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Geometrical Distortions in Octahedral i-Propylcobaloximes

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Recent results [1–4] have shown that the electronic and steric properties of axial ligands induce significant distortions in the vitamin B_{12} model molecules, namely the pseudo-octahedral cobaloximes, $[LCo(DH)_2X]$, where DH = monoanion of dimethylglyoxime, L = neutral ligand and X = negative monodentate ligand. In particular, compounds having the same L but different primary alkyl ($X = CH_2R$) [1, 2] and those having different L ligands but the same $X = CH_2CMe_3$ [3, 4] have been structurally characterized. These results have shown that regular geometrical changes in the bonding of the alkyl groups to cobalt may have implications with respect to the proposed mechanism of the homolytic fission of the Co–C bond in vitamin B_{12} coenzymes [5, 6].

On the other hand, initial observations on the secondary alkyl bound-to-cobalt groups, namely i-propyl [7, 8], indicate that the structural effects may be different to those found for primary alkyl ligands. To obtain further insight into the structural properties of cobaloximes containing secondary alkyl groups, we report the structure of $[(CH_3C(CH_2O)_3PCo(DH)_2(i\text{-}C_3H_7)]$ (I), where the neutral ligand is a phosphite having a very small cone angle [9].

TABLE I. Fractional Coordinates (×10^4) of Non-hydrogen Atoms of I.

	X	Y	Z
Co	2406(1)	2500(0)	2441(1)
P	4314(1)	2500(0)	3433(2)
O(1)	1939(3)	241(2)	3701(4)
O(2)	2911(3)	238(3)	1174(4)
O(3)	4674(3)	1427(3)	4447(5)
O(4)	5350(4)	2500(0)	2237(6)
N(1)	1858(3)	1416(3)	3896(4)
N(2)	2942(3)	1421(3)	965(4)
C(1)	971(4)	1101(6)	6398(6)
C(2)	1398(3)	1859(4)	5138(5)
C(3)	3428(4)	1862(5)	−231(5)
C(4)	3982(6)	1103(8)	−1436(7)
C(5)	5937(4)	1414(5)	5023(7)
C(6)	6595(6)	2500(0)	2839(9)
C(7)	6609(5)	2500(0)	4506(7)
C(8)	7904(5)	2500(0)	5125(10)
C(91)	553(10)	2500(0)	1788(14)
C(92)	783(11)	2500(0)	1128(16)
C(10)	135(5)	1399(5)	1119(7)

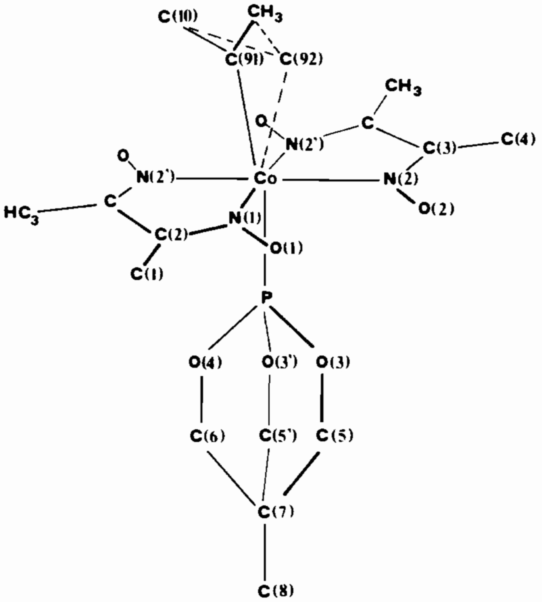

Fig. 1. Numbering scheme for the atoms of (I). The primed symbol indicates the atoms related by the symmetry mirror plane.

Experimental

Crystal data are: Space group $P2_1/m$; $M = 480,4$, $a = 10.995(8)$, $b = 11.342(9)$, $c = 8.891(8)$ Å, $\beta = 90.3(1)°$, $d_{obs} = 1.45$ g cm^{-3}, $d_{calc} = 1.44$ g cm^{-3}, $Z = 2$. Intensity data were collected on a AED Siemens automated diffractometer by a θ–2θ scan technique using MoK_α radiation. The structure was solved by Patterson and Fourier methods, and refined by the anisotropic block-diagonal least-squares method to an R value of 0.038 for 1582 independent reflections having $I > 3\sigma(I)$, including the hydrogen atom contribution ($B = 5$ Å^2). The choice of the centrosymmetric space group $P2_1/m$ was suggested by the vector distribution on the Patterson map and by the final refinement. The carbon atom bonded to cobalt was found to be disordered and was occupying positions lying in the crystallographic mirror plane; these positions were refined isotropically.

