BAE)L], [R–Co(salen)L] complexes[14] and in the

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[12] C. Floriani, M. Puppis, and F. Calderazzo, *J. Organomet. Chem.*, *12*, 209-223 (1968).

[13] R. A. Firth, H. A. O. Hill, J. M. Pratt, R. G. Thorp, and R. J. P. Williams, *Chem. Comm.*, 400 (1967).

[14] L. Stefani *et al.*, *unpublished results.*

organocobinamides and cobalamins.[15] The equilibrium (1) for the $[R\text{–}Co(DH)_2L]$ and $[R\text{–}Co\{(DO)(DOH)pn\}L]^+$ is displaced toward the six-coordinated species relative to the corresponding BAE and salen complexes, suggesting that the *cis*-effect decreases going from BAE and salen to $\{(DO)(DOH)pn\}^-$ complexes.

Going from ligands acting as anions (*e.g.* Cl^-, structure b, scheme I) toward ligands which behave as cations (*e.g.* Na^+, structure g or h, scheme I), the situation gradually changes from that typical of a Co^{III} complex to a limiting case which could be envisaged as that of Co^I complex. For the Co^{III} state the six-coordinated complexes are more stable, while going toward Co^I situation five-coordination or even square planar Co^I anions are preferred. The effective charge on cobalt is influenced, other things being equal, by the nature of the equatorial ligand.

The influence of axial ligands on stereochemistry and equilibrium constant of corrins was previously pointed out, and the term « balanced valence » was proposed to express the breakdown of the rigid distinction between valencies.[15]

The Co^I complexes are characterized by an absorption band in the 14-17 kK region (*e.g.* $[NaCo(I)(BAE)]$ (14.9 kK), $[NaCo(salen)]$ (14.0 kK), $[Co(DH)_2P(C_4H_9)]^-$ (16.5 kK),[16] $[Co(I)\{(DO)(DOH)pn\}P(C_6H_5)_3]^0$ 15.4 kK).

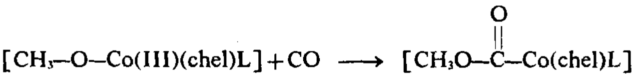
The cobalt atom acts as electrophilic center when the Co^{III} situation is preferred in the transition state as is shown by the mechanism of ligand substitution

$$[X\text{–}Co(DH)_2L]+H_2O \longrightarrow [H_2OCo(DH)_2)L]^+ + X^-$$

by the general reactivity toward Grignard reagent

$$[Cl\text{–}Co(chel)L]^\circ + R\text{–}MgX \rightarrow [R\text{–}Co(chel)L]^\circ + ClMgX$$

and by the reaction of the methoxo-derivatives with carbon monoxide[18]



$$[CH_3\text{–}O\text{–}Co(III)(chel)L] + CO \longrightarrow [CH_3O\text{–}\overset{\overset{\textstyle O}{\|}}{C}\text{–}Co(chel)L]$$

The cobalt atom acts as a nucleophilic center in the Co^I derivatives[3,4]

$$[NaCo(BAE)] + R\text{–}X \longrightarrow R\text{–}Co(BAE) + NaX$$

The $Co^{II}\text{–}R^\circ$ intermediate case (between c and d, scheme I, and d and e scheme II) can be represented by the transition states involved in homolytic (photoreduction) cleavage leading to Co^{II}(chel) complexes.[17]

The gradual change of the overall electron density on the equatorial plane between $Co^{III}\text{–}X^-$ and $Co^I\text{–}X^+$ can be pointed out also by the polarographic reduction data.[19] In the former case the first step involves one-electron transfer leading to Co^{II} complexes. The $E_{1/2}$ is strongly displaced toward more negative potential by increasing the donor power of the axial ligands (the second step implies the reduction $Co^{II} \rightarrow Co^I$). In the metallorganic derivatives R–Co(chel)L the same effect is observed but $E_{1/2}$ overreaches the Co^{II} reduction potential.

The effect of the planar chelate on the nucleophilicity of Co^I. Coming to the comparison of the physico-chemical properties and reactivity of axial position of model molecules with those of Vit. B_{12} group it must be emphasized that (besides the trans effect between axial ligands) the charge on cobalt atom is strongly influenced by the nature of the planar macrocycle.

