

**Structure of *trans*-Bis(2,3-butanedione dioximato-*N,N'*)(imidazole-*N*³)methylcobalt(III),
C₁₂H₂₁CoN₆O₄***

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Abstract. $M_r = 372.28$, monoclinic, $P2_1/n$, $a = 8.075$ (2), $b = 13.969$ (3), $c = 14.892$ (4) Å, $\beta = 97.98$ (2)°, $V = 1664$ Å³, $Z = 4$, $D_x = 1.48$ Mg m⁻³, $Mo K\alpha_1$, $\lambda = 0.70932$ Å, $\mu = 1.05$ mm⁻¹, $F(000) = 776$, $T = 295$ K, final $R(F) = 0.043$ for 2765 significant reflections [$I_{net} > 2\sigma(I_{net})$]. The two butanedione dioximato units and the Co atom lie in a plane with the planar imidazole group perpendicular to the butanedione plane. The Co coordination is a slightly distorted octahedron. The structure has two O—H...O intramolecular hydrogen bonds and chains of hydrogen-bonded molecules are formed almost perpendicular to the bc plane.

Introduction. The title compound is a model compound for the more complex cobalamines like vitamin B₁₂ coenzyme. The structure has been determined as a further aid to understanding the action of the cobalamines.

Experimental. Brown prismatic crystals from a 1:9 water–ethanol mixture. Crystal $0.3 \times 0.2 \times 0.15$ mm, $\theta/2\theta$ scan with line profile analysis (Grant & Gabe, 1978), $2\theta_{max} = 60^\circ$, Picker four-circle automatic diffractometer, graphite-monochromated $Mo K\alpha$ radiation, no absorption correction, data corrected for direct-beam polarization (Le Page, Gabe & Calvert, 1979) and Lorentz effects, unit-cell parameters from least-squares refinement of measured angle values for 37 reflections with $45 < 2\theta < 50^\circ$. 4871 independent measurements, $-11 < h < 11$, $0 \leq k \leq 19$, $0 \leq l \leq 12$, 2765 observed with $I_{net} > 2\sigma(I_{net})$; 3 standard reflections measured every 100 reflections showed no significant variation; structure solution by Patterson and heavy-atom techniques; full-matrix least-squares refinement on $|F|$, isotropic temperature factors, gave $R(F) = 0.090$, $R_w(F) = 0.078$; hydrogen positions, from ΔF synthesis and geometry, refined with isotropic temperature factors; anisotropic refinement for all

Table 1. Positional parameters and equivalent isotropic temperature factors with e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}(\text{Å}^2)^*$
Co	0.16241 (5)	0.11544 (3)	0.27808 (3)	2.51
C(1)	0.2579 (4)	0.0140 (3)	0.54423 (23)	5.09
C(2)	0.2063 (4)	0.06705 (24)	0.45790 (22)	3.28
C(3)	0.1106 (4)	0.15515 (24)	0.45236 (23)	3.47
C(4)	0.0576 (5)	0.2045 (3)	0.53340 (25)	6.25
N(2)	0.2416 (3)	0.03973 (18)	0.37949 (17)	2.89
N(3)	0.0769 (3)	0.18646 (18)	0.36977 (18)	3.38
O(2)	0.3279 (3)	-0.04424 (16)	0.37588 (17)	3.89
O(3)	-0.0124 (3)	0.26635 (16)	0.35200 (17)	5.02
C(1')	0.2731 (5)	0.0298 (3)	0.02586 (24)	5.90
C(2')	0.2194 (4)	0.07940 (24)	0.10656 (22)	3.38
C(3')	0.1184 (4)	0.16632 (25)	0.10121 (23)	3.63
C(4')	0.0590 (5)	0.2191 (3)	0.01603 (24)	6.20
N(2')	0.2561 (3)	0.04795 (17)	0.18816 (17)	2.73
N(3')	0.0854 (3)	0.19341 (18)	0.17941 (18)	3.27
O(2')	0.34998 (24)	-0.03091 (14)	0.20693 (15)	3.43
O(3')	-0.0096 (3)	0.27249 (16)	0.18609 (17)	4.88
N(11)	-0.0458 (3)	0.03423 (17)	0.25230 (16)	2.68
C(12)	-0.2051 (4)	0.06017 (23)	0.24000 (22)	3.53
N(13)	-0.3035 (3)	-0.01539 (24)	0.21811 (20)	4.03
C(14)	-0.2048 (4)	-0.09334 (25)	0.21543 (23)	4.17
C(15)	-0.0465 (4)	-0.06137 (22)	0.23633 (23)	3.60
C(21)	0.3700 (4)	0.19342 (23)	0.29756 (22)	4.14

* B_{eq} is the arithmetic mean of the principal axes of the thermal ellipsoid.

non-hydrogen atoms; final $R(F) = 0.043$, $R_w(F) = 0.027$, including anomalous-dispersion effects for Co, $w = 1/\sigma^2(F_o)$, $S = 1.80$, $R(\text{all}) = 0.100$, $\Delta/\sigma(\text{max}) = 1$, $\Delta/\sigma(\text{mean}) = 0.1$, final difference map within ± 0.3 e Å⁻³. Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). All calculations using the NRC-PDP-8e system of programs (Larson & Gabe, 1978) adapted for the VAX computer. Atomic positions and equivalent isotropic temperature factors for non-hydrogen atoms are listed in Table 1. ‡

