

value of  $0.0020 \text{ \AA}^2$ , calculated from the estimated standard deviation of the  $\beta_{ij}$  of the least-squares refinement, indicates that the rigid-body model is only moderately satisfactory.

This research was supported by the Robert A. Welch Foundation, Houston, Texas. The author wishes to thank Dr John Wainwright of NASA, Lyndon B. Johnson Space Center, Houston, Texas, for assistance in obtaining the diffraction data from the automatic diffractometer in his laboratory, Dr R. Shiono of the University of Pittsburgh for making the *ORTEP* plot, Dr A. L. Ternay Jr of the University of Texas at Arlington for kindly supplying the crystal and many interesting discussions, and Dr Margaret Mangion of this laboratory for her help in processing the data.

### References

- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Oak Ridge National Laboratory Report ORNL-TM-305.
- CHU, S. S. C. (1972). *Acta Cryst.* **B28**, 3625–3632.
- CHU, S. S. C. (1973a). *Acta Cryst.* **B29**, 1690–1696.
- CHU, S. S. C. (1973b). *Structure Interpretation Programs*. Institute of Technology, Southern Methodist Univ.
- CHU, S. S. C. & CHUNG, B. (1973). *Acta Cryst.* **B29**, 2253–2259.
- CHU, S. S. C. & CHUNG, B. (1974a). *Acta Cryst.* **B30**, 235–236.
- CHU, S. S. C. & CHUNG, B. (1974b). *Acta Cryst.* **B30**, 1616–1618.
- CRUCKSHANK, D. W. J. (1965). *Computing Methods in Crystallography*, edited by J. S. ROLLETT, pp. 112–116. New York: Pergamon Press.
- EVANS, S. (1970). Ph.D. thesis, Case Western Reserve Univ., Cleveland, Ohio.
- EVANS, S., DAVENPORT, D. & TERNAY, A. L. JR (1974a). Sixth International Symposium on Organic Sulfur Compounds, Bangor, Wales. Abstract R.B. 1.
- EVANS, S., DAVENPORT, D. & TERNAY, A. L. JR (1974b). *J. Org. Chem.* In preparation.
- EVANS, S. & TERNAY, A. L. JR (1974). *J. Org. Chem.* **39**, 2941–2946.
- GALLANT, D. M. & BISHOP, M. P. (1967). *Psychopharmacology. A Review of Progress*, edited by E. H. EFRON, pp. 1093–1100.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- GILLEAN, J. A. III, PHELPS, D. W. & CORDES, A. W. (1973). *Acta Cryst.* **B29**, 2296–2298.
- International Tables for X-ray Crystallography* (1962). Vol. III, pp. 201–207. Birmingham: Kynoch Press.
- JACKOBS, J. & SUNDARALINGAM, M. (1969). *Acta Cryst.* **B25**, 2487–2496.
- JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL 3794.
- MICHAELIS, W., SCHINDLER, O. & SIGNER, R. (1966). *Helv. Chim. Acta*, **49**, 42–53.
- SCHINDLER, O., LEHNER, H., MICHAELIS, W. & SCHMUTZ, J. (1963). *Helv. Chim. Acta*, **46**, 1097–1108.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
- SHIONO, R. (1971). Technical Report 49, Crystallography Department, Univ. of Pittsburgh.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- TERNAY, A. L. JR, CHASAR, D. W. & SAX, M. (1967). *J. Org. Chem.* **32**, 2465–2470.
- TERNAY, A. L. JR & EVANS, S. (1970). *J. Chem. Soc. (D)*, pp. 407–408.
- ZIRKLE, C. L. & KAISER, C. (1970). *Medicinal Chemistry*, 3rd ed. Edited by A. BURGER, Part II, pp. 1410–1497. New York: Wiley-Interscience.

*Acta Cryst.* (1975). **B31**, 1087

## The Crystal Structure of $\text{Bi}_6\text{O}_7\text{FCl}_3$

BY FREDRIK HOPFGARTEN

Division of Inorganic Chemistry 2, Chemical Center, The Lund Institute of Technology, P. O. B. 740, S-220 07 Lund 7, Sweden

(Received 11 November 1974; accepted 30 November 1974)

The structure of  $\text{Bi}_6\text{O}_7\text{FCl}_3$  has been determined by symbolic addition and Fourier methods and refined to  $R=0.055$  for 1214 independent counter intensities. The crystals are orthorhombic, space group  $Pnma$ , with  $a=20.105$  (6),  $b=3.892$  (2),  $c=15.432$  (5)  $\text{\AA}$ ,  $Z=4$ . The Bi atoms are of two types, one four-coordinated by O or O and F which form a nearly square plane, the other five-coordinated by two F and three O, all on one side of Bi. The Bi–O, F distances range between 2.19 and 2.51  $\text{\AA}$ . The fourfold coordination can be described as a square pyramid with the lone pair of electrons at its apex, and the five-coordination as an octahedron with the lone pair at one corner. The coordination polyhedra are linked by sharing edges and corners to form infinite layers parallel to [010]. Between the nets, trigonal prism columns of chloride ions run in the same direction.