All the Co^I chelates (g, scheme I and II) are characterized by strong nucleophilic reactivity. The nucleophilic power of the cobalt atom is determined by equatorial ligand and can be correlated with the half-wave potential (*vs.* S.C.E.) of the reversible one electron transfer between Co^{II} and Co^I formal oxidation states, increasing in the following order

$$[Co(II)(BAE)]^\circ(\sim-1.5V)[Co(II)salen]^\circ$$

$$(\sim-1.15V)Vit.B_{12}r(\sim-1.02V)^*$$

$$[Co(II)(DH)_2(H_2O)_2]^\circ(\sim-1.0V)$$

$$[Co(II)\{(DO)(DOH)pn\}(H_2O)_2]^+(\sim-0.85V)$$

Furthermore only NaCo(I)(BAE) among the above series of Co^I derivatives reacts with C_6H_5Br.[20] At the other end of the series the reaction rates of $[Co(I)\{(DO)(DOH)pn\}P(C_6H_5)_3]^0$ with R–X decreases in the order $C_2H_5 < CH_3$ while $n\text{–}C_3H_7Br$ does not react even after 24 h.

Vit. B_{12s} appears to be thus intermediate between the most powerful nucleophyle Co(I)(BAE) and the less nucleophilic $[Co(I)\{(DO)(DOH)pn\}L]^0$.

Formal charge in the $\{(DO)(DOH)pn\}^-$ complexes is more close to that in corrins than in cobaloximes or BAE and salen complexes.

In the uncharged complexes (a, scheme II) the cobalt behaves as electrophilic center in the reaction with Grignard reagents.

Reduction of $[Co\{(DO)(DOH)pn\}X_2]$ complexes in the presence of L in alkaline solution leads to a stable five-coordinated uncharged Co^I derivative (g, scheme II; L = triphenylphosphine, imidazole, N–methylimidazole, benzimidazole). The visible spectra show the characteristic Co^I absorption band at 15.4 kK ($L = PPh_3$).

The formation of the organometallic cations derivatives takes place by oxidative addition of R–X to the uncharged Co^I complex, while with BAE, salen and $(DH)_2$ dianions the reaction involves the Co^I complex anion. Alternatively the exchange of H with R from the hydride, formed by addition of H_2O could be assumed

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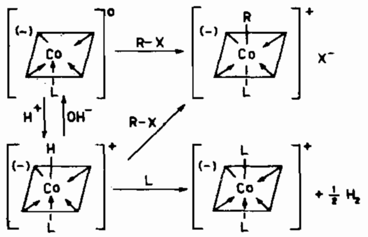

Scheme III

The above reaction scheme shows that in acid solution the electrophilic attack of H^+ on the uncharged complex takes place; the hydrido complex undergoes homolytic cleavage to Co^{II} and molecular hydrogen. This would explain the fact that the Co—H bond was never detected by direct physico-chemical experiments in Vit. B_{12s}.

The alternative reactions mechanism of the cobalt chelates are mainly governed by the charge distribution in the cobalt « upper » ligand bond which in turn is determined by the nature of the upper ligand and by *cis* and *trans* effect.

The complexes $[Co\{(DO)(DOH)pn\}L]^0$ are in our opinion suitable models for Vit. B_{12s} and the observed reactions could be useful guide to the interpretation of the reaction mechanism of Vit. B_{12s}.

Experimental Section

$(DOH)_2pn$ and $(DOH)_2en$ were obtained following E. Uhlig and M. Friedrich.[9]

$[Co(III)\}jDO)(DOH)pn\}Cl_2]$ (**I**). $(DOH)_2pn$ (7.2 g., 30 mmole) dissolved in the minimum amount of acetone was treated with an aqueous solution of $CoCl_2 . 6H_2O$ (7.2 g., 30 mmole). After standing followed by evaporation in a current of air the crystalline grey-green product was precipitated, filtered and washed with water (20% yield). Recrystallized from acetone-ethanol.

$[Co(III)\{(DO)(DOH)pn\}Br_2]$ (**II**). The green complex was obtained as above from $(DOH)_2pn$ (7.2 g, 30 mmole) and $CoBr_2 . 6H_2O$ (9.81 g, 30 mmole) (20% yield). Recrystallized from acetone-water.

$[Co(III)\{(DO)(DOH)pn\}I_2]$ (**III**). The deep green crystalline complex was obtained as above from $(DOH)_2pn$ (7.2 g) and $CoCl_2 . 6H_2O$ (7.2 g) in the presence of KI (5 ml of saturated aqueous solution). Recrystallized from acetone-ethanol.

$[Co(III)\{(DO)(DOH)pn\}(NH_3)_2]Br_2$(**IV**). Was prepared by bubbling gaseous ammonia in the anhydrous ethanol suspension (50 ml) of **II** (0.46 g, 1 mmole). The yellow solid, soluble in water, was recrystallized by precipitation with acetone from a conc. aqueous solution. Dried in a vacuum at 100°C.

