Distortions induced by Electronic and Steric Properties of Axial Ligands in Pseudo-octahedral Cobaloximes. Crystal and Molecular Structures of *trans*-Bis(dimethylglyoximato)n-pentyl(triphenylphosphine)cobalt(III) and *trans*-Aquabis(dimethylglyoximato)n-pentylcobalt(III)

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The crystal structures of two cobaloximes, $[Co(Hdmg)_2(CH_2CMe_3)(OH_2)]$ (1) (Hdmg = dimethylglyoximate monoanion) and $[Co(Hdmg)_2(CH_2CMe_3)(PPh_3)]$ (2), containing a neutral ligand of widely differing bulk *trans* to the same alkyl group, are reported and discussed. Both compounds crystallize in the space group *Pbca* with cell parameters a = 26.91(1), b = 14.449(8), and c = 9.535(6) Å, and Z = 8, for (1) and a = 19.120(8), b = 15.998(8), c = 20.62(1) Å, and Z = 8 for (2). Both structures were solved by Patterson and Fourier methods and refined by anisotropic least-squares methods to a final R 0.045 for (1) and 0.035 for (2) using respectively 1 405 and 2 245 independent reflections having $I \geqslant 3\sigma(I)$, using Mo-K_α radiation to a maximum 2θ = 56°. The H_2O–Co–CH_2CMe_3 fragment in (1) is characterized by an O–Co–C angle of 172.4(3)° and Co–C and Co–O bond lengths of 2.044(7) and 2.056(5) Å. The Co–CH_2–CMe_3 angle is 126.9(5)°. The Ph_3P–Co–CH_2CMe_3 fragment in (2) is characterized by a Co–P distance of 2.460(1) Å which is the longest so far reported for Co^{III}–PPh_3 compounds. The n-pentyl group is disordered with mean Co–C bond lengths of 2.117(9) Å and P–Co–C bond angles of 166.6(2)°. The corresponding Co–CH_2–CMe_3 angles average to 129.2(7)°. Comparative steric effects are discussed on the basis of the increasing bulk of R and L in these and related complexes of formula $[Co(Hdmg)_2(CH_2R)L]$. It is suggested that distortions involving the metal centre and arising from the interaction of the axial CH_2R group and the two equatorial Hdmg ligands affect the co-ordination C–Co–N(equatorial) bond angles, the Co–CH_2–R bond angle, and the Co–C bond length.

OUR previous work on coenzyme B_{12} models, namely pseudo-octahedral cobaloximes $[Co(Hdmg)_2XL]$, where L = neutral ligand, X = negative monodentate ligand, and Hdmg = monoanion of dimethylglyoxime, has shown that a wide range of distortions occur: lenthening of Co–L [1,2] and Co–X bond lengths,[3,4] geometry variations [5,6] in both X and L, bending of Hdmg units, and displacements of the Co atom above the N_4 equatorial plane.[7,8] Attempts to correlate structural deformations with variations in reactivity [9,10] (up to factors of 10^5) and spectral properties [10-15] of this system have been recently reported and the implication of these structural changes with regard to Co–C bond cleavage has been discussed.[3-6]

Particularly, we have shown that in $[Co(Hdmg)_2(CH_2CMe_3)(py)]$ [6] (py = pyridine) both an increase of the Co–C bond length and a widening of Co–CH_2–R angle (up to 130°) occur, with a bending of the two Hdmg units of 5.2° without any appreciable displacement of Co from the N_4 equatorial plane. On the other hand we have shown [3,4] that the substitution of py by PPh_3 in $[Co(Hdmg)_2(R')(py)]$, where R' = Me [16] or i-C_3H_7,[3] leads to a significant increase of the Co–C bond length, of the displacement of the Co atom from the equatorial plane towards P, and of the bending angle (α) between the two Hdmg units.

In order to obtain new insight into the effect of ligands L on structural properties of cobaloximes, it was of interest to structurally characterize n-pentyl cobaloxime derivatives having on the one hand a bulky ligand L such as PPh_3 and on the other, a small ligand such as water. Thus, we report the crystal and molecular structures of *trans*-aquabis(dimethylglyoximato)n-pentylcobalt(III) (1) and *trans*-bis(dimethylglyoximato)n-pentyl(triphenylphosphine)cobalt(III) (2).

