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Evidence of steric influences on the Co–C bond lengths in vitamin B_{12} model compounds

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Abstract

The structures of *trans*-$(NH_2Ph)(Me)Co(DH)_2$ (**1**), *trans*-$(NH_2Ph)(CH_2C(CO_2Et)_2Me)Co(DH)_2$ (**2**), and *trans*-$(PPh(^cHex)_2)(CH_2C(CO_2Et)_2Me)Co(DH)_2$ (**3**), where DH = monoanion of dimethylglyoxime have been determined by X-ray diffraction studies. The variations in the geometry of these octahedral cobalt(III) complexes are interpreted in terms of steric and electronic influences. Linear regression analyses of Co–C bond lengths with α and d (measures of the geometrical deformation of the equatorial moiety) in methyl cobaloximes have confirmed that steric effects play a significant role in the Co–C bond stability in vitamin B_{12} models.

Introduction

Vitamin B_{12} and its derivatives are well established examples of naturally-occurring organometallic compounds [1,2]. To improve understanding of the chemistry of these compounds and knowledge of the nature of the Co–C bond, about three thousand such derivatives or species that can be regarded as models for them have been studied [3–6]. Because of their relative simplicity cobaloximes (compounds containing the $Co(DH)_2$ moiety, where DH is the monoanion of dimethylglyoxime) are extensively studied as models of vitamin B_{12} [3,4].

Steric effects play a significant role in the enzymatic reactions involving the Co–C bond formation and cleavage [2,4,7,8], and can be observed by a study of the steric influences revealed by X-ray structural data for organocobalt complexes [3,4].

We describe here the crystal structures of $CH_2C(CO_2Et)_2MeCo(DH)_2L$, where L = NH_2Ph (**2**) and $PPh(^cHex)_2$ (**3**), which were determined in order to detect structural deformations due to the steric *cis* interaction between axial and equatorial ligands. The substituted alkyl group $CH_2C(CO_2Et)_2Me$ is a bulky ligand bearing electron-withdrawing substituents, and it has been used as a model for a ligand in an organocobalt intermediate involved in the B_{12}-catalyzed isomerization of methylmalonylCoA to succinylCoA [9,10]. We also report the structure of $MeCo(DH)_2NH_2Ph$ (**1**) and present the results of analysis of correlations between structural parameters for deformation of equatorial ligands and the Co–Me bond lengths for several methylcobaloxime derivatives. It has been observed previously that distortions of the $Co(DH)_2$ moiety are related to some extent to the bulk of the axial ligands [3]. Our results provide some evidence in favour of the upward conformational theory [4,11,12], namely that the deformation of the equatorial moiety ("butterfly" bending) can affect the Co–C bond homolysis in the coenzyme B_{12}.

Experimental

The crystals were obtained by slow evaporation from acetone–water for **1** and **2**, and from methylene chloride for **3**. Unit cell parameters were determined from Weissenberg and precession photographs. Diffraction data were then collected with an Enraf–Nonius CAD4 diffractometer using graphite monochromated Mo-K_α radiation. Crystal data are given in Table 1. Three reflections monitored every 100 min, showed no systematic variation in intensity. In all cases reflections with $I > 3\sigma(I)$ were corrected for Lorentz and polarization factors and anomalous dispersion. No absorption correction was applied because of the relatively small size of the crystals used and the low values of the absorption coefficients (Table 1).

All the structures were solved by conventional Patterson and Fourier methods and refined by the full matrix anisotropic least-squares methods to the final R and R_w values given in Table 1. The contributions of the hydrogen atoms, which were kept in calculated positions ($B = 5$ Å^2), were included in the final refinements. The final weighting scheme was $w = 1/(\sigma^2(F) + (p \cdot F)^2 + q)$, where $p = 0.02$ and $q = 1.0$ for all the structures. Atomic scattering factors are as given in Ref. 13. All

Table 1

Crystallographic data and details of refinement for compounds **1–3**. All data collected at 18 °C using graphite-monochromated Mo-K_α radiation ($\lambda = 0.7107$ Å), $2\theta_{max} = 56°$

	1	**2**	**3**
Formula	$CoO_4N_5C_{15}H_{24} \cdot H_2O$	$CoO_8N_5C_{23}H_{36} \cdot H_2O$	$CoPO_8N_4C_{35}H_{36}$
fw	415.3	587.5	750.9
a, Å	8.474(2)	8.643(2)	10.850(3)
b, Å	10.859(1)	10.777(2)	21.487(3)
c, Å	11.654(1)	16.038(2)	16.437(3)
α, deg	65.37(1)	95.56(1)	–
β, deg	84.86(2)	100.39(1)	98.94(2)
γ, deg	81.68(1)	108.63(1)	–
D_{measd}, g cm^{-3}	1.42	1.41	1.30
D_{calcd}, g cm^{-3}	1.43	1.42	1.32
Z	2	2	4
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
μ(Mo-K_α), cm^{-1}	9.1	6.7	5.4
No. of measd. reflcns.	4865	6837	9667
No. of indep. reflcns. $I \geqslant 3\sigma(I)$	3777	4752	4668
No. of param. refined	235	343	442
R	0.034	0.040	0.047
R_w	0.048	0.051	0.057

