

- COCHRAN, W. & WOOLFSON, M. M. (1955). *Acta Cryst.* **8**, 1.
 CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 754.
 CRUICKSHANK, D. W. J. (1965). In *Computing Methods in Crystallography*. Edited by J. S. ROLLETT. p. 114. New York: Pergamon Press.
 DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* A **24**, 390.
 HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 866.
 KARLE, I. L. & KARLE, J. (1963). *Acta Cryst.* **16**, 969.
 LONG, R. E., MADDOX, H. & TRUEBLOOD, K. N. (1969). *Acta Cryst.* B **25**, 2083.
 SASADA, Y., TAKANO, T. & KAKUDO, M. (1964). *Bull. Chem. Soc. Japan*, **37**, 940.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
 TAKAKI, Y., SASADA, Y. & WATANABÉ, T. (1960). *Acta Cryst.* **13**, 693.
 TAKANO, T., SASADA, Y. & KAKUDO, M. (1966). *Acta Cryst.* **21**, 514.
 TAMURA, C. & KUWANO, H. (1962). *Nippon Kagaki Zasshi*, **83**, 971. (*Chem. Abs.* (1963), 10874).
 TAMURA, C., KUWANO, H. & SASADA, Y. (1961). *Acta Cryst.* **14**, 693.
 TURNER, J. D. & LINGAFELTER, E. C. (1955). *Acta Cryst.* **8**, 551.

Acta Cryst. (1972). B **28**, 998

Crystal and Molecular Structure of Bis(amidoxalato-*O,O*)-cobalt(II) Tetrahydrate

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(Received 3 August 1971)

The crystals of bis(amidoxalato-*O,O*)-cobalt(II) tetrahydrate are monoclinic, space group $P2_1/c$. The unit-cell constants are: $a = 5.640$ (5), $b = 13.734$ (12), $c = 7.414$ (6) Å; $\beta = 109.8$ (2)°, $Z = 2$. The three-dimensional intensity data have been measured on a single-crystal automated diffractometer. The structure has been solved by Fourier methods and refined by least-squares methods ($R = 3.7\%$). The structure consists of *trans*-octahedral metal complexes with amidoxalato anion forming chelate pentatomic rings with the amidic oxygen and one carboxylic oxygen as donor atoms. The remaining positions of the octahedron are occupied by water molecules. The complexes are held together by a three-dimensional network of hydrogen bonds. In the ligand the $C_{sp^2}-C_{sp^2}$ distance $C(4)-C(2) = 1.550$ (9) Å, has been found, which is longer than expected for bonds between two sp^2 hybridized carbon atoms.

Introduction

As part of the research on the properties of ligands capable of forming pentatomic chelate rings with divalent metals (Braibanti, Pellinghelli, Tiripicchio & Tiripicchio Camellini, 1971), we have now determined the crystal structure of bis(amidoxalato-*O,O*)-cobalt(II) tetrahydrate.

Experimental

Preparation

The crystals can be obtained by evaporation of an aqueous solution of cobalt carbonate and amidoxalic acid in stoichiometric ratio.

Crystal data

Compound: Bis(amidoxalato-*O,O*)cobalt tetrahydrate, $\text{Co}(\text{H}_2\text{N}-\text{CO}-\text{COO})_2 \cdot 4\text{H}_2\text{O}$.
 Formula weight: 307.09.

Crystal class: monoclinic prismatic.

Unit-cell parameters (determined from rotation and Weissenberg photographs and refined on an automated single-crystal diffractometer, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å):

$a = 5.640$ (5), $b = 13.734$ (12), $c = 7.414$ (6) Å;

$\beta = 109.8$ (2)°; $V = 540.3$ Å³; $Z = 2$;

$D_x = 1.89$, $D_m = 1.88$ g.cm⁻³;

$\mu(\text{Mo } K\alpha) = 154.25$ cm⁻¹; $F(000) = 314$.

Space group: $P2_1/c$ ($C_{2h}(5)$ -No. 14) from systematic absences.

