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A novel polybromide complex of bismuth – $(Et_4N)_3\{[Bi_2Br_9](Br_2)\}$: synthesis and structural features

Sergey A. Adonin,*[a,b] Igor D. Gorokh,[b] Pavel A. Abramov,[a,b] Ilya V. Korolkov,[a,b] Maxim N. Sokolov[a,c] and Vladimir P. Fedin[a,b]

[a] *A. V. Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation. E-mail: adonin@niic.nsc.ru*
[b] *Novosibirsk State University, 630090 Novosibirsk, Russian Federation*
[c] *A. M. Butlerov Institute of Chemistry, Kazan Federal University, 420008 Kazan, Russian Federation*

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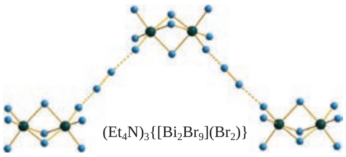
The polybromide complex $(Et_4N)_3\{[Bi_2Br_9](Br_2)\}$ was obtained by reaction of $[BiBr_6]^{3-}$, Br_2 and tetraethylammonium bromide in 2 M HBr. In its crystal structure, bioctahedral $[Bi_2Br_9]^{3-}$ anions are connected by neutral Br_2 linkers into infinite 1D chains *via* terminal bromide ligands.



Despite the fact that the polyhalide ions were discovered almost 200 years ago,[1] their chemistry has been attracting much attention, demonstrating great opportunities of its further development.[2] Within the last years, a number of inspiring and encouraging results were obtained, *e.g.*, polybromides containing more than nine Br atoms,[3–6] including those with 3D structure.[7–8]

Note that the coordination chemistry of complexes containing polyhalide (in particular, polybromide) ligands or, at least, supramolecularly bonded polyhalide units, remains less explored. Such compounds are known only for 6 metals – Pt,[9] Cu,[10] Zn,[11] W,[12] Au[13,14] and Sb.[15,16] Also, there are two examples of heteroligand complexes containing coordinated tribromide – for Cu[17] and Ni,[18] and a complex with Se–Br–Br unit reported fairly recently.[19] In most cases (except for Sb), synthetic procedures involve relatively sophisticated precursors and/or methods, *e.g.* the usage of ionic liquids.

Previously, we noted the ability of Bi^{III} to form complexes, in which polybromide units are either directly coordinated to a Bi atom or 'trapped' in the crystal structure *via* specific supramolecular Br···Br contacts with bromobismuthates $\{Bi_xBr_y\}^{n-}$. The synthesis of such compounds is based on very straightforward strategy: $[BiBr_6]^{3-} + HBr + Br_2 + R^{x+}Br^-_x$. The nature and geometry of the organic cation R^{x+} play the crucial role, determining the structure and composition of the resulting complex; usually, 1D or 2D supramolecular polymers of different topology are formed. Therefore, screening of reactions involving a wide range of cations is essential. Here, we report a novel Bi^{III} polybromide complex $(Et_4N)_3\{[Bi_2Br_9](Br_2)\}$ **1** and its structural features.

Compound **1** was prepared by reaction of $[BiBr_6]^{3-}$ (generated *in situ* by dissolution of BiOBr in HBr), Br_2 and tetraethylammonium (TEA) bromide in 2 M HBr.† Crystals suitable for X-ray diffractometry‡ were selected from the precipitate. According to the PXRD data, **1** can be isolated in pure state, the crystalline phase is detectable only and there are no traces of TEA polybromide salts (see Online Supplementary Materials).

The molecular structure of **1** is similar to those of three Bi^{III} polybromides reported in our previous work.[20] The positions of the ethyl substituents in one of three TEA cations are disordered. There are binuclear ions $[Bi_2Br_9]^{3-}$ built of 'face-shared' $\{BiBr_6\}$ octahedra, the Bi–Br distances (Table 1) are within the range typical of the compounds containing this unit as an isolated anion[21–24] or a fragment of a polymer.[25] Additionally, there is 'trapped' dibromine which is located in two positions with 0.8 : 0.2 occupancies (Figure 1), the Br–Br distances are 2.320(3)–2.330(2) Å. Each $[Bi_2Br_9]^{3-}$ is connected with two (considering the occupancy) $\{Br_2\}$ units *via* terminal bromide ligands [Br···Br = 3.205(3)–3.422(5) Å] thus forming a chain. As stated above, such type of bonding was found previously in Bi^{III}

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† All chemicals were obtained from commercial sources (reagent grade, analytical grade or related Russian qualifications) and used as purchased. BiOBr (50 mg, 0.164 mmol) was dissolved in HBr (3 ml, 2 M), then the solution of Br_2 (4 ml, 1 M) in HBr (2 M) and TEA bromide solution [52 mg in HBr (3 ml, 2 M), 0.246 mmol] were sequentially added. In several minutes, dark orange crystalline precipitate **1** had started to form, the process completed in 3–4 h. Crystals suitable for XRD were selected from the crude precipitate. Yield 89 %. Found (%): C, 17.3; H, 3.8; N, 2.6. Calc. for $C_{24}H_{60}N_3Bi_2Br_{11}$ (%): C, 17.2; H, 3.6; N, 2.5.