EXPERIMENTAL

Crystal Data.—Crystals of $[Co(Hdmg)_2(CH_2CMe_3)(OH_2)]$ (1) were obtained by slow crystallization from a methanol–water solution (1 : 1 v/v) at 25 °C. Crystals of $[Co(Hdmg)_2(CH_2CMe_3)(PPh_3)]$ (2) were obtained from an acetone–water solution (1 : 1 v/v) at 0—5 °C. The cell parameters were determined from Weissenberg and precession photographs and refined on a SIEMENS AED single-crystal diffractometer. Crystal data are given in Table 1. One check reflection intensity, during the collection of diffraction data for both complexes, was measured every 100 reflections and did not show any systematic variation throughout the data re-

TABLE 1

Crystallographic data for (1) and (2)

Formula	$C_{13}H_{27}CoN_4O_5$	$C_{31}H_{40}CoN_4O_4P$
M	378.4	622.7
a/Å	26.91(1)	19.120(8)
b/Å	14.449(8)	15.998(8)
c/Å	9.535(6)	20.62(1)
D_m/g cm^{-3}	1.35	1.31
D_c/g cm^{-3}	1.36	1.31
Z	8	8
Space group	*Pbca*	*Pbca*
μ(Mo-K_α)/cm^{-1}	9.9	6.6
Crystal dimensions/cm	0.05 × 0.02 × 0.07	0.05 × 0.05 × 0.08
No. of collected reflections	5 100	7 500
No. of independent reflections, $I \geqslant 3\sigma(I)$	1 405	2 245
$2\theta_{max.}$/°	56	56
R	0.045	0.035
R'	0.067	0.046

cording. The intensities for which $I \geqslant 3\sigma(I)$ were corrected for Lorentz and polarization factors but not for absorption.

Solution and Refinement of Structures.—Both structures were solved by conventional Patterson and Fourier methods and refined by block-diagonal least-squares methods. The final cycles were done by full-matrix least-squares methods including all hydrogen atom contributions (held constant at $B = 5$ Å^2) and anisotropic temperature factors for non-hydrogen atoms for (1). For (2), the hydrogen atom contributions (held constant at $B = 5$ Å^2) and anisotropic temperature factors for non-hydrogen atoms were included, except those of the n-pentyl group. Final R values are given in Table 1.

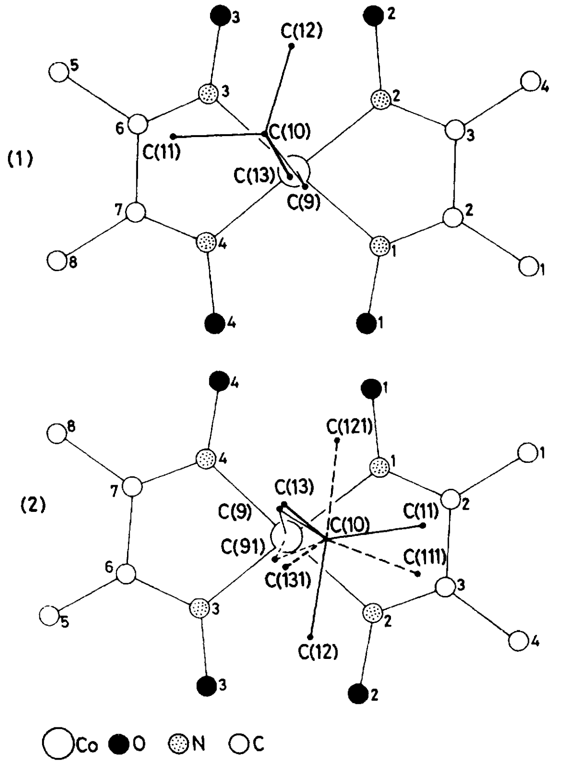

FIGURE 1 A view along the Co–OH$_2$ and Co–P bonds for (1) and (2) respectively. The atom numbering schemes for the Me$_3$CCH$_2$–Co(Hdmg)$_2$ units are also shown

The n-pentyl group in (2) was found to be clearly disordered. Inspection of Fourier and $|F_o - F_c|$ maps, including the contribution of the Ph$_3$P–Co(Hdmg)$_2$ moiety, clearly showed two peaks, C(12) and C(121), with electron densities corresponding to about one-half of a carbon atom each. Furthermore, three broadened banana-shaped peaks were found nearly centred at the midpoint of the pairs C(9) $\cdots$ C(91), C(11) $\cdots$ C(111), and C(13) $\cdots$ C(131), while a well resolved peak, with electron density corresponding to one carbon atom, was found at the C(10) position. From the Fourier map and the geometry of a n-pentyl group, this disorder can be attributed to two different orientations of the alkyl group with respect to the Co(Hdmg)$_2$ plane, as shown in Figure 1. The final refinement confirms this choice and suggests that the occupancies of the C(9)—C(13) and C(91)—C(131) groups of atoms were 0.6 and 0.4 respectively. It may be of interest to note that the two orientations of the n-pentyl group are nearly related by a mirror plane containing Co and C(10) and normal to the Co(Hdmg)$_2$ unit (Figure 1).

