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Solid State and Solution Properties of Vitamin B_{12} Models

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Octahedral organometallic derivatives of cobalt(III) dimethylglyoximates, $LCo(DH)_2R$, where L = neutral ligand, R = alkyl group, DH = monoanion of dimethylglyoxime, the so called alkylcobaloximes, and other organocobalt (III) complexes with macrocyclic equatorial ligands, have been extensively studied for their ability to mimic the behaviour of the more complex system of vitamin B_{12}, the well known cobalamins. Hence, their study has produced an incredible amount of data both in solution and in solid state, which have allowed us to establish empirical relationships between structure and solution properties of these models. Up to date, results relative to the model and comparison, when possible, with cobalamins support the idea that the homolytic cleavage of the Co-C bond in the B_{12} coenzyme is due to a »trigger« mechanism, originated by steric interactions. However, the weakening of this bond may be »helped« by electronic influences due to the lengthening of the ligand trans to the carbon atom bonded to Co.

Analysis of the chemical properties of a large number of derivatives with different alkyl groups shows approximately linear relationships between bond lengths, kinetic, and spectroscopic NMR data. For R = CH_2Y group the above properties can be rationalized on the basis of the σ_I and σ_R constants used in organic chemistry for each *Y* residue. An alternative interpretation is more general, since it can be applied to any alkyl group. It is based on the finding that, when the alkyl group is changed, both Co-L axial distances and kinetics properties vary linearly with an electronic parameter (EP) derived from NMR data for each R group.

INTRODUCTION

Octahedral LCo(chel)R complexes having the Co(III)(chel) equatorial moiety of Figure 1, with L = neutral Lewis base and R = alkyl group or monoanionic ligand, such as Cl^-, contain both metallorganic and non-metallorganic members and form an interesting link between the two types of chemistry. These compounds, having an approximately planar equatorial moiety, are of interest, on the one hand, because of the parallels between the chemistry of their organometallic derivatives and organocobalamins[1-3] (see below) and, on the other, because of their extensive coordination chemi-

stry.[3] For these reasons, they have been intensively studied[3] both in solution and in the solid state, especially as far as the so called cobaloximes (chel = $(DH)_2$, where DH is the monoanion of dimethylglyoxime) are concerned. In this report, the main structural features of these systems and some relationships with solution properties will be reviewed from the point of view of both their relevance to the B_{12} coenzyme biochemistry and their peculiar chemical properties.

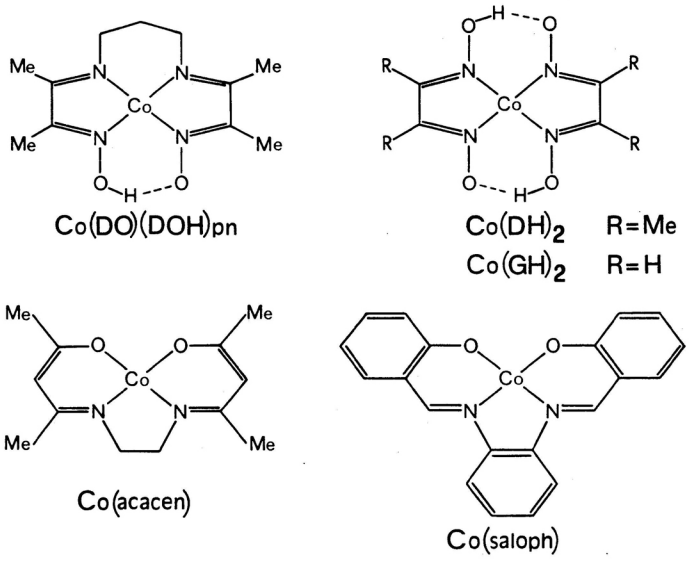

Figure 1. Sketches of the equatorial moiety of vitamin B_{12} models. All the equatorial ligands act as dianions, with the exception of [(DO)(DOH)pn], which is a monanion.

