Inorganica Chimica Acta, *107* (1985) 139–145

An Assessment of the *Cis*-Influence in Coenzyme B_{12} Models. The Structure of the Mixed Schiff-Base/Oxime Complex: Aquo(3,9-dimethyl-2,10-diethyl-1,4,8,11-tetraazaundeca-1,3,8,10-tetraen-11-ol-1-olato)(methyl)cobalt(III)hexafluorophosphate

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Received January 4, 1985

Abstract

The title compound is the first accurately determined structure in the general class of 'Costa' B_{12} models. The data permit comparisons of structural results to other relevant B_{12} models and the construction of a *cis* effect series.

Crystal Data: $C_{14}H_{20}CoF_6N_4O_3P$, M = 504.4, monoclinic, space group $P2_1/c$, $a = 14.316(3)$, $b = 6.819(1)$, $c = 22.741(5)$ Å and $\beta = 99.91(2)°$, $V = 2186.9$ Å^3, $D_m = 1.52$, $Z = 4$, $D_c = 1.53$ g cm^{-3}, $\mu(\text{Mo}K\alpha) = 9.2$ cm^{-1}, $\lambda(\text{Mo}K\alpha) = 0.7107$ Å. Unit cell parameters were refined and intensity data collected on a CAD4 computer-controlled diffractometer, using graphite-monochromated MoKα radiation. A total of 5803 reflections were collected and corrected for Lorentz-polarization factor, 2802 independent reflections with $I > 3\sigma(I)$ being used in the subsequent calculations.

The Co–O bond length to the axial water is 2.102(3) Å. This value places the Costa model structural *cis* influence as being comparatively close to corrin based systems, somewhat greater than cobaloximes and definitely lower than Schiff-base complexes.

Introduction

For some time we have been interested in the dynamic, physical and structural properties of organocobalt compounds which serve as models of B_{12} coenzymes (adenosyl and methyl cobalamins) [1, 2]. One emphasis of such research has been the systematic change of the ligand(s) which occupy the four corrin N equatorial sites in cobalamins, with the goal of obtaining a detailed understanding of the effects due to the corrin in B_{12}. One model system, (DO)(DOH)pn in the scheme, was originally introduced by Costa and co-workers [3]. A modified version [4a], C_2(DO)(DOH)pn [(EMO)(EMOH)pn here], has been recently demonstrated to closely reflect cobalamins in electrochemical behavior [4b]* and to permit better modeling of some B_{12}-dependent enzymic rearrangements [5]†.

One of our interests is to elucidate the relationship between structure and Co–C bond energy. Clear relationships which seem to have emerged are as follows: (1) The Co–C bond lengthens as the bulk of the alkyl group increases [6, 7] and, similarly, the Co–C bond energy or estimated values of this energy decrease [8] (likewise cobalamins with bulky alkyl groups readily decompose [9, 10]); (2) Bulky phosphines, which appear to distort the equatorial ligand moiety in alkyl cobaloximes [1, 11] both increase Co–C bond lengths [1, 11–14] and decrease Co–C bond energy [15]; and (3) For N donor axial ligands *trans* to the alkyl groups, Co–C bond energies appear to be lower [16, 17] in systems where the *trans* Co–N bond length is long [18, 19].

Most studies have been performed with either Schiff-base equatorial ligands or $(DH)_2$ systems. More recently, estimates of Co–C bond energy have become available for (EMO)(EMOH)pn complexes [20]. However, there is only one relevant X-ray structure of a mono alkyl complex in this class,

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*See also discussion in footnote 20 of this paper.

†Interestingly, Rétey and Müller [5c] recently found that the Costa complex was superior to cobaloxime, $CoCl_2$, and even cobalamin catalysts in a model diol dehydratase reaction. This is very probably due to the fact that base-on B_{12} (cobalamins) gives the redox side reaction (to Co(II) + oxidized organic) previously observed [5a, b].

0020-1693/85/$3.30

namely $[H_2OCo((DO)(DOH)pn)CH_3]ClO_4$, **1** [21]. Unfortunately, the accuracy of this structure was limited by ClO_4^- disorder. We have now studied the related $[H_2OCo((EMO)(EMOH)pn)CH_3]PF_6$, 2. Ironically, although the axial ligand *trans* to the alkyl group in cobalamins is an N-donor benzimidazole, the most extensive comparison of bond lengths is possible with O donor ligands. Since the Co–O bond distance has now been accurately determined in a Costa type model, we can now compare structural features of several types of model systems and relate these features to some aspects of solution behavior.