The final weighting scheme was $w = 1/(A + |F_o| + B|F_o|^2)$, where $A = 24.1$ and $B = 0.0046$ for (1) and $A = 36.6$ and $B = 0.005$ for (2) were chosen so as to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of F_o and $\sin(\theta/\lambda)$. Atomic scattering factors were those given in ref. 17. All the calculations were done using the computer pro-

TABLE 2

Fractional atomic co-ordinates ($\times 10^3$ for H, $\times 10^4$ for other atoms) for compounds (1) and (2) with estimated standard deviations in parentheses [a]

Compound (1)	x	y	z
Co	1 268(0)	1 109(1)	2 277(1)
O(1)	1 384(2)	1 166(4)	−688(5)
O(2)	358(2)	1 233(4)	3 854(6)
O(3)	1 162(2)	1 236(4)	5 236(5)
O(4)	2 177(2)	1 000(4)	688(5)
O(5)	1 296(2)	2 531(3)	2 302(5)
N(1)	1 066(3)	1 174(4)	362(6)
N(2)	580(2)	1 169(4)	2 531(6)
N(3)	1 481(2)	1 145(4)	4 173(6)
N(4)	1 961(2)	1 065(4)	1 985(5)
C(1)	353(4)	1 255(8)	−1 272(10)
C(2)	580(3)	1 204(5)	162(9)
C(3)	297(3)	1 239(6)	1 458(9)
C(4)	−246(4)	1 354(8)	1 539(12)
C(5)	2 195(4)	1 241(7)	5 815(9)
C(6)	1 960(3)	1 179(5)	4 362(7)
C(7)	2 242(3)	1 113(5)	3 056(8)
C(8)	2 806(3)	1 098(7)	3 000(11)
C(9)	1 232(3)	−289(5)	1 972(8)
C(10)	1 270(3)	−1 043(5)	3 094(7)
C(11)	1 761(4)	−1 085(7)	3 869(11)
C(12)	835(4)	−978(7)	4 163(10)
C(13)	1 209(4)	−1 963(5)	2 270(10)
H(1)	190	130	0
H(2)	65	120	470
H(3)	120	300	150
H(4)	120	300	300
H(11)	62	121	−202
H(21)	17	186	−140
H(31)	11	74	−143
H(14)	−36	136	257
H(24)	−43	82	108
H(34)	−36	194	110
H(15)	193	128	655
H(25)	242	179	588
H(35)	240	67	599
H(18)	291	106	198
H(28)	294	58	353
H(38)	294	171	338
H(19)	150	−43	126
H(29)	90	−39	150
H(111)	177	−160	456
H(211)	184	−49	434
H(311)	205	−121	316
H(113)	124	−250	292
H(213)	149	−201	154
H(313)	89	−198	178
H(112)	86	−146	490
H(212)	50	−105	367
H(312)	83	−35	464

Compound (2)	x	y	z	B(Å^2)
C(9)	969(4)	744(6)	1 451(4)	3.4(2)
C(11)	1 668(6)	1 435(7)	482(5)	5.7(3)
C(12)	1 899(6)	−94(8)	805(6)	6.6(3)
C(13)	756(6)	290(7)	322(5)	5.5(2)
C(91)	1 315(6)	388(8)	1 463(6)	3.1(2)
C(111)	1 981(7)	1 123(9)	524(7)	4.2(3)
C(121)	630(9)	1 299(11)	653(8)	5.9(4)
C(131)	1 166(8)	−112(11)	328(8)	5.1(3)
Co	1 445(0)	1 091(0)	2 331(0)	
P	1 692(1)	1 632(1)	3 424(1)	

Table 2 (*continued*)

