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Structures of Two Triphenylphosphine Cobaloximes, $PPh_3Co(DH)_2X$ with X = Dichlorocyanomethyl and Isocyanate

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Abstract. (I): *trans*-(Dichlorocyanomethyl)bis(dimethylglyoximato)(triphenylphosphine)cobalt(III), $[Co(C_4H_7N_2O_2)_2(CCl_2CN)\{P(C_6H_5)_3\}]$, $M_r = 660{\cdot}38$, orthorhombic, *Pbca*, $a = 15{\cdot}152\ (2)$, $b = 23{\cdot}261\ (2)$, $c = 16{\cdot}931\ (2)$ Å, $V = 5967{\cdot}3$ Å^3, $Z = 8$, $D_x = 1{\cdot}47$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 7{\cdot}9$ cm^{-1}, $F(000) = 2720$, $T = 293$ K, $R = 0{\cdot}054$ for 2613 unique observed reflections. (II): *trans*-Bis(dimethylglyoximato)isocyanato(triphenylphosphine)cobalt(III), $[Co(C_4H_7N_2O_2)_2(NCO)\{P(C_6H_5)_3\}]$, $M_r = 593{\cdot}5$, monoclinic, *Pn*, $a = 8{\cdot}743\ (1)$, $b = 14{\cdot}875\ (1)$, $c = 10{\cdot}981\ (1)$ Å, $\beta = 101{\cdot}99\ (1)°$, $V = 1396{\cdot}9$ Å^3, $Z = 2$, $D_x = 1{\cdot}41$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 6{\cdot}6$ cm^{-1}, $F(000) = 616$, $T = 293$ K, $R = 0{\cdot}031$ for 2192 unique observed reflections. The axial fragment of the distorted octahedral polyhedron of Co is characterized by Co—C and Co—P distances of 2·089 (7) and 2·371 (2) Å in (I), Co—N and Co—P bond lengths of 1·936 (6) and 2·309 (1) Å in (II). The *trans* influence of the axial ligands is discussed and compared with that of other ligands.

Introduction. Our extensive studies on pseudo-octahedral vitamin B_{12} models, namely cobaloximes $LCo(DH_2)X$, (where L = neutral Lewis base, X = anionic group, DH = monoanion of dimethylglyoxime), have clearly shown that both steric and electronic properties of axial ligands determine the molecular geometry of this class of compounds (Bresciani-Pahor, Forcolin, Marzilli, Randaccio, Summers & Toscano, 1985; Randaccio, Bresciani-Pahor, Zangrando & Marzilli, 1989). P-donor ligands have been used to generate steric distortions in these complexes (Bresciani-Pahor, Randaccio, Toscano, Sandercock & Marzilli, 1982) to simulate those which have been suggested to occur in the B_{12} coenzyme (Chemaly & Pratt, 1980). Moreover, for cobaloximes containing P-donor ligands the Co—C bond-dissociation energy (BDE) decreases with increasing size of the phosphine, and a linear relationship with the Tolman cone angle (Tolman, 1977) has been found (Geno & Halpern, 1987).

As part of our studies to assess the influence of bulky ligands on the ground-state structural parameters of cobaloximes, we report the structures of the two complexes $(PPh_3)Co(DH)_2X$ with $X = CCl_2CN$ (I) and NCO (II).

