# Structural Aspects of a Vitamin $B_{12}$ Model. Crystal and Molecular Structure of *trans*-Cyanobis(dimethylglyoximato)(trimethyl phosphite)-cobalt(III)

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Crystals of the title complex $[Co(Hdmg)_2(CN)\{P(OMe)_3\}]$ are monoclinic, space group $P2_1/c$, with $a$ = 18.431(9), $b$ = 14.082(7), $c$ = 17.651(9) Å, $\beta$ = 121.66(8)°, and $Z$ = 8. The intensities of 3 978 independent reflections [$I \geqslant 3\sigma(I)$] recorded on an automatic diffractometer have been used to solve and refine the structure to $R$ 0.059. The axial $(MeO)_3P$–Co–CN fragments are almost equivalent in the two crystallographically independent pseudo-octahedral molecules with mean Co–P, Co–C distances and P–Co–C angle of 2.225(3), 1.909(8) Å, and 177.8(3)° respectively. The Co–C bond length is the shortest so far reported in organocobaloximes. The *trans* influence of X for the series of complexes $[Co(Hdmg)_2X\{P(OMe)_3\}]$ (X = Cl, CN, or $CH_3$) increases in the order Cl < CN < $CH_3$. A comparison is made of the co-ordination environment of the cobalt atom in cobaloximes and cobalamins.

OUR previous structural studies [1-3] on pseudo-octahedral cobaloximes $[Co(Hdmg)_2(X)L]$ (L = Lewis base, X = anion, Hdmg = monoanion of dimethylglyoxime) have clearly shown that both steric and electronic effects are important in determining the molecular geometry of this class of compounds which model vitamin $B_{12}$. For example, the Co–C bond length in $[Co(Hdmg)_2(R)L]$ [2] (R = alkyl) and the Co–$CH_2$–R′ angle in $[Co(Hdmg)_2(CH_2R')L]$ [3] increase with increasing bulk of R and R′. The Co–C bond lengths so far determined range from 1.966(6) in $[Co(Hdmg)_2(CH{=}CH_2)(py)]$ [4] (py = pyridine) to 2.22(2) Å in $[Co(Hdmg)_2(CHMe_2)(PPh_3)]$.[2] That reported for the $B_{12}$ coenzyme, where R = 5′-deoxy-5′-adenosyl, is 2.03 Å, whereas in vitamin $B_{12}$ itself, where R = CN, and in other cyanocobalamins [5] the Co–C bond length is in the range 1.75—2.02 Å. On the other hand, the *trans* Co–N (benzimidazole residue) bond length is 2.24 Å in the coenzyme but ranges over 1.97—2.06 Å in the cyanocobalamins. These results, although not particularly accurate, suggest that the Co–C bond is exceptionally short in cyanocobalamins with respect to alkylcobalamins. Furthermore, the *trans*-influencing ability of the CN group is significantly smaller than that of an alkyl group. Although many organocobaloxime structures have been determined, no structural data for cyano-derivatives are available for comparison. We

TABLE 1

Atomic positional parameters ($\times 10^4$) with estimated standard deviations in parentheses