### Introduction

By heating  $\text{BiOCl}$  in air above  $600^\circ\text{C}$ , it was totally transformed into a new well defined phase,  $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$

(Sillén & Edstrand, 1942). The substitution of  $\text{O}^{2-}$  by  $\text{F}^-$  in  $\text{BiOCl}$  is useful in preparing compounds with simple and predictable structures, related to the above phase. These substances can serve as models for the

study of principles of syntheses, the non-stoichiometry, and the possible mechanisms of the reactions. Preparative and structural studies are in progress on the systems  $\text{Bi}_2\text{O}_3$ - $\text{BiOCl}$  and  $\text{BiOCl}$ - $\text{BiOF}$ - $\text{Bi}_2\text{O}_3$ . The present paper reports the crystal structure of  $\text{Bi}_6\text{O}_7\text{FCl}_3$ , a new compound in the latter system.

### Experimental

For the preparation of  $\text{Bi}_6\text{O}_7\text{FCl}_3$ , a mixture of  $\text{Bi}_2\text{O}_3$ ,  $\text{BiOCl}$  and  $\text{BiOF}$  in the mole ratio 1:3:1 was heated in a sealed gold capsule for one day at 770°C. The product consisted of colourless needle-shaped crystals. Preliminary Weissenberg photographs indicated orthorhombic symmetry with the systematic absences  $0kl$  and  $hk0$  for  $k+l$  and  $h$  odd, respectively, indicating the space groups  $Pnma$  (No. 62) and  $Pn_2a$  (No. 33\*). Powder photographs were taken in a Guinier-Hägg camera with  $\text{Cu K}\alpha$  radiation and  $\text{KCl}$  ( $a=6.2909 \text{ \AA}$ ) added as an internal standard. Refinement of the cell parameters was performed by least-squares calculations on 27 lines according to Werner (1970). Some crystal data are given in Table 1. Intensities were collected on a Pailred diffractometer with  $\text{Mo K}\alpha$  radiation monochromatized by reflexion off the (002) planes of a graphite crystal, the monochromator angle being 6.08°. The single crystal ( $0.018 \times 0.022 \times 0.32 \text{ mm}$ ) was mounted along the needle axis parallel to  $\mathbf{b}$ . The reflexions  $h0l-h4l$  were collected for the Mo range,  $\sin \theta/\lambda < 0.80$ , by equi-inclination and  $\omega$ -scan techniques, with a scan rate of  $1.0^\circ \text{ min}^{-1}$ . The scan range was  $3.0^\circ$  for all reflexions. The stationary background counts were measured for 40 s at each end of the scan interval. The aperture size of the detector was  $2.0^\circ$ . The intensity of one standard reflexion was measured at regular intervals. The largest variation in its intensity was 2.8%.

Reflexions for which the two measured background values differed by more than 3.09 times the e.s.d. of their difference were omitted. The integrated peak counts  $I$  were calculated from the total integrated peak counts, the background counts, and the counting time in the usual way. If  $\sigma(I)/I \geq 0.387$ , the reflexion was considered unobserved. For each layer line both  $hkl$  and  $\bar{h}\bar{k}\bar{l}$  were measured, a total of 3924 reflexions. The intensities were corrected for Lorentz, polarization and absorption effects; the transmission factors varied from 0.159 to 0.276. The unobserved 1839 reflexions were deleted in the refinement. In the final step, mean values of the intensities of the planes  $hkl$  and  $\bar{h}\bar{k}\bar{l}$  were taken, resulting in 1224 independent reflexions.

### Structure determination and refinement

The positions of  $\text{Bi}(1)$ - $\text{Bi}(6)$  were determined by symbolic addition. The positions of all Cl and O(F) atoms could be deduced from a difference map. The centric

Table 1. *Crystal data*

$\text{Bi}_6\text{O}_7\text{FCl}_3$ , F.W. 1491.23

$Pnma$ ,  $a=20.105$  (6),  $b=3.892$  (2),  $c=15.432$  (5)  $\text{\AA}$   
 $V=1207.8 \text{ \AA}^3$ ,  $Z=4$   
 $D_m=8.27$ ,  $D_x=8.20 \text{ g cm}^{-3}$   
 $\mu(\text{Mo } K\alpha)=835 \text{ cm}^{-1}$

space group  $Pnma$  and the non-centric  $Pn_2a$  are both possible, in view of the systematic absences. The least-squares refinement in  $Pnma$  progressed normally. As a reasonable structure and reasonable thermal parameters were obtained for  $Pnma$ , a refinement in  $Pn_2a$  was not performed. All ligands except Cl were treated as if they were O atoms in the calculations. In the structure there are two possible positions for the F atoms, according to Pauling's second rule in calculating  $\sum s$  (the sum of the strength of the electrostatic valence bonds) (Pauling, 1929). However,  $R$  was equal for both positions.

Table 2. *Positional and thermal parameters obtained in the final least-squares refinement*

The anisotropic thermal parameters are based on the expression  $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2kl\beta_{23}+2hl\beta_{13})]$ . By symmetry  $\beta_{12}=\beta_{23}=0$ . The  $\beta_{ij}$  values are multiplied by  $10^4$ . Estimated standard deviations are given in parentheses.