Experimental. Prismatic red-brown crystals 0·35 × 0·28 × 0·20 mm (I) and 0·40 × 0·40 × 0·25 mm (II), Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$. Measurements were carried out at room temperature; 25 ($9 \le \theta \le 17°$) (I) and 25 ($10 \le \theta \le 21°$) (II) reflections for cell-parameter determinations; two standard reflections [366 and 758 for (I), and 262 and 154 for (II)] measured every three hours showed no significant intensity decay, $\omega/2\theta$ scan, scan angle $(0{\cdot}55 + 0{\cdot}35\tan\theta)°$ (I) and $(0{\cdot}80 + 0{\cdot}35\tan\theta)°$ (II), 5784 reflections measured in the range $1{\cdot}5 \le \theta \le 28°$, $0 \le h \le 20$, $0 \le k \le 30$, $0 \le l \le 22$ for (I) and 3374 in the range $1{\cdot}5 < \theta < 28°$, $-11 \le h \le 11$, $0 \le k \le 19$, $0 \le l \le 14$ for (II). 2613 (I) observed reflections [$I > 2\sigma(I)$] and 2192 (II) [$I > 3\sigma(I)$] used for structure determinations, space group from systematic absences and symmetry requirements, intensities corrected for Lorentz–polarization effects and for absorption based on empirical ψ scan [max. and min. transmission factors 0·99 and 0·95 (I), 0·99 and 0·94 (II)]. The structures were solved by conventional Patterson and Fourier methods, refined through full-matrix least-squares calculations with $\sum w(|F_o| - |F_c|)^2$ being minimized, 370 (I) and 350 (II) parameters were refined, anisotropic temperature factors for all non-H atoms, H atoms were placed in calculated positions (C—H bond distance 1·0 Å) with isotropic B set 1·0 Å^2 higher than the B_{eq} of the bonded atoms, except the oxime protons and one H atom of each methyl group, which were located by means of ΔF maps. $R = 0{\cdot}054$, $wR = 0{\cdot}059$, $w = 1$ for (I) and $R = 0{\cdot}031$,

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Table 1. *Final fractional coordinates and equivalent isotropic thermal parameters for* $(PPh_3)Co(DH)_2CCl_2CN$ (I)

$B_{eq} = \frac{1}{3}\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq} (Å^2)
Co	0·24096 (6)	0·14569 (4)	0·10821 (5)	2·65 (4)
O(1)	0·0750 (3)	0·0970 (2)	0·1500 (3)	4·4 (3)
N(1)	0·1172 (4)	0·1371 (2)	0·1079 (4)	3·5 (3)
C(1)	−0·0246 (5)	0·1734 (4)	0·0575 (6)	6·2 (5)
C(2)	0·0733 (5)	0·1735 (3)	0·0632 (5)	3·7 (3)
C(3)	0·1295 (5)	0·2141 (3)	0·0224 (4)	3·5 (3)
C(4)	0·0969 (6)	0·2598 (4)	−0·0310 (6)	5·5 (4)
N(2)	0·2129 (4)	0·2046 (2)	0·0362 (3)	3·0 (2)
O(2)	0·2747 (3)	0·2370 (2)	0·0000 (3)	4·1 (2)
O(3)	0·4058 (3)	0·1921 (2)	0·0626 (3)	4·2 (2)
N(3)	0·3645 (4)	0·1528 (2)	0·1072 (3)	3·1 (2)
C(5)	0·5060 (5)	0·1135 (4)	0·1544 (6)	5·7 (5)
C(6)	0·4084 (5)	0·1166 (3)	0·1492 (5)	3·7 (3)
C(7)	0·3513 (5)	0·0793 (3)	0·1952 (4)	3·9 (3)
C(8)	0·3828 (6)	0·0352 (4)	0·2543 (5)	5·8 (4)
N(4)	0·2677 (4)	0·0883 (2)	0·1819 (3)	3·4 (3)
O(4)	0·2058 (4)	0·0597 (2)	0·2231 (3)	4·5 (2)
C(9)	0·2351 (6)	0·2064 (3)	0·1989 (4)	4·5 (4)
Cl(1)	0·2906 (3)	0·1882 (1)	0·2886 (2)	8·4 (2)
Cl(2)	0·2880 (4)	0·2757 (2)	0·1716 (2)	14·3 (3)
C(10)	0·138 (2)	0·222 (2)	0·228 (2)	9· (1)
N(5)	0·107 (2)	0·235 (1)	0·224 (1)	10· (1)
P	0·2515 (1)	0·08399 (7)	−0·0029 (1)	2·60 (7)
C(11)	0·3524 (5)	0·0993 (3)	−0·0581 (4)	3·0 (3)
C(12)	0·3616 (5)	0·1434 (4)	−0·1119 (5)	4·4 (4)
C(13)	0·4421 (6)	0·1570 (4)	−0·1448 (5)	5·1 (4)
C(14)	0·5146 (6)	0·1269 (4)	−0·1255 (5)	5·0 (4)
C(15)	0·5077 (6)	0·0821 (4)	−0·0717 (5)	5·1 (4)
C(16)	0·4280 (5)	0·0695 (3)	−0·0379 (5)	4·0 (4)
C(17)	0·2575 (4)	0·0056 (3)	0·0079 (4)	2·9 (3)
C(18)	0·2386 (5)	−0·0229 (3)	0·0769 (5)	3·8 (3)
C(19)	0·2353 (6)	−0·0824 (3)	0·0780 (6)	5·2 (4)
C(20)	0·2514 (6)	−0·1132 (3)	0·0098 (7)	5·5 (5)
C(21)	0·2712 (6)	−0·0852 (4)	−0·0586 (6)	5·3 (4)
C(22)	0·2759 (5)	−0·0253 (3)	−0·0610 (5)	4·0 (3)
C(23)	0·1552 (5)	0·0899 (3)	−0·0676 (4)	3·0 (3)
C(24)	0·1400 (6)	0·1328 (4)	−0·1217 (5)	5·3 (4)
C(25)	0·0627 (6)	0·1351 (4)	−0·1644 (5)	5·8 (5)
C(26)	0·0006 (6)	0·0950 (4)	−0·1555 (5)	5·3 (4)
C(27)	0·0120 (5)	0·0524 (4)	−0·1041 (5)	5·1 (4)
C(28)	0·0885 (5)	0·0493 (4)	−0·0594 (5)	5·1 (4)