Crystal Data

Crystals of $C_{14}H_{20}CoF_6N_4O_3P$, (2), were obtained from H_2O. Crystal data: M = 504.4, monoclinic, space group $P2_1/c$, $a = 14.316(3)$, $b = 6.819(1)$, $c = 22.741(5)$ Å and $\beta = 99.91(2)°$, $V = 2186.9$ Å^3, $D_m = 1.52$, $Z = 4$, $D_c = 1.53$ g cm^{-3}, $\mu(MoK\alpha) = 9.2$ cm^{-1}, $\lambda(MoK\alpha) = 0.7107$ Å. Unit cell parameters were refined and intensity data collected on a CAD4 computer-controlled diffractometer, using graphite-monochromated MoKα radiation. A total of 5803 reflections were collected and corrected for Lorentz-polarization factor, 2802 independent reflections with $I > 3\sigma(I)$ being used in the subsequent calculations. Anomalous dispersion correction for Co and P was applied. No absorption correction was applied because of the small size of the crystal used (0.03 × 0.04 × 0.05 cm^3) and the small value of the absorption coefficient.

Structure Determination and Refinement

The structure was solved by conventional Patterson and Fourier methods and refined by full-matrix anisotropic least-squares method to final R and Rw values of 0.052 and 0.062, respectively. The contribution of hydrogen atoms, held constant at calculated positions (B = 5 Å^2), was included in the final refinement. The final weighting scheme was $w = 1/(\sigma^2(F) + (p \times F)^2 q)$, where $p = 0.02$ and $q = 1.7$. The PF_6^- anion was found to be disordered. The disorder was easily interpreted as being due to two orientations of the PF_6^- anion of about the same occupancy, differing by a rotation of ~30° around the axial F(5)–P–F(6) direction.

Atomic scattering factors were those given in Ref. 22.

All the calculations were done using computer programs from the CAD4-SDP package. Final positional parameters are given in Table I. Anisotropic thermal parameters for non-hydrogen atoms, calculated and observed structure factors and hydrogen atom fractional coordinates, are all available from one of the authors (LR).

Description of the Structure

A drawing of the crystallographically independent cation of (2) and the PF_6^- anion with the atom numbering scheme is given in Fig. 1, where the two orientations of the PF_6^- anion are also shown. The four N atoms of the equatorial ligand are coplanar within ±0.005 Å and the cobalt atom is displaced by 0.01 Å from this mean plane towards the axial water molecule. With the exception of the C(1), C(7), C(13) and the H atoms, the equatorial ligand is nearly planar with the largest displacement being 0.07 Å for C(5). The six-membered ring has the expected flattened chair conformation: the torsional angles around C(6)–C(7) and C(7)–C(8) bonds are −67.8 and 68.3°, respectively, whereas the Co, N(3), N(4), C(6) and C(8) atoms are coplanar within ±0.007 Å. The bond lengths and angles (Table II) are very similar in the two chemically equivalent halves of the equatorial moiety. On the contrary, Co–N(1) and Co–N(2) bond lengths (mean value of 1.884(4) Å) differ significantly from Co–N(4) and Co–N(3) distances (mean value of 1.916(4) Å). A similar difference has already been noticed in $CH_3Co((DO)(DOH)pn)CH_3$ [23] (0.040 Å) and in (**1**) (0.06 Å) [21].

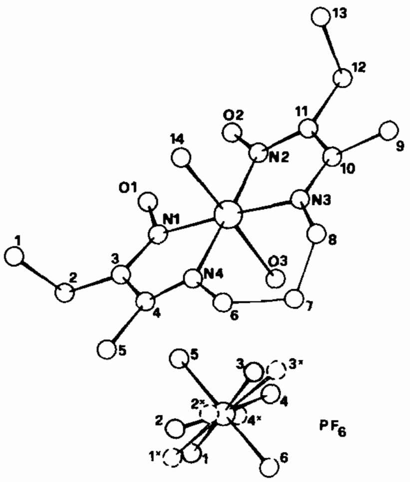


Fig. 1. Numbering scheme for non-hydrogen atoms of the crystallographically-independent cation and PF_6^- anion.