| | Molecule A | | | Molecule B | | |
|---|---|---|---|---|---|---|
| Atom* | *x* | *y* | *z* | *x* | *y* | *z* |
| Co | 1 383(1) | 2 696(1) | 3 122(1) | 6 198(1) | 2 394(1) | 3 076(1) |
| P | 1 548(1) | 1 510(2) | 2 391(2) | 6 689(1) | 3 623(1) | 4 004(1) |
| O(1) | 1 782(3) | 1 524(4) | 4 605(4) | 5 642(4) | 1 574(4) | 4 165(4) |
| O)2) | −241(3) | 3 070(5) | 1 585(3) | 7 759(3) | 2 111(4) | 3 163(4) |
| O(3) | 976(4) | 3 931(5) | 1 675(4) | 6 726(4) | 3 184(4) | 1 957(4) |
| O(4) | 3 005(3) | 2 362(4) | 4 683(3) | 4 596(3) | 2 599(5) | 2 950(4) |
| O(5) | 2 362(6) | 1 420(6) | 2 369(7) | 6 142(4) | 3 723(5) | 4 508(4) |
| O(6) | 881(7) | 1 598(7) | 1 338(5) | 7 572(5) | 3 570(5) | 4 860(4) |
| O(7) | 1 276(5) | 541(4) | 2 600(5) | 6 489(4) | 4 581(4) | 3 518(3) |
| N(1) | 1 157(4) | 1 848(4) | 3 797(4) | 6 281(4) | 1 646(4) | 4 016(4) |
| N(2) | 184(3) | 2 584(4) | 2 348(4) | 7 312(3) | 1 918(4) | 3 537(4) |
| N(3) | 1 606(4) | 3 566(4) | 2 461(4) | 6 085(4) | 3 134(4) | 2 123(3) |
| N(4) | 2 568(3) | 2 837(4) | 3 903(4) | 5 076(4) | 2 840(4) | 2 607(4) |
| N(5) | 1 076(5) | 4 347(6) | 4 021(6) | 5 472(5) | 728(5) | 1 774(5) |
| C(1) | 96(7) | 996(9) | 3 973(9) | 7 215(7) | 697(6) | 5 352(6) |
| C(2) | 374(5) | 1 618(5) | 3 482(5) | 7 014(5) | 1 235(5) | 4 529(5) |
| C(3) | −208(4) | 2 042(8) | 2 613(5) | 7 615(5) | 1 375(5) | 4 237(4) |
| C(4) | −1 146(5) | 1 866(8) | 2 093(6) | 8 467(6) | 931(7) | 4 685(6) |
| C(5) | 2 620(7) | 4 620(8) | 2 400(8) | 5 145(7) | 4 107(7) | 813(5) |
| C(6) | 2 383(5) | 3 873(6) | 2 831(5) | 5 364(5) | 3 538(5) | 1 630(4) |
| C(7) | 2 959(5) | 3 427(6) | 3 666(5) | 4 767(5) | 3 396(5) | 1 919(4) |
| C(8) | 3 892(5) | 3 626(7) | 4 216(6) | 3 902(5) | 3 839(7) | 1 486(6) |
| C(9) | 1 194(5) | 3 728(5) | 3 693(5) | 5 745(4) | 1 339(5) | 2 275(4) |
| C(10) | 3 163(7) | 972(9) | 3 120(7) | 6 407(8) | 3 557(11) | 5 381(6) |
| C(12) | 1 130(9) | −363(8) | 2 132(9) | 6 657(6) | 5 516(6) | 3 948(6) |
| C(11) | 1 198(16) | 2 141(19) | 744(16) | 8 351(8) | 3 708(8) | 4 704(9) |
| C(11′) | 925(16) | 1 530(19) | 613(17) | | | |

* One of the methyl groups of Molecule A occupies two different positions, C(11) and C(11′), due to high thermal motion.

therefore report the structure of cyanobis(dimethylglyoximato)(trimethyl phosphite)cobalt(III).

## EXPERIMENTAL

The compound was prepared according to ref. 6 and the crystals were obtained from methylene chloride–ethanol (1 : 1).

*Crystal Data.*—$C_{12}H_{23}CoN_5O_7P$, $M$ = 439.3, Monoclinic, space group $P2_1/c$, $a$ = 18.431(9), $b$ = 14.082(7), $c$ = 17.651(9) Å, $\beta$ = 121.66(8)°, $U$ = 3 899.9 Å$^3$, $D_m$ = 1.48, $Z$ = 8, $D_c$ = 1.50 g cm$^{-3}$, $\lambda$(Mo-$K_\alpha$) = 0.7107 Å.

Intensity data were collected on a Siemens AED computer-controlled diffractometer with the $\theta$—$2\theta$ scan technique up to $\theta \leqslant 28°$. One standard reflection, measured every 100 reflections, showed no significant variation throughout data collection. 3 978 Reflections having $I \geqslant 3\sigma(I)$ were corrected for Lorentz and polarization effects but not for absorption and used in the subsequent calculations. The structure was solved by conventional Patterson and Fourier methods and refined by block-diagonal anisotropic least-squares methods to a final $R$ value of 0.059. The methoxy-groups showed a high thermal motion and the C(11) methyl group of molecule A (see Table 1) occupies two different positions which were refined isotropically. Therefore, the contribution of the hydrogen atoms, held constant ($B$ = 5 Å$^2$), was included only for the Co(Hdmg)$_2$ moiety. The final weighting scheme was $w = 1/(A + |F_o| + B|F_o|^2)$ where $A$ = 16 and $B$ = 0.008 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. 7. All the calculations were done using computer programs from the ' $X$-Ray '70 ' system.[8]

Final positional parameters of non-hydrogen atoms are given in Table 1, while hydrogen-atom co-ordinates, thermal parameters, and observed and calculated structure factors are deposited in Supplementary Publication No. SUP 23226 (22 pp.).*