	$x$	$y$	$z$	$B (\text{\AA}^2)$
Bi(1)	-0.06855 (9)	$\frac{1}{4}$	0.0478 (2)	[1.91]
Bi(2)	-0.24070 (7)	$\frac{1}{4}$	-0.09002 (9)	[0.64]
Bi(3)	0.09231 (9)	$\frac{1}{4}$	0.16117 (11)	[1.36]
Bi(4)	0.26934 (7)	$\frac{1}{4}$	0.28481 (9)	[0.75]
Bi(5)	0.55672 (7)	$\frac{1}{4}$	0.06361 (10)	[0.78]
Bi(6)	-0.43114 (10)	$\frac{3}{4}$	0.21717 (13)	[2.16]
Cl(1)	0.1390 (5)	$\frac{1}{4}$	0.5617 (8)	1.4 (2)
Cl(2)	0.3176 (5)	$\frac{3}{4}$	0.4369 (7)	1.0 (1)
Cl(3)	0.1418 (5)	$\frac{3}{4}$	0.3129 (7)	1.0 (1)
O(1)	0.20922 (13)	$\frac{1}{4}$	0.1516 (17)	0.5 (4)
O(2)	0.4969 (13)	$\frac{1}{4}$	-0.0604 (19)	0.6 (4)
O(3)	0.0419 (12)	$\frac{1}{4}$	0.0319 (16)	0.8 (3)
O(4)	0.3782 (17)	$\frac{1}{4}$	0.2862 (23)	1.7 (5)
O(5)	-0.2914 (12)	$\frac{1}{4}$	-0.2167 (23)	1.6 (5)
O(6)	0.4829 (22)	$\frac{3}{4}$	0.3431 (31)	3.0 (8)
O(7)	-0.1283 (17)	$\frac{1}{4}$	-0.0944 (24)	1.7 (6)
F	0.5032 (14)	$\frac{1}{4}$	0.1900 (20)	0.9 (4)
		$\beta_{11}$	$\beta_{22}$	$\beta_{33}$
Bi(1)	4.7 (0.4)	283 (14)	72.7 (1.6)	8.6 (0.6)
Bi(2)	4.3 (0.3)	103 (9)	6.3 (0.5)	-0.2 (0.3)
Bi(3)	11.5 (0.4)	258 (12)	9.7 (0.7)	-2.8 (0.4)
Bi(4)	6.1 (0.3)	123 (9)	6.1 (0.5)	-0.4 (0.3)
Bi(5)	3.9 (0.3)	108 (9)	12.7 (0.6)	-1.8 (0.4)
Bi(6)	10.4 (0.4)	703 (19)	15.4 (0.7)	2.4 (0.5)
		$\beta_{13}$		

The F atom was assumed to be in the position given in Table 2. The final refinement in  $Pnma$  by the least-squares method with anisotropic temperature factors for Bi and isotropic for the light atoms, gave  $R=0.055$  and  $R_w=0.071$ , where  $R=\sum||F_o|-|F_c||/\sum|F_o|$  and  $R_w=[\sum w_i(|F_o|-|F_c|)^2/\sum w_i|F_o|^2]^{1/2}$ . Cruickshank's weighting scheme, with  $a=300$ ,  $c=0$  and  $d=0$ , was used.  $[\sum w_i(|F_o|-|F_c|)^2/(m-n)]^{1/2}$ , where  $m$  and  $n$  are the number of observations and parameters varied, was

\* Orientation different from that given in *International Tables for X-ray Crystallography* (1965).

0·69. In the last cycle all parameter shifts were less than 0·01 of the e.s.d. The scattering factors used were those given by Cromer & Waber (1965) for neutral Br and by Hanson, Herman, Lea & Skillman (1964) for neutral Cl, O and F.

Final positional and thermal parameters are given in Table 2, and observed and calculated structure factors in Table 3. All computations were made on the UNIVAC 1108 computer in Lund. A short account of the program system has been given by Stålhandske (1974).

Table 3. Observed and calculated structure factors

The columns list  $h$ ,  $F_0$  and  $|F_c|$ . Reflexions marked with an asterisk were assigned zero weight in the least-squares refinement.

