

Trinuclear Iodobismuthate Complex $[\text{Na}_3(\text{Me}_2\text{CO})_{12}][\text{Bi}_3\text{I}_{12}]$: Synthesis and Crystal Structure

S. A. Adonin^{a, b, *}, E. V. Peresyphkina^{a, b}, M. N. Sokolov^{a, b}, and V. P. Fedin^{a, b}

^a Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences, Novosibirsk, Russia

^b Novosibirsk State University, Novosibirsk, Russia

*e-mail: adonin@niic.nsc.ru

Received May 13, 2014

Abstract—The reaction of BiI_3 and NaI in acetone gives a trinuclear iodobismuthate complex, $[\text{Na}_3(\text{Me}_2\text{CO})_{12}][\text{Bi}_3\text{I}_{12}]$ (**I**), which was studied by X-ray diffraction (CIF file CCDC no. 996330). The centrosymmetric $[\text{Bi}_3\text{I}_{12}]^{3-}$ anions are groups of three distorted $\{\text{BiI}_6\}$ octahedra coupled at the faces. The sodium cations combine six Me_2CO molecules in the bidentate bridging mode to give linear trimers in which the side sodium ions coordinate six terminal acetone molecules.

DOI: 10.1134/S107032841412001X

INTRODUCTION

Polynuclear bismuth iodide complexes (polyiodobismuthates, iodobismuthates) form an extended class of coordination compounds, which has attracted researchers' attention in recent years and is distinguished by unusual structural diversity [1, 2]. Currently, structures have been described for more than 130 complexes of this type, including anions of different nuclearity, particularly bi- [3–7], tri- [8–10], tetra- [11–14], penta- [15, 16], hexa- [17–19], hepta- [20], and octanuclear [16] ones, some of them being subject to structural isomerism. Note that in most cases, these complexes contain organic cations (mainly tetraalkyl- and arylammonium and phosphonium derivatives). As a rule, this is related to the synthetic strategy (dissolution of BiI_3 in some organic solvent in the presence of the iodide of appropriate cation and subsequent crystallization, which often gives a product mixture). Meanwhile, compounds containing inorganic cations have been much less studied. The reaction of lithium iodide with BiI_3 in tetrahydrofuran (THF) afforded the complexes $[\text{Li}(\text{Thf})_4]_2[\text{Bi}_4\text{I}_{14}(\text{Thf})_2]$ and $[\text{Li}(\text{Thf})_4][\text{Bi}_5\text{I}_{16}]$ [14]. When NaI is used, the hexanuclear complex $[\text{Na}(\text{Thf})_6]_4[\text{Bi}_6\text{I}_{22}]$ is formed under similar conditions [14]; complexes containing heavier alkali metal cations are unknown. Note that there are no data about complexes formed upon the reaction of BiI_3 with alkali metal iodides in acetone. In this work, the complex $[\text{Na}_3(\text{Me}_2\text{CO})_{12}][\text{Bi}_3\text{I}_{12}]$ (**I**) was prepared and characterized by X-ray diffraction.

EXPERIMENTAL

All operations were carried out in air. The solvents were purified by standard procedures. The reagent grade chemicals were received from commercial sources. Elemental analysis was performed at the Analytical Laboratory of the Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences, using an EuroEA 3000 CHN-analyzer.

Synthesis of I. A mixture of BiI_3 (250 mg, 0.42 mmol) and NaI (64 mg, 0.42 mmol) was placed in a round-bottom flask. Acetone (15 mL) was added and the mixture was magnetically stirred until BiI_3 completely dissolved (~45 min). Ethanol (7 mL) was added to the bright orange solution with stirring. The resulting mixture was concentrated in air at room temperature. After several hours, bright orange crystals of **I** were deposited on the vessel walls. The yield was 70%. The composition and structure of **I** were determined by X-ray diffraction. During isolation from the mother solution, this compound easily lost acetone molecules being converted to the product $\text{Na}_3\text{Bi}_3\text{I}_{12} \cdot 2\text{Me}_2\text{CO}$.

For $\text{C}_6\text{H}_{12}\text{O}_2\text{I}_{12}\text{Bi}_3\text{Na}_3$		
anal. calcd., %:	C, 3.09;	H, 0.52.
Found, %:	C, 3.07;	H, 0.50.

