Crystal and Molecular Structure of Aquomethylbis(dimethylglyoximato)-cobalt(III)

By **Dennis L. McFadden** and **Andrew T. McPhail,*** Paul M. Gross Chemical Laboratory, Duke University, Durham, North Carolina 27706, U.S.A.

Crystals of the title compound are orthorhombic, space group *Pnma*, with a = 13·182(12), b = 9·115(6), c = 12·132(7) Å, Z = 4. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations to R 0·039 for 1070 independent reflexions collected on an automatic diffractometer. The molecule has C_s symmetry with distorted octahedral co-ordination around the cobalt atom; mean equatorial distances: Co–N 1·890(3) Å; axial lengths: Co–O(H_2O) 2·058(3), Co–C(sp^3) 1·990(5) Å. The intramolecular hydrogen-bonded bridge [O · · · O 2·486(4) Å] is not symmetrical. Comparison of the Co–C(sp^3) axial bond lengths in like complexes is made and shows that there is no clear evidence for a *cis*-influence with variation in equatorial ligand.

SYNTHETIC, mechanistic, and kinetic studies of compounds containing cobalt–carbon σ bonds received great stimulation following the discovery of such a bond in vitamin B_{12}.[1,2] Among the many models studied to date are a number of alkylbis(dimethylglyoximato)cobalt(III) complexes which have proved capable of simulating some of the vitamin B_{12} reactions.[3] Since the detailed molecular geometries of only a few of these compounds are known, we have initiated a programme of *X*-ray studies aimed at providing this information for a variety of ligands. We here report the structure of aquomethylbis(dimethylglyoximato)-cobalt(III) (Figure 1).

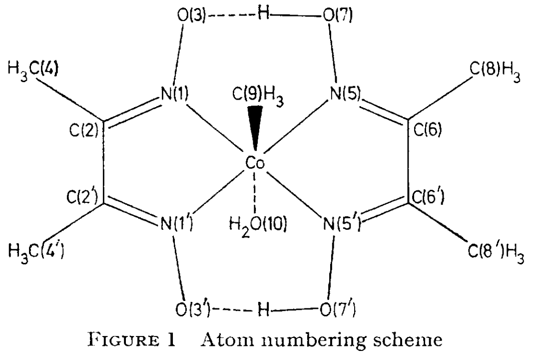

FIGURE 1 Atom numbering scheme

EXPERIMENTAL

Crystal Data.—$C_9H_{19}CoN_4O_5$, M = 322·2, Orthorhombic, a = 13·182(12), b = 9·115(6), c = 12·132(7) Å, U = 1458 Å^3, D_c = 1·468, Z = 4, D_m = 1·47, $F(000)$ = 672. Mo-K_α radiation, λ = 0·71069 Å; μ(Mo-K_α) = 12·5 cm^{-1}. Space group *Pnma* (D_{2h}^{16}) or $Pna2_1$ (C_{2v}^{9}), with b and c axes interchanged, from systematic absences: $0kl$ for $k + l \neq 2n$, and $hk0$ for $h \neq 2n$; shown to be the former by the structure refinement.

Crystallographic Measurements.—A crystal with dimensions *ca.* 0·2 × 0·3 × 0·3 mm was oriented on a glass fibre such that the b axis was parallel to the spindle axis. Preliminary cell dimensions and space-group data were obtained from rotation, Weissenberg, and precession photographs. Accurate cell parameters were obtained by centring 29 high-angle reflexions on an Enraf–Nonius CAD 3 diffractometer (Zr-filtered Mo-K_α radiation, take-off angle 3°). One octant of intensity data for reflexions having $2\theta \leqslant 55°$ was collected (save those excluded by the beam stop) by use of the θ—2θ scanning technique with scanwidths $(0·70 + 0·09 \tan\theta)°$. Attenuators were inserted automatically to ensure that counting rates did not exceed 2500 counts s^{-1}; attenuation factors were derived experimentally. Background counts for a time equal to half the duration of the scan period were made at each end of the scan range. No significant variation of intensity was noted for a standard reflexion measured after every 49 reflexions. Of 2062 independent measurements, 1070 reflexions having $I > 2·0\sigma(I)$ were used in the structure analysis. Lorentz and polarisation corrections were applied but no allowance was made for extinction or absorption.