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TABLE II. Relevant Bond Lengths and Angles.

a) Bond lengths (Å)

Co–N(1)	1.885(3)	P–O(3)	1 564(4)
Co–N(2)	1.891(4)	P–O(4)	1.563(5)
Co–P	2.270(1)	O(3)–C(5)	1.478(6)
Co–C(91)	2.12(1)	O(4)–C(6)	1.466(8)
Co–C(92)	2.13(1)	C(5)–C(7)	1.509(6)
O(1)–N(1)	1.347(4)	C(6)–C(7)	1.48(1)
N(1)–C(2)	1.317(5)	C(7)–C(8)	1.523(8)
C(1)–C(2)	1.490(7)		
O(2)–N(2)	1.355(5)		
N(2)–C(3)	1.294(6)		
C(3)–C(4)	1.505(8)		

b) Bond angles (°)

P–Co–N(1)	91.8(1)	Co–P–O(3)	117.0(1)
P–Co–N(2)	88.8(1)	Co–P–O(4)	114.3(2)
P–Co–C(91)	173.1(3)	O(3)–P–O(4)	102.0(2)
P–Co–C(92)	169.6(4)	O(3)–P–O(3′)	102.1(2)
N(1)–Co–N(2)	99.0(1)	P–O(3)–C(5)	116.3(3)
N(1)–Co–N(1′)	81.4(1)	P–O(4)–C(6)	115.8(5)
N(1)–Co–N(2′)	179.3(2)		
N(1)–Co–C(91)	82.9(3)	O(3)–C(5)–C(7)	110.3(4)
N(1)–Co–C(92)	96.1(3)	O(4)–C(6)–C(7)	111.7(5)
N(2)–Co–C(91)	96.5(3)	C(5)–C(7)–C(6)	107.6(4)
N(2)–Co–C(92)	83.3(3)	C(5)–C(7)–C(8)	110.3(4)
		C(5)–C(7)–C(5′)	109.4(4)
		C(6)–C(7)–C(8)	111.5(5)

TABLE III Some Structural Parameters of (LCo(DH)$_2$i-C$_3$H$_7$) Complexes with Different L Ligands.

L	Co–C (Å)	d (Å)[a]	α (°)[b]	L–Co–C (°)	Cone angle (°)[c]
Py[d]	2.085(3)	0.02	4	175.4(1)	105
P(OCH$_2$)$_3$CCH$_3$[e]	2.122(12)	0.01	4	171.4(3)	101
PPh$_3$[f]	2.22(2)	0.17	14	170.3(6)	155[g]

[a] Displacement of cobalt from the 4-N equatorial towards L. [b] Dihedral angle between the two DH units. [c] Ref. 9. [d] L. G Marzilli, P. J. Toscano, L. Randaccio, N. Bresciani-Pahor and M. Calligaris, *J Am Chem Soc.*, *101*, 6754 (1979). [e] Present work. [f] Ref. 12. [g] N. Bresciani-Pahor, L. Randaccio, P. J Toscano, A C. Sandercock and L G. Marzilli, *J Chem. Soc. Dalton Trans.*, 129 (1982).

A list of the observed and calculated structure factors, tables of hydrogen atom positions and thermal parameters can be obtained from the authors. The final atomic parameters are given in Table I.

Results and Discussion

The numbering scheme for the atoms of the crystallographically independent atoms is shown in Fig 1. Some relevant bond lengths and angles are given in Table II. The crystals consist of discrete molecules of (I), lying across crystallographic mirror planes which bisect the C(2)–C(2′) and C(3)–C(3′) bonds. The carbon atom bonded to cobalt is found to occupy two different positions, both lying in the mirror plane. The geometry of the i-propyl group in the two orientations is characterized by mean C–Me distances and Co–C–Me angles of 1.448(8) Å and 114.5(5)° respectively.

The orientation of the phosphite with respect to the equatorial ligand is dictated by the mirror symmetry, one bridge of the cage lying in the crystallographic mirror plane. The atoms of the other two bridges, referred by the symmetry plane, are coplanar within the experimental errors (±0.007). Bond lengths and angles of the phosphite are given in Table III. The cobalt atom, having a distorted octahedral environment is displaced by 0.01 from the 4-N equatorial donors towards the P atom, whereas the two DH moieties make a dihedral angle, α, of 4.2°. The P–Co–$CHMe_2$ moiety is characterized by Co–P and Co–C distances of 2.270(1) and 2.122(12) Å (mean) and by a mean P–Co–C angle of 171.4(3)°. The Co–P bond length found here is longer than those reported for cobaloximes containing the $P(OMe)_3$ ligand, $(POMe)_3Co(DH)_2X$, where the Co–P distances are 2.188(4) Å (X = Cl), 2.225(3) (X = CN) and 2.256(4) Å (X = Me) [10]. Since we have shown [11] that the Co–P bond lengths in both phosphine and phosphite appear to be a measure of the cone angle of the P-ligand, the large value found in (I) for the 'caged' phosphite, which has a cone angle of 101° as compared with that of 107° of $P(OMe)_3$ [9], may be attributed to the strong electronic *trans*-influence of the i-propyl group. Some geometrical parameters of i-propyl cobaloximes with the different neutral ligands so far structurally characterized, are reported in Table III.

Although the Co–C distances are of different accuracy, the values of Table III show that a lengthening of the Co–C bond may be expected [12] when the L ligand is noticeably bulky (steric *trans*-influence). In fact, the phosphite and py ligands have similar bulk as well as similar Co–C distances, whereas PPh_3 has a larger bulk and a longer distance (although less accurate). This also appears to be supported by the values of α and d, which are significantly larger for the PPh_3 derivative.

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