Table 2

Atomic coordinates of non-hydrogen atoms for compound **1**, with esd's in parentheses

Atom	x	y	z	B (Å^2) [a]	Atom	x	y	z	B (Å^2) [a]
Co	0.22888(3)	0.01316(3)	0.21629(3)	2.036(5)	C3	0.3186(3)	0.2492(2)	0.0335(2)	2.76(5)
O1	0.5373(2)	0.0053(2)	0.3003(2)	3.22(4)	C4	0.3141(4)	0.3814(3)	−0.0795(3)	4.30(7)
O2	0.0668(2)	0.2164(2)	0.0041(2)	3.64(4)	C5	−0.1326(3)	−0.2380(3)	0.3135(3)	3.82(6)
O3	−0.0774(2)	0.0178(2)	0.1319(2)	3.57(4)	C6	0.0115(3)	−0.1707(2)	0.3053(2)	2.70(5)
O4	0.3903(2)	−0.1916(2)	0.4304(2)	3.36(4)	C7	0.1446(3)	−0.2302(2)	0.3911(2)	2.69(5)
O5	0.7764(2)	0.0893(2)	0.3983(2)	3.94(4)	C8	0.1505(4)	−0.3650(3)	0.5013(3)	3.92(6)
N1	0.4262(2)	0.0749(2)	0.2102(2)	2.40(4)	C9	0.3257(3)	−0.0867(2)	0.1125(2)	3.08(5)
N2	0.2010(2)	0.1751(2)	0.0690(2)	2.55(4)	C10	0.1706(3)	0.2459(2)	0.3068(2)	2.48(4)
N3	0.0346(2)	−0.0516(2)	0.2181(2)	2.54(4)	C11	0.2975(3)	0.2554(2)	0.3682(2)	3.15(5)
N4	0.2584(2)	−0.1526(2)	0.3598(2)	2.48(4)	C12	0.3438(4)	0.3821(3)	0.3420(3)	4.04(6)
N5	0.1253(2)	0.1139(2)	0.3323(2)	2.59(4)	C13	0.2645(4)	0.4979(3)	0.2548(3)	4.39(7)
C1	0.5994(3)	0.2562(3)	0.1029(3)	3.74(6)	C14	0.1394(4)	0.4893(3)	0.1926(3)	4.32(7)
C2	0.4528(3)	0.1896(2)	0.1187(2)	2.60(4)	C15	0.0907(3)	0.3626(3)	0.2180(2)	3.42(6)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $\frac{4}{3}\Sigma_i\Sigma_j a_i a_j \beta(i, j)$.

calculations were carried out on a PDP 11/44 computer with the CAD4-SDP package. Final non-hydrogen positional parameters are listed in Tables 2–4. Hydrogen atom coordinates, anisotropic thermal parameters, and a list of final calculated and observed structure factors, as well as a complete list of bond lengths and angles, are available from the authors.

Table 3

Atomic coordinates of non-hydrogen atoms for compound **2** with esd's in parentheses