Structure Analysis.—The structure was solved by the heavy-atom approach. With $Z = 4$ in the centrosymmetric space group *Pnma*, the molecule is constrained to possess C_s symmetry with the cobalt, axial methyl carbon, and water oxygen atoms all lying in the mirror plane. Approximate x and z co-ordinates for the cobalt atom were derived from the three-dimensional Patterson map, and carbon, nitrogen, and oxygen positions were obtained from the three-dimensional cobalt-phased Fourier synthesis (R 0·45). Structure factors calculated with all non-hydrogen atoms located gave R 0·32. Refinement

---

[1] For a recent review, see D. Dodd and M. D. Johnson, *J. Organometallic Chem.*, 1973, **52**, 1.

[2] J. M. Pratt, 'The Inorganic Chemistry of Vitamin B_{12},' Academic Press, New York, 1972.

[3] G. N. Schrauzer, *Accounts Chem. Res.*, 1968, **1**, 97.

of the molecular parameters by full-matrix least-squares calculations reduced R to 0·101 when isotropic temperature factors were assigned, and subsequently to R 0·053 with anisotropic temperature factors. Hydrogen atom positions were obtained from a difference-Fourier map and their inclusion in the next round of structure-factor calculations decreased R to 0·048. Further least-squares calculations in which the hydrogen atom positions and isotropic thermal parameters were also varied brought the refinement to convergence at R 0·039. There was no indication either from the heavier atom thermal parameters or from the refinement of the hydrogen atoms that the molecular symmetry ought to be reduced and consequently the selection of the space group *Pnma* was justified.

Final atomic co-ordinates and thermal parameters are given in Tables 1 and 2. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20888 (9 pp., 1 microfiche).* Neutral atom scattering factors for cobalt, carbon, nitrogen, and oxygen were taken from ref. 4, and anomalous dispersion effects for cobalt[5] were included. For the hydrogen atoms the scattering factor of ref. 6 was used. In the least-squares calculations the weighting scheme employed was $\sqrt{w} = 1$ for $|F_o| \leqslant 20{\cdot}0$ and $\sqrt{w} = 20{\cdot}0|F_o|$ for $|F_o| > 20{\cdot}0$ and this gave satisfactory analysis for $\langle w\Delta^2\rangle$ in ranges of $|F_o|$ and sin θ.

TABLE 1

Fractional atomic co-ordinates ($\times 10^4$) and thermal parameters * ($\times 10^4$) for non-hydrogen atoms, with estimated standard deviations in parentheses

Atom	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Co	1291·8(5)	2500	940·7(6)	41(3)	63(1)	57(1)	0	−8(1)	0
N(1)	1294(2)	3855(3)	−232(3)	45(1)	68(3)	73(2)	0(4)	−5(4)	4(5)
C(2)	1268(3)	3299(4)	−1217(3)	42(2)	101(4)	63(2)	3(6)	9(5)	27(5)
O(3)	1315(2)	5314(3)	−59(3)	62(1)	66(2)	98(2)	−1(4)	−15(4)	22(5)
C(4)	1247(3)	4194(6)	−2242(4)	69(2)	170(6)	77(1)	19(9)	23(7)	66(8)
N(5)	1286(2)	3849(3)	2130(3)	44(5)	117(4)	75(2)	−5(6)	−8(4)	−44(6)
C(6)	1239(3)	3307(5)	3125(4)	46(2)	190(6)	69(3)	2(7)	−10(5)	−30(6)
O(7)	1292(2)	5327(3)	1991(3)	67(2)	99(3)	108(2)	−11(5)	−15(4)	−72(5)
C(8)	1195(4)	4214(8)	4155(4)	88(3)	307(10)	70(3)	7(10)	3(7)	−119(10)
C(9)	2802(4)	2500	928(6)	48(3)	101(6)	89(5)	0	−14(7)	0
O(10)	−268(3)	2500	1012(3)	47(2)	81(4)	79(3)	0	−12(4)	0

* Anisotropic temperature factors are in the form: $B\sin^2\theta/\lambda^2 = b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl$.