X-ray diffraction. The structure of **I** was determined by the standard procedure on a Bruker X8Apex four-circle automated diffractometer equipped with a two-coordinate CCD detector at 150.0(2) K (molybdenum anode, $\lambda = 0.71073 \text{ \AA}$, graphite monochromator). The reflection intensities were measured by φ - and ω scanning of narrow (0.5°) frames to $2\theta = 55^\circ$. The absorp-

Table 1. Crystal data and X-ray diffraction experiment details for compound **I**

Parameter	Value
<i>M</i>	2915.65
Temperature, K	150.0(2)
Radiation (λ , Å)	MoK α (0.71073)
System	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	11.0670(7)
<i>b</i> , Å	25.9515(19)
<i>c</i> , Å	13.9839(11)
β , deg	94.676(2)
<i>V</i> , Å ³	4002.9(5)
<i>Z</i>	2
ρ_{calcd} , g/cm ³	2.419
μ , mm ⁻¹	11.260
<i>F</i> (000)	2604
Crystal size, mm	0.17 × 0.07 × 0.01
Data collection range of θ , deg	1.85–27.50
Ranges of reflection indices	$-14 \leq h \leq 12$, $-33 \leq k \leq 22$, $-3 \leq l \leq 18$
The number of measured reflections	17070
The number of independent reflections (R_{int})	8985 (0.0384)
Reflections with $I \geq 2\sigma(I)$	6357
The number of refinement parameters	327
GOOF	0.976
R_1 ($I > 2\sigma(I)$)	0.0383
wR_2 (all reflections)	0.0655
Residual electron density (min/max), e/Å ³	-1.277/1.188

tion corrections were applied empirically using the SADABS program package [21]. The structure was solved by the direct method and refined by the least-squares method on F^2 in the anisotropic approximation for non-hydrogen atoms (SHELXTL) [22]. One of the crystallographically independent acetone molecules is disordered over two positions with a probability of 0.6/0.4. The oxygen and carbon atoms at the minor positions were refined isotropically. The hydrogen atoms of the coordinated acetone molecules were refined in the riding model in the geometrically calculated positions. The crystal data and structure refinement details are summarized in Table 1 and the selected bond lengths and angles are in Table 2.

Full information on the structure of **I** is deposited at the Cambridge Crystallographic Data Centre (no. 996330; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

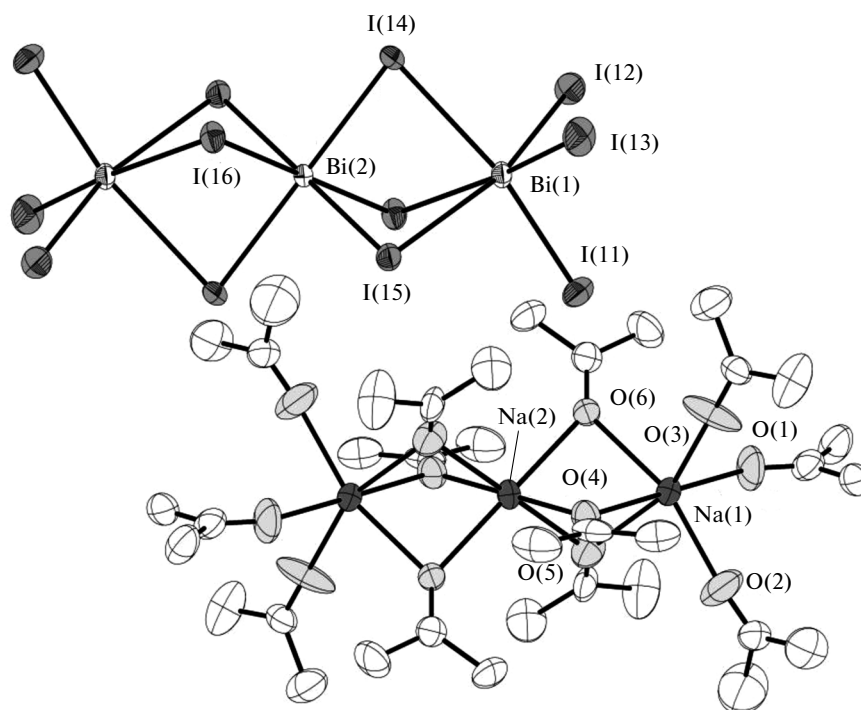
Iodides of some alkali metals are much more soluble in organic solvents, in particular, in acetone, than other halides. For this reason, they can be used as iodide ion sources in the preparation of iodide complexes. This approach was previously used to prepare polynuclear Pb(II) iodide complexes [23] and the heterometallic complex [PtBi₂I₁₂]²⁻ [24]. In all cases, cations of the type [Na_{*x*}(Me₂CO)_{*y*}]^{*x+*} (*x* = 3, *y* = 12; *x* = 4, *y* = 15) are formed during crystallization. Compounds containing such cations are unstable and, as the crystalline samples are kept in air, they lose acetone molecules, as can be ascertained by elemental analysis. The behavior of complex **I** is characteristic: according to the analysis, keeping of the samples in air for several hours results in the loss of, on average, 10 out of the 12 acetone molecules.

