Crystal Structure of a Substituted Alkylcobaloxime

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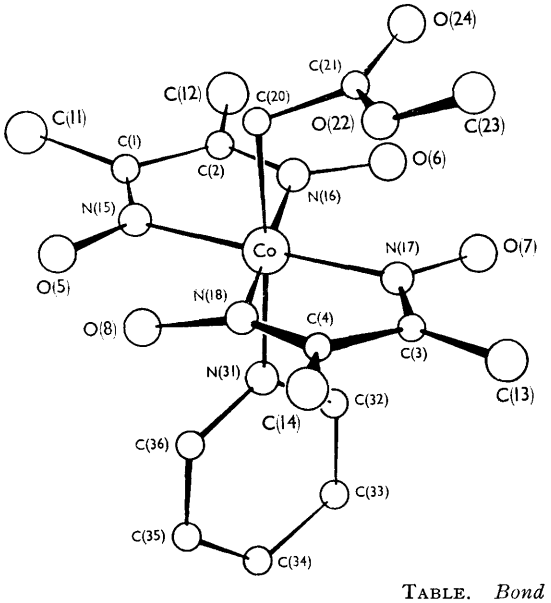
RECENT experiments[1] have shown that alkyl- and alkenyl-cobaloximes of the type reported here mimic many reactions of the vitamin B_{12} coenzymes and alkylcobalamins. This *X*-ray structure analysis was undertaken to compare the cobalt co-ordination in the cobaloximes with that in 5′-deoxyadenosylcobalamin.

The structure of *O*-methyl-(Co-C)carboxymethyl-(bisdimethylglyoximato)pyridinato-cobalt, $C_{16}H_{24}O_6N_5Co$, has been determined. Crystal data: $M = 441{\cdot}33$, monoclinic with $a = 13{\cdot}53$, $b = 9{\cdot}87$, $c = 16{\cdot}08$ Å, $\beta = 115{\cdot}3°$, $V = 1942$ Å^3, $Z = 4$, $D_c = 1{\cdot}512$ g./cm.^{3}, centrosymmetric with space group $P2_1/c$ (C_{2h}^5, No. 14), $\mu = 9{\cdot}6$ cm.$^{-1}$ for Mo-K_α radiation. An uncut crystal approximately $0{\cdot}3 \times 0{\cdot}25 \times 0{\cdot}5$ mm. was used for data collection. It was mounted with the long dimension (*b*) parallel to the ϕ axis on the 4 circle diffractometer. The 2θ scan technique, a NaI scintillation detector using pulse height discrimination, and a 0·001 inch niobium foil incident beam filter were used to collect 1788 reflections out to $\sin\theta/\lambda = 0{\cdot}481$.

The Co–Co peaks were easily located in the Patterson function and an electron density synthesis, calculated with cobalt phases, showed the remainder of the molecule. One difference synthesis was calculated to check the trial structure. Refinement was then carried out by full-matrix least-squares. Anisotropic temperature factors were allowed for the cobalt atom but all other atoms were constrained to isotropic motion. After 3 cycles of refinement, the calculated structure

factors indicated possible errors in several reflections. These were remeasured and refinement continued with 2 further cycles of least squares. R (including unobserved reflections) was 7·7%. Hydrogen atom contributions have not been included in the structure factor calculations but they are clearly evident on a difference synthesis calculated after the last cycle of least squares.

The Figure shows the numbering of the atoms. The bond distances and angles are shown in the Table. The standard deviations, calculated from the least squares process, are 0·006 Å for the cobalt distances and about 0·012 Å for the other bonds. Bond angles about cobalt have standard deviations of 0·3° with 0·6° for other angles. The cobalt atom and the 4 nitrogen atoms of the dimethylglyoxime ligands are planar to about 0·02 Å. The plane of the pyridine ring makes an angle of 88° with the Co–N plane of the dimethylglyoxime ligands and bisects the N(15)–Co–N(18) and N(16)–Co–N(17) angles. The plane of the 4 carboxymethyl atoms [C(20), C(21), O(22), and O(24)] makes an angle of 30° with the Co–N plane. The 95° C(20)–Co–N(17) angle appears to be due to the 2·86 Å contact between the carboxy-carbon, C(21), and the nitrogen, N(17), of the affected angle. The two hydrogen atoms on C(20) are clearly evident on the latest difference synthesis.