Table 2. *Final fractional coordinates and equivalent isotropic thermal parameters for* $(PPh_3)Co(DH)_2NCO$ (II)

$B_{eq} = \frac{1}{3}\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq} (Å^2)
Co	0·25*	0·25180 (4)	0·25*	3·02 (2)
O(1)	0·3667 (5)	0·4229 (3)	0·3356 (4)	5·4 (2)
N(1)	0·2593 (5)	0·3789 (2)	0·2540 (4)	4·1 (2)
C(1)	0·159 (1)	0·5192 (4)	0·1542 (6)	6·7 (3)
C(2)	0·1589 (7)	0·4195 (3)	0·1687 (5)	4·5 (2)
C(3)	0·0536 (6)	0·3581 (4)	0·0863 (5)	4·2 (2)
C(4)	−0·0739 (8)	0·3873 (5)	−0·0165 (6)	6·1 (3)
N(2)	0·0835 (5)	0·2751 (3)	0·1149 (4)	3·6 (2)
O(2)	0·0051 (5)	0·2090 (3)	0·0438 (4)	4·7 (2)
O(3)	0·1448 (5)	0·0790 (3)	0·1589 (4)	5·2 (2)
N(3)	0·2455 (5)	0·1244 (2)	0·2465 (4)	3·8 (2)
C(5)	0·3615 (9)	−0·0179 (4)	0·3350 (8)	6·9 (3)
C(6)	0·3479 (7)	0·0825 (3)	0·3285 (6)	4·5 (2)
C(7)	0·4538 (6)	0·1450 (4)	0·4084 (5)	4·3 (2)
C(8)	0·5832 (7)	0·1159 (4)	0·5146 (7)	6·2 (3)
N(4)	0·4225 (5)	0·2284 (3)	0·3824 (4)	3·7 (2)
O(4)	0·5127 (5)	0·2937 (3)	0·4417 (4)	4·8 (2)
N(5)	0·3913 (7)	0·2506 (3)	0·1356 (6)	5·1 (2)
C(9)	0·4767 (6)	0·2544 (3)	0·0781 (5)	4·5 (2)
O(5)	0·5715 (7)	0·2583 (5)	0·0134 (6)	10·9 (4)
P	0·0682 (2)	0·25261 (6)	0·3753 (1)	2·92 (4)
C(10)	−0·0481 (5)	0·3553 (3)	0·3597 (4)	3·7 (2)
C(11)	−0·1984 (7)	0·3643 (4)	0·2950 (7)	5·6 (2)
C(12)	−0·2724 (9)	0·4469 (5)	0·2894 (9)	7·6 (4)
C(13)	−0·199 (1)	0·5197 (4)	0·350 (1)	8·5 (4)
C(14)	−0·049 (1)	0·5114 (4)	0·415 (1)	8·5 (5)
C(15)	0·0266 (9)	0·4303 (3)	0·4241 (7)	6·3 (3)
C(16)	0·1224 (6)	0·2464 (2)	0·5457 (4)	3·6 (2)
C(17)	0·2734 (7)	0·2546 (3)	0·6154 (5)	4·3 (2)
C(18)	0·3006 (9)	0·2505 (3)	0·7434 (5)	5·3 (2)
C(19)	0·181 (1)	0·2399 (3)	0·8061 (7)	5·2 (2)
C(20)	0·0307 (9)	0·2331 (3)	0·7374 (5)	5·5 (2)
C(21)	0·0007 (7)	0·2369 (3)	0·6075 (5)	4·8 (2)
C(22)	−0·0573 (5)	0·1543 (3)	0·3372 (4)	3·4 (1)
C(23)	−0·0182 (7)	0·0766 (3)	0·4085 (5)	4·5 (2)
C(24)	−0·0986 (8)	−0·0031 (3)	0·3722 (7)	6·1 (3)
C(25)	−0·2197 (8)	−0·0051 (4)	0·2703 (8)	6·9 (3)
C(26)	−0·2560 (8)	0·0708 (4)	0·2005 (7)	6·4 (3)
C(27)	−0·1752 (6)	0·1503 (3)	0·2315 (5)	4·4 (2)