Intensity data

The intensity data were collected on a single-crystal automated Siemens diffractometer on line with a Siemens 304/P computer using Zr-filtered Mo $K\alpha$ radiation and the $\omega-2\theta$ scan technique. A thin tablet crystal of approximate dimensions $0.045 \times 0.180 \times 0.210$ mm was aligned with its [010] axis along the ϕ axis of the diffractometer and all the reflexions with $2\theta < 58^\circ$ were collected. Intensities of 1436 independent reflexions were measured and 833 of them, having $I > 2\sigma(I)$, were used in the crystal analysis.

Calculations

Usual corrections except that for absorption have been applied. The observed factors have been put on an absolute scale by Wilson's (1942) method. Atomic form factors of Cromer & Mann (1968) for non-hydrogen atoms and those of Stewart, Davidson & Simpson (1965) for the hydrogen atom have been employed. The structure has been solved by Patterson and Fourier

* Or diaquobis(amidoxalato-*O,O*)-cobalt(II) dihydrate, $[\text{Co}(\text{H}_2\text{N}-\text{CO}-\text{COO})_2(\text{OH}_2)_2] \cdot 2\text{H}_2\text{O}$.

methods and refined by the full-matrix least-squares method with anisotropic temperature factors, the weighting scheme being $1/w = A + BF_o + CF_o^2$ where $A = 0.42510$, $B = 0.01236$, $C = 0.00008987$.

The hydrogen atoms have been identified in the ($\rho_o - \rho_c$) map. Programs prepared by Immirzi (1967) have been used. The conventional agreement factor is $R = 3.7\%$ (without hydrogen contributions $R = 3.8\%$). All calculations have been performed on a CDC-6600 computer of Consorzio Interuniversitario di Calcolo per l'Italia Nord-Orientale, Bologna.

The results of refinement are summarized in Tables 1 and 2. A list of observed and calculated structure factors is available from the authors on request.

Table 1. Final fractional atomic coordinates ($\times 10^4$) with e.s.d.'s.

	x	y	z
Co	0	0	0
O(1)	-2646 (4)	1136 (2)	-259 (3)
O(2)	1621 (5)	2306 (2)	3713 (4)
O(3)	2019 (4)	943 (2)	2208 (3)
O(4) _w	-1057 (6)	-725 (2)	2028 (4)
O(5) _w	2986 (6)	5418 (3)	1017 (5)
N	-3250 (6)	2485 (2)	1267 (4)
C(1)	-1895 (6)	1752 (2)	1034 (4)
C(2)	831 (6)	1673 (2)	2473 (4)
H(1)	-4822 (96)	2614 (35)	370 (74)
H(2)	-2581 (82)	2907 (32)	2281 (66)
H(3)	-1815 (98)	-1287 (41)	1735 (79)
H(4)	-1782 (97)	-402 (39)	2950 (77)
H(5)	4658 (120)	5582 (44)	1518 (84)
H(6)	2652 (126)	5425 (49)	-54 (106)

Discussion

The structure consists of *trans*-octahedral complexes, in which the amidoxalato anion behaves as a chelate ligand with amidic oxygen O(1) and one carboxylic oxygen, O(3) as donor atoms. The remaining positions of the coordination polyhedron are occupied by two water molecules (Fig. 1). The complexes are held together in the structure by a three-dimensional network of hydrogen bonds OH...O and NH...O in-

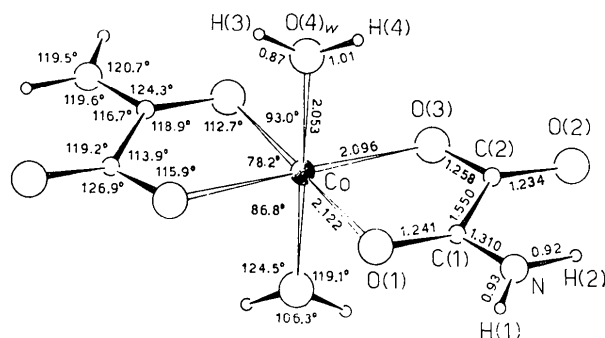


Fig. 1. *trans*-Octahedral complex around cobalt atom.

volving also water molecules not coordinated to the metal. The bonds between cobalt and surrounding atoms (Table 3) are similar but not exactly equal to those found in the zinc compound. Co-O(1) = 2.122 (8) and Co-O(4)_w = 2.053 (6) Å are only slightly shorter than Zn-O(1) = 2.152 (6) and Zn-O(4)_w = 2.088 (5) Å in accordance with small differences in ionic radii. The lengthening of Co-O(3) = 2.096 (3) compared with Zn-O(3) = 2.043 (6) Å is more significant. The coordination polyhedron is fairly regular although a little more distorted than in the zinc complex.

