

Rubidium Iodide Triiodide Hexaiodobismuthate(III) Dihydrate

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Abstract. $\text{Rb}_5\text{I}(\text{I}_3)(\text{BiI}_6)(\text{H}_2\text{O})_2$, trigonal, $R\bar{3}m$; hexagonal axes: $a = 23.380$ (6), $c = 14.959$ (2) Å; $D_o = 3.9$ (1), $Z = 9$, $D_c = 4.097$ g cm⁻³; $R = 0.104$ for 878 reflexions [$I > 2.5\sigma(I)$]. The structure contains rubidium cations, octahedral hexaiodobismuthate(III) anions, iodide anions, linear symmetrical triiodide anions and water molecules.

Introduction. This work is part of a systematic study of bromo- and iodobismuthates(III) (see the preceding paper). It was thought interesting to synthesize a compound containing isolated hexaiodobismuthate(III) anions and to determine its crystal structure. The compound was prepared with a large excess of RbI, because it is possible that the iodide anions present in the structure might prevent the linking of BiI_6 octahedra into the polynuclear species usually found in iodobismuthates(III). Black crystals were grown by very slow evaporation from an aqueous solution, obtained by dissolving $\text{Bi}(\text{OH})_3$ and Rb_2CO_3 in 1:3 molar ratio in a dilute HI solution. During evaporation, some of the iodide ions in the solution were oxidized by air oxygen to triiodide ions (I_3^-). The chemical formula was established by means of standard analytical methods {found: Bi (complexometric) 10.62%, Rb [as $\text{RbB}(\text{C}_6\text{H}_5)_4$] 21.90%, total I (as AgI) 66.03%; calculated: 10.76, 22.01 and 65.37% respectively}. Other crystal structures with isolated hexaiodobismuthate(III) anions are not known; only two structures with hexachlorobismuthate(III) anions have been published: $\text{Cs}_2\text{Na}[\text{BiCl}_6]$ (Morss & Robinson, 1972) and $[\text{Co}(\text{NH}_3)_6][\text{BiCl}_6]$ (Atoji & Watanabé, 1952).

The single crystal selected was ground to a sphere ($r = 0.09$ mm). The intensity data were collected at 20 (1)°C with an Enraf–Nonius CAD-4 diffractometer. Experimental conditions were: Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1.54178$ Å); ω - 2θ scan; $\theta_{\min} = 5.0^\circ$, $\theta_{\max} = 70.0^\circ$; 2θ scan width ($^\circ$): $0.6 + 0.2 \tan \theta$; aperture (mm): $2.4 + 0.87 \tan \theta$; maximum scan time 20 s; background: a quarter of the scan time at each of the scan limits. 4001 reflexions were recorded. After averaging symmetry-related reflexions, 1451 independent reflexions remained (mean discrepancy on I : 12% for 1403 reflexions) and, of these, 878 reflexions, having $I > 2.5\sigma(I)$ (calculations based on counting

statistics), were used in the structure analysis. Corrections were applied for Lorentz and polarization effects and for absorption [$\mu(\text{Cu } K\alpha) = 1091.6$ cm⁻¹]. The absorption corrections A^* , calculated for the spherical crystal ($\mu r = 9.8$), range from 870.1 to 31.9 (*International Tables for X-ray Crystallography*, 1959). The unit-cell parameters were calculated by a least-squares method from the θ values for 15 reflexions measured on the four-circle diffractometer. The systematic absences ($-h + k + l \neq 3n$) and the clearly centrosymmetric distribution of the normalized structure factors indicated space group $R\bar{3}m$.