Atom	x	y	z	B (Å^2) [a]	Atom	x	y	z	B (Å^2) [a]
Co	0.34394(4)	0.20640(3)	0.18058(2)	2.079(5)	C5	−0.0127(3)	0.3656(3)	0.0769(2)	3.73(6)
O1	0.6120(2)	0.1408(2)	0.1302(1)	3.09(4)	C6	0.1298(3)	0.3159(2)	0.0975(2)	2.56(5)
O2	0.2111(2)	0.1542(2)	0.3287(1)	3.95(4)	C7	0.2505(3)	0.3188(2)	0.0441(2)	2.57(5)
O3	0.0598(2)	0.2528(2)	0.2222(1)	3.77(4)	C8	0.2475(4)	0.3752(3)	−0.0371(2)	3.95(6)
O4	0.4760(2)	0.2559(2)	0.0307(1)	3.30(4)	C9	0.4686(3)	0.3947(2)	0.2449(2)	2.62(5)
O5	0.7748(2)	0.3300(2)	0.3898(1)	3.95(4)	C10	0.6525(3)	0.4519(2)	0.2945(2)	2.60(5)
O6	0.5928(2)	0.4182(2)	0.4296(1)	3.62(4)	C11	0.7759(3)	0.4398(3)	0.2392(2)	3.53(6)
O7	0.6151(3)	0.6657(2)	0.2961(2)	8.32(8)	C12	0.6831(3)	0.3921(2)	0.3753(2)	2.76(5)
O8	0.8311(3)	0.6518(2)	0.3848(2)	4.57(5)	C13	0.6933(4)	0.6012(3)	0.3241(2)	3.65(6)
O9	0.7958(3)	−0.0171(2)	0.0743(1)	4.33(5)	C14	0.6264(4)	0.3844(3)	0.5149(2)	4.59(7)
N1	0.5241(2)	0.1428(2)	0.1923(1)	2.46(4)	C15	0.7708(5)	0.4891(4)	0.5732(2)	6.0(1)
N2	0.3303(3)	0.1473(2)	0.2861(1)	2.76(4)	C16	0.8833(5)	0.7921(3)	0.4195(3)	6.2(1)
N3	0.1590(2)	0.2641(2)	0.1659(1)	2.50(4)	C17	1.0311(6)	0.8293(4)	0.4844(4)	8.7(1)
N4	0.3599(2)	0.2668(2)	0.0749(1)	2.37(4)	C18	0.1977(3)	−0.1000(2)	0.1421(2)	2.83(5)
N5	0.1773(3)	0.0162(2)	0.1119(1)	2.85(4)	C19	0.3055(4)	−0.1554(3)	0.1121(2)	3.58(6)
C1	0.6867(4)	0.0298(3)	0.2781(2)	4.38(7)	C20	0.3328(4)	−0.2626(3)	0.1449(2)	4.64(8)
C2	0.5527(3)	0.0890(2)	0.2594(2)	2.91(5)	C21	0.2549(5)	−0.3139(3)	0.2072(2)	5.13(8)
C3	0.4369(3)	0.0917(2)	0.3153(2)	3.14(5)	C22	0.1477(4)	−0.2592(3)	0.2371(2)	4.72(8)
C4	0.4395(4)	0.0328(3)	0.3955(2)	4.81(8)	C23	0.1176(4)	−0.1516(3)	0.2048(2)	3.76(6)

[a] See Table 2.

Table 4

Atomic coordinates of non-hydrogen atoms for compound **3**, with esd's in parentheses

Atom	*x*	*y*	*z*	*B* (Å^2) [a]	Atom	*x*	*y*	*z*	*B* (Å^2) [a]
Co	0.25035(5)	0.08676(2)	0.21317(3)	2.412(8)	C12	0.3806(4)	0.1216(2)	−0.0325(3)	4.3(1)
P	0.17464(9)	0.06738(5)	0.34231(6)	2.60(2)	C13	0.4345(4)	0.1895(2)	0.0831(3)	4.4(1)
O1	0.4217(3)	−0.0124(1)	0.2512(3)	3.75(6)	C14	0.3758(6)	0.0432(3)	−0.1335(3)	7.7(2)
O2	−0.0007(3)	0.0814(2)	0.1303(2)	4.41(7)	C15	0.3174(6)	−0.0154(3)	−0.1513(4)	7.7(2)
O3	0.0772(2)	0.1863(1)	0.1778(2)	3.94(6)	C16	0.6546(6)	0.1974(4)	0.1284(5)	10.3(2)
O4	0.5034(2)	0.0929(1)	0.2910(2)	3.78(6)	C17	0.7467(7)	0.1877(4)	0.0858(6)	12.1(3)
O5	0.4425(4)	0.1526(2)	−0.0712(2)	8.3(1)	C18	0.1219(4)	−0.0135(2)	0.3407(2)	2.89(8)
O6	0.3404(3)	0.0668(2)	−0.0569(2)	5.57(8)	C19	0.2032(4)	−0.0613(2)	0.3709(3)	3.71(9)
O7	0.4195(4)	0.2439(2)	0.0931(2)	6.7(1)	C20	0.1651(5)	−0.1227(2)	0.3676(3)	4.6(1)
O8	0.5440(3)	0.1608(2)	0.1042(2)	5.80(9)	C21	0.0457(5)	−0.1383(2)	0.3336(3)	4.8(1)
N1	0.3074(3)	0.0042(1)	0.2148(2)	2.83(6)	C22	−0.0353(4)	−0.0919(2)	0.3023(3)	4.8(1)
N2	0.1056(3)	0.0491(2)	0.1569(2)	3.19(7)	C23	0.0020(4)	−0.0300(2)	0.3051(3)	3.75(9)
N3	0.1951(3)	0.1694(2)	0.2072(2)	2.99(7)	C24	0.0347(4)	0.1141(2)	0.3551(2)	3.15(8)
N4	0.3993(3)	0.1250(1)	0.2620(2)	2.75(6)	C25	0.0680(4)	0.1824(2)	0.3776(3)	3.9(1)
C1	0.2675(5)	−0.1033(2)	0.1661(3)	5.4(1)	C26	−0.0504(5)	0.2224(2)	0.3660(3)	5.0(1)
C2	0.2322(4)	−0.0368(2)	0.1748(3)	3.60(9)	C27	−0.1441(4)	0.1980(3)	0.4181(3)	5.5(1)
C3	0.1122(4)	−0.0101(2)	0.1412(2)	3.63(9)	C28	−0.1718(4)	0.1293(3)	0.4017(3)	4.9(1)
C4	0.0095(5)	−0.0471(2)	0.0932(3)	5.3(1)	C29	−0.0534(4)	0.0901(2)	0.4134(3)	4.04(9)
C5	0.2472(5)	0.2794(2)	0.2383(3)	5.0(1)	C30	0.2903(4)	0.0694(2)	0.4388(2)	3.08(8)
C6	0.2763(4)	0.2117(2)	0.2365(3)	3.25(8)	C31	0.3626(4)	0.1302(2)	0.4574(3)	3.9(1)
C7	0.3978(4)	0.1853(2)	0.2685(2)	3.14(8)	C32	0.4701(4)	0.1202(2)	0.5268(3)	4.6(1)
C8	0.5063(4)	0.2229(2)	0.3076(3)	4.9(1)	C33	0.4244(5)	0.0981(2)	0.6033(3)	4.9(1)
C9	0.3214(4)	0.0879(2)	0.1029(2)	3.01(7)	C34	0.3452(5)	0.0391(2)	0.5876(3)	4.9(1)
C10	0.3343(4)	0.1437(2)	0.0463(2)	3.31(8)	C35	0.2397(4)	0.0477(2)	0.5161(3)	3.9(1)
C11	0.2118(5)	0.1784(2)	0.0162(3)	4.8(1)					

