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# Preparation and crystal structure of $[\text{Bi}_3\text{I}(\text{C}_4\text{H}_8\text{O}_3\text{H}_2)_2(\text{C}_4\text{H}_8\text{O}_3\text{H})_5]_2\text{Bi}_8\text{I}_{30}$ containing the novel polynuclear $[\text{Bi}_8\text{I}_{30}]^{6-}$ anion

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## Abstract

Preparation and crystal structure of the novel compound  $[\text{Bi}_3\text{I}(\text{C}_4\text{H}_8\text{O}_3\text{H}_2)_2(\text{C}_4\text{H}_8\text{O}_3\text{H})_5]_2\text{Bi}_8\text{I}_{30}$  are reported. The title compound is prepared by heating of  $\text{BiI}_3$  and diethylene glycol at 413 K in a sealed quartz glass tube filled with argon. Deep red single crystals are grown and applied to perform X-ray powder diffraction and X-ray single-crystal diffraction measurements. The compound crystallizes triclinic with space group  $P-1$ :  $Z=2$ ,  $a=13.217(1)\text{Å}$ ,  $b=15.277(1)\text{Å}$ ,  $c=22.498(1)\text{Å}$ ,  $\alpha=84.33(1)^\circ$ ,  $\beta=73.18(1)^\circ$ ,  $\gamma=67.48(1)^\circ$ .  $[\text{Bi}_3\text{I}(\text{C}_4\text{H}_8\text{O}_3\text{H}_2)_2(\text{C}_4\text{H}_8\text{O}_3\text{H})_5]_2\text{Bi}_8\text{I}_{30}$  comprises the novel polynuclear  $[\text{Bi}_8\text{I}_{30}]^{6-}$  anion and  $[\text{Bi}_3\text{I}(\text{C}_4\text{H}_8\text{O}_3\text{H}_2)_2(\text{C}_4\text{H}_8\text{O}_3\text{H})_5]^{3+}$  as the cation. Cation as well as the anion can be assumed to represent intermediates between solid  $\text{BiI}_3$  and  $\text{BiI}_3$  completely dissolved in diethylene glycol.

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**Keywords:** Preparation; Single-crystal structure determination; Bismuth; Iodide

## 1. Introduction

$\text{Cs}_3\text{Bi}_2\text{I}_9$  represents the first known example of a compound containing a polynuclear iodo complex of bismuth [1,2]. Moreover, with this compound the anion  $[\text{Bi}_2\text{I}_9]^{3-}$  consisting of two face-sharing  $\text{BiI}_6$  octahedra was firstly described. Further investigations led to a characterization of  $[\text{Bi}_3\text{I}_{12}]^{3-}$ ,  $[\text{Bi}_4\text{I}_{16}]^{4-}$ ,  $[\text{Bi}_5\text{I}_{19}]^{4-}$ ,  $[\text{Bi}_6\text{I}_{22}]^{4-}$  and  $[\text{Bi}_8\text{I}_{28}]^{4-}$  as additional isolated polynuclear iodo complexes of bismuth [3–8]. To realize the listed compounds, large organic cations such as  $[\text{N}(\text{C}_4\text{H}_9)_4]^+$ ,  $[\text{K}(18\text{-crown-6})]^+$ ,  $[\text{P}(\text{C}_2\text{H}_5)_4]^+$  or  $[\text{Li}(\text{thf})_4]^+$  are applied. These large cations, in principle, separate building units cut out of the  $\text{BiI}_3$  type of structure to form isolated polynuclear anions. Altogether, the number of known bismuth iodo complexes is limited. Exchanging the large organic cations by simple metal ions, a large number of novel compounds is to be expected. As a result, on one hand, a formation of novel anionic building units as well as an interconnection of polynuclear anions via the metal cations seems to be possible. Nowadays, especially the latter type of compounds is becoming more and more interesting

due to potentially anisotropic electrical, magnetical or optical properties [9,10].