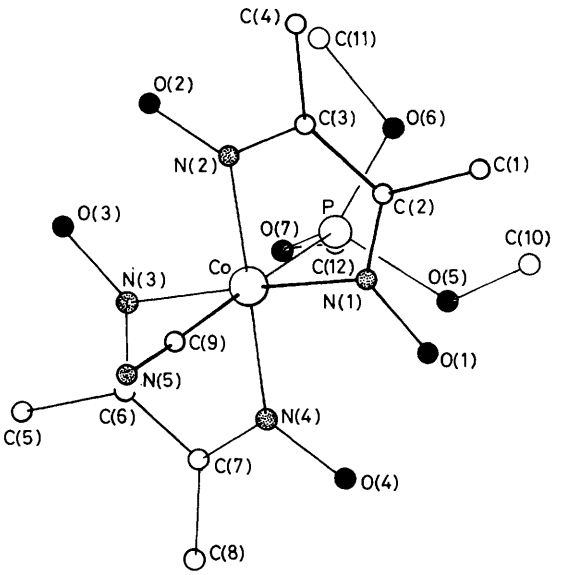
## RESULTS AND DISCUSSION

The numbering scheme for the atoms of both crystallographically independent molecules is shown in the Figure. Relevant bond lengths and angles are given in Table 2.

The two crystallographically independent molecules, A and B, have the four equatorial N atoms coplanar within ±0.002 and ±0.005 Å respectively. The cobalt atom is displaced 0.02 Å from these mean planes towards the phosphite in both molecules. On the contrary, the two Hdmg units are slightly bent towards the CN group in molecule A making an interplanar angle, $\alpha$, of 6.7°, while they are nearly coplanar in molecule B with an interplanar angle of 1°. Such large differences in the bending angle $\alpha$ in the same type of molecule occupying different crystal sites have been observed in other cobaloximes, such as [Co(Hdmg)$_2$Cl{P(OMe)$_3$}].[1] This suggests that crystal packing may influence such bending when the value of $\alpha$ is small.

The CN–Co–P(OMe)$_3$ fragments in A and B are identical within experimental error, see Table 2. The geometrical data are compared in Table 3 with those of

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




Numbering scheme for the non-hydrogen atoms of the two crystallographically independent molecules

TABLE 2

Relevant bond lengths and angles with estimated standard deviations in parentheses

(*a*) Bond lengths (Å)

| | Molecule A | Molecule B |
|---|---|---|
| Co–P | 2.227(3) | 2.222(2) |
| Co–C(9) | 1.903(9) | 1.914(7) |
| Co–N(1) | 1.882(7) | 1.903(7) |
| Co–N(2) | 1.898(5) | 1.892(6) |
| Co–N(3) | 1.880(8) | 1.896(6) |
| Co–N(4) | 1.885(5) | 1.886(6) |
| N(1)–O(1) | 1.357(7) | 1.338(12) |
| N(1)–C(2) | 1.287(10) | 1.302(10) |
| N(2)–O(2) | 1.337(7) | 1.326(11) |
| N(2)–C(3) | 1.297(12) | 1.304(9) |
| N(3)–O(3) | 1.359(7) | 1.360(11) |
| N(3)–C(6) | 1.296(10) | 1.278(9) |
| N(4)–O(4) | 1.351(7) | 1.351(11) |
| N(4)–C(7) | 1.303(12) | 1.299(9) |
| C(1)–C(2) | 1.498(19) | 1.503(13) |
| C(2)–C(3) | 1.461(10) | 1.460(15) |
| C(3)–C(4) | 1.491(11) | 1.475(12) |
| C(5)–C(6) | 1.491(17) | 1.508(13) |
| C(6)–C(7) | 1.433(10) | 1.450(15) |
| C(7)–C(8) | 1.492(11) | 1.495(12) |
| C(9)–N(5) | 1.128(13) | 1.144(10) |

(*b*) Bond angles (°)

| | | |
|---|---|---|
| N(1)–Co–N(2) | 81.0(3) | 81.7(3) |
| N(1)–Co–N(3) | 178.7(3) | 178.6(3) |
| N(1)–Co–N(4) | 99.2(3) | 97.7(3) |
| N(1)–Co–P | 91.9(2) | 88.5(2) |
| N(1)–Co–C(9) | 89.2(4) | 91.1(3) |
| N(2)–Co–N(3) | 99.1(3) | 99.5(3) |
| N(2)–Co–N(4) | 178.4(3) | 178.6(3) |
| N(2)–Co–P | 89.0(2) | 91.6(2) |
| N(2)–Co–C(9) | 88.7(3) | 89.8(3) |
| N(3)–Co–N(4) | 80.7(3) | 81.0(3) |
| N(3)–Co–P | 89.4(2) | 92.2(2) |
| N(3)–Co–C(9) | 89.5(4) | 88.2(3) |
| N(4)–Co–P | 92.6(2) | 89.6(2) |
| N(4)–Co–C(9) | 89.8(3) | 89.0(3) |
| P–Co–C(9) | 177.2(2) | 178.4(3) |
| Co–C(9)–N(5) | 179.1(7) | 177.7(8) |