1	204	224	1	123	100	2	116	15	14	310	377	26	92	4R	1	148	193	24	172	171	1	216	142	1	93	52	304	119	1	155	213	15	160
2	106	597	581	2	227	277	3	244	251	27	91	96	4R	1	145	190	24	171	170	1	215	141	1	92	51	303	118	1	154	212	15	161	
3	345	311	1	124	152	2	117	14	14	311	378	26	97	4R	1	146	194	24	170	220	25	235	236	1	93	52	302	117	1	153	211	15	162
4	147	201	1	125	145	2	115	17	15	315	377	27	99	4R	1	147	195	24	171	170	1	216	142	1	92	51	303	118	1	154	212	15	161
5	145	493	480	2	115	157	3	245	275	27	100	120	4R	1	148	196	24	172	227	25	236	237	1	93	52	302	117	1	153	211	15	160	
6	145	491	482	2	116	157	3	245	275	27	101	121	4R	1	149	197	24	173	228	25	237	238	1	93	52	303	118	1	154	212	15	161	
7	144	91	2	119	212	12	76	64	25	98	100	4R	1	150	198	24	174	229	25	238	239	1	94	53	304	119	1	155	213	15	162		
8	114	92	2	119	159	12	76	64	25	99	100	4R	1	151	199	24	175	230	25	239	240	1	94	53	304	119	1	155	213	15	162		
9	147	57	2	119	157	10	94	92	25	245	264	1	152	197	24	176	231	25	240	241	1	94	53	304	119	1	155	213	15	162			
10	572	57	2	119	157	10	94	92	25	245	264	1	153	198	24	177	232	25	241	242	1	94	53	304	119	1	155	213	15	162			
11	142	64	2	115	155	12	76	64	25	98	100	4R	1	154	199	24	178	233	25	242	243	1	94	53	304	119	1	155	213	15	162		
12	142	64	2	115	155	12	76	64	25	99	100	4R	1	155	200	24	179	234	25	243	244	1	94	53	304	119	1	155	213	15	162		
13	142	64	2	115	155	12	76	64	25	100	100	4R	1	156	201	24	180	235	25	244	245	1	94	53	304	119	1	155	213	15	162		
14	142	64	2	115	155	12	76	64	25	101	100	4R	1	157	202	24	181	236	25	245	246	1	94	53	304	119	1	155	213	15	162		
15	142	64	2	115	155	12	76	64	25	102	100	4R	1	158	203	24	182	237	25	246	247	1	94	53	304	119	1	155	213	15	162		
16	142	64	2	115	155	12	76	64	25	103	100	4R	1	159	204	24	183	238	25	247	248	1	94	53	304	119	1	155	213	15	162		
17	142	64	2	115	155	12	76	64	25	104	100	4R	1	160	205	24	184	239	25	248	249	1	94	53	304	119	1	155	213	15	162		
18	142	64	2	115	155	12	76	64	25	105	100	4R	1	161	206	24	185	240	25	249	250	1	94	53	304	119	1	155	213	15	162		
19	142	64	2	115	155	12	76	64	25	106	100	4R	1	162	207	24	186	241	25	250	251	1	94	53	304	119	1	155	213	15	162		
20	142	64	2	115	155	12	76	64	25	107	100	4R	1	163	208	24	187	242	25	251	252	1	94	53	304	119	1	155	213	15	162		
21	142	64	2	115	155	12	76	64	25	108	100	4R	1	164	209	24	188	243	25	252	253	1	94	53	304	119	1	155	213	15	162		
22	142	64	2	115	155	12	76	64	25	109	100	4R	1	165	210	24	189	244	25	253	254	1	94	53	304	119	1	155	213	15	162		
23	142	64	2	115	155	12	76	64	25	110	100	4R	1	166	211	24	190	245	25	254	255	1	94	53	304	119	1	155	213	15	162		
24	142	64	2	115	155	12	76	64	25	111	100	4R	1	167	212	24	191	246	25	255	256	1	94	53	304	119	1	155	213	15	162		
25	142	64	2	115	155	12	76	64	25	112	100	4R	1	168	213	24	192	247	25	256	257	1	94	53	304	119	1	155	213	15	162		
26	142	64	2	115	155	12	76	64	25	113	100	4R	1	169	214	24	193	248	25	257	258	1	94	53	304	119	1	155	213	15	162		
27	142	64	2	115	155	12	76	64	25	114	100	4R	1	170	215	24	194	249	25	258	259	1	94	53	304	119	1	155	213	15	162		
28	142	64	2	115	155	12	76	64	25	115	100	4R	1	171	216	24	195	250	25	259	260	1	94	53	304	119	1	155	213	15	162		
29	142	64	2	115	155	12	76	64	25	116	100	4R	1	172	217	24	196	251	25	260	261	1	94	53	304	119	1	155	213	15	162		
30	142	64	2	115	155	12	76	64	25	117	100	4R	1	173	218	24	197	252	25	261	262	1	94	53	304	119	1	155	213	15	162		
31	142	64	2	115	155	12	76	64	25	118	100	4R	1	174	219	24	198	253	25	262	263	1	94	53	304	119	1	155	213	15	162		
32	142	64	2	115	155	12	76	64	25	119	100	4R	1	175	220	24	199	254	25	263	264	1	94	53	304	119	1	155	213	15	162		
33	142	64	2	115	155	12	76	64	25	120	100	4R	1	176	221	24	200	255	25	264	265	1	94	53	304	119	1	155	213	15	162		
34	142	64	2	115	155	12	76	64	25	121	100	4R	1	177	222	24	201	256	25	265	266	1	94	53	304	119	1	155	213	15	162		
35	142	64	2	115	155	12	76	64	25	122	100	4R	1	178	223	24	202	257	25	266	267	1	94	53	304	119	1	155	213	15	162		
36	142	64	2	115	155	12	76	64	25	123	100	4R	1	179	224	24	203	258	25	267	268	1	94	53	304	119	1	155	213	15	162		
37	142	64	2	115	155	12	76	64	25	124	100	4R	1	180	225	24	204	259	25	268	269	1	94	53	304	119	1	155	213	15	162		
38	142	64	2	115	155	12	76	64	25	125	100	4R	1	181	226	24	205	260	25	269	270	1	94	53	304	119	1	155	213	15	162		
39	142	64	2	115	155	12	76	64	25	126	100	4R	1	182	227	24	206	261	25	270	271	1	94	53	304	119	1	155	213	15	162		
40	142	64	2	115	155	12	76	64	25	127	100	4R	1	183	228	24	207	262	25	271	272	1	94	53	304	119	1	155	213	15	162		
41	142	64	2	115	155	12	76	64	25	128	100	4R	1	184	229	24	208	263	25	272	273	1	94	53	304	119	1	155	213	15	162		
42	142	64	2	115	155	12	76	64	25	129	100	4R	1	185	230	24	209	264	25	273	274	1	94	53	304	119	1	155	213	15	162		
43	142	64	2	115	155	12	76	64	25	130	100	4R	1	186	231	24	210	265	25	274	275	1	94	53	304	119	1	155	213	15	162		
44	142	64	2	115	155	12	76	64	25	131	100	4R	1	187	232	24	211	266	25	275	276	1	94	53	304	119	1	155	213	15	162		
45	142	64	2	115	155	12	76	64	25	132	100	4R	1	188	233	24	212	267	25	276	277	1	94	53	304	119	1	155	213	15	162		
46	142	64	2	115	155	12	76	64	25	133	100	4R	1	189	234	24	213	268	25	277	278	1	94	53	304	119	1	155	213	15	162		
47	142	64	2	115	155	12	76	64	25	134	100	4R	1	190	235	24	214	269	25	278	279	1	94	53	304	119	1	155	213	15	162		
48	142	64	2	115	155	12	76	64	25	135	100	4R	1	191	236	24	215	270	25	279	280	1	94	53	304	119	1	155	213	15	162		
49	142	64	2	115	155	12	76	64	25	136	100	4R	1	192	237	24	216	271	25	280	281	1	94	53	304	119	1	155	213	15	162		
50	142	64	2	115	155	12	76	64	25	137	100	4R	1																				

