Relation between Cobalt–Carbon Bond Lengthening and Conformational Changes in Octahedral Neopentylcobaloximes. Crystal and Molecular Structure of Bis(dimethylglyoximato)neopentyl(trimethylphosphine)cobalt(III) †

Nevenka Bresciani-Pahor, Mario Calligaris, Giorgio Nardin, and Lucio Randaccio *
Istituto di Chimica, Università di Trieste, 34127 Trieste, Italy

The crystal structure of a cobaloxime, $[Co(Hdmg)_2(CH_2CMe_3)(PMe_3)]$ (Hdmg = monoanion of dimethylglyoxime), is reported and discussed. The crystals are monoclinic, space group $P2_1/c$ with cell parameters $a = 11.807(7)$, $b = 12.136(7)$, $c = 15.225(9)$ Å, $\beta = 95.42(8)°$, and $Z = 4$. The structure was solved by Patterson and Fourier methods and refined by block-diagonal anisotropic least-squares methods to a final R of 0.028, using 2 580 independent reflections. The $Me_3P–Co–CH_2CMe_3$ fragment is characterized by a C–Co–P angle of 173.68(9)° and Co–P and Co–C bond lengths of 2.316(1) and 2.084(3) Å respectively. The $Co–CH_2–C$ angle is greatly widened to 130.2(2)°. The P–C bond lengths and the C–P–C bond angles average 1.813(4) Å and 103.1(2)° respectively, being significantly different from those in free PMe_3 [1.846(3) Å and 98.6(3)°]. The two Hdmg units make an interplanar angle (α) of 5° bending towards the phosphine ligand, and the Co atom lies approximately in the N_4 equatorial donor plane. The Co–C bond lengths, α angles, and the displacement of Co out of the N_4 donor plane (d) are compared in the series $[Co(Hdmg)_2(CH_2CMe_3)L]$ (L = H_2O, pyridine, PMe_3, and PPh_3). This shows that the lengthening of the Co–C bond is accompanied by movement of the Hdmg ligands from downward- to the upward-pointing (with respect to the alkyl group), which appears to be determined by the increasing bulk of L. Comparison with the analogous methyl derivatives shows also that the Co–L and Co–C bond lengths are influenced by the bulk of both the axial ligands.

Recently, Chemaly and Pratt [1] have suggested that neopentylcobalamin provides a model for the labilization of the Co–C bond in the vitamin B_{12} coenzyme. These authors have ascribed the origin of such a labilization to the distortion of the bond angles around C_α with a concomitant increase of the $Co–C_\alpha$ bond length. They conclude that such distortions arise from the steric interaction of the bulky neopentyl group with upward-projecting side groups of the corrin ring and that such interaction does not occur in simple model compounds such as cobaloximes, accounting for the stability of neopentyl cobaloximes. However, we have recently shown [2,3] that large distortions, such as $Co–C_\alpha$ bond lengthening and $Co–CH_2–CMe_3$ bond-angle widening (up to 130°), do occur in $[Co(Hdmg)_2(CH_2CMe_3)L]$ models [Hdmg = monoanion of dimethylglyoxime; L = H_2O, pyridine (py), or PPh_3]. On the other hand, it has been shown [2] that the steric interaction of the alkyl group (R) with the Hdmg ligands (steric *cis* influence [4]) causes a lengthening of the Co–C bond of up to 0.1 Å with increasing bulk of R in the complexes $[Co(Hdmg)_2R(py)]$. Furthermore, there was evidence that the length of the Co–C bond is also influenced by the bulk of the *trans* neutral ligand [3,5] (steric *trans* influence). To gain new insight into the above effects, it was of interest to extend the neopentyl series to ligands (L) of intermediate bulk. In fact, structural variations due to the change in the bulk of the ligand L may give indications of the structural changes associated with the ' base-on ' $\rightleftharpoons$ ' base-off ' mechanism in alkylcobalamins.[1,6,7] Thus we report the crystal and molecular structure of $[Co(Hdmg)_2R(PMe_3)]$ (1; R = CH_2CMe_3). Furthermore, since the structures of the derivatives with R = Me having the same *trans* ligands L have already been reported,[4,8,9] a structural comparison with the analogous neopentyl complexes was of interest.