Former experiments have evidenced that polynuclear iodo complexes of bismuth can be realized by heating  $\text{BiI}_3$  together with additional metal iodides in diethylene glycol at comparably low temperatures ( $<200^\circ\text{C}$ ) [4,11,12]. Here, with  $[\text{Bi}_8\text{I}_{30}]^{6-}$  in  $[\text{Bi}_3\text{I}(\text{C}_4\text{H}_8\text{O}_3\text{H}_2)_2(\text{C}_4\text{H}_8\text{O}_3\text{H})_5]_2\text{Bi}_8\text{I}_{30}$ , the largest isolated bismuth iodo complex known till now is described.  $[\text{Bi}_3\text{I}(\text{C}_4\text{H}_8\text{O}_3\text{H}_2)_2(\text{C}_4\text{H}_8\text{O}_3\text{H})_5]^{3+}$  representing the cationic substructure of the title compound also contains bismuth and iodine. For such a situation also only a few examples have been reported, yet [12,13]. The composition of both species, anion as well as cation, allow a view on the relevant species being present by dissolving  $\text{BiI}_3$  in diethylene glycol.

## 2. Experimental

### 2.1. Syntheses

To prepare  $[\text{Bi}_3\text{I}(\text{C}_4\text{H}_8\text{O}_3\text{H}_2)_2(\text{C}_4\text{H}_8\text{O}_3\text{H})_5]_2\text{Bi}_8\text{I}_{30}$ , 8.5 mmol  $\text{BiI}_3$  (Aldrich, 99%) and 5 ml diethylene glycol (Aldrich, 99%) were filled in a quartz glass tube ( $\varnothing = 15\text{ mm}$ ). The quartz glass tube was sealed under

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argon and heated for 4 days at 413 K in a tube furnace. The resulting transparent, air-stable and deep red crystals of  $[\text{Bi}_3\text{I}(\text{C}_4\text{H}_8\text{O}_3\text{H}_2)_2(\text{C}_4\text{H}_8\text{O}_3\text{H})_5]_2\text{Bi}_8\text{I}_{30}$  were washed with acetone in order to remove diethylene glycol. According to the results of X-ray powder diffraction analysis, the title compound was yielded as a pure compound.

## 2.2. EDX analysis

Semiquantitative elemental analysis was performed with the use of an energy-dispersive X-ray (EDX)

Table 1

X-ray crystallographic details for  $[\text{Bi}_3\text{I}(\text{C}_4\text{H}_8\text{O}_3\text{H}_2)_2(\text{C}_4\text{H}_8\text{O}_3\text{H})_5]_2\text{Bi}_8\text{I}_{30}$

Space group	<i>P</i> -1 (no. 2)
<i>a</i> (Å)	13.217(1)
<i>b</i> (Å)	15.277(1)
<i>c</i> (Å)	22.498(1)
$\alpha$ (deg)	84.33(1)
$\beta$ (deg)	73.18(1)
$\gamma$ (deg)	67.48(1)
<i>V</i> (Å <sup>3</sup> )	4016.3(1)
<i>Z</i>	2
<i>F</i> (0 0 0)	3530
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	3.44
$\mu$ (MoK) (cm <sup>-1</sup> )	2.148
Crystal color and habit	Dark red rods
Crystal size (mm)	0.08 × 0.07 × 0.15
Range in $\theta$	2.9–23
Range in <i>hkl</i>	±14, ±16, ±24
Measured reflections	31287
Independent reflections/parameter	11515 ( <i>R</i> <sub>int</sub> 0.097)/650
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.982
<i>R</i> ( <i>F</i> ) <sup>a</sup>	0.051
<i>wR2</i> ( <i>F</i> <sup>2</sup> ) <sup>b</sup>	0.116
Largest diff. peak and hole (e/Å <sup>3</sup> )	3.14 and –1.96

<sup>a</sup>  $R(F) = \sum(|F_o| - |F_c|) / \sum|F_o|$ ; Denotes value of the residual considering only the reflections with  $I > 2\sigma(I)$ .

<sup>b</sup>  $wR2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$ ,  $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ ;  $P = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)]/3$ , denotes value of the residual considering all the reflections.