[a] See Table 2.

Since some discrepancies were noted in previous papers for the interplanar angles, α, between DH units owing to the choice of the set of atoms, four different dihedral angles, $\alpha 1$–$\alpha 4$, were calculated in the present study, involving several sets, as shown in Table 5. Some calculations were performed on data from the Cambridge Structural Database [14] (CSD 4.3, version of July 1990 with 82129 entries). Atomic coordinates of 13 methylcobaloximes structures were retrieved (Refcodes [14] reported in Table 5).

Results and discussion

The atom numbering schemes and ORTEP drawings for the crystallographically independent molecules **1**, **2** and **3** are depicted in Figs. 1, 2, and 3, respectively. In all the complexes the cobalt center exhibits a distorted octahedral geometry, with the $(DH)_2$ units occupying the four equatorial positions. The displacement, *d*, of the cobalt atom from the plane of the four N equatorial donors is +0.035 Å in **1**, −0.014 Å in **2**, and +0.053 Å in **3**. The corresponding dihedral angles, $\alpha 1$, between the two DH units (see below) are +3.8, −2.6 and +8.9°, respectively; a positive sign of *d* and α indicates displacement towards the neutral ligand and bending towards the alkyl group (R), respectively.

Table 5

Geometry of the R–Co–L axial fragment [a] and d and α [b] values for $LCo(DH)_2Me$ complexes

