Crystal and Molecular Structure of Cobalt(II) Monoglycerolate

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A three-dimensional structural analysis and infra-red data for a new metal alkoxide, cobalt(II) mono-glycerolate has been obtained. The complex, which can be assigned the formula $[Co(C_3H_6O_3)]_n$, crystallizes in space group $P2_1/c$, with unit-cell dimensions $a = 8\cdot15$, $b = 6\cdot44$, $c = 8\cdot57$ Å, $\beta = 93\cdot96°$. Least-squares refinement led to a final agreement index for the observed reflections: $R = 0\cdot12$. The complex is polymeric in two directions; the b-axis linkage is through a system of five-membered rings with a common C–O group; along c, alkoxide bridges form four-membered rings. The oxygen atoms form a distorted trigonal bipyramidal environment about the cobalt atoms. The polymeric units are linked in the a direction by van der Waals forces. A magnetic moment of $3\cdot94$ B.M. has been determined. Infra-red data show the presence of hydrogen bonding.

Introduction

The amount of information available on the structures of metal alkoxides is very limited, probably because they are difficult to obtain in a crystalline form. X-ray studies have established the structural characteristics of tetrameric thallium(I) methoxide (Dahl, Davis, Wampler & West, 1962) and of several tetrameric alkoxides of titanium(IV) (Witters & Caughlan, 1965; Ibers, 1963). These studies have shown that the alkoxide group frequently forms a bridge between two or more metal atoms and that polynuclear molecular clusters determine the structural chemistry of these compounds. Fuls, Rodrique & Fripiat (1970) have proposed a structure for iron alkoxide in which octahedral layers are not linked. This feature along with five-membered rings and alkoxide bridges commends their hypothetical model.

The crystal structure of cobalt(II) monoglycerolate was investigated as part of a programme on metal glycerolates developed in this laboratory, (Radoslovich, Raupach, Slade & Taylor, 1970). Our work has shown that this compound can be well crystallized and that it is polymeric in two directions with alkoxide bridges as basic units.

Experimental

Crystals were prepared for analysis by heating 50 ml glycerol with about 10g of cobalt acetate for two days at 140°C. The reaction vessel was heated in an oil bath to minimize convection. The product was washed with water, alcohol and acetone and then dried at 100°C.

The crystals of $Co[C_3H_6O_3]$ are magenta coloured and tabular (100).

Crystal data

Cobalt (II) monoglycerolate
Co(II) $[C_3H_6O_3]$, M.W. 149·02
Crystal class: monoclinic

$a = 8\cdot147 \pm 0\cdot006$, $b = 6\cdot435 \pm 0\cdot0006$, $c = 8\cdot567 \pm 0\cdot006$Å
$\beta = 93\cdot96 \pm 0\cdot06°$
Unit-cell volume $U = 448\cdot0 \pm 0\cdot4$ Å^3, $Z = 4$, $D_m = 2\cdot19$
(determined by the flotation method),
$D_c = 2\cdot21$ g.cm^{-3}, $F(000) = 472$.
$\mu = 76\cdot56$ cm^{-1} (Co $K\alpha$).
The systematic absences are: $h0l$ absent when l is odd and $0k0$ absent when k is odd. There are no systematic absences in hkl reflexions so the space group is $P2_1/c$.

The three-dimensional intensity data were recorded with iron-filtered Co $K\alpha$ radiation ($\lambda = 1\cdot7889$ Å), by means of Weissenberg photographs, with the multiple-exposure technique and integration processes. A crystal of natural habit ($0\cdot22 \times 0\cdot26 \times 0\cdot03$ mm) was used. Five layers with [100] as rotation axis ($h = 0$ to 4) were taken.

A total of 564 reflexions were measured with a Zeiss microdensitometer and processed with a program written by E. W. Radoslovich. Corrections were made for Lorentz and polarization factors, and for the absorption factor by the integration method (Busing & Levy, 1957).

Determination of the structure

The structure was determined by the heavy-atom method. The cobalt atoms were located by calculation of the three-dimensional Patterson function for that part of the unit cell bounded by $a = 0$ to 1, $b = 0$ to $\frac{1}{2}$ and $c = 0$ to $\frac{1}{4}$. The cobalt positional parameters were then refined by least-squares adjustment. Phases based upon the refined cobalt positions were then assigned to the observed structure factors which enabled a three-dimensional Fourier synthesis to be calculated. Although images of all the other atoms were revealed by the first three-dimensional Fourier synthesis the resolution about one carbon atom [C(1)] was poor, owing to its proximity to the metal and the consequent influence of series termination errors. After least-

squares refinement of isotropic temperature factors and positional parameters of the cobalt, three oxygen and two of the three carbon atoms a difference Fourier synthesis confirmed the position of the third carbon. Least-squares adjustment of isotropic temperature factors and positional parameters of all atoms in the asymmetric unit resulted in a R value of 0·16.