The average Co–N distance for the equatorial ligands is 1·88 Å. This compares with average values of 1·94 Å for the 4 equatorial ligands in 5′-deoxyadenosylcobalamin,[2] 1·86 Å in the wet crystals of cyanocobalamin[3] and 1·91 Å in the dry crystals of cyanocobalamin.[4] Due to the lower accuracy attained in the more complex crystal structures, the differences are probably not significant, except possibly in the coenzyme. The axial Co–N distance is 2·04 Å in this cobaloxime, 2·23 Å in the coenzyme[2] and it averages 2·02 Å in the cyanocobalamin structures. The Co–C bond distances are identical in the coenzyme and in this cobaloxime: 2·05 and 2·04 Å, respectively. The Co–C-cyano bonds in cyanocobalamin average 1·97 Å as compared with 1·89 Å reported[5] in $Co^{III}(CN)_6$.

TABLE. *Bond distances and angles*

Atoms	Distance	Atoms	Distance	Atoms	Distance	Atoms	Distance
Co–N(15)	1·88 Å	C(1)–C(11)	1·52 Å	C(3)–C(4)	1·47 Å	N(31)–C(32)	1·34 Å
Co–N(16)	1·87	C(1)–C(2)	1·45	C(4)–C(14)	1·51	C(32)–C(33)	1·39
Co–N(17)	1·88	C(2)–C(12)	1·52	C(4)–N(18)	1·27	C(33)–C(34)	1·38
Co–N(18)	1·89	C(2)–N(16)	1·28	N(18)–O(8)	1·39	C(34)–C(35)	1·35
Co–N(31)	2·04	N(16)–O(6)	1·37	C(20)–C(21)	1·48	C(35)–C(36)	1·39
Co–C(20)	2·04	O(7)–N(17)	1·36	C(21)–O(24)	1·22	C(36)–N(31)	1·36
O(5)–N(15)	1·37	N(17)–C(3)	1·30	C(21)–O(22)	1·34	O(6) · · · O(7)	2·51
N(15)–C(1)	1·29	C(3)–C(13)	1·46	O(22)–C(23)	1·46	O(5) · · · O(8)	2·49

Atoms	Angle	Atoms	Angle	Atoms	Angle
N(15)–Co–N(16)	80·7°	N(15)–C(1)–C(11)	122·7	C(3)–C(4)–C(14)	123·0
N(16)–Co–N(17)	99·7	C(11)–C(1)–C(2)	124·9	C(14)–C(4)–N(18)	124·5
N(17)–Co–N(18)	80·0	C(2)–C(1)–N(15)	112·3	C(3)–C(4)–N(18)	112·5
N(18)–Co–N(15)	99·6	C(1)–C(2)–C(12)	123·8	Co–N(18)–C(4)	118·2
N(15)–Co–C(20)	84·6	C(12)–C(2)–N(16)	124·0	Co–N(18)–O(8)	121·5
N(15)–Co–N(31)	90·7	N(16)–C(2)–C(1)	112·2	O(8)–N(18)–C(4)	119·7
N(16)–Co–C(20)	89·4	C(2)–N(16)–O(6)	120·4	Co–N(31)–C(32)	123·5
N(16)–Co–N(31)	90·8	Co–N(16)–O(6)	121·7	Co–N(31)–C(36)	119·0
N(17)–Co–C(20)	94·9	Co–N(16)–C(2)	117·7	C(36)–N(31)–C(32)	117·5
N(17)–Co–N(31)	89·7	Co–N(17)–O(7)	123·1	N(31)–C(32)–C(33)	122·6
N(18)–Co–C(20)	87·8	Co–N(17)–C(3)	117·9	C(32)–C(33)–C(34)	119·1
N(18)–Co–N(31)	92·1	C(3)–N(17)–O(7)	118·9	C(33)–C(34)–C(35)	118·8
Co–N(15)–O(5)	122·3	N(17)–C(3)–C(13)	124·0	C(34)–C(35)–C(36)	120·3
Co–N(15)–C(1)	116·9	C(13)–C(3)–C(4)	125·0°	C(35)–C(36)–N(31)	121·6
C(1)–N(15)–O(5)	120·8°	C(4)–C(3)–N(17)	111·0		

The similarity between the cobalt bonds of the cobaloxime and the vitamin B_{12} coenzyme strongly support the claim that the cobalt ligand fields are closely similar in both molecules. The shorter Co–N axial bond in the cobaloxime implies slightly tighter bonding for the base than in vitamin B_{12} coenzyme.

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