Table 2

Atomic coordinates (×10<sup>4</sup>) and equivalent isotropic displacement parameters for  $[\text{Bi}_3\text{I}(\text{C}_4\text{H}_8\text{O}_3\text{H}_2)_2(\text{C}_4\text{H}_8\text{O}_3\text{H})_5]_2\text{Bi}_8\text{I}_{30}$

Atom	Wyckoff-position	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> <sub>eq</sub> (Å <sup>2</sup> ) <sup>a</sup>
Bi1	2i	8772(1)	1229(1)	3106(1)	25(1)
Bi2	2i	9466(1)	557(1)	977(1)	26(1)
Bi3	2i	1467(1)	2242(1)	1447(1)	26(1)
Bi4	2i	842(1)	3067(1)	3621(1)	33(1)
Bi5	2i	6120(1)	7426(1)	2153(1)	18(1)
Bi6	2i	4224(1)	6110(1)	2171(1)	24(1)
Bi7	2i	5593(1)	7929(1)	3834(1)	26(1)
I1	2i	8786(1)	2423(1)	1722(1)	31(1)
I2	2i	1402(1)	1100(1)	2764(1)	31(1)
I3	2i	25(1)	8634(1)	395(1)	44(1)
I4	2i	2143(1)	306(1)	831(1)	42(1)

Table 2 (continued)

Atom	Wyckoff-position	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> <sub>eq</sub> (Å <sup>2</sup> ) <sup>a</sup>
I5	2i	6388(1)	1378(1)	3388(1)	47(1)
I6	2i	9396(1)	9476(1)	2164(1)	44(1)
I7	2i	3831(1)	2042(1)	1125(1)	51(1)
I8	2i	8040(1)	3034(1)	3770(1)	49(1)
I9	2i	641(1)	4071(1)	2229(1)	51(1)
I10	2i	9375(1)	9900(1)	4048(1)	46(1)
I11	2i	1033(1)	3383(1)	355(1)	49(1)
I12	2i	7093(1)	1168(1)	1029(1)	59(1)
I13	2i	3283(2)	2374(1)	3267(1)	60(1)
I14	2i	606(2)	4895(1)	4017(1)	70(1)
I15	2i	506(1)	2370(1)	4874(1)	70(1)
I16	2i	7722(1)	8229(1)	3618(1)	50(1)
O1	2i	4320(8)	7502(7)	2332(5)	25(3)
O2	2i	2211(10)	7431(9)	2528(7)	49(4)
O3	2i	2316(13)	5591(10)	2504(9)	74(5)
O4	2i	4153(11)	5956(8)	3117(5)	37(3)
O5	2i	4821(12)	4386(8)	2436(6)	44(4)
O6	2i	4962(12)	4749(9)	1214(6)	49(4)
O7	2i	7978(12)	7829(10)	1985(8)	58(4)
O8	2i	8106(9)	6041(7)	1696(5)	29(3)
O9	2i	6008(9)	5963(7)	1968(5)	26(3)
O10	2i	6180(13)	7650(9)	958(7)	56(4)
O11	2i	5542(11)	9127(7)	1733(5)	35(3)
O12	2i	5354(10)	8596(7)	2926(5)	31(3)
O13	2i	4142(11)	7154(10)	3879(7)	58(4)
O14	2i	3320(12)	8907(10)	4452(7)	59(4)
O15	2i	4855(15)	9710(10)	4256(8)	71(5)
O16	2i	6405(10)	6826(7)	3079(5)	25(3)
O17	2i	6650(12)	6287(9)	4228(6)	47(4)
O18	2i	5459(17)	7708(11)	5098(6)	83(6)
O19	2i	4710(15)	6839(11)	864(9)	85(6)
O20	2i	3141(16)	6071(14)	758(9)	97(7)
O21	2i	3440(3)	4350(2)	202(18)	205(15)
C1	2i	3351(13)	8380(11)	2402(11)	53(6)
C2	2i	2258(15)	8228(14)	2769(11)	61(7)
C3	2i	1294(16)	7180(16)	2915(10)	64(7)
C4	2i	1281(15)	6384(14)	2563(11)	67(8)
C5	2i	4178(19)	5091(11)	3440(9)	53(6)
C6	2i	5069(18)	4253(13)	3029(7)	51(6)
C7	2i	5336(18)	3607(11)	2013(8)	51(6)
C8	2i	4820(3)	3887(14)	1469(11)	77(9)
C9	2i	9034(15)	7043(12)	1833(9)	49(6)
C10	2i	9008(15)	6364(13)	1395(8)	40(5)
C11	2i	7956(15)	5425(12)	1327(7)	35(5)
C12	2i	6987(12)	5133(11)	1718(8)	35(5)
C13	2i	6050(3)	8531(12)	660(10)	79(9)
C14	2i	5630(4)	9318(15)	1105(8)	129(16)
C15	2i	5310(3)	9837(13)	2137(8)	86(10)
C16	2i	5150(2)	9565(11)	2796(8)	51(6)
C17	2i	3101(17)	7437(16)	4363(11)	76(8)
C18	2i	2532(17)	8524(16)	4385(13)	89(10)
C19	2i	2890(2)	9911(13)	4374(12)	70(7)
C20	2i	3687(18)	240(17)	4591(11)	73(8)
C21	2i	6947(17)	5830(10)	3196(8)	39(5)
C22	2i	7520(17)	5719(15)	3720(8)	61(7)
C23	2i	7010(2)	6234(16)	4769(8)	83(10)
C24	2i	6000(2)	6768(13)	5305(9)	73(9)
C25	2i	3830(2)	7366(17)	583(14)	88(10)
C26	2i	3330(3)	6770(2)	346(15)	136(16)
C27	2i	2240(3)	5810(3)	709(16)	125(14)
C28	2i	2580(3)	5230(2)	123(16)	126(14)