Experimental

Crystal Data.—$C_{16}H_{34}CoN_4O_4P$, $M = 378.0$, Monoclinic, space group $P2_1/c$, $a = 11.807(7)$, $b = 12.136(7)$, $c = 15.225(9)$ Å, $\beta = 95.42(8)°$, $U = 2\,172.2$ Å^3, $D_m = 1.33$, $Z = 4$, $D_c = 1.34$ g cm^{-3}, λ(Mo-K_α) = 0.7107 Å.

Intensity data were collected on a Siemens AED computer-controlled diffractometer with the θ—2θ scan technique up to $\theta \leqslant 28°$. One standard reflection, measured every 100 reflections, showed no significant variation throughout data collection. 2 580 Reflections having $I > 3\sigma(I)$ were corrected for Lorentz and polarization factors, but not for absorption, and were used in the subsequent calculations. The structure, solved by conventional Patterson and Fourier methods, was refined by block-diagonal anisotropic least-squares methods to a final R value of 0.028. The contribution of the hydrogen atoms, held constant ($B = 5$ Å^2), was included. The final weighting scheme was $w = 1/(A + |F_o| + B|F_o|^2)$, where $A = 16.0$ and $B = 0.011$ 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. 10. All calculations were done using computer programs from the *X*-RAY 70 system.[11]

Final positional parameters of non-hydrogen atoms are given in Table 1 and bond distances and angles are in Table 2.

Results and Discussion

A view of the crystallographically independent molecule of (1) is shown in Figure 1, together with the numbering scheme for

---

† *Supplementary data available* (No. SUP 23380, 16 pp.): observed and calculated structure factors, thermal parameters, hydrogen-atom co-ordinates. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Positional parameters of non-hydrogen atoms ($\times 10^4$) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Co	2 361(1)	507(1)	2 243(1)
P	2 247(1)	1 953(1)	1 245(1)
O(1)	1 542(2)	1 942(2)	3 521(1)
O(2)	1 083(2)	−795(2)	947(1)
O(3)	3 185(2)	−904(2)	949(2)
O(4)	3 640(2)	1 898(2)	3 476(1)
N(1)	1 271(2)	1 197(2)	2 874(2)
N(2)	1 051(2)	−108(2)	1 644(2)
N(3)	3 457(2)	−187(2)	1 619(2)
N(4)	3 669(2)	1 146(2)	2 821(2)
C(1)	−756(3)	1 450(4)	3 095(3)
C(2)	201(3)	957(3)	2 641(2)
C(3)	79(3)	189(3)	1 905(2)
C(4)	−1 036(3)	−184(3)	1 438(3)
C(5)	5 482(3)	−346(4)	1 343(3)
C(6)	4 515(3)	86(3)	1 824(2)
C(7)	4 644(3)	885(3)	2 534(2)
C(8)	5 758(3)	1 358(4)	2 925(3)
C(9)	2 335(3)	−884(3)	3 043(2)
C(10)	2 865(3)	−1 075(3)	3 982(2)
C(11)	4 176(4)	−1 031(5)	4 031(4)
C(12)	2 580(4)	−2 259(3)	4 247(3)
C(13)	2 478(7)	−289(4)	4 642(3)
C(14)	858(3)	2 220(4)	667(3)
C(15)	3 162(4)	1 825(4)	358(3)
C(16)	2 644(5)	3 277(3)	1 723(3)