The water molecule O(4)_w is bound to the metal in a way which can be considered as intermediate between classes 1 and 2 of Chidambaran, Sequeira & Sikka (1964).

The distances and angles in the ligand (Table 4) repeat in several details those found in the zinc compound.

The molecule as a whole (Table 5) is not planar but the bond systems around the carbon atom of the carboxylic group and around the amidic nitrogen are both planar. The angle between the two planes is 2.3° against 1.3° in the zinc compound. The bond C(1)-C(2) = 1.550 (9) Å, comparable with 1.546 (6) Å of the zinc compound, is longer than the bond length as expected between two *sp*² hybridized carbon atoms, $C_{sp^2}-C_{sp^2} = 1.515$ Å, (Almenningen, Bastiansen & Skancke, 1958) and 1.499 Å (Bart, 1968). The lengthening of the

Table 2. Thermal parameters with e.s.d.'s (Å²)

$B_{ij} = 8\pi^2 U_{ij}$ are referred to a^* , b^* , c^* .

	B_{11} or B	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	1.703 (18)	1.076 (16)	1.369 (17)	0.006 (25)	0.300 (14)	-0.025 (25)
O(1)	1.820 (83)	1.802 (83)	1.761 (84)	0.221 (68)	0.046 (67)	-0.399 (69)
O(2)	2.226 (103)	1.728 (88)	2.642 (104)	0.111 (76)	-0.137 (77)	-0.730 (78)
O(3)	1.713 (84)	1.835 (85)	2.225 (88)	0.332 (70)	-0.025 (71)	-0.355 (72)
O(4) _w	4.018 (126)	1.766 (98)	3.110 (111)	-0.229 (90)	2.020 (99)	0.021 (86)
O(5) _w	3.112 (120)	5.277 (162)	2.623 (126)	-1.568 (117)	0.772 (98)	0.209 (114)
N	2.189 (121)	1.849 (106)	2.111 (118)	0.477 (93)	0.078 (89)	-0.481 (90)
C(1)	1.919 (111)	1.335 (103)	1.473 (106)	-0.242 (91)	0.317 (88)	0.083 (86)
C(2)	1.688 (108)	1.280 (103)	1.696 (106)	0.061 (85)	0.294 (88)	0.119 (87)
H(1)	4.61 (1.15)					
H(2)	3.58 (0.95)					
H(3)	5.51 (1.33)					
H(4)	5.56 (1.28)					
H(5)	6.70 (1.52)					
H(6)	7.52 (1.87)					

Table 3. Bond distances and angles in the coordination polyhedron

Co—O(1)	2.122 (8) Å	O(1)—Co—O(3)	78.2 (1)°
Co—O(3)	2.096 (3)	O(1)—Co—O(4) _w	93.0 (1)
Co—O(4) _w	2.053 (6)	O(3)—Co—O(4) _w	86.8 (1)
		Co—O(1)—C(1)	112.7 (2)
		Co—O(3)—C(2)	115.9 (2)