Compound (2)	*x*	*y*	*z*
O(1)	774(2)	2 640(2)	1 993(2)
O(2)	2 859(2)	600(2)	2 094(2)
O(3)	2 095(2)	−483(2)	2 605(2)
O(4)	12(2)	1 552(2)	2 510(2)
N(1)	1 382(2)	2 196(2)	2 011(2)
N(2)	2 377(2)	1 220(3)	2 052(2)
N(3)	1 492(2)	−27(2)	2 616(2)
N(4)	498(2)	948(3)	2 581(2)
C(1)	2 002(4)	3 406(4)	1 529(3)
C(2)	1 958(3)	2 535(3)	1 803(2)
C(3)	2 555(3)	1 962(3)	1 840(2)
C(4)	3 290(3)	2 164(4)	1 635(3)
C(5)	861(4)	−1 252(4)	3 063(3)
C(6)	918(3)	−363(3)	2 833(2)
C(7)	324(3)	217(3)	2 820(2)
C(8)	−402(3)	6(4)	3 047(3)
C(10) [b]	1 320(3)	656(3)	774(3)
C(14)	2 576(3)	1 806(3)	3 761(2)
C(15)	3 185(2)	1 580(3)	3 426(2)
C(16)	3 836(3)	1 695(4)	3 718(3)
C(17)	3 893(3)	2 022(4)	4 339(3)
C(18)	3 293(3)	2 243(4)	4 663(3)
C(19)	2 638(3)	2 138(4)	4 381(3)
C(20)	1 353(3)	991(3)	4 098(2)
C(21)	1 633(3)	177(4)	4 140(3)
C(22)	1 462(4)	−341(4)	4 662(3)
C(23)	1 026(5)	−49(5)	5 133(4)
C(24)	753(5)	740(6)	5 112(4)
C(25)	911(4)	1 281(5)	4 591(3)
C(26)	1 288(3)	2 671(3)	3 507(2)
C(27)	1 695(3)	3 392(3)	3 449(3)
C(28)	1 382(3)	4 181(4)	3 468(3)
C(29)	671(3)	4 251(4)	3 546(3)
C(30)	262(3)	3 543(4)	3 590(3)
C(31)	559(3)	2 751(4)	3 569(3)
H(1)	30	210	220
H(2)	255	10	235
H(11)	153	369	155
H(21)	216	339	106
H(31)	235	375	178
H(14)	361	165	171
H(24)	349	263	189
H(34)	331	229	116
H(15)	133	−155	304
H(25)	51	−157	280
H(35)	70	−127	353
H(18)	−72	50	300
H(28)	−39	−16	352
H(38)	−60	−48	280
H(115)	316	133	298
H(116)	427	155	347
H(117)	435	210	455
H(118)	333	247	511
H(119)	221	229	463
H(121)	196	−2	379
H(122)	167	−91	469
H(123)	89	−43	550
H(124)	44	91	547
H(125)	71	188	457
H(127)	222	335	340
H(128)	167	469	342
H(129)	45	482	357
H(130)	−26	359	363
H(131)	25	224	360

[a] The isopropyl C atoms of (2) are treated isotropically. [b] $B = 3.7(1)$ Å^2.

grams from *X*-RAY 70.[18] Final positional parameters are given in Table 2. Anisotropic thermal parameters, calculated and observed structure factors, and deviations from least-squares planes are listed in Supplementary Publication No. SUP 23201 (27 pp.).*

RESULTS AND DISCUSSION

Description of the Structures.—The atom numbering scheme of the crystallographically independent molecules of (1) and (2) is given in Figures 1 and 2. Bond lengths and angles are listed in Table 3.

The four N atoms of the Co(Hdmg)$_2$ unit are coplanar within ±0.03 Å for (1) (with a slight tetrahedral distortion) and ±0.003 Å for (2). The cobalt atom is displaced 0.043 Å from their mean plane towards the n-pentyl group in (1) and 0.037 Å towards PPh$_3$ in (2). The Co(Hdmg)$_2$ unit of (1) deviates from planarity with a bending angle of −6.9° while it is nearly planar in (2), the angle α being 2.2°. These differences can best be seen from the side views in Figure 2. Bond lengths and angles of the Co(Hdmg)$_2$ moiety are quite normal in both compounds.

In (1), the H_2O–Co–CH_2CMe_3 fragment is characterized by a O–Co–C angle of 172.4(3)° and Co–C and Co–O bond lengths of 2.044(7) and 2.056(5) Å respectively. The Co–CH_2–CMe_3 angle is 126.9(5)°.

In (2), the Ph_3P–Co–CH_2CMe_3 fragment is characterized by a Co–P distance of 2.460(1) Å which is longer than those already reported (Table 4). The Co–C bond lengths and P–Co–C bond angles in the two orientations of the n-pentyl group are 2.104(8) and 2.13(1) Å and 165.0(2) and 168.2(3)° respectively. The corresponding Co–CH_2–CMe_3 angles are 127.7(5) and 130.7(8)° respectively. Finally, the n-pentyl geometries in (1) and (2) exhibit similar distortions of bond angles (Table 3).