RELEVANCE OF THE MODELS TO B_{12} COENZYME BIOCHEMISTRY

A knowledge of the factors affecting the strength of the Co-C bond is important to clarify the mechanism of this bond homolysis, which is an essential step in the enzymic processes involving the B_{12} coenzyme, *i.e.* the 5-deoxyadenosylcobalamin. Cobalamins are a class of compounds with cobalt(III) coordinated in the equatorial plane by four corrin N atoms and in the axial position by a 5,6-dimethylbenzimidazole nucleotide. The other axial position may be occupied by a CN group, in vitamin B_{12} itself, by a 5-deoxyadenosyl residue in the B_{12} coenzyme or by an alkyl group in alkylcobalamins. The corrin ring distortions, possibly originated by protein conformational variations, are thought[1-3] to be important in weakening the Co-C bond that binds the 5-deoxyadenosyl residue to Co, by inducing variations in the metal coordination sphere through a »trigger« mechanism. Structural data on cobalamins and related systems have been recently reviewed.[4] Due to the intrinsic difficulty in obtaining single crystals, suitable for accurate X-ray analyses, the structural characterizations of cobalamins are few and of low accuracy. However, the simple models LCo(chel)R have been shown[3-6] to be very useful in providing a foundation for understanding the structural aspects of the more complex cobalamins.

TABLE I

Some Co-C distances (Å) in alkylcobalamins and in LCo(chel)R complexes. Estimated standard deviations are given in parentheses. Data are from refs. 3 and 6.

alkylcobalamins					
Co-CN 1.91(3)	Co-Me	1.99(3)	Co-CH_2Y		2.00(1) – 2.08(3)
		chel = $(DH)_2$			
R/L	H_2O	py	Me_3Bzm	$P(OMe)_3$	PPh_3
CN	1.906(5)	–	–	1.909(9)	–
Me	1.990(5)	1.998(5)	1.989(5)	2.01(1)	2.026(6)
CH_2CN	–	2.024(6)	–	2.036(7)	2.043(3)
Et	–	2.035(5)	–	–	2.045(5)
CH(CN)Me	–	2.053(6)	–	–	2.08(1)
$CH(CH_2CN)CN$	–	–	2.061(3)	–	–
CH_2CMe_3	2.044(7)	2.060(6)	–	–	2.117(9)
i-Pr	–	2.085(3)	2.076(2)	2.13(1)	–
adamantyl	2.133(2)[a]	2.160(4)	2.179(5)	2.214(3)	–
		chel = (DO)(DPH)pn			
	py	Me_3Bzm		NH_2Ph	H_2O
Me	2.003(3)	2.011(3)		1.991(4)	1.997(4)
CH_2CF_3	–	2.026(4)		2.009(2)	2.005(4)
Et	–	2.041(4)		2.030(4)	2.020(3)
CH_2Ph	–	–		–	2.052(2)
CH_2CMe_3	2.083(4)	–		–	–
i-Pr	–	–		–	2.072(4)
c-C_6H_{11}	2.129(5)	–		–	–

[a] to be published

Co-C distances in some LCo(chel)R complexes are given in Table I where they are compared with the values reported[4] for alkylcobalamins. The data available show that the Co-C bond lengths increase with the increasing bulk of R, regardless of the nature of the chel and L ligands. Thus, for L = $P(OMe)_3$, the Co-C distance increases from 2.01(1) Å in the Me derivative to 2.214(3) Å in the adamantyl analogue. This trend is mainly determined by the steric interaction between the R and chel ligands (steric *cis*-influence[3]), and follows the same trend reported for the Co-C Bond Dissociation Energy (BDE) in the series pyCo(chel)R with R of different bulk[1] (Table II). The high value of the Co-CH_2-Y angle (125°) found in the coenzyme structure[4] is another consequence of this steric interaction.[5] However, this should not destabilize the Co-C bond, since angles up to 130° have been found in many stable LCo(chel)CH_2Y derivatives[6], where Y is a bulky group such as CMe_3. On the other hand, the nature of the L ligand also contributes to influence the Co-C bond. Halpern and coworkers[1] have shown that the Co-C BDE, in the series LCo$(DH)_2CH_2$Ph, linearly decreases with the increasing bulk of L, when L is a phosphine of different bulk, as reported in Table II. The diagram shown on Figure 2 suggests that the increase in the bulk of L provokes also a significant lengthening of the *trans* Co-C distance, especially with bulky alkyl groups. Thus, bond lengths and BDE energies are influenced by the bulk of L in a similar way. Correspondingly, the bending angle, α, between the two DH units varies gradually from negative values (bending towards L) to positive values (bending towards R), as shown in Figure 2. This result appears to support the »trigger« mechanism described above

