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Polymer Chlorobismuthate Complex *catena*-$\{((\mathrm{Me,Me})\mathrm{Bpe})[\mathrm{BiCl_5}]\}_n$: Synthesis and Crystal Structure

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Abstract—The reaction of $\mathrm{BiCl_3}$ and *N*,*N*-dimethyl-1,2-bis(pyridyl)ethane chloride (Me,Me-Bpe) in 2 M HCl affords a polymer chlorobismuthate complex $\{((\mathrm{Me,Me})\mathrm{Bpe})[\mathrm{BiCl_5}]\}_n$ (**I**). The structure of complex **I** is determined by X-ray diffraction analysis (CIF file CCDC 1058842). The anionic moiety of the complex is presented by a 1D coordination polymer $([\mathrm{BiCl_5}]^{2n-})_n$ consisting of octahedral blocks $\{\mathrm{BiCl_6}\}$ linked by μ_2-bridging chloride ligands into infinite zigzag chains.

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INTRODUCTION

The chemistry of polynuclear bismuth(III) halide complexes (polyhalide bismuthates) attracts intense attention of researchers during recent decades [1, 2]. From the viewpoint of fundamental inorganic chemistry, this class of compounds is distinguished by a variety of structural types. Depending on the reaction conditions, one can obtain anionic complexes of different nuclearity, including bi- [3, 4], tri- [5–7], tetra- [8, 9], penta- [10], hexa- [11, 12], hepta- [13, 14], and octanuclear complexes [15, 16], a series of heterometallic derivatives [17, 18], and a number of coordination polymers [19–22]. At the same time, interest in Bi(III) halide complexes is due to a series of their physical properties valuable from the viewpoint of materials science: thermochromism [16, 23], luminescence and photochromism [24–27], etc. In the latter two cases, both the structure and composition of the anionic moiety of the complex and also the choice of an organic cation play the key role. In the most cases, various viologens (N-alkylated derivatives of 4,4-bipyridine) are used in order to attain high luminescence intensity and quantum yield [25–29]. Data on the synthesis of polyhalide bismuthates with other aromatic cations and studies of their properties are nearly lacking. In this work, we synthesized and structurally characterized the polymer complex $\{((\mathrm{Me,Me})\mathrm{Bpe})[\mathrm{BiCl_5}]\}_n$ (**I**) containing the cation based on N-alkylated 1,2-bis(pyridyl)ethane.

EXPERIMENTAL

The synthesis was carried out in air. Initial $\mathrm{AgNO_3}$, HBr, 1,2-bis(pyridyl)ethane, iodomethane, and BiOBr (reagent grade or analogous grade) were commercially available and used without additional purification. 4,4-Ethylenebis(1-methylpyridinium) iodide was synthesized by the reaction of 1,2-bis(pyridyl)ethane and iodomethane in DMF according to a described procedure [30]. Elemental analysis was carried out on an Euro EA 3000 CHN analyzer at the Analytical Laboratory of the Nikolaev Institute of Inorganic Chemistry (Siberian Branch, Russian Academy of Sciences).

Synthesis of $\{((\mathrm{Me,Me})\mathrm{Bpe})[\mathrm{BiCl_5}]\}_n$ (I). 4,4-Ethylenebis(1-methylpyridinium) iodide (100 mg, 0.21 mmol) was dissolved in $\mathrm{H_2O}$ (5 mL), and $\mathrm{AgNO_3}$ (73 mg, 0.43 mmol) was added to the solution with magnetic stirring. After 15 min, precipitated AgI was separated and a calculated amount (necessary for attaining a concentration of 2 mol/L) of concentrated HCl was added to the mother liquor. The solution was repeatedly filtered to remove insignificant amounts of AgCl, and BiOBr (65 mg, 0.21 mmol) in 2 M HCl (5 mL) was added to the solution. The solution was evaporated by approximately 1/4, and colorless crystals of complex **I** suitable for X-ray diffraction analysis were obtained. The yield was 32%.

For $\mathrm{C_{14}H_{18}N_2Cl_5Bi}$

anal. calcd., %:	C, 28.00;	H, 3.02;	N, 4.66.
Found, %:	C, 28.09;	H, 3.14;	N, 4.83.