* Origin assignment

$wR = 0{\cdot}036$, $w = 1$ for (II); $-0{\cdot}80 < \Delta\rho < 0{\cdot}30$ (I) and $-0{\cdot}25 < \Delta\rho < 0{\cdot}32$ e Å^{-3} (II). Max. Δ/σ 0·46 (I) and 0·19 (II). In (I) the CCl_2CN group appeared disordered, possibly due to two group orientations differing by a rotation of 120° around the Co—C(9) bond direction (and overlap of one Cl atom and the CN group). Nevertheless, all attempts to treat the disorder problem in this way failed to produce satisfactory results, either in terms of geometry or of reliability indices. The atoms of the CCl_2CN group were refined starting from the positions of the electronic density peaks located on the Fourier map, producing an inconsistent location of N(5) [C(9)—C(10)—N(5) bond angle of 148 (8)°]. However, this did not affect the accuracy of the other bond lengths and angles, especially the Co—C distance. Complex neutral-atom scattering factors were from *International Tables for X-ray Crystallography* (1974). No correction for secondary extinction was applied. Calculations were carried out on a Cray X-MP/48 computer, using the *SHELX*76 (Sheldrick, 1976) system of progams.

Discussion. Final fractional coordinates and equivalent isotropic thermal parameters of non-H atoms of (I) and (II) are reported in Tables 1 and 2.* *ORTEP* (Johnson, 1965) drawings of molecules (I) and (II) with the atom-numbering schemes are depicted in Figs. 1 and 2, respectively. In both structures, the $(DH)_2$ ligand occupies the four equatorial positions of a distorted octahedron around Co, the axial positions being occupied by PPh_3 and *X*. The Co atom is displaced 0·02 Å from the mean plane passing through the four N equatorial donors towards PPh_3 in (II) and essentially in the mean plane in (I). The two DH units are approximately planar [within ±0·035 (I) and ±0·028 Å in (II)] and make a dihedral angle, α, of −3·9 and 0·8° in (I) and (II), respectively. (A negative sign of α indicates a bending towards the neutral ligand.)