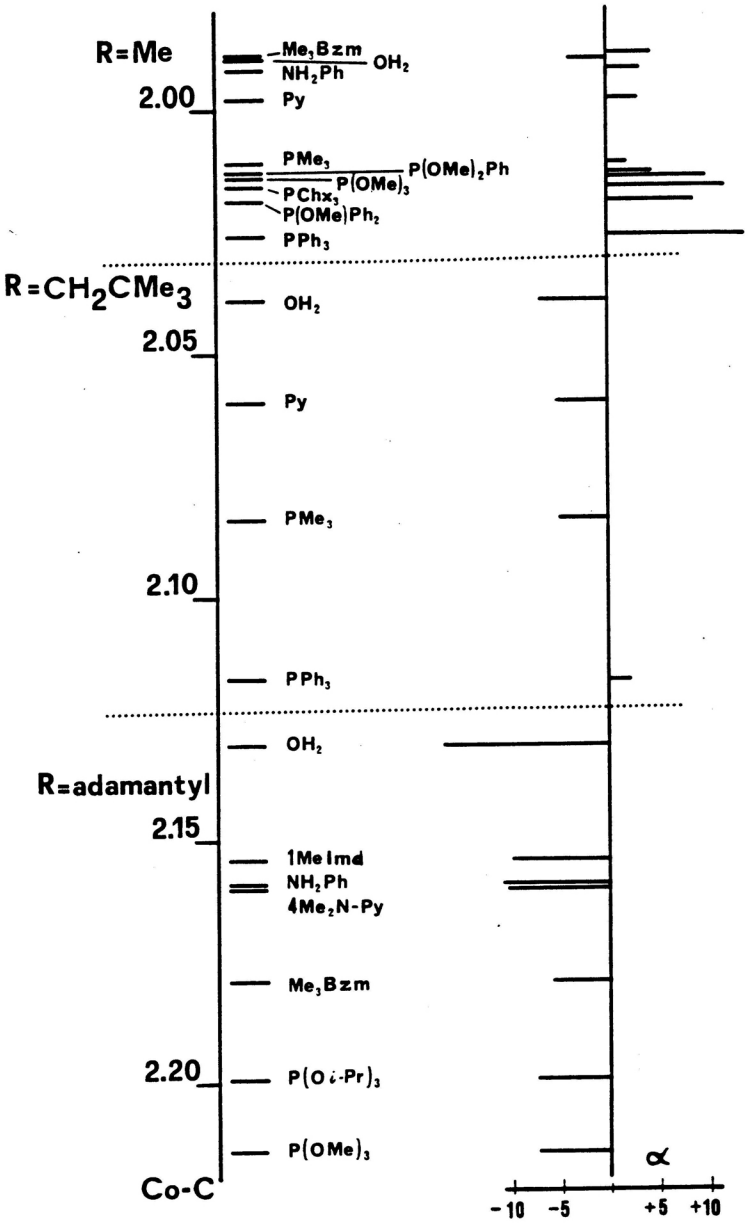

Figure 2. Variation of the Co-C distances (Å) and of the bending angle α (°) in the series $RCo(DH)_2L$ with different L ligands and R = Me, CH_2CMe_3, adamantyl.

TABLE II

Co-C bond dissociation energies (BDE, in kcal/mol) in pyCo(chel)R and in LCo(DH)$_2$CH$_2$Ph.