Refinement

To bring the reliability index below the value quoted above, Cruickshank's weighting scheme was applied.

Also a facility was introduced into Busing, Martin & Levy's (1962) *ORFLS* program whereby approximately 10% of reflections with $|(|F_o| - |F_c|)/\sigma|F_o||$ greater than an adjustable value could be rejected. Reflexions thus rejected were accounted for by measurement difficulties, extinction and high backgrounds due to white radiation. Two cycles of refinement using these restrictions produced an R value of 0·14. At this stage weak reflexions and those with $(\sin \theta/\lambda)^2 > 0.25$ were deleted and anisotropic temperature factors were tried. However, this altered several bond lengths to unreasonable values and therefore isotropic temperature factors only

Table 1. *Comparison of observed and calculated structure factors*

were used for the final two cycles of refinement. An R value of 0·12 resulted.

The atomic scattering curves for Co^{2+}, C, and O^- were taken from Table 3.3.1 A, *International Tables for X-ray Crystallography* (1962).

The observed and calculated structure factors are compared in Table 1 which does not list those 10% of reflexions rejected by the weighting scheme when $|(F_o| - |F_c|)/\sigma|F_o||$ was greater than 0·4. Tables 2 and 3 give the final positional and temperature parameters with their standard deviations. The interatomic distances and bond angles were calculated by the *ORFFE* program of Busing, Martin & Levy (1964). Intramolecular distances and bond angles are reported in Tables 4 and 5 respectively and in Fig. 1. The closest intermolecular distances are reported in Table 6 and in Fig. 2.

Table 2. *Positional parameters in fractional coordinates, followed by standard deviations*

	x	y	z
Co	0·4499 (7)	0·0736 (7)	0·1636 (5)
C(1)	0·7727 (48)	0·1503 (45)	0·0728 (31)
C(2)	0·6992 (49)	0·3629 (49)	0·0951 (33)
C(3)	0·1675 (47)	0·0158 (44)	0·3560 (32)
O(1)	0·3463 (30)	0·4806 (29)	0·4531 (21)
O(2)	0·5723 (31)	0·3338 (29)	0·1972 (21)
O(3)	0·2483 (29)	0·1884 (29)	0·2733 (21)

Table 3. *Isotropic temperature factors, followed by standard deviations*

Co	2·5	±0·2
C(1)	2·7	±0·6
C(2)	3·1	±0·6
C(3)	2·7	±0·6
O(1)	1·5	±0·4
O(2)	1·8	±0·4
O(3)	2·0	±0·4

Table 4. *Bond distances, with their standard deviations*

Bond	Distance	s.d.
Co^i—O(1)	1·97 Å	±0·02 Å
Co^i—O(1)	2·07	±0·02
Co^i—O(2)	1·98	±0·02
Co^{iii}—O(2)	1·95	±0·02
Co^i—O(3)	1·98	±0·04
O(1)–C(1)	1·49	±0·04
O(2)–C(2)	1·32	±0·04
O(3)–C(3)	1·45	±0·03
C(1)–C(2)	1·50	±0·04
C(2)–C(3)	1·54	±0·05
Co^{iii}—Co^{iv}	3·66	±0·00
O(1)–O(3)	2·59	±0·03

The structure consists of five-membered rings composed of Co–O–C–C–O– interlinked with similar rings by sharing carbon–oxygen pairs C(2)–O(2). These rings form an array of chains which extend infinitely in the direction of the b axis. Cross linking between chains is

achieved by the familiar alkoxide bridges which operate approximately in the c direction. The combined effect of these primary structural units is to produce a two-dimensional polymer in the bc plane. The cobalt atoms are each bonded to five oxygen atoms situated at the apices of distorted trigonal bipyramids. Bond angles around the coordination spheres of the cobalt atoms are reported in Table 5. The structure is represented in Fig. 1(a) and 1(b).