TABLE 2

Fractional atomic co-ordinates ($\times 10^3$) and isotropic thermal parameters for hydrogen atoms, labelled according to the atoms to which they are bonded

Atom	x	y	z	B/Å^2
H(4α)	169(5)	406(6)	−271(5)	9(2)
H(4β)	60(4)	395(6)	−270(5)	9(2)
H(4γ)	119(3)	522(6)	−215(4)	6(1)
H(7)	132(3)	538(6)	108(3)	7(1)
H(8α)	186(5)	395(7)	455(6)	12(2)
H(8β)	109(4)	524(7)	388(4)	8(1)
H(8γ)	66(5)	398(7)	436(5)	9(2)
H(9α)	304(8)	250	20(8)	11(3)
H(9β)	304(4)	337(6)	111(4)	7(1)
H(10)	−52(3)	324(5)	75(4)	5(1)

DISCUSSION

Interatomic distances and angles are given in Table 3, and the atom numbering scheme is shown in Figure 1. The $MeCo(dmg)_2(H_2O)$ molecules (dmg = monoanion of dimethylglyoxime) lie across crystallographic mirror planes of symmetry which bisect the C(2)–C(2′) and C(6)–C(6′) bonds. The cobalt atom is in a distorted octahedral environment and lies in the equatorial plane (Δ 0·003 Å) through the approximately equidistant nitrogen atoms while the methyl group and water molecule occupy the axial positions. The mean Co–N distance [1·890(3) Å], is in excellent agreement with the corresponding mean of 1·90 in $PhCo(bae)(H_2O)$[7] [bae = dianion of bis(acetylacetone)ethylenedi-imine] and $[EtCo(dmg)(dmgH)Cl],H_2O$,[8] and 1·89 Å in Co(salen) complexes [salen = dianion of bis(salicylaldehyde)ethylenedi-imine] with a variety of axial ligands.[9]

In a recent article describing the results of a structural study of $[(CH_2{:}CH)Co(salen)(py)]$ (py = pyridine),[10] Randaccio *et al.* surveyed the then known axial Co–C lengths in octahedral organocobalt complexes and suggested that there was possibly sufficient evidence to indicate the existence of a *cis*-influence of the different quadridentate ligands on the axial bonds. The entries in Table 4 include the results of the present study and of our earlier work on $[EtCo(dmg)(dmgH)Cl],H_2O$.[8] From these we conclude that there is no evidence from the available structural data to support their contention, for the Co–C(sp^3) lengths are seen to be essentially constant (mean 2·00 Å), despite the variation in equatorial ligand. In this series further studies on bae complexes would be highly desirable to obtain more accurate values for the Co–C(sp^3) distances in such species since only one value is available at present.

---

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue (items less than 10 pp. are supplied as full size copies).

[4] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[5] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

[6] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[7] S. Brückner, M. Calligaris, G. Nardin, and L. Randaccio, *Chem. Comm.*, 1970, 152.

[8] A. L. Crumbliss, J. T. Bowman, P. L. Gaus, and A. T. McPhail, *J.C.S. Chem. Comm.*, 1973, 415.

[9] M. Cesari, C. Neri, G. Perago, E. Perrotti, and A. Zazzetta, *Chem. Comm.*, 1970, 276.

[10] M. Calligaris, G. Nardin, and L. Randaccio, *J.C.S. Dalton*, 1972, 1433.