Table 4. Bond distances and angles in amidoxalato anion

C(1)—O(1)	1.241 (4) Å	O(1)—C(1)—N	124.3 (3)°
C(1)—N	1.310 (6)	O(1)—C(1)—C(2)	118.9 (3)
C(2)—O(2)	1.234 (4)	N—C(1)—C(2)	116.7 (3)
C(2)—O(3)	1.258 (5)	C(1)—C(2)—O(2)	119.2 (3)
C(1)—C(2)	1.550 (9)	C(1)—C(2)—O(3)	113.9 (3)
		O(2)—C(2)—O(3)	126.9 (3)

carbon-carbon bonds in derivatives of oxalic acid is confirmed by a long list of data both by X-rays (Beagley & Small, 1963; Sequeira, Srikanta & Chidambaram, 1970; Delaplane & Ibers, 1969; Haas, 1964; Dougill & Jeffrey, 1953; Robertson, 1965) and by neutrons (Sabine, Cox & Craven, 1969; Coppens & Sabine, 1969). Coppens, Sabine, Delaplane & Ibers (1969) by combining F_o from X-ray measurements and F_c from neutron determination of α -oxalic acid dihydrate found some residual electron density along the line joining carbon to carbon; even the final difference map from an X-ray determination (Beagley & Small, 1953; Braibanti, Pellinghelli, Tiripicchio & Tiripicchio Camellini, 1971) revealed the same residual. This is confirmed also by the final difference map of the present determination, where a peak of height half that of the

hydrogen atoms has been found. The distances and angles involving hydrogen atoms with O (Table 6) and with N (Table 7) are in reasonable agreement with values quoted in the literature. The distances O—H and N—H are on the average 0.1 Å longer than the distances in the zinc compound, but they are shorter than the values determined by neutron diffraction. Short distances X—H are expected because of the unequal

Table 5. Analysis of planarity in amidoxalato anion

The plane of best fit is defined by atoms with an asterisk.

Equation of the plane of the amidic group:

$$3.1998x + 7.7698y - 5.5990z - 0.1800 = 0$$

	Δ	σ	
Co	-0.1800 Å	0.0000 Å	O(1)
*O(1)	0.0009	0.0026	C(1)—N
O(2)	0.0515	0.0032	C(2)
O(3)	-0.0376	0.0026	$\sum \left(\frac{\Delta}{\sigma}\right)^2 = 1.954$
*N	0.0014	0.0033	
*C(1)	-0.0041	0.0033	
*C(2)	0.0011	0.0033	

Equation of the plane of the carboxylic group:

$$3.2445x + 7.3232y - 5.7716z - 0.0706 = 0$$

	Δ	σ	
Co	-0.0706 Å	0.0000 Å	C(1)
O(1)	0.0523	0.0026	O(3)—C(2)
*O(2)	0.0011	0.0032	O(2)
*O(3)	0.0007	0.0026	$\sum \left(\frac{\Delta}{\sigma}\right)^2 = 1.077$
N	-0.0365	0.0034	
*C(1)	0.0008	0.0034	
*C(2)	-0.0031	0.0034	