The structure was solved by the heavy-atom method and refined by least squares with anisotropic thermal parameters for Bi, I and Rb atoms, isotropic for O, and with anomalous-dispersion corrections for Bi, I and Rb. The function minimized in the least-squares procedure was $\sum w(F_o - F_c)^2$. The weighting scheme applied was as follows: $|F_o| < 100$: $w_F = (|F_o|/100)^{1.0}$; $\sin \theta < 0.55$: $w_S = (\sin \theta/0.55)^{3.0}$; $100 < |F_o| \leq 400$: $w_F = 1.0$; $0.55 < \sin \theta \leq 0.80$: $w_S = 1.0$; $|F_o| \geq 400$: $w_F = (400/|F_o|)^{3.5}$; $\sin \theta \geq 0.80$: $w_S = (0.80/\sin \theta)^{2.0}$; $w = 0.05w_Fw_S$.

Rb(3) is statistically distributed at the Wyckoff 18(h) position with a population parameter of 0.5, according to the actual number of atoms in the unit cell and to the peak height in the electron-density map. This population parameter did not change significantly during the refinement. An attempt to refine the structure in the noncentrosymmetric space group $R3m$ was unsuccessful (higher R value, unreasonable temperature factors for all atoms). No attempts have been made to locate H atoms. An isotropic extinction parameter (Zachariasen, 1963; Larson, 1967) was also included in the final stage of the refinement ($g = 6.0 \times 10^{-3}$). Final R values are $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.104$ and $R_w = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2} = 0.103$ for 878 reflexions and 56 parameters. Unfortunately, the poor quality of the crystal ground to a sphere did not allow us to achieve a better agreement index. The average parameter shift-to-error ratio was 0.06 in the final cycle.

All calculations were performed on the CDC Cyber 72 computer of RRC Ljubljana with the XRAY 72 system (Stewart, Kruger, Ammon, Dickinson & Hall,

Table 1. *Final positional parameters* ($\times 10^4$) *with standard deviations in parentheses*

W = Wyckoff position, P = population parameter.

	W	P	x	y	z
Bi	9(e)	1	0	$\frac{1}{2}$	0
I(1)	18(h)	1	$=2y-1$	4992 (1)	2050 (2)
I(2)	36(i)	1	1085 (1)	4619 (1)	-22 (1)
I(3)	3(a)	1	0	0	1
I(4)	6(c)	1	0	0	3153 (4)
I(5)	9(d)	1	$\frac{1}{6}$	$\frac{1}{3}$	$\frac{2}{3}$
I(6)	18(h)	1	994 (1)	$=2x$	9062 (2)
Rb(1)	18(g)	1	0	3307 (2)	$\frac{1}{2}$
Rb(2)	18(h)	1	708 (1)	$=2x$	1651 (3)
Rb(3)	18(h)	$\frac{1}{2}$	697 (3)	$=2x$	5171 (7)
O	18(f)	1	0	2667 (20)	0

Table 2. *Interatomic distances* (\AA) *and angles* ($^\circ$) *with standard deviations in parentheses*