TABLE 3

Geometrical parameters of the L–Co–X fragment, the bending angle, $\alpha$, and the displacement, $d$ (see text), of the Co atom in some $[Co(Hdmg)_2(X)L]$ complexes. Corresponding values for cobalamins are given for comparison

(*a*) Cobaloximes

| L | X | Co–P/Å | Co–X/Å | α/° | d/Å | PCoX/° |
|---|---|---|---|---|---|---|
| $P(OMe)_3$ | Cl [a] | 2.165(4) | 2.272(4) | 7 | 0.03 | 178.0(2) |
| | | 2.211(4) | 2.289(5) | 1 | 0.01 | 175.7(2) |
| $P(OMe)_3$ | CN [b] | 2.227(3) | 1.903(9) | 7 | 0.02 | 177.2(2) |
| | | 2.222(2) | 1.914(7) | 1 | 0.02 | 178.4(2) |
| $P(OMe)_3$ | $CH_3$ [c] | 2.256(4) | 2.014(14) | 10 | 0.10 | 177.2(5) |

(*b*) Cobalamins [d]

| L | X | Co–N(bzm)/ Å | Co–C/ Å | d/Å | C–Co–N-(bzm)/° |
|---|---|---|---|---|---|
| bzm [e] | CN [f] | 1.97 | 1.92 | 0.05 | 174 |
| bzm | CN [g] | 2.06 | 2.02 | 0.07 | 175 |
| bzm | CN [h] | 2.05 | 1.75 | 0.02 | 176 |
| bzm | Adenosyl | 2.24 | 2.03 | 0.01 | 171 |

[a] Ref. 1. [b] This work. [c] G. Stucky and J. S. Swanson, personal communication. [d] Data from ref. 5. [e] bzm = benzimidazole residue. [f] Vitamin $B_{12}$ wet crystals. [g] Vitamin $B_{12}$, dry crystals. [h] Neovitamin $B_{12}$.

other phosphite–cobaloximes, together with the bending angle, $\alpha$, and the displacement, $d$, of the cobalt atom out of the co-ordination plane towards the phosphite ligand. The most relevant result is the mean Co–CN bond length of 1.909(8) Å which falls in the range 1.88—1.92 Å (mean 1.89 Å) reported for typical octahedral $Co^{III}$–CN distances.[9] This is the shortest value so far reported for organocobaloximes, *ca.* 0.1 Å shorter than the corresponding Co–$CH_3$ bond length [10] (Table 3). This difference may be mainly attributed to the different C($sp$) and C($sp^3$) covalent radii. In $[Co(Hdmg)_2R(py)]$, R = $CH_3$ [11] or $CH{=}CH_2$,[5] the Co–C bonds are 1.998(5) and 1.966(6) Å corresponding to C($sp^3$) and C($sp^2$) covalent radii respectively. Since about the same difference (0.03 Å) should be expected between the Co–C($sp^2$) and Co–C($sp$) distance, a value of 1.93 Å for the latter is only slightly greater than those found for Co–CN bonds. On the other hand, the existence of a certain amount of double-bond character in the Co–C bond must not be ruled out.

The Co–P bond lengths in Table 3 show that the *trans* influence of the CN group is slightly, but noticeably, greater than that of Cl but smaller than that of the methyl group. Similar observations regarding the relative order of *trans* influences, Cl < CN < $CH_3$, have previously been noted in the solution $^{13}C$ and $^{31}P$ n.m.r. spectra of cobaloximes containing trimethyl phosphite,[12,13] as well as in the nucleophilic attack of bromide ion on these complexes.[6] These results follow the same trend as that observed for cobalamins (Table 3), where the Co–CN bonds average 1.90 Å and the Co–adenosyl bond length is 2.03 Å. Furthermore, the Co–N(benzimidazole residue) bond lengths in cyanocobalamins are *ca.* 0.2 Å shorter than that found in the coenzyme. The above data lend support to a significant similarity in structural behaviour, at least for the cobalt co-ordination sphere, between cobaloximes and cobalamins.

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