The N–O, N–C(sp^2) and C(sp^2)–C(sp^2) mean bond lengths of 1.338(5), 1.284(5) and 1.472(7) Å, respectively, are in agreement with those of 1.338(7), 1.309(8) and 1.452(9) Å, respectively reported for the dimethyl derivative.

The two axial $Co–CH_3$ and $Co–OH_2$ bonds have lengths of 1.977(4) and 2.103(3) Å, respectively, and make an angle of 178.8(2)°. These bond lengths should be compared with the much less accurate value of 1.99(4) and 2.14(2) Å, respectively reported for the analogous perchlorate derivative (**1**) [21]. On the other hand, the Co–C distance is significantly

TABLE I. Positional Parameters and their Estimated Standard Deviations.[a]

Atom	x	y	z	B(Å^2)
Co	0.37050(4)	0.2098(1)	0.14659(2)	3.63(1)
O1	0.2476(3)	−0.1086(6)	0.1592(2)	6.14(9)
O2	0.3991(3)	−0.1100(6)	0.2280(2)	6.4(1)
O3	0.4282(2)	0.0360(5)	0.0854(1)	4.33(7)
N1	0.2590(3)	0.0590(7)	0.1309(2)	4.68(9)
N2	0.4356(3)	0.0545(7)	0.2092(2)	4.79(9)
N3	0.4854(3)	0.3614(6)	0.1643(2)	4.58(9)
N4	0.3021(3)	0.3663(6)	0.0842(2)	4.64(9)
C1	0.0301(6)	0.073(2)	0.1083(5)	14.2(4)
C2	0.1004(4)	0.009(1)	0.0730(3)	8.8(2)
C3	0.1922(3)	0.1202(9)	0.0894(2)	5.5(1)
C4	0.2184(4)	0.3047(9)	0.0629(2)	5.9(1)
C5	0.1493(5)	0.404(1)	0.0155(3)	8.8(2)
C6	0.3411(5)	0.5442(9)	0.0621(3)	6.7(2)
C7	0.4478(4)	0.5370(8)	0.0683(2)	6.7(1)
C8	0.4998(4)	0.5404(9)	0.1319(3)	6.7(1)
C9	0.6406(5)	0.385(1)	0.2301(3)	8.7(2)
C10	0.5462(4)	0.294(1)	0.2067(2)	5.8(1)
C11	0.5196(4)	0.110(1)	0.2335(2)	5.8(1)
C12	0.5807(5)	−0.007(1)	0.2832(3)	9.8(2)
C13	0.5614(8)	0.052(2)	0.3414(4)	13.6(3)
C14	0.3147(4)	0.3624(9)	0.2059(2)	5.9(1)
P	0.2986(1)	−0.0111(3)	−0.08420(6)	5.20(3)
F1	0.2411(8)	−0.159(2)	−0.1233(5)	14.5(3)
F2	0.2197(7)	0.140(2)	−0.1041(5)	13.9(3)
F3	0.3568(6)	0.155(1)	−0.0435(4)	9.8(2)
F4	0.3792(6)	−0.157(1)	−0.0640(5)	12.0(3)
F5	0.2518(3)	−0.0571(8)	−0.0288(2)	11.1(1)
F6	0.3549(3)	0.0346(8)	−0.1360(2)	10.6(1)
F1*	0.2082(5)	−0.045(2)	−0.1284(4)	10.8(3)
F2*	0.2761(8)	0.206(1)	−0.0826(5)	12.3(3)
F3*	0.3935(6)	0.021(2)	−0.0407(4)	12.7(3)
F4*	0.3228(8)	−0.236(1)	−0.0848(4)	12.0(3)

[a]Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3) \times [a^2B_{1,1} + b^2B_{22} + c^2B_{33} + abB_{1,2}\cos\gamma + acB_{1,3}\cos\beta + bcB_{2,3}\cos\alpha]$

TABLE II. Bond Lengths (Å) and Angles (°) with e.s.d. s in Parentheses.