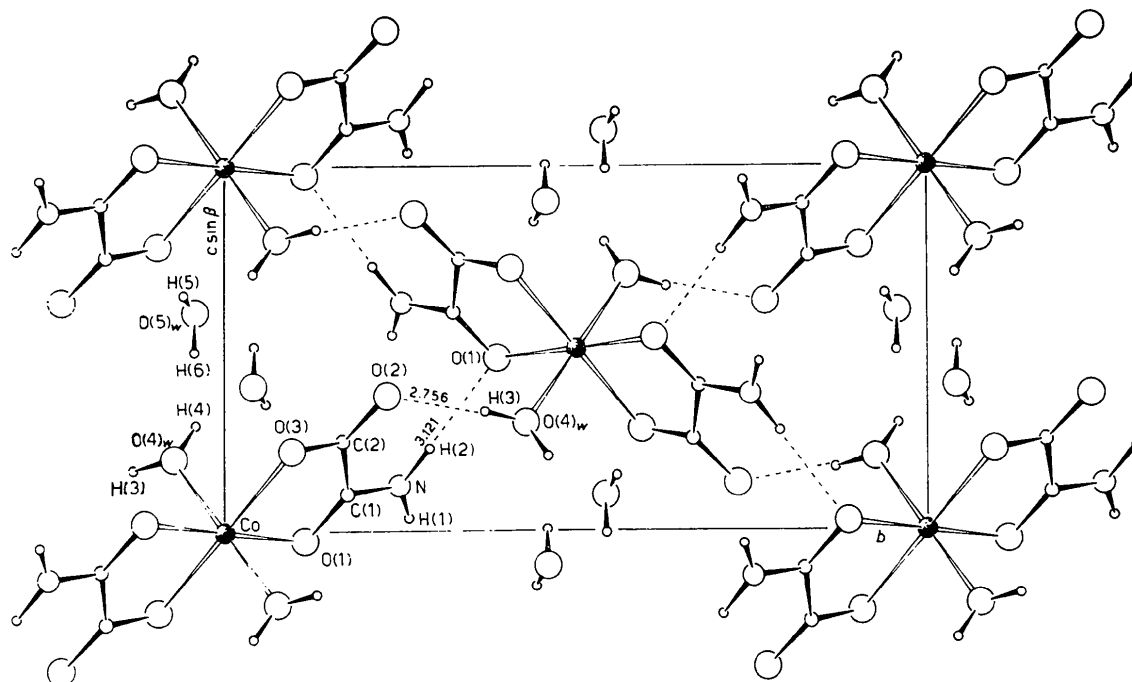


Fig. 2. Projection of the structure down [100].

Table 6. *Environment of water molecules, O(4)_w and O(5)_w*

O(4) _w -H(3)	0.87 (6) Å	H(3)—O(4) _w —H(4)	106.3 (4.9)°
O(4) _w -H(4)	1.01 (6)	Co—O(4) _w —H(3)	119.1 (3.7)
O(4) _w -H(3)···O(2 ⁱⁱ)	2.756 (4)	Co—O(4) _w —H(4)	124.5 (3.1)
H(3)···O(2 ⁱⁱ)	1.970 (56)	Co—O(4) _w ···O(2 ⁱⁱ)	111.9 (1)
O(4) _w -H(4)···O(5 ⁱⁱ) _w	2.611 (9)	Co—O(4) _w ···O(5 ⁱⁱ) _w	113.2 (1)
H(4)···O(5 ⁱⁱ) _w	1.634 (55)	O(4) _w —H(3)···O(2 ⁱⁱ)	149.1 (5.4)
O(5) _w -H(5)	0.92 (7)	O(4) _w —H(4)···O(5 ⁱⁱ) _w	161.4 (4.9)
O(5) _w -H(6)	0.75 (7)	O(2 ⁱⁱ)···O(4) _w ···O(5 ⁱⁱ) _w	131.2 (2)
O(5) _w -H(5)···O(3 ⁱⁱⁱ)	2.771 (17)	H(3)—O(4) _w ···O(2 ⁱⁱ)	21.5 (3.8)
H(5)···O(3 ⁱⁱⁱ)	1.858 (68)	H(4)—O(4) _w ···O(5 ⁱⁱ) _w	11.5 (3.0)
Co—O(4) _w	2.053 (6)	H(5)—O(5) _w —H(6)	106.3 (6.9)
		O(5) _w —H(5)···O(3 ⁱⁱⁱ)	173.5 (5.7)
		H(5)—O(5) _w ···O(3 ⁱⁱⁱ)	4.4 (3.8)

Table 6 (cont.)

Asymmetric units

	<i>x</i> ,	<i>y</i> ,	<i>z</i>
i	<i>x</i> ,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$
ii	$-x$,	$-\frac{1}{2}+y$,	$\frac{1}{2}-z$
iii	$1-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$
iv	$-1+x$,	$\frac{1}{2}-y$,	$-\frac{1}{2}+z$

distribution of the electron cloud around the hydrogen nucleus (Sabine, Cox & Craven, 1969). The complexes are held together by strong hydrogen bonds. Bonds

O(4)_w-H(3)···O(2)=2.756 (4) and N-H(2)···O(1)=3.121 (5) Å hold together the complexes in layers parallel to (100) (Fig. 2). These layers are joined to one another by hydrogen bonds O(4)_w-H(4)···O(5)_w=2.611(9), O(5)_w-H(5)···O(3)=2.771(17), and N-H(1)···O(2)=2.885 (15) Å (Fig. 3).