R	chel = saloph[a]	chel = (DH)$_2$[b]
Me	–	33
n-Pr	25	–
benzyl	22	31
i-Pr	20	21
neo-pentyl	18	–

L	PMe_2Ph	PBu_3^n	$PEtPh_2$	PPh_3	$P(c\text{-}C_6H_{11})_3$
BDE[c]	30.4	28.9	26.8	25.8	22.8

[a] T. T. Tsou, M. Loots, and J. Halpern, *J. Amer. Chem. Soc.* **104** (1982) 623. [b] P. J. Toscano, A. L. Seligson, M. T. Curran, A. T. Skrobutt, and D. C. Somenberger, *Inorg. Chem.* **28** (1989) 166. [c] Ref. 1.

TABLE III

Co-N(axial) distances (Å) and α bending angles (°) in parantheses for some pyCo(chel)R complexes. Data are from refs. 3 and 6.

chel/R	CH_2CN	CH_2CF_3	Me	Et	$CH2CMe_3$
$(DH)_2$	2.024(6) (4.7)	2041(4) (1.0)	2.068(3) (3.2)	2.081(3) (9.1)	2.081(4) (–5.2)
(DO)(DOH)pn	–	–	2.106(3) (6.9)	–	2.121(3) (14.3)
saloph	2.098(4) (16.2)	2.124(9) (17.0)	–	2.215(4) (–25.0)	–

for the coenzyme. No significant change in Co-C bond lengths was detected when the basicity of L was changed. Furthermore, the Co-C distances, in complexes with the same L-Co-R axial fragment, are not significantly influenced by the nature of the chel ligand, as shown in Table I, where the values for Co-CN, Co-Me and Co-CH_2Y distances are very similar for the different chel ligands, including corrin.

Structural data for the models indicate that the Co-N axial distances are strongly influenced by the σ-donor power of the *trans* R group, by the nature of the equatorial ligand (Table III) and by the bulk of the L ligand (Table IV). The rate constants, k, for displacement of the L ligand, which is a pseudo-first order reaction, follow the same trend of the Co-L distances[7], as shown by the values of log k given in Table IV. When the equatorial ligand is varied, the following order of increasing Co-N(axial) distances, for the same axial fragment L-Co-R, may be derived:[8,9]

$$(DH)_2 < (DO)(DOH)pn < saloph < corrin$$

which parallels the trend of the increasing flexibility of chel, as indicated by the α values given in Table III. Recent results[9,10] suggest that a significant part of the Co-L lengthening in (DO)(DOH)pn complexes having planar L ligands, when compared with $(DH)_2$ analogues, is due to the different orientation of L with respect to the equatorial moiety, as shown in Figure 3. A similar relationship between orientation and axial dis-

TABLE IV

Co-N(axial) distances (Å) and log k for the series LCo(DH)$_2$R with R = Me, i-Pr, and different L ligands[a]. Estimated standard deviations are given in parentheses. Data are from refs. 3 and 6.

R/L		1-MeIm	py	Me$_3$Bzm	1,2-Me$_2$py	2-NH$_2$py
Me	Co-N	2.019(3)[b]	2.068(3)	2.060(2)	2.086(1)	–
	log *k*	–3.60	–2.10	–2.38	–1.96	2.12
i-Pr	Co-N	–	2.099(2)	2.097(2)	2.121(2)	2.194(4)
	log *k*	–0.80	0.48	0.58	1.04	[c]

[a] 1-MeIm = 1-methylimidazole; Me$_3$Bzm = 1,5,6-trimethylbenzimidazole; 1-2-Me$_2$Im = 1,2-dimethylimidazole; 2-NH$_2$py = 2-aminopyridine.
[b] This value refers to the imidazole ligand.
[c] Too high to be measured.

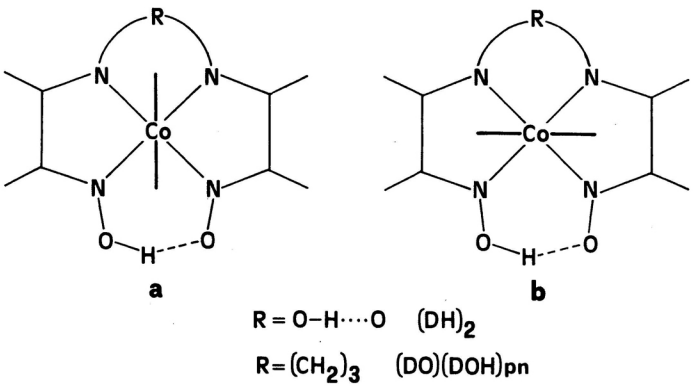

Figure 3. Orientations of the L planar ligand (heavy line represents the trace of the ligand plane) with respect to the equatorial moiety in cobaloximes (**a**) and in (DO)(DOH)pn analogues (**b**).