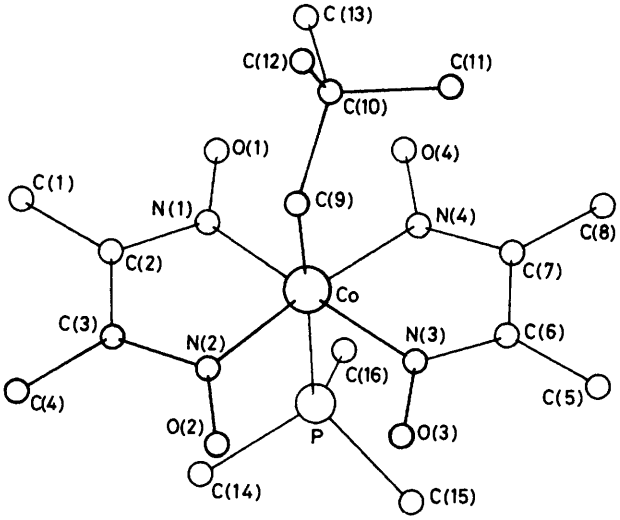

Figure. View of the crystallographically independent molecule together with the atomic numbering scheme

Table 2. Bond distances (Å) and angles (°)

(*a*) Distances

Co–P	2.316(1)	C(1)–C(2)	1.503(5)
Co–C(9)	2.084(3)	C(2)–C(3)	1.455(5)
Co–N(1)	1.875(3)	C(3)–C(4)	1.506(5)
Co–N(2)	1.875(2)	C(5)–C(6)	1.508(5)
Co–N(3)	1.876(3)	C(6)–C(7)	1.450(5)
Co–N(4)	1.871(2)	C(7)–C(8)	1.506(5)
N(1)–O(1)	1.354(3)	C(9)–C(10)	1.523(5)
N(1)–C(2)	1.312(4)	C(10)–C(11)	1.543(6)
N(2)–O(2)	1.353(3)	C(10)–C(12)	1.538(5)
N(2)–C(3)	1.300(4)	C(10)–C(13)	1.489(6)
N(3)–O(3)	1.356(3)	P–C(14)	1.816(4)
N(3)–C(6)	1.301(4)	P–C(15)	1.814(4)
N(4)–O(4)	1.355(3)	P–C(16)	1.808(4)
N(4)–C(7)	1.308(4)		

(*b*) Angles

P–Co–C(9)	173.68(9)	N(4)–Co–C(9)	96.8(1)
N(1)–Co–N(2)	81.5(1)	Co–C(9)–C(10)	130.2(2)
N(1)–Co–N(3)	179.6(1)	C(9)–C(10)–C(11)	111.2(3)
N(1)–Co–N(4)	98.6(1)	C(9)–C(10)–C(12)	108.0(3)
N(1)–Co–P	89.84(8)	C(9)–C(10)–C(13)	114.2(3)
N(1)–Co–C(9)	90.8(1)	C(11)–C(10)–C(12)	105.3(4)
N(2)–Co–N(3)	98.8(1)	C(11)–C(10)–C(13)	108.4(4)
N(2)–Co–N(4)	178.7(1)	C(12)–C(10)–C(13)	109.4(4)
N(2)–Co–P	89.31(8)	Co–P–C(14)	116.6(2)
N(2)–Co–C(9)	84.6(1)	Co–P–C(15)	114.9(1)
N(3)–Co–N(4)	81.2(1)	Co–P–C(16)	114.4(1)
N(3)–Co–P	90.49(8)	C(14)–P–C(15)	103.2(2)
N(3)–Co–C(9)	88.9(1)	C(14)–P–C(16)	102.9(2)
N(4)–Co–P	89.38(8)	C(15)–P–C(16)	103.0(2)