## Discussion

Interatomic distances and angles are given in Table 4.

The coordination around Bi can be described in the following two ways: Bi(1)-Bi(4) (Table 2) are each surrounded by four O atoms, Bi(5) by one F and three O atoms, the ligand atoms in each case forming a nearly square plane (*cf.* Table 4). The lone pair of electrons can be imagined as completing a square pyramid. This coordination polyhedron has been found previously in BiOCl (Bannister & Hey, 1935) and

Table 4. Interatomic distances and angles

Interatomic distances ( $\text{\AA}$ ) in  $\text{Bi}_6\text{O}_7\text{FCl}_3$  compared with the corresponding distances in  $\text{BiOF}$  and  $\text{BiOCl}$  (Aurivillius, 1964a. The estimated standard deviations are given in parentheses.

	$\text{Bi}_6\text{O}_7\text{FCl}_3$	$\text{BiOF}$	$\text{BiOCl}$		$\text{Bi}_6\text{O}_7\text{FCl}_3$	$\text{BiOF}$	$\text{BiOCl}$
Bi-Bi	$\geq 3.584$ (3)	$\geq 3.694$ (3)	$\geq 3.71$ (1)				
Bi(1)-2Cl(2)	3.168 (8)			Bi(4)-2O(5)	2.25 (2)		
Bi(2)-2Cl(1)	3.135 (9)			Bi(5)-2O(2)	2.23 (1)		
Bi(2)-2Cl(2)	3.212 (9)			Bi(5)-O(2)	2.26 (3)		
Bi(3)-2Cl(3)	3.203 (9)		3.49 (4)	Bi(6)-2O(4)	2.46 (2)		
Bi(4)-2Cl(2)	3.143 (9)		3.07 (2)	Bi(6)-O(6)	2.20 (5)		
Bi(4)-2Cl(3)	3.247 (8)			Bi(1)-2O(6)	2.77 (3)		
Bi(5)-2Cl(1)	3.204 (10)			Bi(3)-2O(6)	2.94 (3)		
Bi(5)-2Cl(3)	3.217 (8)			Bi(5)-F	2.22 (3)		
Bi(1)-O(7)	2.51 (4)			Bi(6)-2F	2.46 (2)	2.75 (2)	
Bi(1)-2O(3)	2.36 (1)			Cl-O	3.32 (3)-3.43 (2)		$\geq 3.25$ (3)
Bi(1)-O(3)	2.24 (2)			F-O	$\geq 2.79$ (3)	2.75 (5)	
Bi(2)-2O(1)	2.26 (1)			F-F	3.892 (-b)	3.44 (8)	
Bi(2)-O(5)	2.21 (3)			Cl-Cl	3.84 (2)-3.90 (2)		3.48 (5)
Bi(2)-O(7)	2.26 (3)			O(1)-2O(5)	2.74 (3)		
Bi(3)-O(1)	2.36 (3)	2.273 (2)	2.309 (4)	O(1)-2O(7)	2.69 (3)		
Bi(3)-O(3)	2.24 (2)			O(2)-2O(2)	2.70 (4)		
Bi(3)-2O(7)	2.31 (2)			O(3)-2O(7)	2.78 (3)	2.6494 (4)	2.7457 (5)
Bi(4)-O(1)	2.37 (3)			O(3)-2O(3)	2.76 (3)		
Bi(4)-O(4)	2.19 (3)			O(4)-2O(5)	2.82 (4)		
				O(4)-2O(6)	3.00 (4)		