Thanks are due to Professor A. Braibanti for helpful suggestions and discussions. We also thank the Consiglio Nazionale delle Ricerche, Rome for financial help.

Table 7. *Environment of amidic group*

N—H(1)	0.93 (5) Å	C(1)—N—H(1)	120.7 (3.1)
N—H(2)	0.92 (5)	C(1)—N—H(2)	119.6 (3.0)
N—H(1)···O(2 ^{iv})	2.885 (15)	H(1)—N—H(2)	119.5 (4.2)
H(1)···O(2 ^{iv})	1.969 (56)	N—H(1)—O(2 ^{iv})	169.3 (4.6)
N—H(2)···O(1 ⁱ)	3.121 (5)	N—H(2)···O(1 ⁱ)	155.4 (4.2)
H(2)···O(1 ⁱ)	2.258 (46)	C(1)—N···O(2 ^{iv})	119.3 (2)
N—C(1)	1.310 (6)	C(1)—N···O(1 ⁱ)	132.0 (2)
		O(1 ⁱ)···N···O(2 ^{iv})	106.6 (1)
		H(1)—N···O(2 ^{iv})	7.3 (3.2)
		H(2)—N···O(1 ⁱ)	17.5 (3.0)

For asymmetric units see Table 6.

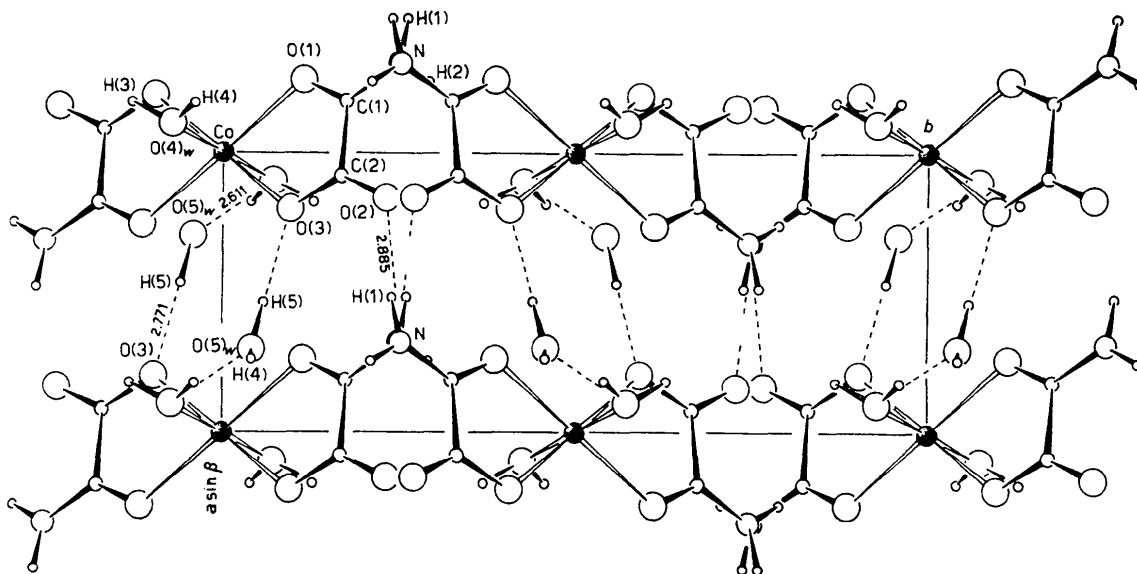


Fig. 3. Projection of the structure down [001].