the atoms. The four *N*-donors of the Hdmg units are coplanar within ±0.013 Å with a slightly tetrahedral distortion, the cobalt atom being in their mean plane. The two Hdmg units make an angle of 4.8°, bending towards PMe_3. The P–Co–CH_2CMe_3 fragment is characterized by a P–Co–C(9) angle of 173.68(9)° and Co–P and Co–C(9) bond lengths of 2.316(1) and 2.084(3) Å respectively. As already found [2,3] in other neopentylcobaloximes the Co–CH_2–C angle is largely distorted, at 130.2(2)°. The value of this angle allows the atoms C(10), C(11), and C(13) to lie in a plane nearly parallel to the equatorial plane. Analogously, the orientation of the alkyl group is such that the C(9)–C(10) bond lies nearly on the Co–N(4) bond. Thus the angles N(2)–Co–C(9) and N(4)–Co–C(9) are 84.6(1) and 96.8(1)° respectively, the other two angles N–Co–C(9) being nearly 90°. The CH_2–CMe_3 group appears significantly distorted, the C(9)–C(10) bond length and the angles around C(10) deviating significantly from the ideal values (see Table 2). Similar distortions have been observed previously in other neopentylcobaloximes.[2,3] The P–Me bond lengths and C–P–C bond angles average 1.813(4) Å and 103.1(2)° respectively, in agreement with the mean values of 1.816(6) Å and 103.6(3)° reported for the methyl analogue.[4] It is of interest to compare the above values with those found in free PMe_3 [12] and in the adduct $PMe_3{\cdot}BCl_3$,[13] where the P–C distances are 1.846(3) and 1.800(4) Å and the C–P–C angles are 98.6(3) and 109.3(3)° respectively. The above comparison suggests that the *s* character in the P–C bonds increases for the above compounds in the following order $PMe_3 <$ (1) $< PMe_3{\cdot}BCl_3$. Alternatively, the repulsion exerted on the electron pairs of the P–C bond by the fourth electron pair increases in the opposite order. This suggests that ' compression ' around the P atom in (1) is not so dramatic.

Some structural data for the series of complexes [Co(Hdmg)$_2$(CH$_2$CMe$_3$)$_2$L] and [Co(Hdmg)$_2$(Me)L] are compared in Table 3. As already observed,[2,3] substitution of Me by neopentyl for the same ligand L produces an increase in the Co–C bond. However, this increase ranges from 0.054 to 0.092 Å when L varies from H_2O to PPh_3, showing a clear influence of the bulkiness of L on the Co–C distance. The Co–L distance increases in the same direction, although when L = H_2O it is the same in both the Me and CH_2CMe_3 derivatives. This increase ranges from 0.013 to 0.042 when L varies from py to PPh_3. The above findings show that the axial bond lengths are significantly influenced by the bulk of both axial ligands. Finally, the P–Co–C angles are always

Table 3. Comparison of some structural parameters for the two series of complexes [Co(Hdmg)$_2$(R)L]

L	Co–L/Å	Co–C/Å	PCoC/°	α/° [a]	d/Å [a]	Co–CH$_2$–CMe$_3$/°
(*a*) R = CH$_2$CMe$_3$						
H$_2$O [b]	2.056(5)	2.044(7)	172.4(3)	−7	−0.04	126.9(5)
py [c]	2.081(4)	2.060(6)	174.7(2)	−5	*ca.* 0	130.3(4)
PMe$_3$ [d]	2.316(1)	2.084(3)	173.68(9)	−5	*ca.* 0	130.2(2)
PPh$_3$ [b]	2.460(1)	2.118(9)	166.6(3)	+2	+0.04	129.2(7)
(*b*) R = Me						
H$_2$O [e]	2.058(3)	1.990(5)	178.0(2)	−4	*ca.* 0	
py [f]	2.068(3)	1.998(5)	178.0(2)	+3.2	+0.04	
PMe$_3$ [g]	2.294(1)	2.015(3)	178.5(2)	+4.0	+0.05	
PPh$_3$ [h]	2.418(1)	2.026(6)	175.4(2)	+14.0	+0.11	

[a] Positive values of α and *d* indicate that the two Hdmg units bend towards the alkyl group, and that the displacement of Co from the N$_4$ equatorial donor set is towards L; negative values indicate bending and displacement in the opposite direction. [b] Ref. 3. [c] Ref. 2. [d] This work. [e] Ref. 9. [f] Ref. 8. [g] Ref. 4. [h] N. Bresciani-Pahor, M. Calligaris, L. Randaccio, and L. G. Marzilli, *Inorg. Chim. Acta*, 1979, **32**, 181.

smaller in the neopentyl derivatives, while the Co–CH$_2$–CMe$_3$ angle does not show large variations with L, if L = H$_2$O is excluded. In the latter case, probably the overall strain within the molecule does not require the widening of the Co–CH$_2$–CMe$_3$ angle as large as in other compounds with bulkier ligand L.