The orientation of the alkyl group with respect to the equatorial plane, defined by the dioxime ligands, in (1) and (2) is shown in Figure 1. As previously observed,[6] the C(9)–C(10) bond lies preferentially almost over one of the equatorial Co–N bonds (see below). We note that the two orientations found in (2) correspond to the C(9)–C(10) bond being almost oriented along the Co–N(2) bond and C(91)–C(10) along Co–N(1) respectively. In both cases, the CMe$_2$ grouping lies in a plane nearly parallel to the CoN$_4$ equatorial plane.

Structural Comparisons.—Comparative steric effects can best be discussed by first considering the effects of separately increasing the bulk of R and L and then by considering molecules containing R and L which are both bulky. For this discussion we use the compound [Co(Hdmg)$_2$(CH$_3$)(OH$_2$)] [19] as a reference (Table 4). Bond angle changes are considered in detail later.

Increasing the bulk of CH$_2$R from methyl to n-pentyl has the following consequences: (*a*) the Co–C bond length increases by 0.05 Å; (*b*) the Co atom moves out of the plane of the four equatorial N atoms towards the n-pentyl group, and (*c*) the angle (α) between the Hdmg units becomes appreciable (−6.9°). In contrast, the Co–OH$_2$ bond is little affected. This is the first case we have found where the displacement of Co is clearly towards CH$_2$R (by 0.043 Å). Complex (1) appears, then, to be a clear-cut example of the Co(Hdmg)$_2$ unit responding to changes in the bulk of R rather than that of L.

Increasing the bulk of L from H_2O to PPh$_3$ with R = H

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

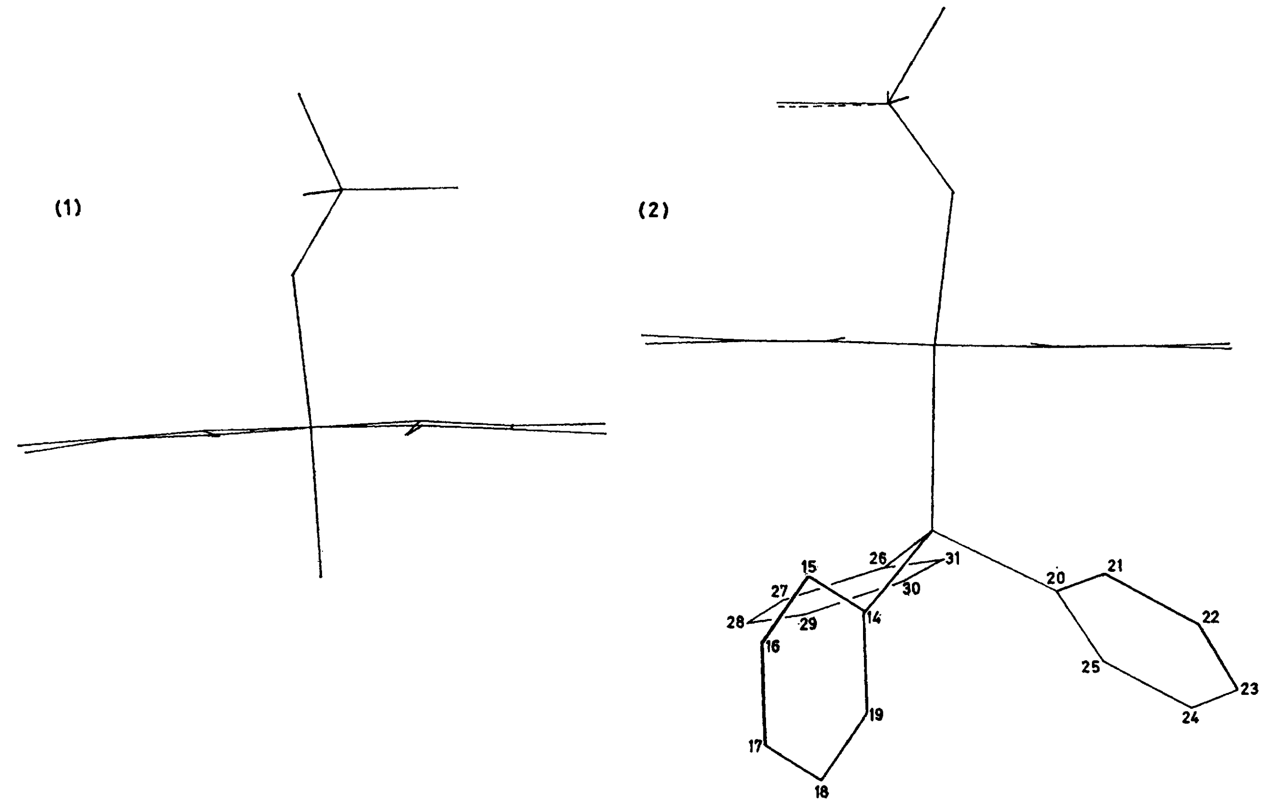

FIGURE 2 Side-views of molecules of (1) and (2). The numbering scheme for carbon atoms of the PPh$_3$ ligand in (2) is also shown