<sup>a</sup> *U*<sub>eq</sub> is defined as one third of the trace of the orthogonalized *U*<sub>ij</sub> tensor.

spectrometry equipped Philips SEM 525R scanning electron microscope: for  $[\text{Bi}_3\text{I}(\text{C}_4\text{H}_8\text{O}_3\text{H}_2)_2(\text{C}_4\text{H}_8\text{O}_3\text{H})_5]_2\text{Bi}_8\text{I}_{30}$  the Bi/I ratio was determined to be 1/2.36(4) (theoretical value: 1/2.29).

### 2.3. Crystal structure analyses

A summary of the crystallographic data for  $[\text{Bi}_3\text{I}(\text{C}_4\text{H}_8\text{O}_3\text{H}_2)_2(\text{C}_4\text{H}_8\text{O}_3\text{H})_5]_2\text{Bi}_8\text{I}_{30}$  is given in Tables 1 and 2. The data set of the compound was collected on a Siemens Platform/CCD automated diffractometer. The structure was solved by direct methods (SHELXS-97) [14] and refined by full-matrix least squares procedures, based on  $F^2$ , of the positional and anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97) [15]. Finally, numeric correction of absorption was carried out (WinGX-1.64.02) [16]. Structural diagrams were performed with KXPLOT [17]. Lattice parameters were also verified by X-ray powder diffraction analysis.

Further details of the crystal structure investigation are also available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-412536, the name of the author, and citation of the paper.

### 3. Results and discussion

The novel compound  $[\text{Bi}_3\text{I}(\text{C}_4\text{H}_8\text{O}_3\text{H}_2)_2(\text{C}_4\text{H}_8\text{O}_3\text{H})_5]_2\text{Bi}_8\text{I}_{30}$  consists of isolated polynuclear  $[\text{Bi}_8\text{I}_{30}]^{6-}$  anions and  $[\text{Bi}_3\text{I}(\text{C}_4\text{H}_8\text{O}_3\text{H}_2)_2(\text{C}_4\text{H}_8\text{O}_3\text{H})_5]^{3+}$  as the cationic building unit. The  $[\text{Bi}_8\text{I}_{30}]^{6-}$  anion is established by eight bismuth atoms, each of them coordinated by six iodine atoms to form distorted octahedra (Fig. 1). Six  $\text{BiI}_6$  octahedra are linked by edge-sharing to three additional octahedra, the two residual octahedra are connected to only two octahedra.