No.	L	Co–L (Å)	Co–C (Å)	L–Co–C (°)	d (Å)	$\alpha 1$ (°)	$\alpha 2$ (°)	$\alpha 3$ (°)	$\alpha 4$ (°)	Refcode [c]
1	H_2O	2.055(8)	1.978(11)	178.0(3)	+0.001	−4.4	−5.1	−4.9	−5.3	AMGXCO01
2	H_2O	2.058(3)	1.990(5)	178.0(2)	−0.002	−4.6	−4.2	−5.1	−4.6	AMGXCO
3	Im	2.019(3)	1.985(3)	177.2(1)	+0.029	−1.5	−1.9	−1.9	−2.0	CIHNOW
4	$NH_4CH(Me)Ph$	2.087(9)	1.988(19)	173.7(5)	+0.036	+2.4	+2.5	+2.1	+2.4	MBAGCO
5	Me_3Bzm	2.060(2)	1.989(2)	176.8(1)	+0.056	+3.0	+4.7	+2.8	+3.7	
6	NH_2Ph (**1**)	2.129(1)	1.992(2)	178.2(1)	+0.035	+3.8	+3.5	+5.0	+4.1	
7	anisidine	2.118(2)	1.995(3)	179.1(1)	+0.033	+3.9	+3.4	+5.7	+4.2	
8	py	2.068(3)	1.998(5)	178.0(2)	+0.054	+1.6	+4.2	+0.7	+2.5	GXMPYC10
9	1,2-Me_2Im	2.086(1)	2.001(2)	176.6(1)	+0.062	+1.6	+3.4	+2.0	+2.0	
10	N-iminopy	2.038(6)	2.006(8)	172.6(3)	+0.059	+1.3	+2.7	+1.0	+1.3	GLYICO
11	1MeIm	2.058(5)	2.009(7)	178.0(3)	+0.061	+4.1	+4.4	+3.9	+4.2	MGXIMC
12	PMe_3	2.291(1)	2.011(3)	179.2(2)	+0.035	+2.4	+1.8	+3.2	+2.0	BECTEI
13	$P(OMe)_2Ph$	2.287(1)	2.013(5)	178.4(2)	+0.060	+3.5	+4.8	+2.3	+3.1	DARCEE
14	$P(OMe)_3$	2.256(4)	2.014(14)	177.2(5)	+0.093	+10.2	+10.6	+7.2	+8.6	
15	$P(^cHex)_3$	2.463(5)	2.016(5)	179.1(2)	+0.123	+8.6	+12.5	+2.7	+8.6	BECTIM
16	PMe_3	2.295(1)	2.019(3)	178.5(2)	+0.058	+5.4	+5.6	+5.3	+5.5	BECTEI
17	$P(OMe)Ph_2$	2.352(1)	2.019(6)	175.1(2)	+0.089	+6.5	+8.8	+3.8	+7.0	DARCII
18	PPh_3	2.418(1)	2.026(6)	175.4(2)	+0.111	+11.2	+13.6	+9.2	+12.1	MGLPCO
19	Ph(CO)CHpy	2.19(1)	2.04(1)	174.9(4)	+0.074	+12.0	+11.7	+12.6	+12.1	BPMGCP

[a] Bond lengths and bond angles from Refs. 3 and 4. Im = imidazole, Me_3Bzm = 1,5,6-trimethylbenzimidazole, pyCH(CO)Ph = benzoyl(1-pyridinio)methanide. [b] $\alpha 1$ = dihedral angle between mean planes N1–2, C2–3 and N3–4, C6–7; $\alpha 2$ = N1–2, C1–4 and N3–4, C5–8; $\alpha 3$ = O1–2, N1–2, C2–3 and O3–4, N3–4, C6–7; $\alpha 4$ = O1–2, N1–2, C1–4 and O3–4, N3–4, C5–8; (for numering scheme see Figs. 1–3). [c] Refcodes [14] from the Cambridge Structural Database.

Bond lengths and angles of the $Co(DH)_2$ moiety are very similar in all the complexes, and fall within the range reported for several organometallic cobaloximes [4].

In **1** and **2** a water molecule of crystallization forms hydrogen bonds to the oxime bridge oxygens. In each structures the water molecule bridges two molecules of the complexes through short contacts, as follows: with O(1) (2.839(2) Å in **1** and 2.859(2) Å in **2**) of the molecule at x, y, z; and O(4) (2.846(2) Å in **1** and 2.974(2) Å in **2**) of the molecules at $1 - x$, $-y$, $1 - z$ in **1** and $1 - x$, $-y$, $-z$ in **2**, respectively. There are additional short contacts with N(5) of 3.010(2) Å in **1** and of 3.038(3) Å in **2**.

The orientation of $PhNH_2$ with respect to the equatorial moiety is essentially the same in **1** and **2**, and is sketched in Fig. 4a; that of $PPh(^cHex)_2$ (**3**) is shown in Fig. 4b. The phenyl groups of both $PhNH_2$ and $PPh(^cHex)_2$ lie above one of the five membered ring of the DH unit. The N–Co–C axial fragments are characterized by the geometrical values reported in Table 5 and 6, in which the d and α values are also shown and compared with those or some closely related cobaloximes. The distortions of the Co–R fragment are very similar in **2** and **3**, with Co–C–C angles largely distorted from the tetrahedral value. These angles are similar to those found in the analogous py and PPh_3 derivatives [15] (Table 6) and in cobaloximes with neopentyl (neo-C_5H_{11}) groups [16].