Co–O3	2.102(3)	N1–C3	1.291(6)	C3–C4	1.471(7)
Co–N1	1.881(4)	N2–C11	1.291(6)	C4–C5	1.495(7)
Co–N2	1.887(4)	N3–C8	1.459(6)	C6–C7	1.511(8)
Co–N3	1.925(4)	N3–C10	1.271(6)	C7–C8	1.508(8)
Co–N4	1.907(4)	N4–C4	1.282(6)	C9–C10	1.500(7)
Co–C14	1.977(4)	N4–C6	1.459(6)	C10–C11	1.472(7)
O1–N1	1.336(5)	C1–C2	1.458(10)	C11–C12	1.527(8)
O2–N2	1.338(5)	C2–C3	1.506(7)	C12–C13	1.456(11)
P–F1	1.497(14)	P–F5	1.558(3)	P–F3*	1.553(11)
P–F2	1.536(13)	P–F6	1.569(3)	P–F4*	1.572(14)
P–F3	1.602(10)	P–F1*	1.513(11)		
P–F4	1.536(13)	P–F2*	1.516(12)		
O3–Co–N1	89.1(1)	Co–N1–O1	123.1(3)	C2–C3–C4	127.0(5)
O3–Co–N2	89.0(1)	Co–N1–C3	117.4(4)	N4–C4–C3	114.4(4)
O3–Co–N3	91.3(1)	O1–N1–C3	119.5(4)	N4–C4–C5	125.7(6)
O3–Co–N4	91.9(1)	Co–N2–O2	122.8(3)	C3–C4–C5	119.9(5)

(Continued overleaf)

TABLE II. *(Continued)*

O3-Co-C14	177.4(2)	Co-N2-C11	117.6(4)	N4-C6-C7	112.4(4)
N1-Co-N2	97.5(2)	O2-N2-C11	119.7(4)	C6-C7-C8	114.4(4)
N1-Co-N3	178.8(2)	Co-N3-C8	122.3(4)	N3-C8-C7	112.4(4)
N1-Co-N4	81.6(2)	Co-N3-C10	114.4(4)	N3-C10-C9	125.2(6)
N1-Co-C14	89.3(2)	C8-N3-C10	123.4(5)	N3-C10-C11	115.6(4)
N2-Co-N3	81.4(2)	Co-N4-C4	115.1(3)	C9-C10-C11	119.2(5)
N2-Co-N4	178.7(2)	Co-N4-C6	122.9(4)	N2-C11-C10	111.1(4)
N2-Co-C14	89.2(2)	C4-N4-C6	122.0(5)	N2-C11-C12	122.5(5)
N3-Co-N4	99.6(2)	C1-C2-C3	111.7(6)	C10-C11-C12	126.4(5)
N3-Co-C14	90.4(2)	N1-C3-C2	121.5(6)	C11-C12-C13	110.8(7)
N4-Co-C14	89.8(2)	N1-C3-C4	111.5(4)		
F1-P-F2	88.6(9)	F3-P-F5	85.9(5)	F6-P-F1*	91.2(6)
F1-P-F3	177.0(1)	F3-P-F6	90.6(5)	F6-P-F2*	87.9(6)
F1-P-F4	93.0(1)	F4-P-F5	91.9(7)	F6-P-F3*	86.7(6)
F1-P-F5	94.3(8)	F4-P-F6	84.1(7)	F6-P-F4*	92.6(6)
F1-P-F6	89.3(8)	F5-P-F6	174.7(2)	F1*-P-F2*	90.2(9)
F2-P-F3	88.9(8)			F1*-P-F3*	177.8(7)
F2-P-F4	179.0(1)	F5-P-F1*	94.0(6)	F1*-P-F4*	90.7(9)
F2-P-F5	88.6(8)	F5-P-F2*	93.1(6)	F2*-P-F3*	90.6(9)
F2-P-F6	95.3(8)	F5-P-F3*	88.0(6)	F2*-P-F4*	179.0(1)
F3-P-F4	89.8(9)	F5-P-F4*	86.3(6)	F3*-P-F4*	88.5(9)

TABLE III. Comparison of some Relevant Structural Parameters in some Co(chel) Units, where Chel contains at Least one Oxime Bridge. Distances are in Å and Angles in Degrees.