* Lists of structure factors, anisotropic thermal parameters for non-H atoms, positional parameters for H atoms, bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52942 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The axial fragment Ph_3P—Co—C in (I) is characterized by Co—P, Co—C bond lengths and P—Co—C bond angle of 2·371 (2), 2·089 (7) Å and 174·5 (2)°, respectively. The corresponding Co—C distance in the 1,2-Me_2imidazole (1,2Me_2Im) analogue (Bresciani-Pahor, Geremia, Lopez, Randaccio & Zangrando, 1990), 1,2-Me_2ImCo$(DH)_2CCl_2CN$ is 2·047 (4) Å. This lengthening could be attributed to the steric *trans* influence exerted by PPh_3 being larger than that of 1,2-Me_2Im. The Co—P bond length of 2·371 (2) Å indicates that the CCl_2CN group has an electronic *trans* influence comparable with the corresponding $(PPh_3)Co(DH)_2X$ derivatives with other electron-withdrawing groups such as CH_2CF_3, CH_2CN and CH_2Br, where the Co—P distances are 2·383 (1), 2·391 (1) and 2·399 (3) Å. On the other hand, this bond length is shorter than the values of 2·418 (1) and 2·460 (1) Å, found in the methyl and neopentyl derivatives, respectively (Bresciani Pahor *et al.*, 1985).

In the Ph_3P—Co—NCO fragment of (II) the Co—P and Co—N bond lengths and the P—Co—N bond angle are 2·309 (1), 1·936 (6) Å and 176·3 (2)°, respectively. These values are very similar to those of other non-organometallic complexes as in the azido derivative $(PPh_3)Co(DH)_2N_3$ (Nelson, Takach, Bresciani-Pahor, Randaccio & Zangrando, 1984) where the Co—P and Co—N bond lengths are 2·311 (1) and 2·014 (4) Å, and as in the less accurately determined isothiocyanate $(PPh_3)Co(DH)_2NCS$ derivative (Botoshanskii, Simonov, Ablov, Malinovskii & Bologa, 1978), where the corresponding figures are 2·286 (8) and 1·93 (4) Å.

The trend of the Co—P distances in $(PPh_3)Co(DH)_2X$ complexes (Bresciani-Pahor *et al.*, 1985), as a function of the σ-donating ability of the ligand *trans* to the phosphine, indicates that the NCO group is among the less *trans* influencing groups.

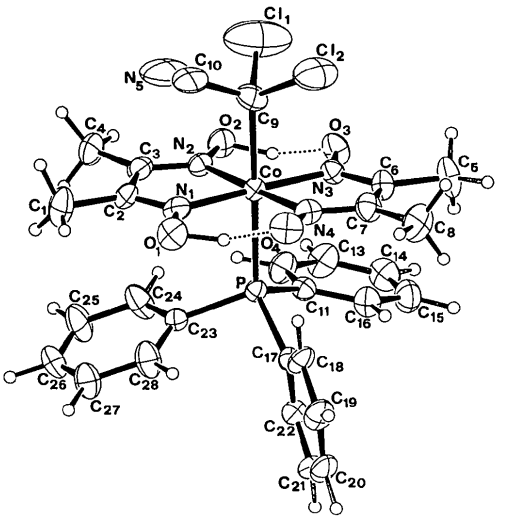

Fig. 1. *ORTEP* drawing and atom-numbering scheme of (PPh_3)-$Co(DH)_2CCl_2CN$ (I) (thermal ellipsoids at 35% probability). H atoms are represented as spheres of radius 0·10 Å.

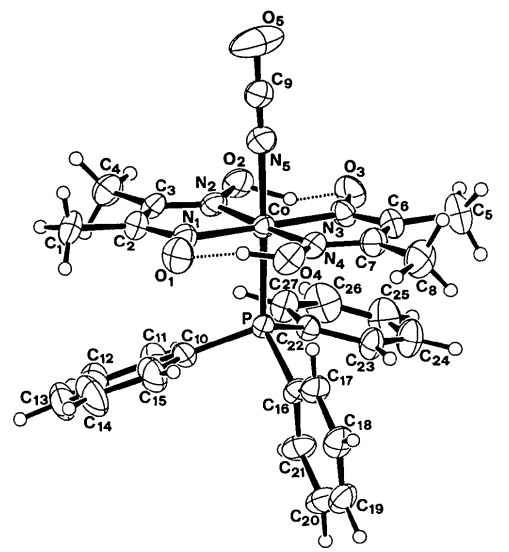

Fig. 2. *ORTEP* drawing and atom-numbering scheme of (PPh_3)-$Co(DH)_2NCO$ (II) (thermal ellipsoids at 35% probability). H atoms are represented as spheres of radius 0·10 Å.

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