The cationic substructure of the compound also contains bismuth and iodine (Fig. 2). Here, three bismuth atoms (Bi5, Bi6, Bi7) are coordinated by altogether seven molecules of diethylene glycol. In addition, one iodine atom (I16) is linked to Bi7. The composition of both building units, cation as well as anion, is described for the first time. The anion  $[\text{Bi}_8\text{I}_{30}]^{6-}$  represents the largest isolated polynuclear bismuth iodo complex described till now.

As expected, the Bi–I distances in the  $[\text{Bi}_8\text{I}_{30}]^{6-}$  anion are very similar to other polynuclear anions containing comparably interconnected  $\text{BiI}_6$  octahedra (Table 3). Taking the reduced symmetry of the  $[\text{Bi}_8\text{I}_{30}]^{6-}$  anion into account, the  $\mu_2(\text{Bi}-\text{I})$ -distances are also very similar to the situation in  $\text{BiI}_3$  [18]. In fact,  $[\text{Bi}_8\text{I}_{30}]^{6-}$  can be assumed to represent a building unit which is cut out of a layer of the hexagonal  $\text{BiI}_3$  type of structure. The variation of the I–Bi–I angles ( $76$ – $102^\circ$  and  $164$ – $179^\circ$ ) must be attributed to the different connectivity of iodine. Deviations to the ideal octahedra are largest in case of  $\mu_3$ -bridging and very similar to comparable polynuclear bismuth iodo complexes [6,8,12]. Since  $\text{Bi}^{3+}$  is surrounded by iodine, the influence of the lone-pair is, as expected, less pronounced [18,19]. The Bi–I distance in the  $[\text{Bi}_3\text{I}(\text{C}_4\text{H}_8\text{O}_3\text{H}_2)_2(\text{C}_4\text{H}_8\text{O}_3\text{H})_5]^{3+}$  cation matches exactly with the  $\mu_1(\text{Bi}-\text{I})$ -distance of the anion (Table 4). In case of the cation, bismuth is furthermore coordinated by seven molecules of diethylene glycol (Fig. 2). Thereof, four molecules are linked to two bismuth atoms. Two further molecules of diethylene glycol are coordinated to only one bismuth atom via all of the three oxygen atoms. The residual molecule of diethylene glycol is connected only with one oxygen atom (O19) to bismuth (Bi6). The significantly enlarged parameters of thermal motion for this latter molecule, especially for O20 and O21, are in accordance with the fact that only O19 is coordinated to bismuth (Table 2, Fig. 2).

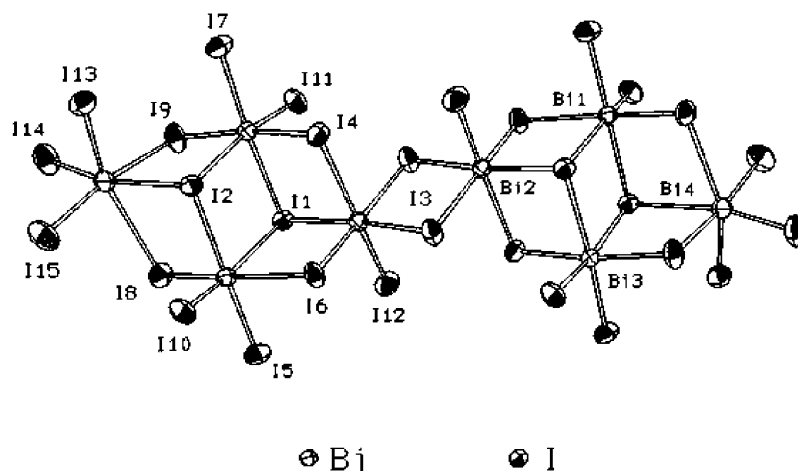


Fig. 1. View on the  $[\text{Bi}_8\text{I}_{30}]^{6-}$  anion (anisotropic displacement with 50% probability of finding).