	Co[(DO)(DOH)pn][a]	Co[(EMO)(EMOH)pn]	Co$(DH)_2$[b]	Co$[(AO)_2$-H][c]	Co(PnAO-H)[d]
Co-N(O)	1.859(6)	1.884(4)	1.8901(9)	1.891(2)	1.900(3)
O-N	1.338(7)	1.338(5)	1.3492(9)	1.345(3)	1.353(3)
N-C(sp^2)	1.309(8)	1.284(5)	1.301(1)	1.279(3)	1.276(3)
C(sp^2)-C(sp^2)	1.452(9)	1.472(7)	1.462(3)	–	–
O···O	2.461(6)	2.445(5)	2.487(2)	2.422(3)	2.432(3)
Co-N-O	124.2(4)	123.0(3)	122.63(7)	120.7(1)	121.0(2)
Co-N-C	117.8(5)	117.5(4)	116.60(7)	119.9(2)	119.9(2)
O-N-C	118.0(6)	119.6(4)	120.61(9)	119.3(2)	119.3(2)
(O)N-Co-N(O)	97.4(2)	97.5(2)	98.57(8)	99.0(1)	98.6(1)

[a] Ref. 23. [b] Data are mean values of about 300 measurements as reported in Ref. 1. [c] Ref. 33. [d] Ref. 34.

shorter than the mean value of 2.047(8) Å reported for the two axial Co–C distances in $CH_3Co((DO)(DOH)pn)CH_3$ [23]. The O···O distance of 2.445(5) Å is similar to the value of 2.461(6) found in the dimethyl compound.

Discussion

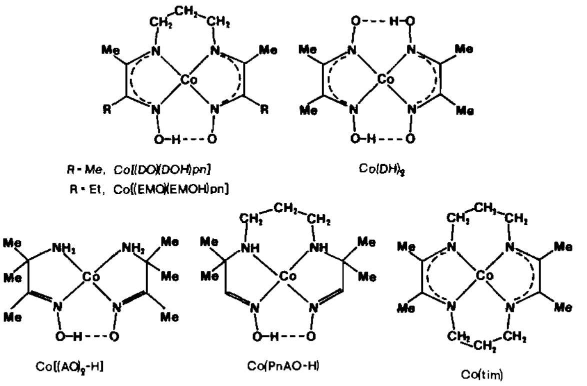
A comparison of some relevant structural parameters of the equatorial moiety in this and similar cobalt complexes (see scheme) with at least one oxime bridge is presented in Table III, where the mean values of the chemically-equivalent bond lengths and angles are given. The general trends of bond lengths and angles in these systems are very similar, with differences only in fine details. These are: (i) a systematic increase of the O···O distance in the order $(AO)_2$–H ~ (pnAO–H) < (DO)(DOHpn ~ (EMO)(EMOH)pn < $(DH)_2$. This trend should parallel the increasing ease of the oxime bridge deprotonation in the above complexes. This suggestion is supported by the slower exchange of the proton in the OHO bridge of (DO)(DOH)pn complexes with free water as compared to that of complexes of $(DH)_2$ with similar axial ligands [1, 25]. (ii) The bond angles around the N atom are all close to 120° in $(AO)_2$–H and pnAO–H, while the Co–N–O and Co–N–C angles are significantly larger and narrower respectively than 120° in complexes of (DO)(DOH)pn, (EMO)(EMOH)pn and $(DH)_2$. These two observations suggest that the electron charge distribution in the oxime bridge is influenced by the nature of the equatorial ligand.

TABLE IV. Co–C(Å) and Co–O(Å) Axial Bond Lengths in some RCo(chel)(O–ligand) Complexes with Different Equatorial Chel Ligand.

R	Chel	O–ligand	Co–C	Co–O
Ph	acacen[a]	H_2O	1.93(3)	2.33(2)
$CH{=}CH_2$	acacen[a]	H_2O	1.89(1)	2.221(7)
CH_2COCH_3	salen[a]	CH_3OH	2.02(1)	2.202(9)
CH_3	(DO)(DOH)pn[b]	H_2O	1.99(4)	2.14(2)
CH_3	(EMO)(EMOH)pn[c]	H_2O	1.977(4)	2.102(3)
CN	cobyrinic acid[d]	H_2O	1.85	2.06
$CH_2C(CH_3)_3$	$(DH)_2$[e]	H_2O	2.044(7)	2.056(5)
CH_3	$(DH)_2$[e f]	H_2O	1.990(5)	2.058(5)
CN	$(DH)_2$[g]	H_2O	1.906(3)	1.992(4)

[a] Ref. 35. [b] Ref. 21. [c] Present work. [d] Ref. 36. [e] Ref. 37. [f] Ref. 38. [g] Ref. 39.