$[Co(III)\{(DO)(DOH)pn\}(NH_3)_2]I_2$ (**V**). Was prepared (a) as above from **III** or (b) by exchange of Br^- with I^- from **IV** (aq. solution) with KI (sat. aq. solution. Recrystallized from warm water; yellow crystals.

$[Co(III)\{(DO)(DOH)pn\}(NH_3)_2](ClO_4^-)_2$(**VI**). Was obtained by the above procedure (b) using $NaClO_4$ (sat. aqueous solution) as yellow crystalline solid; slightly soluble in water.

$[Co(III)\{(DO)(DOH1pn\}(C_4H_6N_2)_2](ClO_4)_2$(**VII**). The suspension of II (0.46 g, 1 mmole) in ethanol (50 ml) was treated with N–methylimidazole (0.5 ml). From the green suspension a brown solution was gradually obtained. By addition of conc. aqueous $NaClO_4$ and evaporation, a yellow solid was precipitated. Recrystallized from acetone-ethanol.

$[Co(III)(DOpn)_2]ClO_4 . H_2O$ (**VIII**); *$[Co(III)(DOen)_2]ClO_4$* (**IX**). $(DOH)_2pn$ (4.8 g, 20 mmole) or $(DOH)_2en$ (4.6 g, 20 mmole) were dissolved in ethanol (25 cc) and treated with ethanol solution (50 ml of $Co(CH_3COO)_2 . 4H_2O$ (5 g, 20 mmole). By addition of $NaClO_4$ (aq. solution) an orange-yellow solid was precipitated. Soluble in water, methanol, acetone.

$[R–Co\{(DO)(DOH)pn\}H_2O] . ClO_4$; $R = CH_3$(X); C_2H_5 (**XI**); *$C_6H_5CH_2$* (**XII**). (a) The suspension of **II** (0.92 g, 2 mmole) in anhydrous THF (100 ml) were treated (–60°, under nitrogen) with the appropriate freshly prepared Grignard reagent RMgBr (4 mmole). Within about 2 hours the parent complex **II** was completely reacted and an orange-red solution was formed. The solution was poured in cool water (10 ml) and neutralized with 2 N HCl. After partial evaporation of the solvent, excess $NaClO_4$ was added. By standing orange-red crystals were obtained. Recrystallized from acetone-water or from hot water.

(b) The suspension of **II** (0.92 g, 2 mmole) in methanol-water (100 ml, 10% water) was reduced in the presence of the appropriate alkyl halide RX by stepwise addition of $NaBH_4$. The reaction was completed when, after addition of further amounts of $NaBH_4$, the transient formation of deep-blue colour (Co^I intermediate) was no more noticed. The solution was filtered and treated with $NaClO_4$. By evaporation of methanol and standing the organometallic derivative was precipitated.

$[R–Co\{(DO)(DOH)pn\}H_2O]B(C_6H_5)_4$; $R = CH_3$ (**XIII**); *C_2H_5* (**XIV**) Were obtained as above by addition of $NaB(C_6H_5)_4$ (sat. aq. solution) instead of $NaClO_4$ to **X** or **XI** respectively. Alternatively the tetraphenylborates could be obtained by precipitation with $NaB(C_6H_5)_4$ from aqueous solutions of the perchlorates. Recrystallized from methanol-water. The complexes are soluble in methanol, acetone, CH_2Cl_2, $CHCl_3$.

$[R–Co\{(DO)(DOH)pn\}(C_3H_4N_2)]X$; $R = CH_3$, $X = B(C_6H_5)_4$ (**XV**); $R = CH_3$, $X = PF_6$ (**XVI**); $R = C_2H_5$, $X = B(C_6H_5)_4$ (**XVII**); $R = C_2H_5$, $X = PF_6^-$ (**XVIII**); $R = C_3H_7$, $X = B(C_6H_5)_4$ (**XIX**); $R = C_6H_5CH_2$, $X = ClO_4^-$ (**XX**).

(a) A suspension of **II** (0.92 g, 2 mmole) in methanol (100 ml) was treated under nitrogen with imidazole (1 g). An orange-yellow solution was obtained. After addition of the appropriate alkyl halide the complex is reduced by stepwise addition of excess

$NaBH_4$(see-preparation of **X**, **XI**, **XII**, procedure (b)). The products are recrystallized from acetone-water.

(b) The aquo complexes **X** to **XIV** were converted in the imidazole complexes by treatment with slight excess of imidazole.