tances was also observed[8] in saloph derivatives. This observation suggests that a lengthening of the Co-N(axial) bond due to corrin distortions may derive also from changes in the orientation of the benzimidazole moiety. The weakening of this bond decreases the electron donation from the axial ligand to cobalt, destabilizing Co(III) with respect to Co(II) and, hence, facilitates the Co-C bond homolytic cleavage.[1] Therefore, assuming that the corrin upwards distortion, which displaces the adenosyl group of the B_{12} coenzyme with a consequent lengthening of the Co-CH_2Y bond may also induce changes in the benzimidazole orientation, a further weakening of the trans Co-C bond occurs. In this hypothesis, the cleavage of the Co-C bond should require corrin distortions less severe than those needed for only a »direct« weakening of this bond.

CHEMICAL RELATIONSHIPS IN SOLUTION AND IN THE SOLID STATE

The enormous amount of data obtained for understanding the limits of these models to mimic the biological system has furnished a great variety and abundance of information about the dependence of the L ligand dissociation rates, axial coordination bond lengths *etc.*, upon the nature of the R and L groups bound to cobalt. Neverthe-

less, the empirical relationships have not been fully understood and several anomalies were noted and persisted in the literature for some time.[3] Recently, two observations appear to hold promise as a means of quantitatively predicting the relationships between rates, structures and spectra of diverse, and as yet unsynthesized, organocobalt compounds.[11,12]

TABLE V

Rate and NMR spectroscopic data for $LCo(DH)_2CH_2Y$ and organic substituent constants from the literature, rescaled to $\sigma_{Me} = 0$. Data are from ref. 11.

Y/L	log k		γ-^{13}C(py)	σ_I	σ_R^o	σ_R^+
	4-CNpy	4-MeOPhNH$_2$				
OMe	1.38	2.18	137.24	0.31	−0.34	−0.77
Me	−0.018	0.892	137.34	0	0	0
Ph	−0.48	0.447	137.36	0.14	0.00	−0.05
$SiMe_3$	−0.37	0.152	137.42	−0.06	0.17	0.31
H	−1.39	−0.328	137.48	0.04	0.11	0.25
Cl	−2.51	−1.47	137.91	0.50	−0.12	−0.11
COMe	−3.23	−2.49	137.95	0.32	0.27	0.41
Br	−2.59	−1.76	137.96	0.48	−0.08	−0.05
CO_2Me	−3.57	−2.62	137.97	0.34	0.25	0.39
I	−2.80	−2.03	137.98	0.43	−0.05	0.00
CF_3	−3.57	−2.96	138.03	0.49	0.19	0.33
CN	−4.52	−3.77	138.25	0.60	0.24	0.38
NO_2	−5.37	–	138.46	0.69	0.26	0.40

In a first set of observations, kinetic and spectral data for $LCo(DH)_2CH_2Y$ compounds were reproduced using a dual substituent parameter (DSP) approach.[11] It was found that, when L = 4-cyanopyridine (4-CNpy), for cobaloximes with the Y groups given in Table V, the 4-CNpy dissociation rate increases by a factor of more than 10^6 (Table V) and the log k can be expressed by the equation $\log k = a\sigma_x + b\sigma_R^+$, where σ_x and σ_R^+ are the organic inductive and resonance substituent constants given in Table V and a and b are the relative coefficients. Using σ_x and $\sigma_R^+ = 0$ for Y = Me (*i.e.* the ethylcobaloxime), the linear correlation coefficient, r was 0.996 for 13 points and the goodness of fit, f, was excellent (0.093), with a ratio $b/a = 0.667$. The same analysis with L = anisidine (Table V) gave similar results ($r = 0.998$, $f = 0.073$, $b/a = 0.665$). For the same series of alkylcobaloximes with L = py, the DSP approach works well for NMR shifts of the γ-^{13}C atom of the pyridine ligand (Table V) when the resonance parameter employed is σ_R.[11] The r and f values are 0.998 and 0.1655, respectively.