However, the most interesting aspect is the trends in the values of α (the angle between the planes of the two Hdmg ligands) and *d* (the displacement of Co out of the N$_4$ donor plane) with the bulk of L. For both the series (R = Me or CH$_2$CMe$_3$) the bending angle α goes from negative (bending towards L) to positive values (bending towards R) with increasing bulk of L. Of course, the ' crossover point ' depends upon the nature of R, being somewhere between L = PMe$_3$ and L = PPh$_3$ in the neopentyl series and near to L = H$_2$O in the methyl series. A similar trend appears to occur for values of *d*. Although five-co-ordinate cobaloximes have so far not been isolated and structurally characterized, the change in the bulk of L from the small water molecule to the bulky PPh$_3$ group may give indications about the possible structural changes which may occur on passing from five- to six-co-ordinate species. The results, reported in Table 3, show that the regular change of α and *d* from negative to positive values is accompanied by a lengthening of the Co–C bond, when the bulk of L increases. This effect is particularly marked when R = neopentyl. The above results for cobaloximes seem to support the mechanism of the Co–C bond cleavage proposed by Schrauzer and Grate[7] for neopentylcobalamin. These authors have proposed that the Co–C bond cleavage starts by the bending of the corrin ligand towards the alkyl group upon formation of the ' base-on ' species. In addition we suggest that such a movement is accompanied by a Co–C bond lengthening.[2] However, in the cobalamins the additional interaction of the alkyl group with the upward-projecting side groups of the corrin ring may enhance the distortions observed in cobaloximes, provoking a further labilization of the Co–C bond.

Acknowledgements

This work was supported in part by a N.A.T.O. grant (to L. R.) and in part by a grant (to L. R.) from C.N.R., Rome. We are grateful to Professor L. G. Marzilli and Mr. P. J. Toscano for kindly supplying the crystals.

References

1. S. M. Chemaly and J. M. Pratt, *J. Chem. Soc., Dalton Trans.*, 1980, 2274.
2. L. Randaccio, N. Bresciani-Pahor, P. J. Toscano, and L. G. Marzilli, *J. Am. Chem. Soc.*, 1981, **103**, 6347.
3. N. Bresciani-Pahor, L. Randaccio, P. J. Toscano, and L. G. Marzilli, *J. Chem. Soc., Dalton Trans.*, 1982, 567.
4. N. Bresciani-Pahor, L. Randaccio, P. J. Toscano, A. C. Sandercock, and L. G. Marzilli, *J. Chem. Soc., Dalton Trans.*, 1982, 129.
5. L. Randaccio, N. Bresciani-Pahor, P. J. Toscano, and L. G. Marzilli, *J. Am. Chem. Soc.*, 1980, **102**, 7372.
6. J. H. Grate and G. N. Schrauzer, *J. Am. Chem. Soc.*, 1979, **101**, 4601.
7. G. N. Schrauzer and J. H. Grate, *J. Am. Chem. Soc.*, 1981, **103**, 541.
8. A. Bigotto, E. Zangrando, and L. Randaccio, *J. Chem. Soc., Dalton Trans.*, 1976, 96.
9. D. L. McFadden and A. T. McPhail, *J. Chem. Soc., Dalton Trans.*, 1974, 363.
10. F. H. Moore, *Acta Crystallogr.*, 1963, **16**, 1169.
11. J. M. Stewart, F. A. Kundal, and J. C. Baldwin, ' The *X*-RAY System,' University of Maryland, 1970.
12. L. S. Bartell and L. O. Brockway, *J. Chem. Phys.*, 1960, **32**, 512.
13. K. Iijima and S. Shibata, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 3204.

Received 8th April 1982; *Paper* 2/603