(c) 0.92 g (2 mmole) of **II** in methanol-water was treated under nitrogen with imidazole (1 g) and NaOH (0.24 g, 6 mmole). The solution is reduced with $NaBH_4$. A deep blue stable solution is formed. By treatment with R–X, the organometallic derivatives were obtained.

$[R–Co\{(DO)(DOH)pn\}(C_4H_6N_2)]ClO_4$; R = CH_3 (**XXI**); C_2H_5 (**XXII**); $C_6H_5CH_2$ (**XXIII**). Prepared as above from **II** or from the appropriate aquo complexes by reaction with N-methylimidazole in slight excess. Recrystallized from acetone-water.

$[CH_3Co\{(DO)(DOH)pn\}(C_7H_6N_2)]ClO_4$ (**XXIV**). Was obtained from a methanol solution of **X** by treatment with a slight excess of benzimidazole dissolved in the minimum amount of ethanol.

$[CH_3Co\{(DO)(DOH)pn\ NH_3]B(C_6H_5)_4$ (**XXV**). Was prepared by bubbling gaseous ammonia in the corresponding aquo-complex (**XIII**) dissolved in the minimum amount of methanol. After standing the product precipitated as yellow needles. Recrystallized from acetone-ethanol.

$[CH_3Co\{(DO)(DOH)pn\}X]$; X = I (**XXVI**), SCN (**XXVII**). Was prepared following the same procedure as for **X**, using KI and KSCN respectively.

$[C_6H_5Co\{(DO)(DOH)pn\}Br]$ (**XXVIII**). Was obtained by the same procedure (a) adopted for preparation of complexes **X** to **XII**. The hydrolysis was performed with dil. HBr. The yellow solid precipitated on evaporation of the solvent and was recrystallized from CH_2Cl_2–C_2H_5–O–C_2H_5.

$[C_6H_5Co\{(DO)(DOH)pn\}H_2O]ClO_4$ (**XXIX**). The bromoderivative **XXVIII** was dissolved in hot water and treated with sat. aqueous solution of $NaClO_4$; an orange-yellow solid is obtained and recrystallized from acetone-water.

$[C_6H_5Co\{(DO)(DOH)pn\}I]$(**XXX**). The bromo derivative **XXVIII** was dissolved in hot water and treated with sat. solution of KI. After recrystallization from diethylether–CH_2Cl_2, the product was obtained as orange-red needles.

$[Co(II)\{(DO)(DOH)pn\}(H_2O)_2]B(C_6H_5)_4$ (**XXXI**). The methanol suspension of **II** (0.92 g, 2 mmole in methanol-water (100 ml, 10% water) was treated under nitrogen with a slight excess of $NaBH_4$. The transient deep blue colour (Co^I was noticed firstly, then a stable purple solution was obtained. After addition of deareated aqueous solution of $NaB(C_6H_5)_4$ the product was precipitated on evaporation of the solvent under vacuum. Filtered under nitrogen and washed with deareated water dried under vacuum at room temperature.

Reaction of the Co^{II} complexes with $C_6H_5CH_2Cl$ The suspension of **II** (0.92 g, 2 mmole) in methanol-water (100 ml, 10% water) was treated with N-methylimidazole (1 ml) and reduced with $NaBH_4$. The resulting solution of the Co^{II} complex was treated with $C_6H_5CH_2Cl$ (0.3 ml) and NaOH until pH 12 was reached. Within 2 hours an orange-red solution was formed. By pouring in a few ml of water and adding $NaClO_4$ a crystalline orange-yellow product identical to **XXIII** was obtained.

$[Co(I)\{(DO)(DOH)pn\}P(C_6H_5)_3]$ (**XXXII**). The suspension of **II** (0.92 g, 2 mmole) in anhydrous ethanol was treated under nitrogen with $P(C_6H_5)_3$ (0.52 g) and reduced with $NaBH_4$. A deep blue solution (stable under nitrogen but sensitive to air) together with a crystalline precipitate of the same colour were obtained. The precipitate was filtered under nitrogen, washed with light petroleum. Soluble in benzene, ethyl ether, methanol, ethanol.

Oxidative addition. **XXXII** (0.5 g) was dissolved in deareated benzene and reacted with $C_6H_5CH_2Cl$. An orange-yellow solution was slowly obtained. After evaporation of the solvent under a vacuum the residue was treated with water (5 ml) and a slight excess of imidazole. The resulting yellow solution was filtered and $NaClO_4$ was added. The precipitated yellow solid was recrystallized from acetone-water. The product was found to be identical to **XX**.

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