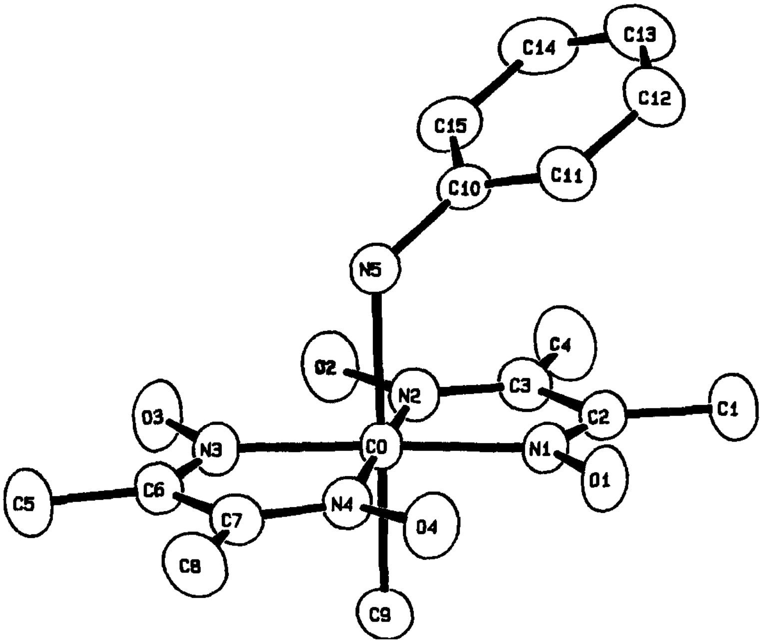

Fig. 1. ORTEP drawing (50% probability thermal ellipsoids) and labeling scheme for non-hydrogen atoms of **1**.

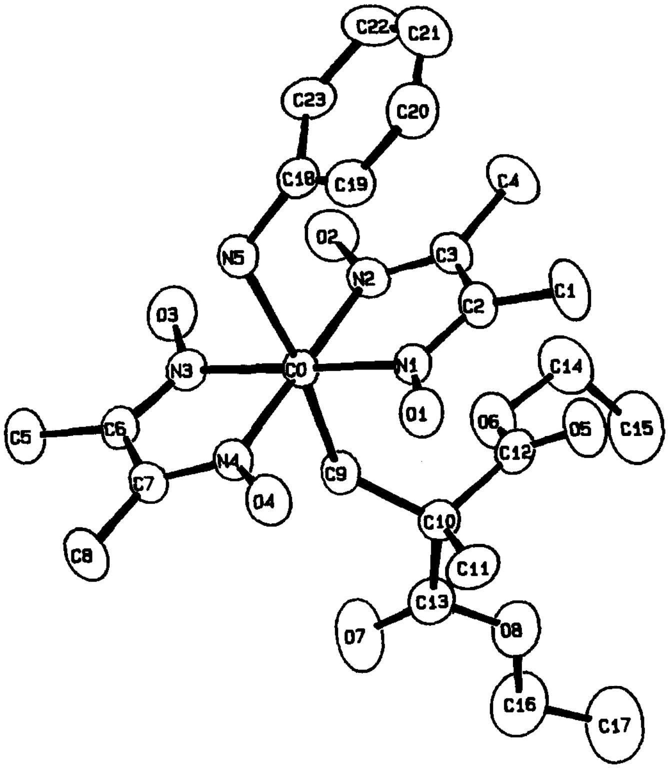

Fig. 2. ORTEP drawing (50% probability thermal ellipsoids) and labeling scheme for non-hydrogen atoms of **2**.

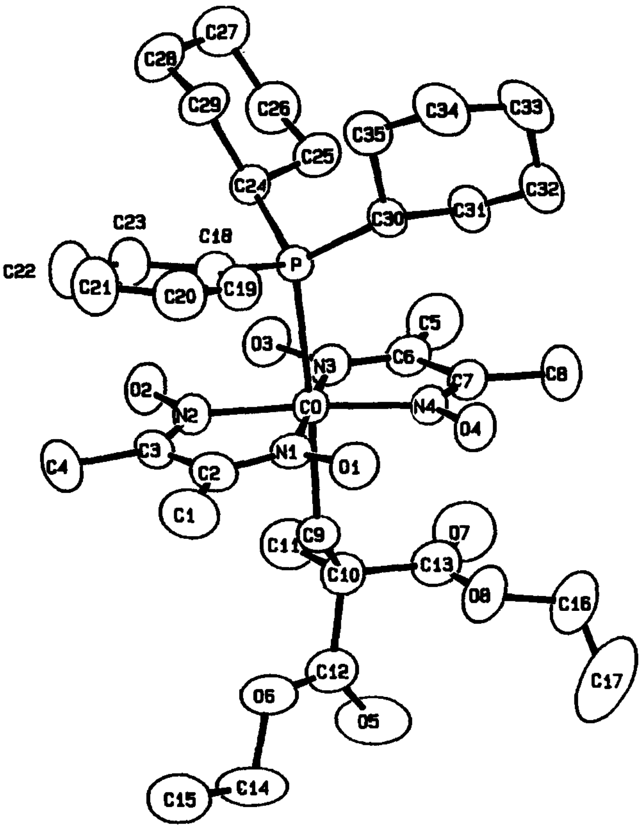

Fig. 3. ORTEP drawing (50% probability thermal ellipsoids) and labeling scheme for non-hydrogen atoms of 3.