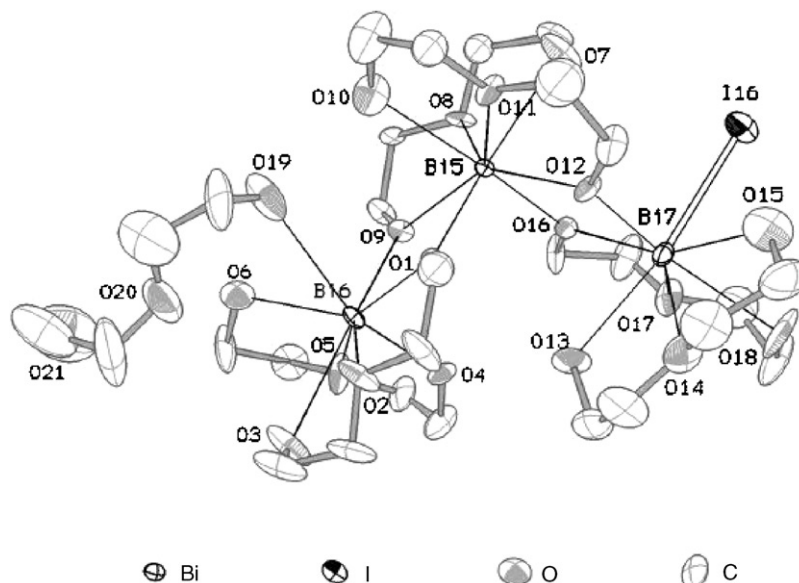


Fig. 2. View on the  $[\text{Bi}_3\text{I}(\text{C}_4\text{H}_8\text{O}_3\text{H}_2)_2(\text{C}_4\text{H}_8\text{O}_3\text{H})_5]^{3+}$  cation (anisotropic displacement with 50% probability of finding).

Table 3  
Selected interatomic distances (Å) for the  $[\text{Bi}_8\text{I}_{30}]^{6-}$  anion and comparison with related compounds

	$[\text{Bi}_3\text{I}(\text{C}_4\text{H}_8\text{O}_3\text{H}_2)_2(\text{C}_4\text{H}_8\text{O}_3\text{H})_5]_2\text{Bi}_8\text{I}_{30}$	$[\text{Bi}_2(\text{C}_4\text{H}_8\text{O}_3\text{H}_2)(\text{C}_4\text{H}_8\text{O}_3\text{H})_3]\text{CuBi}_5\text{I}_{19}$ [12]	$\text{BiI}_3$ [18]
Bi– $\mu_3$ –I	3.137(1)–3.450(2)	3.14–3.45	/
Av Bi– $\mu_3$ –I	3.318(2)	3.31	/
Bi– $\mu_2$ –I	2.952(1)–3.640(2)	2.99–3.43	3.05–3.12
Av Bi– $\mu_2$ –I	3.203(2)	3.18	3.09
Bi– $\mu_1$ –I	2.852(1)–2.952(1)	2.87–2.99	/
Av Bi– $\mu_1$ –I	2.895(1)	2.91	/

With regard to the value of the Bi–O distances, the situation is very different. Firstly, with 2.10(1)–2.38(1) Å altogether nine comparably short Bi–O distances are observed (Table 4, Fig. 2). These distances agree well with the sum of ionic radii ( $\text{Bi}^{3+}$ – $\text{O}^{2-}$  [CN6]: 2.43 Å) [20] and the Bi–O bond length in  $\text{Bi}_2\text{O}_3$  (2.13–2.56 Å) [21]. All the five oxygen atoms involved here are terminal atoms of diethylene glycol molecules. Next with around 2.60(1) Å, there is a group of significantly enlengthened Bi–O distances. These distances belong to oxygen atoms forming the ether bridge of diethylene glycol (Table 4, Fig. 2). Again, the observed values are in good agreement to compounds exhibiting a comparable bonding situation (2.59–2.74 Å) [13]. Even longer are bond distances (2.59(1)–3.04(1) Å) to the residual terminal oxygen atoms. Considering these findings, it must be concluded that the five oxygen atoms showing significantly shortened distances are deprotonated. In contrast, the other eight terminal oxygen atoms with Bi–O distances longer than the ether-bound oxygen atoms belong to hydroxyl groups. Consequently, the  $[\text{Bi}_3\text{I}(\text{C}_4\text{H}_8\text{O}_3\text{H}_2)_2(\text{C}_4\text{H}_8\text{O}_3\text{H})_5]^{3+}$  cation is with two mole-