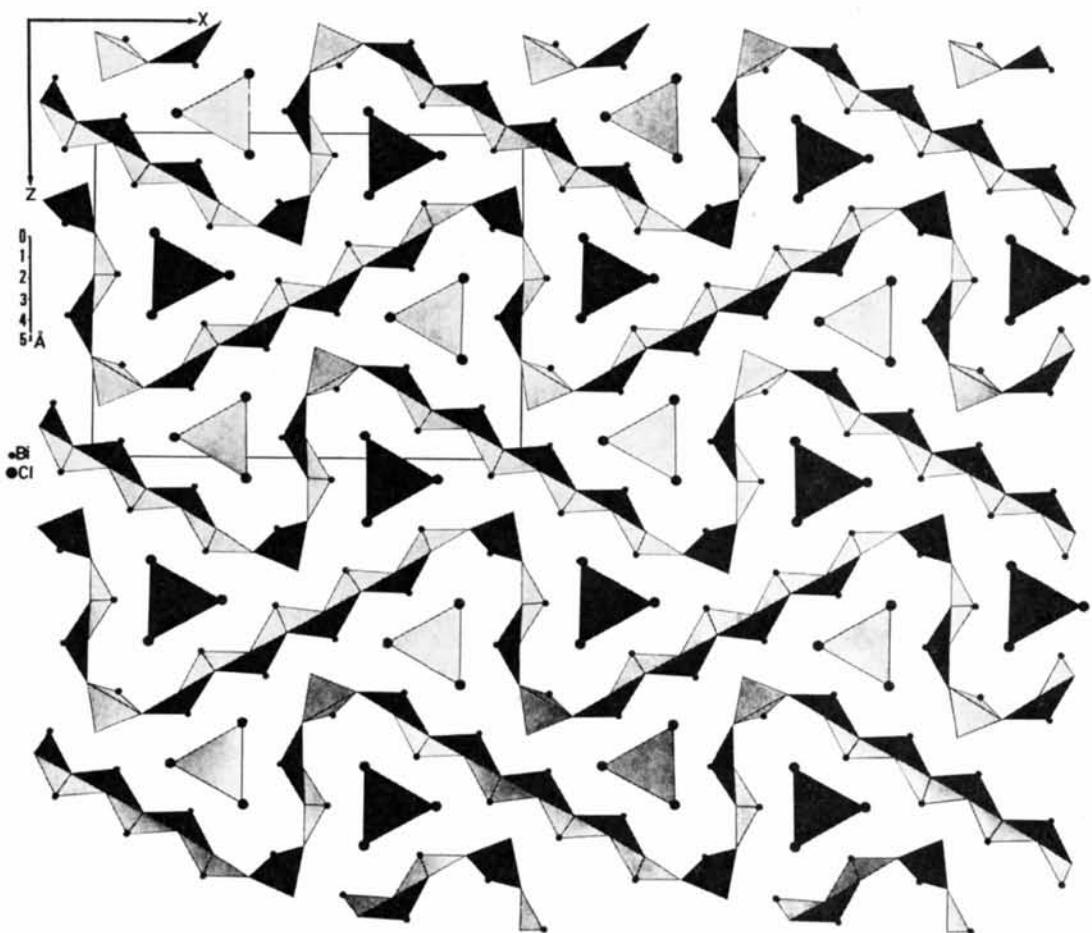


Fig. 1. The structure of  $\text{Bi}_6\text{O}_7\text{FCl}_3$  projected along the  $y$  axis. The bismuth atoms are coordinated to oxygen (fluorine) atoms in the form of square pyramids and octahedra, connected to infinite layers parallel to  $[010]$ . The heavier and the lighter polyhedra are  $b/2$  apart. The chloride ions form trigonal prisms, running in the same direction. All atoms are at the heights  $y=\frac{1}{4}$  or  $\frac{3}{4}$ .