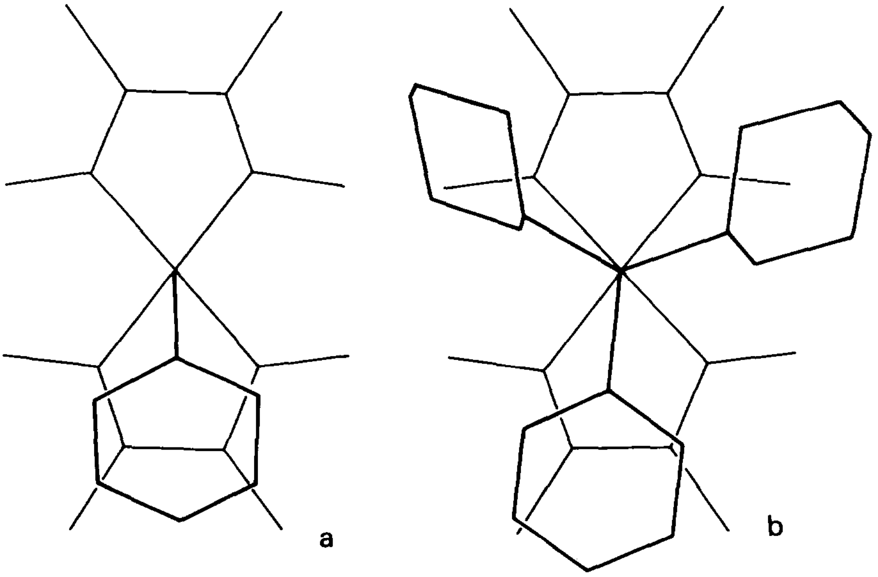

Fig. 4. Orientation of NH_2Ph (a) and $PPh(^cHex)_2$ ligand (b) with respect to the equatorial moiety $Co(DH)_2$ in compound 2 and 3, respectively.

Table 6

Geometry of the R–Co–L axial fragment [a] and d and $\alpha 1$ [b] values for $LCo(DH)_2CH_2C(CO_2Et)_2Me$ complexes

L	Co–L (Å)	Co–C (Å)	L–Co–C (°)	C–C (Å)	Co–C–C (°)	d (Å)	$\alpha 1$ (°)	Refcode [c]
NH_2Ph (**2**)	2.143(2)	2.035(2)	170.9(1)	1.537(3)	126.8(2)	−0.014	−2.6	
py	2.075(4)	2.047(5)	176.0(2)	1.537(7)	125.4(4)	−0.030	−11.0	CUKLUP
PPh_3	2.460(1)	2.062(2)	173.3(2)	1.550(4)	127.2(2)	+0.018	−5.2	CUKLOJ
$PPh(^cHex)_2$ (**3**)	2.428(1)	2.078(3)	170.6(1)	1.538(4)	128.1(2)	+0.053	+8.9	

[a] Bond lengths and bond angles from Refs. 3 and 4. [b] $\alpha 1$ defined in Table 5. [c] Refcodes [14] from the Cambridge Structural Database.

Table 7

Linear regression parameters and correlations coefficients of Co–Me bond lengths vs. d and αi ($n = 19$, see Table 5)

	d	$\alpha 1$	$\alpha 2$	$\alpha 3$	$\alpha 4$
a	1.984(11)	1.994(9)	1.993(9)	1.996(10)	1.994(9)
b	0.36(8)	0.0029(5)	0.0025(4)	0.0029(6)	0.0028(5)
r	0.742	0.839	0.822	0.778	0.833