Bi ⁱ -I(1 ^{i,ii})	3.067 (3)	Rb(1 ⁱ)-O ^{ix, vii}	2.96 (2)
Bi ⁱ -I(2 ^{i,ii,iii,iv})	3.079 (3)	Rb(2 ⁱ)-I(4 ⁱ)	3.643 (5)
I(5 ⁱ)-I(6 ^{i,v})	2.935 (2)	Rb(2 ⁱ)-I(2 ^{vii, xiii})	3.697 (4)
I(6 ⁱ)-I(3 ⁱ)	4.261 (2)	Rb(2 ⁱ)-I(6 ^{xiv, xv})	3.744 (4)
I(6 ⁱ)-I(1 ^{vi})	4.276 (3)	Rb(2 ⁱ)-I(3 ^{xvi})	3.785 (3)
Rb(1 ⁱ)-I(2 ^{vii, viii})	3.726 (5)	Rb(2 ⁱ)-I(1 ^x)	3.888 (3)
Rb(1 ⁱ)-I(2 ^{ix, x})	3.746 (3)	Rb(3 ⁱ)-I(4 ^{xvi})	3.776 (8)
Rb(1 ⁱ)-I(1 ^{xi, xii})	3.909 (3)	Rb(3 ⁱ)-I(2 ^{viii, xvii})	3.886 (8)
		Rb(3 ⁱ)-I(2 ^{vii, xiii})	3.923 (9)
I(1 ⁱ)-Bi ⁱ -I(2 ^{i,iii})	91.04 (5)	I(2 ⁱ)-Bi ⁱ -I(2 ^{iv})	90.99 (6)
I(1 ⁱⁱ)-Bi ⁱ -I(2 ^{ii, iv})	91.04 (5)	I(2 ⁱⁱ)-Bi ⁱ -I(2 ⁱⁱⁱ)	90.99 (6)
I(1 ⁱ)-Bi ⁱ -I(1 ⁱⁱ)	180.00	I(2 ⁱ)-Bi ⁱ -I(2 ⁱⁱ)	180.00
I(1 ⁱ)-Bi ⁱ -I(2 ^{ii, iv})	88.96 (5)	I(2 ⁱⁱⁱ)-Bi ⁱ -I(2 ^{iv})	180.00
I(1 ⁱⁱ)-Bi ⁱ -I(2 ^{i, iii})	88.96 (5)	I(6 ⁱ)-I(5 ⁱ)-I(6 ^v)	180.00
I(2 ⁱ)-Bi ⁱ -I(2 ⁱⁱⁱ)	89.00 (6)	I(3 ⁱ)-I(6 ⁱ)-I(5 ⁱ)	177.4 (1)
I(2 ⁱⁱ)-Bi ⁱ -I(2 ^{iv})	89.00 (6)		

Symmetry code

(i)	x, y, z	(x)	$-\frac{1}{3}+y, \frac{1}{3}+x, \frac{1}{3}-z$
(ii)	$-x, 1-y, -z$	(xi)	$\frac{1}{3}+x-y, -\frac{1}{3}-x+y, \frac{2}{3}-z$
(iii)	$x, 1+x-y, z$	(xii)	$-\frac{1}{3}-x+y, -\frac{2}{3}-2x+2y, \frac{1}{3}+z$
(iv)	$-x, -x+y, -z$	(xiii)	$\frac{2}{3}-y, \frac{1}{3}-x, \frac{1}{3}+z$
(v)	$\frac{1}{3}-x, \frac{2}{3}-y, \frac{5}{3}-z$	(xiv)	$y, -x+y, 1-z$
(vi)	$-\frac{1}{3}+y, \frac{1}{3}+x, \frac{4}{3}-z$	(xv)	$x-y, x, 1-z$
(vii)	$-\frac{1}{3}-x+y, \frac{1}{3}-x, \frac{1}{3}+z$	(xvi)	$x, y, 1-z$
(viii)	$\frac{1}{3}+x-y, \frac{2}{3}-y, \frac{2}{3}-z$	(xvii)	$\frac{1}{3}-x, \frac{2}{3}-y, \frac{2}{3}-z$
(ix)	$\frac{1}{3}-y, \frac{2}{3}+x-y, \frac{2}{3}+z$		

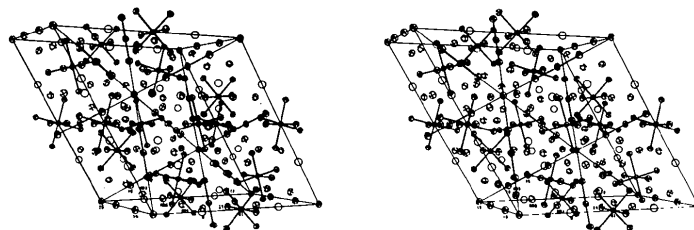


Fig. 1. A stereoscopic drawing of the unit cell viewed approximately along [001]. The atoms are represented by thermal ellipsoids drawn at the 60% probability level. For Rb(3) incomplete ellipsoids are used to stress the 50% occupancy.