Table 4  
Selected interatomic distances (Å) for the  $[\text{Bi}_3\text{I}(\text{C}_4\text{H}_8\text{O}_3\text{H}_2)_2(\text{C}_4\text{H}_8\text{O}_3\text{H})_5]^{3+}$  cation (ether-bound oxygen atoms bold)

Bi5–O1	2.25(1)	Bi6–O4	2.10(1)	Bi7–O16	2.24(1)
Bi5–O16	2.27(1)	Bi6–O9	2.19(1)	Bi7–O12	2.24(1)
Bi5–O12	2.34(1)	Bi6–O1	2.25(1)		
Bi5–O9	2.38(1)			<b>Bi7–O17</b>	<b>2.57(1)</b>
		<b>Bi6–O5</b>	<b>2.51(1)</b>	Bi7–O13	2.59(1)
<b>Bi5–O11</b>	<b>2.58(1)</b>	<b>Bi6–O2</b>	<b>2.60(1)</b>	Bi7–O15	2.68(1)
<b>Bi5–O8</b>	<b>2.65(1)</b>	Bi6–O3	2.82(1)	Bi7–O18	2.78(1)
Bi5–O10	2.66(1)	Bi6–O6	2.83(1)	<b>Bi7–O14</b>	<b>2.78(1)</b>
Bi5–O7	2.67(1)	Bi6–O19	3.04(1)	Bi7–I16	2.92(1)

cules of diethylene glycol and five deprotonated molecules. In contrast to a coordination sphere with iodine, the influence of the lone-pair is clearly visible while chelating  $\text{Bi}^{3+}$  with oxygen-containing ligands [13]. As a result, the short Bi–O distances mentioned above are observed in one coordination hemisphere around Bi5, Bi6 and Bi7, the significantly longer distances in the opposite hemisphere (Table 4, Fig. 2).