TABLE 3

Bond lengths (Å) and selected bond angles (°) for compounds (1) and (2) with e.s.d.s in parentheses

Compound (1)

(*a*) Bond lengths

Co–O(5)	2.056(5)	N(4)–C(7)	1.273(9)
Co–C(9)	2.044(7)	C(1)–C(2)	1.500(13)
Co–N(1)	1.907(6)	C(2)–C(3)	1.452(12)
Co–N(2)	1.869(6)	C(3)–C(4)	1.474(13)
Co–N(3)	1.897(6)	C(5)–C(6)	1.526(12)
Co–N(4)	1.887(6)	C(6)–C(7)	1.462(10)
N(1)–O(1)	1.317(8)	C(7)–C(8)	1.517(12)
N(1)–C(2)	1.322(11)	C(9)–C(10)	1.530(10)
N(2)–O(2)	1.399(8)	C(10)–C(11)	1.515(13)
N(2)–C(3)	1.279(10)	C(10)–C(12)	1.556(13)
N(3)–O(3)	1.335(8)	C(10)–C(13)	1.553(11)
N(3)–C(6)	1.303(10)	O(1) ··· O(4)	2.517(8)
N(4)–O(4)	1.370(7)	O(2) ··· O(3)	2.534(8)

(*b*) Bond angles

N(1)–Co–N(2)	80.8(3)	N(3)–Co–C(9)	100.2(3)
N(1)–Co–N(3)	175.6(3)	N(4)–Co–O(5)	89.9(3)
N(1)–Co–N(4)	98.2(3)	N(4)–Co–C(9)	89.6(3)
N(1)–Co–O(5)	88.5(2)	O(5)–Co–C(9)	172.4(3)
N(1)–Co–C(9)	84.2(3)	Co–C(9)–C(10)	126.9(5)
N(2)–Co–N(3)	100.1(3)	C(9)–C(10)–C(11)	115.4(7)
N(2)–Co–N(4)	178.7(3)	C(9)–C(10)–C(12)	111.4(7)
N(2)–Co–O(5)	89.4(3)	C(9)–C(10)–C(13)	104.4(6)
N(2)–Co–C(9)	91.0(3)	C(11)–C(10)–C(12)	109.8(7)
N(3)–Co–N(4)	80.9(3)	C(11)–C(10)–C(13)	107.8(7)
N(3)–Co–O(5)	87.2(2)	C(12)–C(10)–C(13)	107.6(7)

Compound (2)

(*a*) Bond lengths

TABLE 3 (*continued*)

Compound (2)

Co–P	2.460(1)	C(3)–C(4)	1.504(8)
Co–C(9)	2.104(8)	C(5)–C(6)	1.503(8)
Co–C(91)	2.128(12)	C(6)–C(7)	1.467(7)
Co–N(1)	1.891(4)	C(7)–C(8)	1.503(8)
Co–N(2)	1.884(4)	C(9)–C(10)	1.555(10)
Co–N(3)	1.885(4)	C(10)–C(11)	1.536(12)
Co–N(4)	1.896(4)	C(10)–C(12)	1.635(13)
N(1)–O(1)	1.363(6)	C(10)–C(13)	1.541(12)
N(1)–C(2)	1.301(7)	C(91)–C(10)	1.484(13)
N(2)–O(2)	1.358(5)	C(10)–C(111)	1.557(15)
N(2)–C(3)	1.309(7)	C(10)–C(121)	1.690(18)
N(3)–O(3)	1.364(6)	C(10)–C(131)	1.563(17)
N(3)–C(6)	1.301(7)	P–C (mean)	1.845(5)
N(4)–O(4)	1.349(5)	C–C(phenyl) (mean)	1.389(9)
N(4)–C(7)	1.312(7)		
C(1)–C(2)	1.505(8)	O(1) ··· O(4)	2.507(5)
C(2)–C(3)	1.466(8)	O(2) ··· O(3)	2.501(5)