It has been shown [24] that axial Co–N and Co–O bond lengths are indicative of the following order of the *cis* influence in different coenzyme B_{12} models:



$$(DH)_2 < \text{salen} < \text{acacen} \qquad (1)$$

The tetradentate ligands salen (dianion of bis(salicylidene)-ethylenediamine) and acacen (dianion of bis(acetylacetone)-ethylenediimine) differ from the ligands in the scheme in that they have 2 Schiff-base N donors and 2 oxygen donors. In this comparison, $(DH)_2$ has the strongest axial cobalt ligand bonds and acacen the weakest. To provide a framework for developing further insights from the structural results it is useful at this point to summarize relevant results for B_{12} model ligand association (K_{assoc}) and substitution ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$) reactions in solution.

Recently, Brown and Flay [26] have suggested on the basis of thermodynamic measurements (K_{assoc}), and earlier work by Courtright and Drago [27] that the order of the *cis*-influence in different coenzyme B_{12} model systems (*cis* activating or labilizing influence)[#], is described by series (1) above. Furthermore, activation $\Delta H^{\ddagger}$ values [28], for $(DH)_2$ complexes are *ca.* 2 kcal/mol larger than for (DO)(DOH)-pn analogues. Finally, dehydration results [25] for the $H_2OCo(chel)CH_3$ series, where chel = $(DH)_2$, (DO)(DOH)pn, and tim, indicate that H_2O binds cobalt relatively strongly for tim. Combined, these results suggest that the *cis*-labilizing sequence in (1) could be extended as follows:

$$\text{tim} < (DH)_2 < (DO)(DOH)pn < \text{salen} < \text{acacen} \qquad (2)$$

This order parallels the increasing order of the 'electron richness' [16] of the Co(chel) moiety. If it is assumed that most of the $\Delta H^{\ddagger}$ variation is due to changes in the ground state and that the ground state is mainly affected by the change of the equatorial ligand, the $\Delta H^{\ddagger}$ comparison suggests a Co–O axial bond in the $(DH)_2$ complexes stronger than that in (DO)(DOH)pn analogues. There is a discrepancy, however, in that the order found by Guschl and Brown for dehydration and for CH_3CN exchange in $CH_3CNCo(chel)CH_3$ is tim < (DO)(DOH)pn < $(DH)_2$ [25]. Previous work on the *cis* and *trans* effects in B_{12} concluded that 'the main factor is the amount of negative charge donated to the cobalt atom through the σ-bond [29] in these 'soft, class B' systems [25, 26]. It is of interest to examine which trend is suggested by the structural data. Some relevant Co–C and Co–O bond lengths for a series (O-ligand)Co(chel)R, having different chel equatorial ligands, are listed in Table IV. As already observed [19], the Co–C bond length is not influenced by the electronic nature of the chel ligand. The differences in Co–C bond lengths reported in Table IV reflect mainly the different hybridization states of the C bonded to Co or different steric interactions between the axial alkyl and the equatorial ligands (steric *cis* influence). On the contrary, the Co–O bond lengths are strongly affected by the nature of the chel ligand. The order of decreasing Co–O bond lengths derived from data of Table IV is:

[#] Brown and Flay cite their data (see p. 68) [26] as a *cis*-deactivating rather than activating order, $(DH)_2$ > salen.

$$\text{acacen} > \text{salen} > \text{DO(DOH)pn} \sim \text{(EMO)(EMOH)pn} \sim \text{cobyrinic acid} > \text{(DH)}_2 \qquad (3)$$

A similar trend for the Co–N bond lengths but based on fewer observations has been reported for analogous complexes containing pyridine [19]. The present series is derived with the consideration that the Co–OH_2 bond is also affected by *trans*-influence since the axial ligands *trans* to O in the complexes in Table IV are different. It has been shown that a CH_3 group produces a lenthening of the *trans* bond in the range 0.05–0.1 Å, as compared with a CN group [30] as shown for $H_2OCo(DH)_2X$ complexes (R = CH_3, CN) of Table IV.

Similar lengthening is observed in the cobalamin system [31] for N-containing neutral ligands. Thus, a bond length of at least 2.1 Å is assumed to be reasonable for the methyl analogue of the CN derivative of the cobyrinic acid of Table IV in the derivation of the above trend.