TABLE 3

Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Intramolecular distances

Co–N(1)	1·884(3)	C(2)–C(4)	1·488(6)
Co–N(5)	1·896(3)	C(2)–C(2′)	1·456(5)
Co–C(9)	1·990(5)	N(5)–C(6)	1·306(5)
Co–O(10)	2·058(3)	N(5)–O(7)	1·358(4)
N(1)–C(2)	1·298(5)	C(6)–C(8)	1·499(7)
N(1)–O(3)	1·347(3)	C(6)–C(6′)	1·471(7)
C(4)–H(4α)	0·83(6)	C(8)–H(8β)	1·01(6)
C(4)–H(4β)	1·04(5)	C(8)–H(8γ)	0·78(6)
C(4)–H(4γ)	0·95(5)	C(9)–H(9α)	0·88(5)
O(7)–H(7)	1·11(4)	C(9)–H(9β)	0·94(9)
C(8)–H(8α)	1·03(7)	O(10)–H(10)	0·80(5)
O(3) · · · O(7)	2·486(4)	N(1) · · · H(9α)	2·66(5)
O(3) · · · H(4γ)	2·55(5)	N(5) · · · H(9β)	2·66(5)

(*b*) Some intermolecular distances

O(10) · · · O(3^{I})	2·69	O(7) · · · C(4^{II})	3·40
C(4) · · · O(7^{I})	3·39	O(8) · · · O(3^{II})	3·44

(*c*) Valency angles

N(1)–Co–N(5)	98·6(1)	C(2)–N(1)–O(3)	122·0(3)
N(1)–Co–N(1′)	81·9(1)	N(1)–C(2)–C(4)	123·7(3)
N(1)–Co–N(5′)	179·4(1)	N(1)–C(2)–C(2′)	113·0(3)
N(1)–Co–C(9)	89·6(2)	C(4)–C(2)–C(2′)	123·3(3)
N(1)–Co–O(10)	91·9(1)	Co–N(5)–C(6)	117·3(3)
N(5)–Co–N(5′)	80·8(1)	Co–N(5)–O(7)	123·3(2)
N(5)–Co–C(9)	90·6(2)	C(6)–N(5)–O(7)	119·4(3)
N(5)–Co–O(10)	87·9(1)	N(5)–C(6)–C(8)	124·3(4)
C(9)–Co–O(10)	178·0(2)	N(5)–C(6)–C(6′)	112·2(3)
Co–N(1)–C(2)	116·0(2)	C(8)–C(6)–C(6′)	123·5(4)
Co–N(1)–O(3)	122·0(2)		
C(2)–C(4)–H(4α)	119(4)	C(6)–C(8)–H(8α)	103(4)
C(2)–C(4)–H(4β)	110(3)	C(6)–C(8)–H(8β)	104(3)
C(2)–C(4)–H(4γ)	117(3)	C(6)–C(8)–H(8γ)	99(4)
H(4α)–C(4)–H(4β)	101(5)	H(8α)–C(8)–H(8β)	119(5)
H(4α)–C(4)–H(4γ)	106(5)	H(8α)–C(8)–H(8γ)	124(6)
H(4β)–C(4)–H(4γ)	102(4)	H(8β)–C(8)–H(8γ)	104(5)
H(10)–O(10)–H(10′)	111(4)		

Roman numeral superscripts refer to the following transformations of the co-ordinates of Table 1:

I, $-x, \frac{1}{2}+y, -z$ II, $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$

TABLE 4

Equations of least-squares planes in the form $AX + BY + CZ + D = 0$, where X, Y, and Z, are in Å, and displacements (Å) of atoms from the plane

Plane (A): Co, N(1), C(2), O(3), C(4), N(5), C(6), O(7), C(8)

$$-0{\cdot}9999X + 0{\cdot}0115Y - 0{\cdot}0082Z + 1{\cdot}6412 = 0$$

[Co − 0·045, N(1) − 0·021, C(2) 0·017, O(3) − 0·036, C(4) 0·064, N(5) − 0·035, C(6) 0·012, O(7) −0·026, C(8) 0·069, C(9) − 2·034, O(10) 2·011]