References

- ALMENNINGEN, A., BASTIANSEN, O. & SKANCKE, P. N. (1958). *Acta Chem. Scand.* **12**, 1215.
- BART, J. C. J. (1968). *Acta Cryst.* **B24**, 1277.
- BEAGLEY, B. & SMALL, R. W. H. (1963). *Proc. Roy. Soc. A* **275**, 469.
- BRAIBANTI, A., PELLINGHELLI, M. A., TIRIPICCHIO, A. & TIRIPICCHIO CAMELLINI, M. (1971). *Acta Cryst.* **B27**, 1240.
- CHIDAMBARAM, R., SEQUEIRA, A. & SIKKA, S. K. (1964). *J. Chem. Phys.* **41**, 3616.
- COPPENS, P. & SABINE, T. M. (1969). *Acta Cryst.* **B25**, 2442.
- COPPENS, P., SABINE, T. M., DELAPLANE, R. G. & IBERS, J. A. (1969). *Acta Cryst.* **B25**, 2451.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321.
- DELAPLANE, R. G. & IBERS, J. A. (1969). *Acta Cryst.* **B25**, 2423.
- DOUGILL, M. W. & JEFFREY, G. A. (1953). *Acta Cryst.* **6**, 831.
- HAAS, D. J. (1964). *Acta Cryst.* **17**, 1511.
- IMMIRZI, A. (1967). *Ric. Sci.* **37**, 743.
- ROBERTSON, J. H. (1965). *Acta Cryst.* **18**, 410.
- SABINE, T. M., COX, G. W. & CRAVEN, B. M. (1969). *Acta Cryst.* **B25**, 2437.
- SEQUEIRA, A., SRIKANTA, S. & CHIDAMBARAM, R. (1970). *Acta Cryst.* **B26**, 77.
- STEWART, R. F., DAVIDSON, R. D. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
- WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 152.

Acta Cryst. (1972). **B28**, 1002

The Crystal Structure of Dibenzofuran

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(Received 7 July 1971)

The crystal and molecular structure of dibenzofuran $C_{12}H_8O$ has been determined by X-ray diffraction techniques. The space group is *Pnam* with four molecules per unit cell of dimensions $a = 7.702 \pm 0.010$, $b = 5.825 \pm 0.006$, $c = 19.185 \pm 0.020$ Å (at room temperature). Three-dimensional intensity data were collected with a Weissenberg type diffractometer about two crystal axes. The structure was refined by least-squares methods to a final *R* value of 0.073; the e.s.d.'s in bond lengths and angles not involving hydrogen atoms are about 0.003 Å and 0.13°. The anisotropic temperature factors of the C and O atoms have been accounted for by a rigid-body treatment; on this basis, corrections to the values of the observed bond distances and angles are in the ranges 0.006–0.013 Å and $\pm 0.3^\circ$. The two benzene rings are planar with angle value of 2.2° between them. A crystallographic mirror plane normal to the *c* axis passes through the oxygen atom.

Introduction

This work has emerged from an E.P.R. study of the triplet state of a few organic molecules oriented in a dibenzofuran host crystal. Another purpose is to obtain precise experimental values of C–C and C–O bond lengths to be compared with theoretical models. In relation to crystal structure, we are enabled further, to explain such physical properties as cleavage, melting point and optical sign.

Experimental

The dibenzofuran crystals recrystallized from ethanol are colourless transparent plates with well developed (001) faces. The density was measured by flotation in a $ZnSO_4$ solution. The melting point is low and the crystals are sublimable. Crystal data are given in Table 1. The sample mounted for X-ray analysis ($0.3 \times 0.3 \times 0.2$ mm) was cut off a monocystal obtained

by the Bridgman–Stockbarder method. It was sealed in a Lindemann capillary. For the determination of the structure, the intensities of 700 independent reflexions belonging to layers 0–4 along *b* and 0–1 along *a*, were measured on a Weissenberg type automatic diffractometer (Stoe), with Cu $K\alpha$ radiation. After correction for Lorentz and polarization factors, the structure factors on various layers were correlated and scaled to a common base. Since $\mu R \sim 0.2$, no absorption correction was applied. The agreement between values of structure factors of equivalent reflexions $F_e(h)$ may be used to assess the degree of internal consistency $R_c = (\sum_h \sum_e |F_e(h) - \bar{F}(h)|) / \sum_h \sum_e |F_e(h)|$. This produced an R_c value of 0.041. A Wilson plot was then made to estimate the scale factor and an overall temperature factor. The value of *B* was found to be 4.95 \AA^2 . Fig. 1 gives the distribution function of the normalized structure factors E^2 compared with theoretical curves for centro- and non-centrosymmetrical cases.