An important conclusion of the present work is that the bond length trend is in agreement with the trend (2) established from ligand association (K_{assoc}) values and ligand substitution $\Delta H^{\ddagger}$ values for $Co(DH)_2$ and Co[(DO)(DOH)pn] aquo complexes. It would be useful to extend the work of Guschl and Brown [25] for a comparison to trend (2) by obtaining kinetic, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for ligand substitutions on tim *vs.* $(DH)_2$ and (DO)(DOH)pn aquo complexes. The discrepancy between trend (2) and the kinetic, $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ data reported for substitution of axial $P(OMe)_3$ or CH_3CN ligands and for dehydration in tim, $(DH)_2$ and (DO)(DOH)pn cobalt complexes† is not understood. One possible explanation is that $\Delta H^{\ddagger}$ for ligand substitution can be a variable measure of the Co–L bond strength (depending upon the transition state structure), since $\Delta H^{\ddagger}$ will reflect the difference in all the axial R, L and equatorial N and O to cobalt bond strengths between the transition and ground states.

A second important conclusion is that by the structural *cis* influence criterion, the [(EMO)(EMOH)pn] model system is a better mimic of cobalamins than cobaloximes. Support for this conclusion was offered previously [4] on the basis of electrochemical, ligand charge, ligand symmetry, and axial base binding constant data††. Subtle but important differences in the redox behavior of the [(EMO)(EMOH)pn] model *vs.* B_{12} have recently been observed* and, importantly, the differences between the available Co–C BDE's as a function of the B_{12} models are relatively small**.

Acknowledgements

This work was supported by grants to LR from M.P.I. and C.N.R. (Rome), to LGM from NIH (Grant 29225) and to RGF from NIH (Grant AM-26241). We are grateful to these organizations. LGM thanks the Alexander von Humboldt Foundation for a Senior U.S. Scientist Award which facilitated this research, and RGF thanks the Dreyfus and Sloan Foundations for fellowships.

References

1 N. Bresciani-Pahor, M. Forcolin, L. G. Marzilli, L. Randaccio, M. F. Summers and P. J. Toscano, *Coord. Chem. Rev.*, in press.
2 R. G. Finke, D. A. Schiraldi and B. J. Mayer, *Coord. Chem. Rev., 54,* 1 (1984).
3 G. Costa, *Pure Appl. Chem., 30,* 355 (1972) and refs. therein.
4 (a) R. G. Finke, B. L. Smith, W. A. McKenna and P. L. Christian, *Inorg. Chem., 20,* 687 (1981); (b) C. M. Elliot, E. Hershenhart, R. G. Finke and B. L. Smith, *J. Am. Chem. Soc., 103,* 5558 (1981) and refs. therein.
5 (a) R. G. Finke, W. P. McKenna, D. A. Schiraldi, B. L. Smith and C. Pierpoint, *J. Am. Chem. Soc., 105,* 7592 (1983); (b) R. G. Finke and D. A. Schiraldi, *J. Am. Chem. Soc., 105,* 7605 (1983) and refs. therein; (c) P. Müller and J. Rétey, *J. Chem. Soc., Chem. Commun.,* 1342 (1983).
6 L. G. Marzilli, P. J. Toscano, L. Randaccio, N. Bresciani-Pahor and M. Calligaris, *J. Am. Chem. Soc., 101,* 6754 (1979).
7 N. Bresciani-Pahor, L. G. Marzilli, L. Randaccio, P. J. Toscano and E. Zangrando, *J. Chem. Soc., Chem. Commun.,* in press.
8 T.-T. Tsou, M. Loots and J. Halpern, *J. Am. Chem. Soc., 104,* 623 (1982) and refs. therein.
9 J. H. Grate, J. W. Grate and G. N. Schrauzer, *J. Am. Chem. Soc., 104,* 1588 (1982) and refs. therein.
10 S. M. Chemaly and J. M. Pratt, *J. Chem. Soc., Dalton Trans.,* 2259 (1980) and refs. therein.
11 N. Bresciani-Pahor, M. Calligaris, L. Randaccio and L. G. Marzilli, *Inorg. Chim. Acta, 32,* 181 (1979).
12 L. Randaccio, N. Bresciani-Pahor, P. J. Toscano and L. G. Marzilli, *J. Am. Chem. Soc., 102,* 7372 (1980).
13 N. Bresciani-Pahor, L. Randaccio, P. J. Toscano and L. G. Marzilli, *J. Chem. Soc., Dalton Trans.,* 567 (1982).
14 L. Randaccio, N. Bresciani-Pahor, J. D. Orbell, M. Calligaris, M. F. Summers, B. Snyder, P. J. Toscano and L. G. Marzilli, *Organometallics,* in press.
15 F. T. T. Ng, G. L. Rempel and J. Halpern, *Inorg. Chim. Acta, 77,* L165 (1983).
16 J. Halpern, in D. Dolphin (ed.), 'B_{12}', (2 vols.), Wiley, New York, 1982, p. 501.