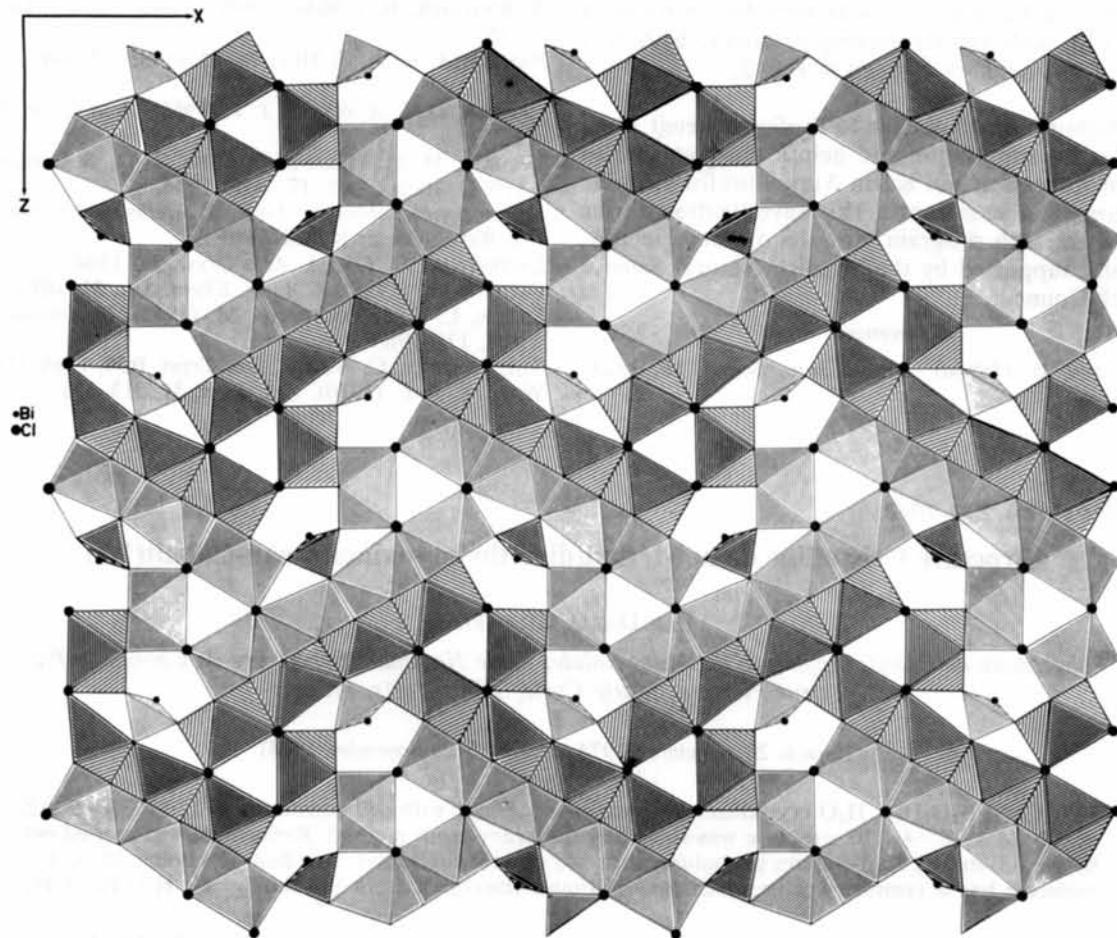


Fig. 2. The structure of  $\text{Bi}_6\text{O}_7\text{FCl}_3$  projected along the  $y$  axis. The coordination polyhedra of bismuth are described as octahedra and square antiprisms, the bismuth atoms in the latter case coordinated to eight ligands (oxygen, fluorine and chlorine). The polyhedra are fused to a three-dimensional network, interleaved by tunnels running along  $[010]$ . The heavier and lighter polyhedra are  $b/2$  apart. All atoms are at the heights  $y=\frac{1}{4}$  or  $\frac{3}{4}$ .

Table 4 (cont.)

Selected angles ( $^\circ$ ) in  $\text{Bi}_6\text{O}_7\text{FCl}_3$

The square plane

$\text{O}(5)-\text{O}(1)-\text{O}(5)$	90.4 (1.3)	$\text{O}(7)-\text{O}(3)-\text{O}(7)$	88.7 (1.2)
$\text{O}(7)-\text{O}(1)-\text{O}(7)$	92.7 (1.4)	$\text{O}(7)-\text{O}(3)-\text{O}(3)$	90.8 (0.6)
$\text{O}(2)-\text{O}(2)-\text{O}(2)$	92.3 (1.8)	$\text{O}(5)-\text{O}(4)-\text{O}(5)$	87.4 (1.4)
$\text{O}(2)-\text{O}(2)-\text{F}$	89.5 (0.7)	$\text{O}(4)-\text{O}(5)-\text{O}(1)$	91.1 (0.6)
$\text{F}-\text{O}(2)-\text{F}$	88.6 (1.2)	$\text{O}(1)-\text{O}(7)-\text{O}(3)$	89.3 (0.5)
$\text{O}(3)-\text{O}(3)-\text{O}(3)$	89.7 (1.4)		

In the octahedron

$\text{O}(4)-\text{O}(4)-\text{F}$	90.00 (0.0)	$\text{O}(4)-\text{O}(6)-\text{O}(4)$	81.0 (1.4)
$\text{F}-\text{F}-\text{O}(4)$	90.00 (0.0)	$\text{O}(4)-\text{O}(6)-\text{F}$	57.2 (1.0)
$\text{F}-\text{O}(6)-\text{F}$	78.0 (1.3)		

The trigonal prism

$\text{Cl}(1)-\text{Cl}(2)-\text{Cl}(3)$	59.5 (0.3)
$\text{Cl}(1)-\text{Cl}(3)-\text{Cl}(2)$	61.0 (0.3)
$\text{Cl}(2)-\text{Cl}(1)-\text{Cl}(3)$	59.5 (0.3)

$\text{BiOF}$  (Aurivillius, 1964a).  $\text{Bi}(6)$  (Table 2), on the other hand, is surrounded by two F and three O atoms, all on one side. The lone pair of electrons completes a

distorted octahedron (Table 4). The square pyramids are joined by sharing edges, forming layers which are connected to the octahedra by sharing corners. The nets of formula  $[\text{Bi}_6\text{O}_7\text{F}^{3+}]_n$  zigzag through the structure parallel to  $\mathbf{b}$ . Between them are trigonal prism columns of chloride ions, running in the same direction. A projection of the described layer structure is given in Fig. 1. In the structure of red  $\text{PbO}$  (Leciejewicz, 1961), there are similar layers consisting of square pyramids.

The coordination around  $\text{Bi}(1)-\text{Bi}(5)$  can also be described as a square antiprism.  $\text{Bi}(1)$ ,  $\text{Bi}(3)$  are each surrounded by two Cl and six O atoms,  $\text{Bi}(2)$ ,  $\text{Bi}(4)$  by four Cl and four O atoms and  $\text{Bi}(5)$  by four Cl one F and three O atoms. This type of coordination polyhedron of bismuth has also been found in the structure of  $\text{BiOHCrO}_4$  (Aurivillius 1964b). The square antiprisms are joined by sharing faces and edges with other antiprisms, forming blocks, which are connected by sharing corners with the described above octahedra. The structure can in this way be described as being

built up of a three-dimensional network of formula  $[\text{Bi}_6\text{O}_7\text{FCl}_3]_n$  with tunnels running parallel to **b**. A projection of this network is given in Fig. 2.