‡ *Crystallographic data for* **1**. The measurements were made on a New Xcalibur Agilent Technologies diffractometer with MoKα radiation (λ = 0.71073 Å). Absorption correction was done empirically using SCALE3 ABSPACK (CrysAlisPro, Agilent Technologies, Version 1.171.37.35, release 13-08-2014 CrysAlis171 .NET). The structure was solved by direct method and refined by the full-matrix least-squares treatment against F^2 in the anisotropic approximation with SHELX 2014/7 in ShelXle program.[41] Hydrogen atoms were refined in geometrically calculated positions.

Crystals of $C_{24}H_{60}Bi_2Br_{11}N_3$, M = 1687.658, are orthorhombic, space group $P2_12_12_1$ (as racemic twin with BASF gives value 0.42; one of the Et_4N^+ cations is disordered over two positions with occupancies 0.7/0.3), at 130 K: a = 10.1867(2), b = 18.0615(5) and c = 24.4002(5) Å, V = = 4489.32 (18) Å^3, Z = 4, μ = 17.64 mm^{-1}, F(000) = 3104. Intensities of 16165 reflections were measured and 8092 independent reflections (R_{int} = 0.025) were used in a further refinement. The refinement converged to $wR(F^2)$ = 0.092 and GOF = 1.08 for all independent reflections [R_1 = = 0.042 was calculated against F^2 for 7418 observed reflections with $I > 2\sigma(I)$].

The main geometrical parameters are summarized in Table S1 (see Online Supplementary Materials).

CCDC 1543028 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

Table 1 Distances between Br atoms in various polybromide complexes and solid Br_2.

Compound	Br–Br distances in $\{Br_2\}$ unit/Å	$Br_{term}\cdots Br_{Br_2}$ distances	Reference
1	2.320–2.330	3.205–3.422	This work
$(4\text{-MePyH})_3\{[Bi_2Br_9](Br_2)\}$	2.317–2.324	2.933–3.191	20
$(N\text{-MePy})_3\{[Bi_2Br_9](Br_2)\}$	2.238–2.390	3.224–3.384	26
$(PyH)_3\{[Bi_2Br_9](Br_2)\}$	2.319	3.139	27
Solid Br_2	2.27	3.31	28
$(Me_4N)_3\{[Sb_2Br_9](Br_2)\}$	2.31	2.89	15
$\{[P(o\text{-tolyl})_3]Br\}_2[Cu_2Br_6](Br_2)$	2.341	3.153	10

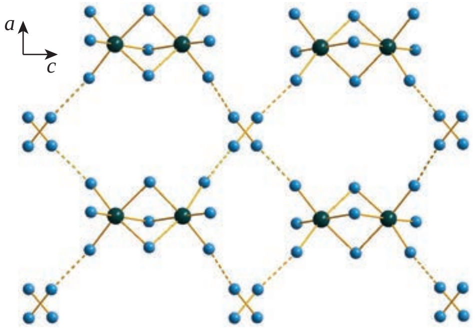

Figure 1 Fragment of the anionic substructure in **1** (black Bi, blue Br, Br···Br contacts are dashed).

polybromides, however the occupancy of Br positions may vary (0.5 : 0.5[20,26] or full[27]). Interestingly, this structural type seems to be the most common throughout polyhalides in general, as **1** is the fourth among the complexes of Bi^{III}, and the only known example of Sb^{III} polybromide reveals the same geometry.[15] Comparison of selected geometric parameters found in other polybromides, as well as in solid Br_2, is given in Table 1.

Among numerous undertaken attempts of isolation and characterization of polybromides containing other tetraalkylammonium cations there were no successful ones. In the case of Me_4N^+, a dark red product formed, which, most probably, was Bi^{III} polybromide (EDX analysis confirmed the presence of Bi and Br). However, the crystals we managed to obtain were not suitable for XRD, although the cell parameters were determined reliably. For Pr_4N^+ and Bu_4N^+, our preparations resulted in mixtures of light yellow polycrystalline precipitates (most likely bromobismuthates) and, in some cases, red crystals identified as polybromide salts of corresponding cation. These data are in good agreement with the observation made by us earlier: in the presence of some cations, formation of polybromide complexes *via* $[BiBr_6]^{3-}$ + HBr + Br_2 + $R^{x+}Br_x^-$ strategy does not occur.[27] Obviously, this phenomenon, as well as the establishment of possible correlations, requires additional studies which are underway. The obtained results may be of interest for further theoretical studies in terms of the halogen bonding concept, which has been attracting a great attention of chemical community within the last decade,[29–34] in particular, for the chemistry of halide complexes.[35–40]

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.01.012.

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