1972) adapted by Professor L. Golič. Atomic scattering factors for neutral atoms tabulated by Cromer & Mann (1968), and the values of $\Delta f'$ and $\Delta f''$ for anomalous-dispersion correction tabulated by Cromer & Liberman (1970) were applied.

The positional parameters are listed in Table 1.* A stereoscopic drawing (Johnson, 1965) of the structure and the atom-numbering system used are shown in Fig. 1. Some important interatomic distances and angles are given in Table 2.

Discussion. The structure of the title compound consists of Rb⁺ cations, isolated octahedral [BiI₆]³⁻ anions, I⁻ anions, symmetrical linear I₃⁻ anions and water molecules, coordinated to the cations. The almost regularly octahedral hexaiodobismuthate(III) anions (angles between 88.96 and 91.04°) are not linked to form polynuclear species as is usually found in iodo-bismuthates(III) (Robertson, McPherson & Meyers, 1967; Lindqvist, 1968). This may be caused by the excess iodide and triiodide anions in the crystal structure. A stereochemical influence of the Bi electron lone pair cannot be observed, probably because of the bulky ligands (Porter & Jacobson, 1970). The triiodide anions are linear and symmetrical with an I(5)-I(6) distance of 2.935 (2) Å, very similar to the 2.90 (2) Å of symmetrical anions in (C₆H₅)₄AsI₃ (Mooney-Slater, 1959). The I₃⁻ anions are linked by van der Waals bonds [4.261 (2) Å] to some of the I⁻ anions [I(3)], forming endless, nearly linear chains [I(3)-I(6)-I(5) 177.4 (1)°]. At each I(3), three such chains intersect. A contact between the triiodide and hexaiodobismuthate(III) anions was also observed [I(6ⁱ)-I(1^{vi}) 4.276 (3) Å]. Some I⁻ anions [I(4)] have no contact with other anions, but are only coordinated to the cations. The coordination polyhedra around the cations are thoroughly irregular.

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32452 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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2-Deoxy-12-oxolemnacarnol; A Case of Twinning

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Abstract. $C_{15}H_{22}O_3$, triclinic, $P1$, $a = 13.70(2)$, $b = 7.29(1)$, $c = 7.53(1)$ Å, $\alpha = 89.6(1)$, $\beta = 109.8(1)$, $\gamma = 95.2(1)^\circ$, $Z = 2$, $D_m = 1.184$, $D_x = 1.180$ g cm $^{-3}$. The crystals are twins, with the $(\bar{1}60)$ net as twin net and a rotation angle of 180° . The twinning is explained in terms of an approximate non-crystallographic twofold screw axis. The compound was isolated from soft corals of the genera *Lemnalia* and *Paralemnalia*.

Introduction. We describe here the X-ray diffraction analysis of the title compound, which was undertaken in order to add an independent proof to the chemical analysis (Daloze, Braekman, Georget & Tursch, 1977), and to establish the configuration at C(7).

Fig. 1 shows the molecule with the absolute configuration obtained by chemical correlation with lemnacarnol (Tursch, Colin, Daloze, Losman & Karlsson, 1975).

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A Philips PW 1100 diffractometer with graphite-monochromatized Cu $K\alpha$ radiation was used to determine lattice constants and to collect data. Two crystals were used, one for data up to 40° in θ , and another for data between 40 and 60° in θ , their volumes being respectively 3×10^{-3} and 50×10^{-3} mm 3 .

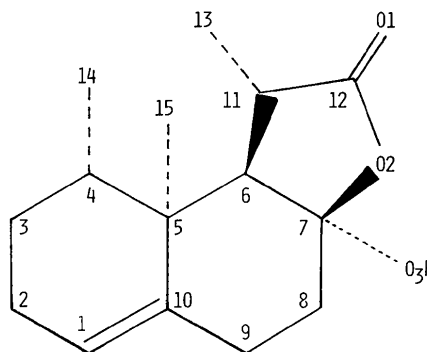


Fig. 1. The absolute configuration of 2-deoxy-12-oxolemnacarnol.