Table 5. *Bond angles, with standard deviations*

	Bond angle	s.d.
$O(2^i)$—Co^{iii}—$O(2^{iii})$	127°21′	1°20′
$O(2^i)$—Co^{iii}—$O(1^{ii})$	111 52	2 0
$O(2^{iii})$—Co^{iii}—$O(1^{ii})$	120 32	2 10
$O(1^i)$—Co^{iii}—$O(3^{iii})$	175 34	2 30
$O(2^{iii})$—Co^{iii}—$O(3^{iii})$	91 27	0 41
$O(2^i)$—Co^{iii}—$O(3^{iii})$	88 2	0 40
$O(3^{iii})$—Co^{iii}—$O(1^{ii})$	95 51	0 41
$O(1^i)$—Co^{iii}—$O(2^{iii})$	85 8	0 40
$O(1^i)$—Co^{iii}—$O(1^{ii})$	83 29	0 40
$O(1^i)$—Co^{iii}—$O(2^i)$	96 18	0 40
C(1)—C(2)–C(3)	109 29	2 43
C(1)—C(2)–O(2)	104 2	2 12
C(2)—C(1)–O(1)	115 28	2 37
C(2)—C(3)–O(3)	108 26	2 26
C(3)—C(2)–O(2)	116 21	2 8
Co^i—O(1)–C(1)	103 41	1 23
Co^i—O(2)–C(2)	113 45	1 30
Co^i—O(3)–C(3)	106 17	1 27
Co^{iii}—O(1)–Co^{iv}	96 31	0 45
Co^{iii}—O(2)–Co^i	136 59	2 30
Co^{iii}—O(2)–C(2)	109 10	1 2

Stacking of the polymeric sheets on their (100) faces apparently gives rise to weak intermolecular interactions of the van der Waals type, explaining the observed cleavage in this direction. The distances between C(1)–C(1) and C(1)–C(3) are very close to twice the van der Waals radius of the methylene group, CH_2, to which Pauling (1960) has assigned an effective van der Waals radius of 2·0 Å.

Table 6. *Shortest intercell distances*

See also Fig. 2.

C(1)···C(1)	4·29 Å
C(3)···O(3)	4·20
C(3)···C(1)	4·25
C(3)···C(3)	4·67

The distance (3·02 Å) between cobalt atoms comprising the four-membered rings is very likely too great to allow any direct spin-spin coupling by overlap of orbitals so that the low magnetic moment for the complex, 3·94 B.M., needs an alternative explanation. The observed moment is close to the spin-only value of 3·88 B.M. which suggests that the asymmetric field in which the cobalt atoms are sited has produced almost complete quenching of the orbital contribution. A possible second explanation for the low moment could be in terms of spin coupling through bridging

oxygens. Further work is needed to decide between the above possibilities.

The lengths of bonds $Co^i-O(1^{ii})$, $CO^i-O(1^{iv})$ and $O(2)-C(2)$ are of interest. The lengths of the Co–O bonds of the alkoxide bridge differ and suggest a

charge transfer thus:

The longer bonds results from the consequent reduction of ionic character. The $O(2)-C(2)$ distance is shorter than either that for $O(1)-C(1)$ or $O(3)-C(3)$, which are close to accepted lengths of carbon–oxygen single bonds (1·43 Å). The reason for this shortening is not immediately obvious even by analogy with oxalato and carbonato metal comp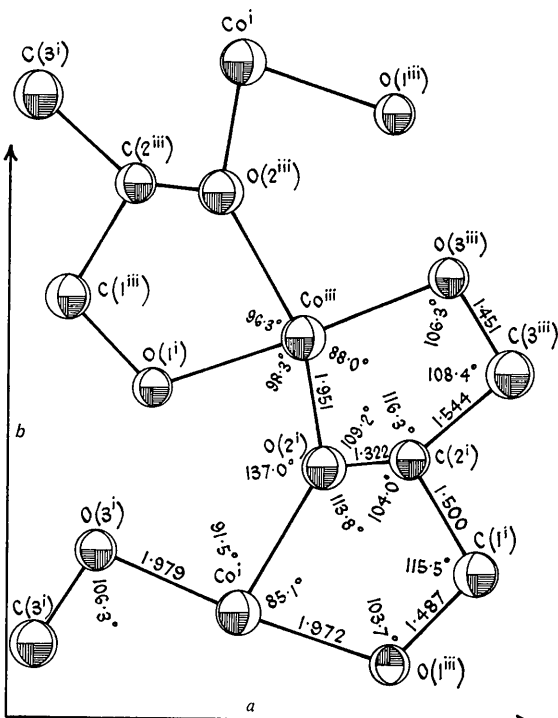lexes, where a carbon–oxygen distance of 1·32 Å has been reported (Van Niekerk & Schoening, 1951; Fujita, Martell & Nakamoto, 1962). A possible explanation is in terms of charge withdrawal from $O(2)$, by both its attached cobalt atoms, so increasing the ionic character of the $O(2)-C(2)$ bond. A distance between that for a carbon–oxygen single and a carbon–oxygen double bond results.