The island crystal structure of **I** consists of [Bi₃I₁₂]³⁻ anions and solvated sodium cations (Fig. 1). The structure of the centrosymmetric [Bi₃^{III}I₁₂]³⁻ anion can be represented as three distorted {BiI₆} octahedra coupled at the faces. Due to the stereochemical activity of the lone electron pair (EP) of bismuth, the Bi–I distances vary over broad limits, while the IBI angles of 78.088(13)°–95.427(18)° substantially deviate from the right angle. The coordination polyhedron of the central Bi(III) atom is a distorted octahedron with close Bi–I bond lengths of 3.0696(5)–3.0768(5) Å. The peripheral bismuth atoms have a highly distorted coordination and form each three short (2.8758(6)–2.8808(6) Å) and three long (3.3330(6)–3.4084(6) Å) bonds with terminal and bridging iodine atoms, respectively.

Sodium cations and acetone molecules form linear trimers [Na₃(Me₂CO)₁₂]³⁺. The sodium cation coordinates each of the six acetone molecules through the oxygen atoms at the octahedron vertices (Fig. 1). Out of the 12 acetone molecules, six molecules are coordi-

Table 2. Selected bond lengths and bond angles in compound **I**

Bond	$d, \text{Å}$	Bond	$d, \text{Å}$	Bond	$d, \text{Å}$
Bi(1)–I(11)	2.9267(6)	Bi(1)–I(14)	3.3330(6)	Bi(2)–I(14) \times 2	3.0768(5)
Bi(1)–I(12)	2.8758(6)	Bi(1)–I(15)	3.4084(6)	Bi(2)–I(15) \times 2	3.0696(5)
Bi1–I(13)	2.8808(6)	Bi(1)–I(16) \times 2	3.3478(6)	Bi(2)–I(16) \times 2	3.0721(5)
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
I(11)Bi(1)I(12)	95.427(18)	I(12)Bi(1)I(16)	91.861(18)	I(15)Bi(2)I(16)	91.595(14)
I(11)Bi(1)I(13)	94.850(19)	I(13)Bi(1)I(14)	93.558(17)	I(15)Bi(2)I(16)	88.405(14)
I(11)Bi(1)I(15)	95.048(16)	I(14)Bi(1)I(16)	80.203(13)	I(15)Bi(2)I(14)	92.589(13)
I(11)Bi(1)I(16)	90.885(17)	I(13)Bi(1)I(15)	95.479(18)	I(15)Bi(2)I(14)	87.411(13)
I(12)Bi(1)I(13)	92.92(2)	I(14)Bi(1)I(15)	78.088(13)	I(16)Bi(2)I(14)	88.832(14)
I(12)Bi(1)I(14)	90.199(15)	I(16)Bi(1)I(15)	78.654(15)	I(16)Bi(2)I(14)	91.168(14)

**Fig. 1.** Cation and anion in the crystal structure of **I** (50% probability ellipsoids). The second (minor) position of the acetone molecule disordered over two positions is not shown.

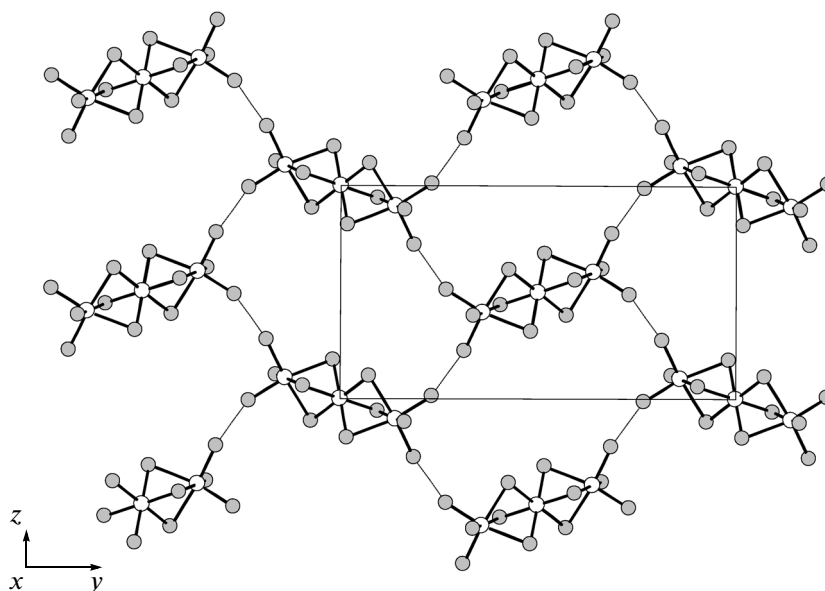


Fig. 2. View of the crystal structure of I in the yz plane. The anionic layer formed by shortened I...I contacts.

nated in the bidentate bridging mode and the other six are coordinated in the monodentate mode. The Na—O bond lengths vary over the usual limits of 22.280(7)—2.476(7) Å.