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†Dependent upon the original axial ligand, the $\Delta G^{\ddagger}$ for ligand substitution are tim ~ (DO)(DOH)pn ~ $(DH)_2$ (for $P(OMe)_3$) to $\Delta G^{\ddagger}$ tim > (DO)(DOH)pn > $(DH)_2$ (for CH_3CN).

††Note that recent work [19] shows that both Co(saloph) and B_{12} are *ca.* 10^7 more labile towards substitution than $Co(DH_2)$ complexes.

*See reference 5b and footnote 19 therein.

**For example compare the $\Delta H^{\ddagger}$ = 28.6 ± 10.8 kcal/mol and $\Delta S^{\ddagger}$ = 14 ± 3 e.u. found by Espenson [32] to the values listed in Table 1 of reference 20.

17 J. Halpern, *Pure Appl. Chem., 55,* 1059 (1983).

18 M. F. Summers, P. J. Toscano, N. Bresciani-Pahor, G. Nardin, L. Randaccio and L. G. Marzilli, *J. Am. Chem. Soc., 105,* 6259 (1983).

19 M. F. Summers, L. G. Marzilli, N. Bresciani-Pahor and L. Randaccio, *J. Am. Chem. Soc., 106,* 4478 (1984).

20 R. G. Finke, B. L. Smith, B. J. Mayer and A. A. Molinero, *Inorg. Chem., 22,* 3677 (1983).

21 S. Bruckner, M. Calligaris, G. Nardin and L. Randaccio, *Inorg. Chim. Acta, 3,* 278 (1969).

22 'International Tables for X-ray Crystallography, Vol. IV', Kynoch Press, Birmingham, 1974.

23 M. Calligaris, *J. Chem. Soc., Dalton Trans.,* 1628 (1974).

24 A. Bigotto, E. Zangrando and L. Randaccio, *J. Chem. Soc., Dalton Trans.,* 96 (1976).

25 R. J. Guschl and T. L. Brown, *Inorg. Chem., 13,* 959 (1974).

26 D. G. Brown and R. B. Flay, *Inorg. Chim. Acta, 57,* 63 (1982).

27 R. L. Courtright, R. S. Drago, J. P. Nusz and M. S. Nozari, *Inorg. Chem., 12,* 2809 (1973).

28 R. Dreos-Garlatti, G. Tauzher, G. Costa and M. Green, *Inorg. Chim. Acta, 50,* 95 (1981).

29 R. A. Firth, H. A. O. Hill, J. M. Pratt, R. G. Thorp and R. J. P. Williams, *J. Chem. Soc. A:,* 2428 (1968).

30 N. Bresciani-Pahor, M. Calligaris, L. Randaccio and P. J. Toscano, *J. Chem. Soc., Dalton Trans.,* 1009 (1982).

31 M. Rossi, J. P. Glusker, L. Randaccio, M. F. Summers, P. J. Toscano and L. G. Marzilli, submitted for publication.

32 A. Bakac, J. H. Espenson, *J. Am. Chem. Soc., 106,* 5197 (1984).

33 E. O. Schlemper, S. J. la Placa, B. R. Davis and W. C. Hamilton, *Acta Crystallogr., Sect. B:, 34,* 918 (1978).

34 R. K. Murmann and E. O. Schlemper, *Inorg. Chem., 12,* 2625 (1973).

35 M. Calligaris, G. Nardin and L. Randaccio, *Coord. Chem. Rev., 7,* 385 (1972).

36 K. Venkatesan, D. Dale, D. G. Hodgkin, C. E. Nockolds, F. H. Moore and B. H. O'Connor, *Proc. R. Soc. London, Ser. A:, 323,* 455 (1971).

37 N. Bresciani-Pahor, L. Randaccio, P. J. Toscano and L. G. Marzilli, *J. Chem. Soc., Dalton Trans.,* 567 (1982).

38 D. L. McFadden and A. T. McPhail, *J. Chem. Soc., Dalton Trans.,* 363 (1974).

39 S. Alvarez and C. Lopez, *Inorg. Chim. Acta, 64,* L99 (1982).