(*b*) Bond angles

N(1)–Co–N(2)	81.4(2)	P–Co–C(91)	168.2(3)
N(1)–Co–N(3)	177.5(2)	Co–C(9)–C(10)	127.7(5)
N(1)–Co–N(4)	98.5(2)	Co–C(91)–C(10)	130.7(8)
N(1)–Co–P	90.2(1)	C(9)–C(10)–C(11)	117.8(6)
N(1)–Co–C(9)	85.3(3)	C(9)–C(10)–C(12)	108.9(6)
N(1)–Co–C(91)	101.1(4)	C(9)–C(10)–C(13)	106.1(6)
N(2)–Co–N(3)	98.9(2)	C(91)–C(10)–C(111)	117.4(8)
N(2)–Co–N(4)	177.9(2)	C(91)–C(10)–C(121)	108.3(8)
N(2)–Co–P	93.4(1)	C(91)–C(10)–C(131)	109.6(8)
N(2)–Co–C(9)	100.1(3)	C(11)–C(10)–C(12)	108.4(7)
N(2)–Co–C(91)	84.9(3)	C(11)–C(10)–C(13)	112.0(7)
N(3)–Co–N(4)	81.1(2)	C(12)–C(10)–C(13)	102.6(7)
N(3)–Co–P	92.2(1)	C(111)–C(10)–C(121)	107.0(9)
N(3)–Co–C(9)	92.2(3)	C(111)–C(10)–C(131)	109.5(9)
N(3)–Co–C(91)	76.5(4)	C(121)–C(10)–C(131)	104.2(9)
N(4)–Co–P	88.7(1)	Co–P–C(14)	125.0(2)
N(4)–Co–C(9)	77.8(3)	Co–P–C(20)	115.3(2)
N(4)–Co–C(91)	93.1(3)	Co–P–C(26)	108.8(2)
P–Co–C(9)	165.0(2)		

leads to the following changes: (*a*) the Co–C bond length is slightly increased, (*b*) the Co atom moves out of the N_4 equatorial plane by a substantial amount (0.1 Å) towards PPh_3, and (*c*) the Hdmg units make a large (14°) angle with each other.

Simultaneous increase in the bulk of R and L, as represented in the complex $[Co(Hdmg)_2)(CH_2CMe_3)(PPh_3)]$, has the following structural consequences: (*a*) the Co–C bond length is further increased {0.08—0.10 Å longer than in $[Co(Hdmg)_2(CH_3)(PPh_3)]$}, (*b*) the Co out-of-plane displacement is towards PPh_3 but by only 0.037 Å, and (*c*) the angle between the Hdmg units is away from PPh_3 but is only *ca.* 2°.

The Co–P bond length increase in the n-pentyl derivative may be a consequence of the better electron donation of this group or to a steric *trans* influence.

One excellent way to see the consequence of the bulky t-butyl group of the n-pentyl ligand is to compare bond angles with other $[Co(Hdmg)_2(CH_2R)L]$ compounds (Table 5). From previous studies [6] it is known that in response to steric strain, one C(9)–Co–N (equatorial) bond angle is larger and one smaller and this is also the case for (1) and (2) (Table 3). The substituent R on the $-CH_2-$ group lies preferentially over one N which we call the adjacent N (N_A). The *trans* or ' opposite ' N we label N_o (see Figure 1).

TABLE 4

Axial bond lengths (Å) and bending angles (°) for a series of $[Co(Hdmg)_2(CH_2R)L]$ compounds

CH_2R	Co–C			Co–L			α		
L	CH_3	i-C_3H_7	CH_2CMe_3	CH_3	i-C_3H_7	CH_2CMe_3	CH_3	i-C_3H_7	CH_2CMe_3
PPh_3	2.026(6)	2.22(2)	2.12(1)	2.418(1)	2.412(4)	2.460(1)	14	14	2
py	1.998(5)	2.085(3)	2.060(6)	2.068(3)	2.099(2)	2.081(4)	3	4	−5
H_2O	1.990(5)		2.044(7)	2.058(3)		2.056(5)	0		−7

The results in Table 4 for $[Co(Hdmg)_2(CH_2CMe_3)(PPh_3)]$ fit into the trend if we recognise that py is of a size intermediate between H_2O and PPh_3. However, the Co–N(py) bond length responds slightly more to a change from methyl to n-pentyl than is found in the two analogous complexes with L = H_2O above. Similarly, there is an increase in the Co–P bond length in going from methyl to n-pentyl in the compounds with L = PPh_3. The effects are small. However, all the alkyl compounds exhibit a significant *trans* influence. For example, in $[Co(Hdmg)(NO_2)(OH_2)]$ [20] the Co–OH_2 bond length is found to be 1.980(6) Å and for other compounds a ' normal ' Co^{III}–OH_2 distance is in the range 1.94(2) [21] to 1.948(7) Å.[22]