The author is much obliged to Professor Bengt Aurivillius for his stimulation and helpful interest, and to Drs Sten Andersson and Karin Aurivillius for valuable discussions and comments. This investigation forms part of a research program, on salts of heavy metals, financially supported by the Swedish Natural Science Research Council.

#### References

- AURIVILLIUS, B. (1964a). *Acta Chem. Scand.* **18**, 1823–1830.

- AURIVILLIUS, B. (1964b). *Acta Chem. Scand.* **18**, 1937–1957.
- BANNISTER, F. A. & HEY, M. H. (1935). *Miner. Mag.* **24**, 49.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
- HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.
- International Tables for X-ray Crystallography* (1965). Vol. I. Birmingham: Kynoch Press.
- LECIEJEWICZ, J. (1961). *Acta Cryst.* **14**, 1304.
- PAULING, L. (1929). *J. Amer. Chem. Soc.* **51**, 1010–1026.
- SILLÉN, L. G. & EDSTRAND, M. (1942). *Z. Kristallogr. (A)* **104**, 178–196.
- STÅLHANDSKÉ, C. (1974). *Acta Cryst. B* **30**, 1586–1589.
- WERNER, P.-E. (1970). *Ark. Kem.* **31**, 513–516.

*Acta Cryst.* (1975). **B31**, 1092

## Structure Cristalline de la Méthyl(diméthylglyoximato)eau-Cobalt(III)

PAR DARIA GINDEROW

*Laboratoire de Chimie Appliquée de l'Etat Solide, Ecole Nationale Supérieure de Chimie de Paris,  
11 rue Pierre et Marie Curie, 75005 Paris, France*

(Reçu le 20 septembre 1974, accepté le 29 novembre 1974)

$\text{CH}_3\cdot\text{Co}(\text{C}_4\text{N}_2\text{O}_2\text{H}_7)_2\cdot\text{H}_2\text{O}$  cristallizes in space group *Pnma*, with cell constants  $a=13\cdot136$ ,  $b=9\cdot112$ ,  $c=12\cdot114$  Å,  $Z=4$ . The structure was solved by the heavy-atom method. Refinement was carried out by the full-matrix least-squares procedure, with 946 observed reflexions; the final *R* value is 10%. The molecule has a symmetry plane which passes through the cobalt atom and the ligands  $\text{H}_2\text{O}$  and  $\text{CH}_3$ .

#### Introduction

La méthyl(diméthylglyoximato)eau-cobalt(III) fait partie de la série des méthylcobaloximes synthétisées et étudiées par Benlian & Hernandoren (1971). Nous avons entrepris l'étude cristallographique du composé pour examiner s'il y a une influence *trans* sensible du ligand  $\text{H}_2\text{O}$  sur le ligand  $\text{CH}_3$ .

#### Partie expérimentale

Les cristaux sont des aiguilles rouge-brun qui cristallisent dans l'eau. Le groupe spatial et les dimensions de la maille ont été déterminés par enregistrement en chambre de Weissenberg. Les valeurs des paramètres de la maille et les intensités des réflexions ont été mesurées au laboratoire de recherche Philips à Eindhoven sur le diffractomètre à quatre cercles PW 1100. Les intensités ont été mesurées avec la radiation du molybdène pour les angles  $\theta$  inférieurs à  $25^\circ$ .

Sur 1356 réflexions indépendantes, 946 réflexions répondant au critère  $I > 2\sigma(I)$  ont été utilisées pour la détermination et l'affinement de la structure. Les intensités diffractées ont été corrigées des facteurs de Lorentz et de polarisation. Les effets de l'absorption ont été négligés. Les données cristallographiques sont

les suivantes:  $\text{C}_9\text{N}_4\text{O}_5\text{H}_{19}\text{Co}$ ,  $M=322,21$ ; orthorhom-bique *Pnma*,  $a=13,136$  (5);  $b=9,112$  (3);  $c=12,114$  (4) Å;  $V=1450,1$  Å<sup>3</sup>;  $Z=4$ ;  $D_m=1,45$ ;  $D_c=1,48$  g cm<sup>-3</sup>;  $\mu=12,53$  cm<sup>-1</sup> pour  $\lambda$  (Mo  $K\alpha$ ).

#### Détermination de la structure et affinement

La structure a été résolue par la technique de l'atome lourd. L'étude de la fonction de Patterson tridimensionnelle a permis de localiser l'atome de cobalt ainsi que l'atome de carbone de la liaison Co-CH<sub>3</sub> et l'atome d'oxygène de la liaison Co-H<sub>2</sub>O, ceux-ci sont en position spéciale sur les plans de symétrie de la maille. Les positions des autres atomes ont été déterminées par des synthèses de Fourier successives.

L'affinement des coordonnées atomiques et des coefficients de température a été réalisé par la méthode des moindres carrés (matrice complète). Pour tous les atomes avec des facteurs d'agitation thermique isotrope, le facteur *R* est égal à 0,12 ( $R=\sum|\Delta F|/\sum|F_o|$ ).

L'affinement de la structure a été poursuivi avec des facteurs d'agitation thermique anisotrope sans les atomes d'hydrogène, car ceux-ci ne sont pas repérables avec précision sur la série de densité électronique différence. En fin d'affinement, nous avons utilisé un schéma de pondération de la forme:  $w=5-0,125|F_o|+$