Plane (B): Co, N(1), C(2), O(3), C(4)

$$-0{\cdot}9995X + 0{\cdot}0209Y + 0{\cdot}0230Z + 1{\cdot}6334 = 0$$

[Co 0·005, N(1) − 0·004, C(2) − 0·008, O(3) 0·000, C(4) 0·007, C(9) − 1·984, O(10) 2·063, H(4α) − 0·60, H(4β) 0·85, H(4γ) 0·10]

Plane (C): Co, N(5), C(6), O(7), C(8)

$$-0{\cdot}9991X + 0{\cdot}0167Y - 0{\cdot}0392Z + 1{\cdot}7194 = 0$$

[Co 0·011, N(5) − 0·017, C(6) − 0·010, O(7) 0·004, C(8) 0·012, C(9) − 0·976, 0(10) 2·063, H(8α) − 0·89, H(8β) 0·18, H(8γ 0·71]

Dihedral angle between planes: (*B*)–(*C*) 3·5°.

The mean dimensions of the dmg ligand, N–C(*sp*^{2}) 1·302(5), N–O 1·353(4), C(*sp*^{2})–C(*sp*^{3}) 1·497(7), and C(*sp*^{2})–C(*sp*^{2}) 1·464(7) Å, are close to the corresponding values found in other transition-metal complexes: $(MeO_2C{:}CH_2)Co(dmg)_2(py)$ [11] 1·29(1), 1·37(1), 1·50(1), 1·46(1); $(dmg)_2(imidazole)_2Fe$ [12] 1·317(9), 1·387(9), 1·528(10), 1·467(9); (EtMeglyoximato)Ni [13] 1·298(5), 1·347(5), 1·503(7), 1·462(7) Å. In all these compounds the bond lengths are indicative of the presence of cyclic delocalisation. It has been noted elsewhere [12] that N–O distances appear to be sensitive indicators of the bridging proton position in $(dmg)_2$ complexes, dissimilar lengths implying that the proton is not symmetrically located with respect to the bridging oxygen atoms but that it lies closer to that oxygen atom which is associated with the longer N–O length. While there is only a small difference between the N–O lengths found in the present study (Δ/σ 3), nonetheless the

TABLE 5

Axial Co–C(*sp*^{3}) bond lengths (Å) in some Co^{III} complexes

Compound	Co–C(*sp*^{3})	*cis*-Ligand
$(MeO_2C{\cdot}CH_2)Co(dmg)_2(py)$ [a]	2·040(6)	dmg
$[EtCo(dmg)(dmgH)Cl],H_2O$ [b]	2·000(14)	dmg
$MeCo(dmg)_2(H_2O)$ [c]	1·990(5)	dmg
$[EtCo(salen)]_2$ [d]	1·990(7)	salen
$[(NC{\cdot}CH_2)Co(salen)]_n$ [e]	1·99(2)	salen
$[(MeCO{\cdot}CH_2)Co(salen)(MeOH)]$ [e]	2·02(2)	salen
[MeCo(bae)] [f]	1·95(2)	bae

[a] Ref. 11. [b] Ref. 8. [c] Present work. [d] M. Calligaris, D. Minichelli, G. Nardin, and L. Randaccio, *J. Chem. Soc.* (*A*), 1971, 2720. [e] Ref. 9. [f] S. Brückner, M. Calligaris, G. Nardin, and L. Randaccio, *Inorg. Chim. Acta*, 1969, **3**, 308.