The isopropyl series is of interest although only the py and PPh_3 complexes have been structurally characterized. It appears that the rather weak Co–C bond does not allow this group to exhibit as strong a *trans* influence as one might expect for an isopropyl group. The presence of the two methyl groups does not permit angular distortions (within the ethyl group) which appear to allow the shorter Co–C bonds seen in the n-pentyl derivatives. This leads to the remarkably long Co–C bond seen in the $[Co(Hdmg)_2(i\text{-}C_3H_7)(PPh_3)]$ derivative. The Co–P bond in this compound has about the same length as in the methyl derivative, presumably because of the weakened *trans* influence of the isopropyl group.

In Table 5, the four angles, C(9)–Co–N_A(N_o) and L–Co–N_A(N_o), are reported for a series of $[Co(Hdmg)_2(CH_2R)L]$ compounds. Their sum is always very close to 360°, showing that such a distortion takes place nearly in the plane defined by the two equatorial N atoms, Co, the L donor atom, and C(9), without involving the other two equatorial N atoms which are aligned on a line nearly normal to the above plane. The distortion may be viewed as a bending in that plane of C(9) towards N_o. This interpretation is also supported by the values of C(9)–Co–L(donor atom) angles reported in Table 5.

Bond angle changes within the alkyl group are less easily evaluated since accurate positions are not available for the H atoms. However, rather large distortions are found for the n-pentyl group with the Co–C(9)–C angles being appreciably greater than tetrahedral. For (1), this angle is 126.9(5)° and for the two forms of (2), the values are 127.7(5) and 130.7(8)°. These do not differ greatly from the value found for the pyridine derivative of 130.3(4)°. It seems likely that this angle may be about the maximum distortion which is energetically feasible and that when larger steric effects are introduced, other changes occur, such as the lengthening of the Co–C bond. In the isopropyl compounds, Co–C bond lengthening appears to be an energetically more reasonable option than angular distortions within the alkyl group. Thus, distortions involving the metal centre and

TABLE 5

Deformation of the co-ordination bond angles in a series of $[Co(Hdmg)_2(CH_2R)L]$ complexes; all e.s.d.s are $\leqslant 0.4°$

R/L	C(9)–Co–N_A	C(9)–Co–N_o	L–Co–N_A	L–Co–N_o	Sum	C(9)–Co–L
NO_2/py [a]	94.2	85.1	89.8	91.0	360.1	176.0
CO_2Me/py [b]	94.9	84.6	89.7	90.7	359.9	
CMe_3/py [c]	96.0	85.0	88.6	90.4	360.0	174.7
CMe_3/H_2O [d]	100.2	84.2	88.5	88.7	360.1	172.4
CMe_3/PPh_3 [d]	100.1	77.8	93.4	88.7	360.0	165.0
	101.1	76.5	90.2	92.2	360.0	168.2

[a] See ref. 5. [b] P. G. Lenhert, *Chem. Commun.*, 1967, 980. [c] See ref. 2. [d] This work.

arising from the interaction of the axial CH_2R group and the equatorial ligands affect (*i*) co-ordination C–Co–N-(equatorial) bond angles, (*ii*) the $Co{-}CH_2{-}R$ bond angle, and (*iii*) the Co–C bond length. Since distortion (*i*) is observed also when R is not bulky and without distortions (*ii*) and (*iii*), as in the case of $[Co(Hdmg)_2(CH_2NO_2)(py)]$,[5] and distortion (*iii*) is observed especially in $[Co(Hdmg)_2(i\text{-}C_3H_7)L]$ [3,4] (L = py or PPh_3) where other distortions cannot take place, it is interesting to speculate that the above order may be indicative of the relative energy needed to produce structural changes. In addition, such distortions are difficult to explain in terms of repulsions between *d* electrons of Co and bonding electron pairs in the alkyl groups as suggested by Chemaly and Pratt [23] for alkyl cobalamins.

This work has been carried out with partial financial support by a N.A.T.O. grant (to L. G. M. and L. R.), by a grant from C.N.R., Roma (to L. R.), and by N.I.H. grant GM 29225 (to L. G. M.).

[1/1108 *Received*, 14*th July*, 1981]

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