In the crystal structure, the cations and the anions are packed in layers along the yz plane. In the layer formed by the $[\text{Bi}_3\text{I}_{12}]^{3-}$ anions, the iodine atoms formed shortened I...I contacts of 3.70 Å (Fig. 2a). In the presence of large cations (Fig. 2b), the shortest interatomic I...I contacts between the layers 5.5 Å.

ACKNOWLEDGMENTS

This study was supported by the Russian Research Foundation, project no. 14-23-00013.

REFERENCES

1. Wu, L.-M. and Wu, X.-T., and Chen, L., *Coord. Chem. Rev.*, 2009, vol. 253, p. 2787.
2. Mercier, N., Louvain, N., and Bi, W., *CrystEngComm*, 2009, vol. 11, p. 720.
3. Zhu, X.-H., Mercier, N., Frere, P., et al., *Inorg. Chem.*, 2003, vol. 42, p. 5330.
4. Sharutin, V.V., Senchurin, V.S., Sharutina, O.K., et al., *Russ. J. Gen. Chem.*, 2012, vol. 82, p. 194.
5. Sharutin, V.V., Egorova, I.V., Klepikov, N.N., et al., *Russ. J. Gen. Chem.*, 2008, vol. 78, p. 1326.
6. Dobrzycki, L. and Wozniak, K., *J. Mol. Struct.*, 2009, vol. 921, p. 18.
7. Goforth, A.M., Tershansy, M.A., Smith, M.D., et al., *J. Am. Chem. Soc.*, 2011, vol. 133, p. 603.
8. Sharutin, V.V., Egorova, I.V., Klepikov, N.N., et al., *Russ. J. Inorg. Chem.*, 2009, vol. 54, p. 53.
9. Okrut, A. and Feldmann, C., *Z. Anorg. Allg. Chem.*, 2006, vol. 632, p. 409.
10. Carmalt, C.J., Farrugia, L.J., and Norman, N.C., *Z. Anorg. Allg. Chem.*, 1995, vol. 621, p. 47.
11. Carmalt, C.J., Farrugia, L.J., and Norman, N.C., *Z. Naturforsch., B: Chem. Sci.*, 1995, vol. 50, p. 1591.
12. Bi, W. and Mercier, N., *Chem. Commun.*, 2008, p. 5743.
13. Goforth, A.M., Gardinier, J.M., Smith, M.D., et al., *Inorg. Chem. Commun.*, 2005, vol. 8, p. 684.
14. Krautscheid, H., *Z. Anorg. Allg. Chem.*, 1994, vol. 620, p. 1559.
15. Sharutin, V.V., Egorova, I.V., Sharutina, O.K., et al., *Russ. J. Coord. Chem.*, 2004, vol. 30, p. 925.
16. Krautscheid, H., *Z. Anorg. Allg. Chem.*, 1995, vol. 621, p. 2049.
17. Liu, B., Xu, L., Gou, G.-C., et al., *J. Solid State Chem.*, 2006, vol. 179, p. 1611.
18. Goforth, A.M., Peterson, Jr.L., Smith, M.D., et al., *J. Solid State Chem.*, 2005, vol. 178, p. 3529.
19. Tershansy, M.A., Goforth, A.M., Smith, M.D., et al., *Acta Crystallogr., Sect. E: Structure Reports Online*, 2006, vol. 62, p. m3269.
20. Monakhov, K.Yu., Gourlaouen, C., Pattacini, R., et al., *Inorg. Chem.*, 2012, vol. 51, p. 1562.
21. Sheldrick, G.M., *SADABS. Program for Empirical X-ray Absorption Correction*, Bruker-Nonius, 1990.
22. *SHELXTL. Version 6.22*, Madison (WI, USA): Bruker AXS Inc., 2003.
23. Krautscheid, H., Lefieffre, J.-F., and Besinger, J., *Z. Anorg. Allg. Chem.*, 1996, vol. 622, p. 1781.
24. Adonin, S.A., Sokolov, M.N., Smolentsev, A.I., et al., *Dalton Trans.*, 2013, vol. 42, p. 9818.

Translated by Z. Svitanko