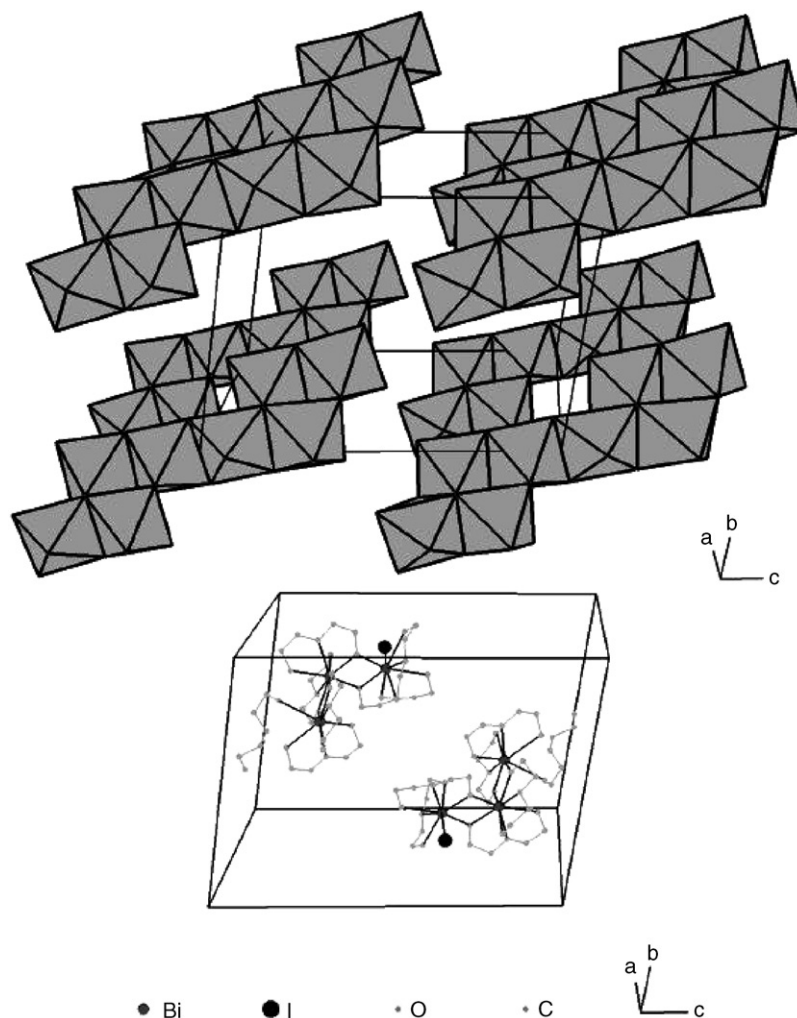


Fig. 3. View on the unit cell of  $[\text{Bi}_3\text{I}(\text{C}_4\text{H}_8\text{O}_3\text{H}_2)_2(\text{C}_4\text{H}_8\text{O}_3\text{H})_5]_2\text{Bi}_8\text{I}_{30}$  showing the anionic substructure (top) and the cationic substructure (bottom).

The three-dimensional packing of  $[\text{Bi}_3\text{I}(\text{C}_4\text{H}_8\text{O}_3\text{H}_2)_2(\text{C}_4\text{H}_8\text{O}_3\text{H})_5]_2\text{Bi}_8\text{I}_{30}$  based on the unit cell is shown in Fig. 3.  $[\text{Bi}_8\text{I}_{30}]^{6-}$  anions are located at the corner of the unit cell. As a result, the arrangement of the polynuclear anions is like chlorine or cesium of the CsCl type of structure. The anions are directed with the long axis along  $[001]$  and with the anion's plane slightly tilted equiangular against  $[101]$ . In contrast to the CsCl type of structure, the cation is not located in the center of the unit cell. Instead, the unit cell is occupied by two  $[\text{Bi}_3\text{I}(\text{C}_4\text{H}_8\text{O}_3\text{H}_2)_2(\text{C}_4\text{H}_8\text{O}_3\text{H})_5]^{3+}$  cations separating the polynuclear anions.

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#### References

- [1] O. Lindquist, *Acta Chem. Scand.* 22 (1968) 2943.
- [2] B. Chabot, E. Parthe, *Acta Crystallogr. B* 34 (1978) 645.
- [3] U. Geiser, E. Wade, H.H. Wang, J.M. Williams, *Acta Crystallogr. C* 46 (1990) 1547.
- [4] C. Feldmann, unpublished results.
- [5] R. Kubiak, K. Ejsmont, *J. Mol. Struct.* 474 (1999) 275.
- [6] H. Krautscheid, *Z. Anorg. Allg. Chem.* 620 (1994) 1559.
- [7] W. Clegg, R.J. Errington, G.A. Fisher, M.E. Green, D.C.R. Hockless, N.C. Norman, *Chem. Ber.* 124 (1991) 2457.
- [8] H. Krautscheid, *Z. Anorg. Allg. Chem.* 621 (1995) 2049.
- [9] G.C. Papavassiliou, I.B. Koutselas, A. Terzis, M.H. Whangbo, *Solid State Commun.* 91 (1994) 695.
- [10] C.R. Kagan, D.B. Mitzi, C.D. Dimitrakopoulos, *Science* 286 (1999) 945.
- [11] C. Feldmann, *Z. Kristallogr. NCS* 216 (2001) 465.
- [12] C. Feldmann, *Inorg. Chem.* 40 (2001) 818.

- [13] R.D. Rogers, A.H. Bond, S. Aguinaga, A. Reyes, *J. Am. Chem. Soc.* 114 (1992) 2967.
- [14] G.M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Germany, 1997.
- [15] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
- [16] L.J. Farrugia, WinGX-1.64.02, *J. Appl. Cryst.* 32 (1999) 837.
- [17] R. Hundt, KPLOTT Program for Drawing and Investigation of Crystal Structures, University of Bonn, Germany, 2000.
- [18] M. Ruck, *Z. Kristallogr.* 210 (1995) 650.
- [19] N.N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Oxford, 1997.
- [20] R.D. Shannon, *Acta Crystallogr. A* 32 (1976) 751.
- [21] H.A. Harwig, *Z. Anorg. Allg. Chem.* 444 (1978) 151.