‡ Lists of structure factors, atomic parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39328 (36 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Discussion. A stereoview of the molecule is shown in Fig. 1 and Fig. 2 shows the bond lengths and angles. The numbering scheme has been chosen to emphasize the similarity between the two butanedione groups. No crystallographic symmetry is present or implied. The distances and angles observed in the equatorial plane [*viz* the plane of the bis(butanedione) and Co atom] are comparable with those observed in other related structures (Palenik, Sullivan & Naik, 1976; Pannhorst, 1977). The Co—C(21) distance [1.985 (3) Å] is significantly shorter than the distances observed in the

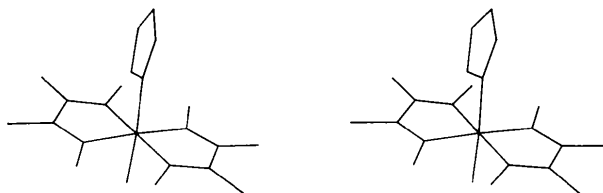


Fig. 1. Stereoview of the molecule.

vitamin B₁₂ coenzyme, 2.05 Å (Lenhert, 1968), and 2.06 Å in cobaloxime (Pannhorst, 1977). The coordination around the Co atom deviates only slightly from octahedral geometry. The N(11)—Co—C(21) angle is 177.2 (1)° and the four other N—Co—C angles vary between 88.1 (1) and 90.2 (1)°.

The two butanedione dioximato groups are almost coplanar with a dihedral angle of 1.8 (2)°. The imidazole group is planar ($\chi^2 = 1.4$) and its position is close to that of a theoretical perpendicular mirror plane between the two butanedione groups. The dihedral angles between the imidazole group and the two planes N(2), Co, N(3'), N(11) and N(2'), Co, N(3), N(11) are 55.2 (2) and 44.0 (2)°, respectively, and thus the group is about 5° from this ideal plane. In spite of this there was no evidence of any disorder or librational motion of this plane. The bonds N(3)—O(3) and N(2')—O(2') show some evidence of double-bond character, although the lengths are not markedly different from those of N(2)—O(2) and N(3')—O(3') (see Fig. 2). The main evidence is the clear indication of hydrogen atoms attached to O(2) and O(3') and the lack of such evidence for O(2') and O(3). In the imidazole ring there is a double bond between C(14) and C(15) and the two C(12)—N bonds are significantly shorter than C—N single bonds.

The intramolecular distances between O(3)···O(3') and O(2)···O(2') are 2.475 (3) and 2.553 (3) Å, suggesting hydrogen bonding. The H(3')···O(3) and H(2)···O(2') distances are 1.29 (4) and 1.64 (3) Å, respectively, though the large difference may not be real as H(3')—O(3') is 1.20 (4) and H(2)—O(2) is 0.94 (3) Å. The O(3')—H···O(3) angle is 168 (3)° and the O(2)—H···O(2') angle is 163 (3)°. There is an intermolecular hydrogen bond between O(2') and N(13) at 1 + x, y, z. The O(2')···N(13) distance is 2.834 (6) Å and the O(2')···H(13) distance is 1.98 (2) Å. The bond is closely parallel to the *a* axis and chains of hydrogen-bonded molecules are formed almost perpendicular to the *bc* plane.

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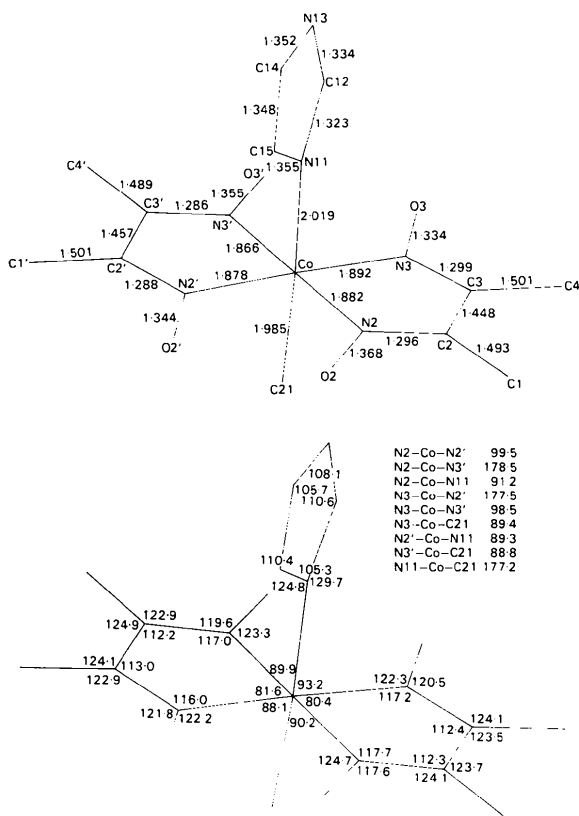


Fig. 2. Bond lengths (Å) and angles (°) with average e.s.d.'s 0.005 Å and 0.3° in bonds and angles involving C, N, O, and 0.003 Å and 0.12° in distances and angles involving Co.

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