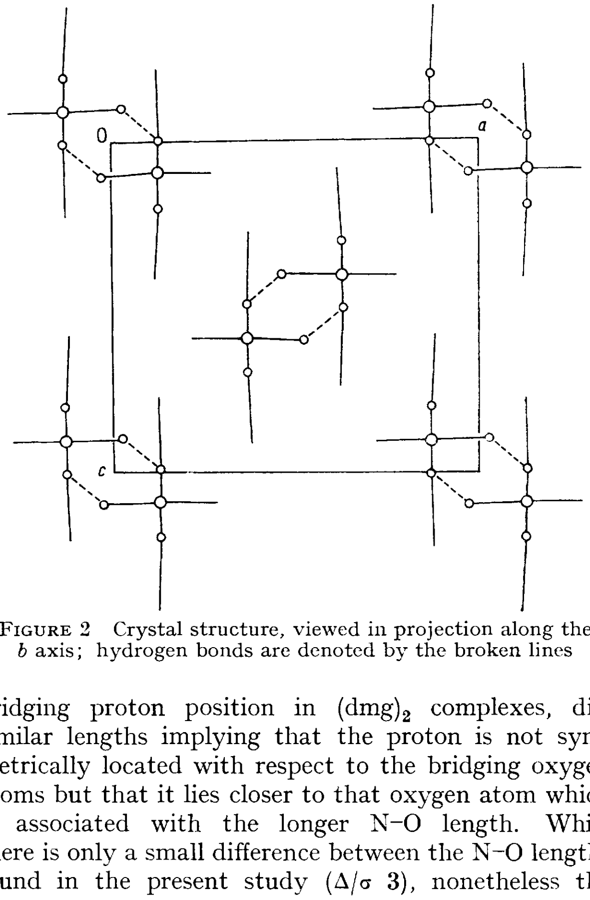

FIGURE 2 Crystal structure, viewed in projection along the *b* axis; hydrogen bonds are denoted by the broken lines

---

[11] P. G. Lenhert, *Chem. Comm.*, 1967, 980.

[12] K. Bowman, A. P. Gaughan, and Z. Dori, *J. Amer. Chem. Soc.*, 1972, **94**, 727.

[13] R. H. Bowers, C. V. Banks, and R. A. Jacobson, *Acta Cryst.*, 1972, **B28**, 2318.

refined position for the bridging hydrogen atom is in accord with this concept for it lies closer to O(7) than to O(3) [N(1)–O(3) 1·347(3), N(5)–O(7) 1·358(4), O(7)–H(7) 1·11(4), O(3)–H(7) 1·38(4) Å].

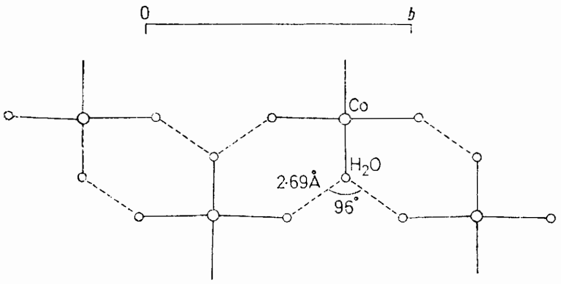

FIGURE 3 Intermolecular hydrogen bonding arrangement viewed in projection along the *c* axis

Table 5 lists displacements of selected atoms from least-squares planes through groups of atoms. The dmg ligands are essentially planar and are mutually inclined at an angle of 3·5°. The small, but significant, deviation of the C(9)–Co–O(10) angle, 178·0(2)°, from an ideal linear value does not appear to be a consequence of intramolecular non-bonded interactions but it seems to arise in order to achieve a desirable geometry to yield an extensive intermolecular hydrogen bonded arrangement about centres of symmetry in the crystal. Figure 2 shows a view of the molecular packing in the crystal, and the intermolecular hydrogen bonding scheme is shown more clearly in Figure 3.

We thank Dr. A. L. Crumbliss for supplies of the crystals used in this analysis, and the U.S. National Science Foundation for funds for purchase of the diffractometer. Calculations were performed on an IBM 370/65 computer at the Triangle Universities Computation Centre, North Carolina.

[3/1720 *Received*, 14*th August*, 1973]