These results indicate that when Y is varied, the *trans*-effect (kinetic) and the *trans*-influence (spectroscopic) follow the same trend, which is interpreted on the basis of the DSP approach using the appropriate σ_R constants. This approach confirms also that the CH_2OMe and *i*-Pr groups have essentially the same *trans*-effect[12], although they have very different Taft σ^* constants. Furthermore, it allows reproduction of the observed trend of the *trans*-labilizing effect of CH_2Y groups (Y = halogen), which increases in the order I < Br < Cl.[13]

In another set of observations[14], it was found that for $pyCo(DH)_2CY^1Y^2Y^3$ compounds with several Y^1 substituents, the differences in NMR shifts of py γ-^{13}C atom

TABLE VI

Mean values of $d_{Co\text{-}N}$ *(Å). log* k, $\Delta C(Y^1Y^2Y^3)$ *and the* EP *parameter*

		$d_{Co\text{-}N}$	log k	$\Delta C(Y^1Y^2Y^3)$	EP
1	CCl_2CN	1.992			−1.48
2	$CHClCN$	2.019	−4.85	−1.09	−1.13
3	$CH(CH_2CN)CN$	2.039	−4.47	−1.12	−1.12
4	CH_2NO_2	2.023	−5.42	−0.96	−0.96
5	$CHBr_2$		−3.28	−0.80	−0.82
6	CH_2CN	2.016	−4.52	−0.77	−0.78
7	$CHCl_2$	2.047	−2.95		−0.70
8	CHMeCN	2.047	−2.88	−0.66	−0.63
9	CH_2CF_3	2.041	−3.56	−0.53	−0.53
10	CH_2I		−2.79	−0.47	−0.47
11	CH_2CO_2Me	2.039	−3.57	−0.46	−0.46
12	CH_2COMe		−3.23	−0.45	−0.44
13	CH_2Br		−2.68	−0.43	−0.41
14	CH_2Cl		−2.43	−0.38	−0.35
15	CH_2CH_2Me	2.050	−1.59	−0.33	−0.34
16	$CHMeCO_2Me$	2.058			−0.31
17	$CH=CH_2$	2.073	−1.65	−0.20	−0.20
18	$CH_2C(CO_2Et)_2Me$	2.075	−0.54	−0.02	−0.02
19	Me	2.064	−1.31	0.00	0.00
20	CH_2Ph		−0.48	0.08	0.08
21	CH_2SiMe_3	2.091	−0.49	0.10	0.10
22	Et	2.081	0.00	0.16	0.15
23	CH_2i-Pr		0.19	0.18	0.18
24	CH_2CMe_3	2.081	1.00	0.18	0.18
25	CH_2CH_2Me		0.08	0.19	0.20
26	CH_2OMe		1.38	0.27	0.27
27	*i*-Pr	2.098	1.43	0.31	0.30
28	CHMeEt		1.55	0.34	0.34
29	cyclohexyl	2.106	1.61	0.36	0.35
30	$CHEt_2$		2.00	0.41	0.40
31	adamantyl	2.134	2.57	0.51	0.51

with respect to the R = CH_3 derivative, $\Delta(CY^1Y^2Y^3) = \delta^{13}C(CH_3) - \delta^{13}C(CY^1Y^2Y^3)$, were additive. Thus, using these chemical shifts, the differences $\delta^{13}C(CH_3) - \delta^{13}C(CH_2Y)$ were defined as ΔY. Having obtained such constants ΔY^1, ΔY^2, ΔY^3 for three substituents Y^1, Y^2 and Y^3, their sum was assumed to be the electronic parameter, *EP*, of the $CY^1Y^2Y^3$ group:

$$EP = \Delta Y^1 + \Delta Y^2 + \Delta Y^3 \qquad (1)$$

The good agreement between the *EP* parameters and the observed $\Delta(CY^1Y^2Y^3)$ values supports the validity of equation (1).[14] The *EP* values correlate linearly with Co-N (axial) distances and log *k* for the series $pyCo(DH)_2R$.[14] More recently[15], it was found that the differences in chemical shifts, $\Delta(CY^1Y^2Y^3)$, the log *k* values and the axial bond lengths, $d_{Co\text{-}N}$, in several $LCo(DH)_2R$ series, with L ligands other than py, are linearly related to the corresponding data for the series with L = py. The correlation coefficients varied from 0.992 to 0.999. This offers the opportunity to test the validity of the EP approach using a more extended set of L and R ligands. After rescaling to L = py,

the values were averaged obtaining for each R group the data given in Table VI. Application of equation (1) to the values provided the EP scale reported in Table VI for a large number of R groups. Plots of $d_{Co\text{-}N}$ and log k mean values against EP parameters showed fairly linear relationships with the following best fit equations:

$$\log k = -0.4(6) + 4.6(2) \cdot EP \qquad r = 0.965 \qquad (2)$$

$$D_{Co\text{-}N} = 2.08(1) + 0.058(4) \cdot EP \qquad r = 0.943 \qquad (3)$$

This finding confirms that both *trans*-influence (distances) and *trans*-effect (log k's) reflect mainly the σ-donor ability of R, as measured by the EP parameter. However, significant deviations above the best line are observed in both trends, especially at the extreme »sides« of the *EP* values, *i.e.* for strong σ-donating and σ-withdrawing R groups. These groups are generally those with more than one substituent Y at the C atom bonded to Co and presumably with a larger bulk. This suggests that other influences, mainly steric in origin, may contribute to defining the overall trend. In fact, when the linear regressions given above are limited to cobaloximes with alkyl groups having negligible bulk, *i.e.* CH_2Y groups, the correlation factors improve to 0.979 and 0.967 for equations (2) and (3), respectively. Although this analysis suggests that steric influences play a role in defining the above properties, no indication is available for their quantitation. Therefore, extension of these studies to analogous complexes containing Rh instead of Co was undertaken.[16] In Rh complexes, the steric influences should be reduced, since the Rh ionic radius, larger then that of Co, leads to longer axial distances with consequent relief of the steric interaction between axial and equatorial ligands. Preliminary results[16] indicate that the increase of the Rh-C distance from Me to *i*-Pr, in $pyRh(DH)_2R$ derivatives, is significantly smaller than that of the corresponding Co-C distances. In fact, the Rh-Me and Rh-*i*-Pr bond lengths are 2.063(5) and 2.107(5) Å, respectively, and they should be compared with the analogous distances of 1.998(5) and 2.085(3) Å in $pyCo(DH)_2R$.

The exciting prospect of these observations is that a unified set of constants may eventually be derived for predicting the properties of a diverse range of organometallic compounds, not only those relevant to coenzyme B_{12}. Although the first approach has the advantage of transferring to organometallic chemistry substituent constants from organic chemistry, at present it is limited to groups R = CH_2Y. In contrast, the EP approach may be applied not only to any axial alkyl group but also to monoanionic ligands such as N_3^- or Cl^-. However, as expected, the EP approach to log k and $d_{Co\text{-}N}$ indicates that these properties cannot be interpreted only on the basis of the electronic properties of the R groups. The steric influences are especially important in determining the trend of log k, since they could also play a role in the transition state.[17]

In conclusion, it may be derived that, so far the structural properties of $LCo(DH)_2R$ complexes in the solid state have been very useful in interpreting solution data, although further studies are needed to assess the relative role played by the steric and the electronic factors on the chemical properties of these complexes.

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SAŽETAK

Svojstva modela vitamina B_{12} u čvrstom stanju i u otopinama

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Razmatrana su strukturna svojstva nekih spojeva koji mogu poslužiti kao modeli za vitamin B_{12} i njemu srodne sustave. Analizirani su njihovi kristalografski podaci kako bi se izvela neka opća pravila u strukturama u čvrstom i tekućem stanju.