Table 7 gives possible assignments of the absorption bands in the infrared spectrum* of cobalt monoglycerolate. This table has been arrived at by comparison of the infrared data for the cobalt complex with data for

* Infrared spectra were recorded with KBr discs, attenuated total-reflectance techniques and hand-oriented groups of small crystals in Nujol on a Perkin–Elmer 521 spectrophotometer.

Fig. 1. (a) The unit cell contents as viewed along [001]. (b) The molecular structure of $Co(C_3H_6O_3)$.
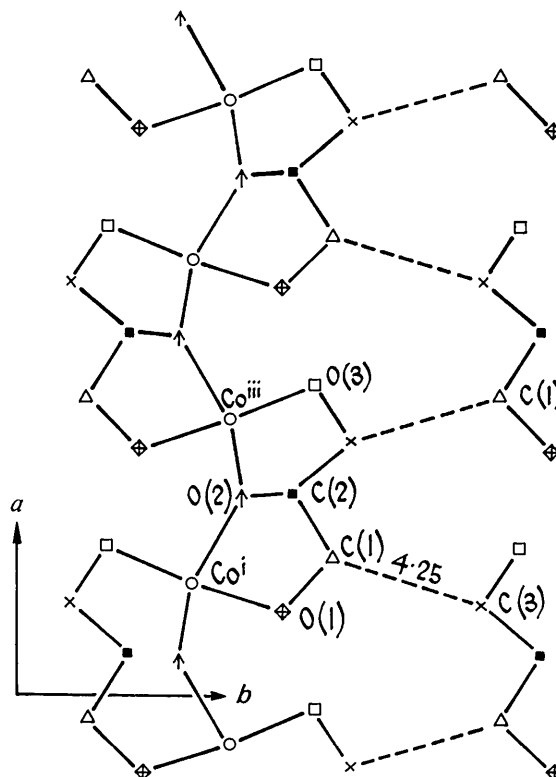
Fig. 2. View along [001] showing the shortest intercell distance nearest the [001] plane.

similar structures including: substituted 1:3-dioxolans (Barker, Bourne, Pinkard & Whiffen, 1959); ethylene glycol (Buckley & Giguère, 1967); cobalt complexes of the ethylene glycols (Miyake, 1959); metal oxalates and acetylacetone complexes (Nakamoto, 1963); see also Jones & Sandorfy (1956), and Silverstein & Bassler (1963). Deuteration and polarization studies have also been used to help with the assignments. Coupled vibrations within the ring structures would give more complex assignments in some instances. The vibrational assignments agree with those expected from the X-ray structure.

Table 7. *Infrared absorption frequencies of cobalt monoglycerolate*

v cm^{-1}	Assignment
3410smb	O–H stretch
2929s	CH$_2$ stretch (asymmetric)
2893sh	CH stretch
2873s	CH$_2$ stretch
2846s ⎱ d	(symmetric)
2839s ⎰	
2510bm	O–H --- O stretch
2710sm	O–H---O?
1945s	O–H---O·bend
1650sm	H–O–H bend
1461s	CH$_2$ scissor
1441m	CH bond
1377s	
1366m	CH$_2$ wag
1346s	
1277m	
1232m	CH$_2$ twist
1110vs	C–O stretch
1072sh	C–C stretch
1063vs	C–O stretch
991vs	CH bend (out of plane)
910m	
863vs	CH$_2$ rock
650vs	
514s	C–C–O in plane bend + Co–O
476m	C–C–O out of plane
415m	bend + Co–O
348s	Co–O + C–O
293s	Co–O (+ ring deformation)

Abbreviations: v=very; s=strong; m=medium; sm=small; b=broad; d=doublet; sh=shoulder

The chemical formula for cobalt glycerolate requires the positioning of six hydrogen atoms within each formula unit. The accuracy of the X-ray data does not allow the hydrogens to be included in the structure determination but some information about their posi-

tions can be inferred. Five hydrogens can be related to the three carbons within such a unit (as in glycerol) and the infra-red data allow the position of the sixth to be deduced. The peaks at 2510 and 1945 cm^{-1} which vanish on deuteration, indicate that a hydrogen bond operates within the structure. The higher-frequency band enables the O–O distance (2·59 Å) to be calculated (Feilchenfeld, 1958). From Table 4 it can be seen that the O(1)–O(3) distance agrees with the calculated length so that these oxygens are hydrogen bonded. As O(3) is the least coordinated oxygen the hydrogen is formally attached to this oxygen.

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