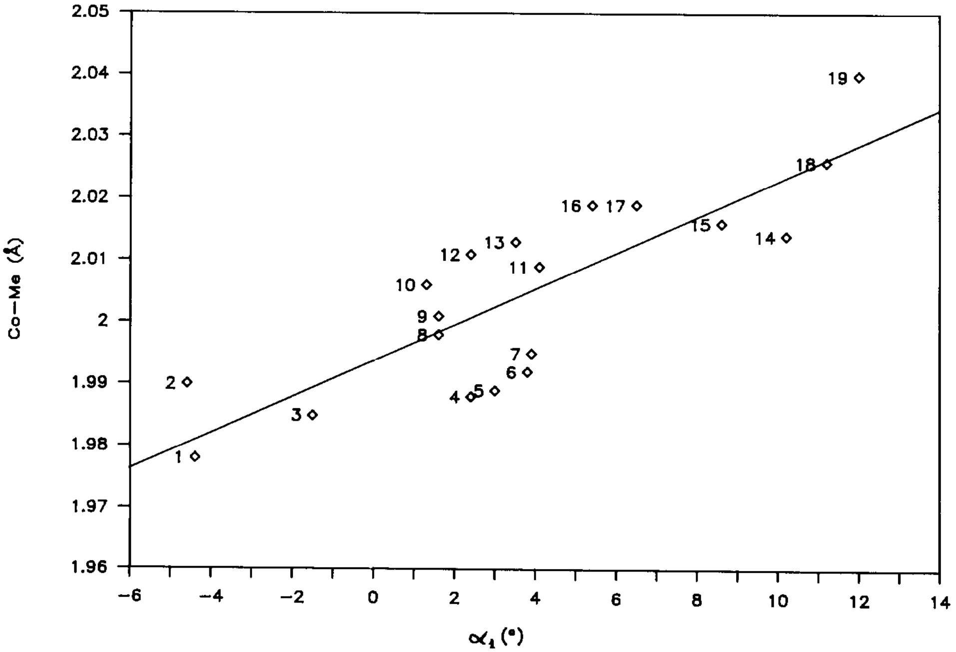

Fig. 5. Plot of Co–Me bond lengths vs. $\alpha 1$ for the cobaloximes listed in Table 5.

Comparison of the $PhNH_2$ cobaloximes with the py analogues reveals an increase of the Co–N(axial) bond length of 0.06–0.07 Å, but no appreciable difference in the Co–C distance. However, the Co–C bond lengths are slightly but significantly smaller than those in the P-donor cobaloximes (Table 5 and 6). It has been suggested [3,4] that the effective bulk of the axial ligands in cobaloximes may be assessed in terms of the amount of the Co–C bond lengthening and of the values of d and α. This is confirmed by the data in Table 5 and 6, where both for R = Me and $CH_2C(CO_2Et)_2Me$, increase in the bulk of the neutral ligand causes an increase in the Co–C bond length, which parallels the increase in d and α values towards positive values ("*trans* steric influence" [16]). That is, the lengthening of the Co–C bond is accompanied by a bending of the DH ligands from downward- to upward-pointing (with respect to the alkyl group). The structural trend is similar to that previously noted for neo-$C_5H_{11}Co(DH)_2L$ complexes [17].

Although slight differences are observed in the dihedral angles α for the same molecule depending upon the choice of the atom set, the displacement d of the cobalt atom and the interplanar angles vary in parallel, and exhibit a fairly linear correlation with the Co–Me bond lengths; linear regression equations and correlation coefficients, r, are listed in Table 7. A plot of Co–Me bond lengths vs. $\alpha 1$, showing the best least-squares line, is presented in Fig. 5. The dihedral angle, $\alpha 1$, is calculated by omitting oxygen and methyl carbon atoms that are in terminal positions and so may be influenced by packing forces.

The observed structural deformations have implications for the energy terms in the Co–C homolysis. From the results of kinetic and thermodynamic studies Halpern [2,18] concluded that increase in the bulk of L significantly decreases the Co–C bond dissociation energy of model compounds. The results provide support for the view that conformational changes in the corrinoid promote Co–C bond weakening and thus make easier its cleavage in B_{12}-dependent catalytic reactions [1,16,19].

Furthermore, the data in Table 6 show that for the $CH_2C(CO_2Et)_2Me$ group, the L–Co–C angle significantly deviates from the ideal value of 180°, and this effect is particularly marked when the neutral ligand is "not symmetric" such as $PhNH_2$, and $PPh(^cHex)_2$. The distortion of the L–Co–C angle acts to reduce the effective bulk of the "unsymmetrical" ligands such as $CH_2C(CO_2Et)_2Me$, relieving some of the steric strain that would otherwise require larger distortions of the Co–C, d and α parameters. On the other hand, if these "unsymmetrical" ligands have side groups, such as phenyls, which can stack with the DH ligands (Fig. 4) there may be a further decrease in the α value, especially in the presence of bulky R groups. In terms of this hypothesis, from the data in Table 5 we can conclude that $PhNH_2$ and py have, as a whole, a similar bulk, although they cause somewhat different distortions.

Balancing of the various kinds of distortion, depending upon the "shape" of the neutral ligand, may be also responsible for the shorter Co–P distance in the $PPh(^cHex)_2$ derivative compared with that in the PPh_3 analogue (Table 5); conclusions based on the bulk of each ligand would lead to an inverted order.

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