Table 1. Crystallographic parameters and diffraction experimental details for structure **I**

Parameter	Value
Empirical formula	$C_{14}H_{18}N_2Cl_5Bi$
FW	600.53
Crystal system	Orthorhombic
Space group	*Pbcn*
a, Å	10.81049(17)
b, Å	21.4071(3)
c, Å	16.6264(2)
V, Å^3	3847.70(10)
Z	8
ρ_{calcd}, g/cm^3	2.073
μ, mm^{-1}	9.856
F(000)	2272
Crystal size, mm	0.340 × 0.270 × 0.200
Scan θ range, deg	3.421–29.524
Index range *hkl*	$-12 \leqslant h \leqslant 15$, $-29 \leqslant k \leqslant 26$, $-22 \leqslant l \leqslant 23$
N_{hkl} of measured/independent reflections	14637/4718
R_{int}	0.0156
N_{hkl} with $I > 2\sigma(I)$	3943
T_{max}/T_{min}	1.000/0.553
GOOF (F^2)	1.033
R factors ($I > 2\sigma(I)$)	$R_1 = 0.0299$, $wR_2 = 0.0825$
R factors (for all reflections)	$R_1 = 0.0381$, $wR_2 = 0.0878$
$\Delta\rho_{max}/\Delta\rho_{min}$, *e* Å^{-3}	2.730/–1.477

The crystals of compound **I** are dissolved again on storage in the mother liquor and further evaporation.

X-ray diffraction analysis. Diffraction data for a single crystal of compound **I** were obtained on an Agilent Xcalibur automated diffractometer equipped with an Atlas S2 two-coordinate detector (graphite monochromator, $\lambda(MoK_\alpha) = 0.71073$ Å). Integration, absorption correction, and unit cell parameter determination were applied using the CrysAlisPro program package [31]. The structure was solved by a direct method and refined by the full-matrix least-squares method in the anisotropic approximation (except for hydrogen atoms) using the SHELX-2013 program package [32]. The positions of the hydrogen atoms of the organic cation were calculated geometrically and refined by the riding model. The central fragments CH_2–CH_2– of the organic cation are disordered over two orientations. The X-ray diffraction analysis details and the main crystallographic data are presented in Table 1. Selected interatomic distances and bond angles are given in Table 2. The full tables of interatomic distances and bond angles, atomic coordinates, and atomic displacement parameters were deposited with the Cambridge Crystallographic Data Centre (CCDC 1058842; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif) and are also available from the authors.

RESULTS AND DISCUSSION

As already mentioned above, Bi(III) halide complexes, including the chloride complexes, can contain both isolated anions of different nuclearity and polymer structures of diverse topology. Three variants of the structure of 1D *catena*-coordination polymers

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

Bond	*d*, Å	Bond	*d*, Å
Bi(1)–Cl(1)	2.5970(10)	Bi(2)–Cl(3)	2.7852(9)
Bi(1)–Cl(2)	2.6946(11)	Bi(2)–Cl(4)	2.7035(10)
Bi(1)–Cl(3)	2.9753(9)	Bi(2)–Cl(5)	2.7096(10)
Angle	ω, deg	Angle	ω, deg
$Cl(1)^iBi(1)Cl(1)$	95.69(5)	Cl(4)Bi(2)Cl(3)	88.71(3)
$Cl(1)Bi(1)Cl(2)^i$	85.72(3)	$Cl(4)Bi(2)Cl(3)^{ii}$	91.29(3)
Cl(1)Bi(1)Cl(2)	88.48(4)	$Cl(4)^{ii}Bi(2)Cl(4)$	180.0
Cl(1)Bi(1)Cl(3)	90.20(3)	Cl(4)Bi(2)Cl(5)	87.73(3)
$Cl(1)Bi(1)Cl(3)^i$	172.58(3)	$Cl(4)Bi(2)Cl(5)^{ii}$	92.27(3)
$Cl(2)^iBi(1)Cl(2)$	171.36(5)	$Cl(5)Bi(2)Cl(3)^{ii}$	85.15(3)
Cl(2)Bi(1)Cl(3)	89.93(3)	Cl(5)Bi(2)Cl(3)	94.85(3)
$Cl(2)Bi(1)Cl(3)^i$	96.48(3)	$Cl(5)Bi(2)Cl(5)^{ii}$	180.0
$Cl(3)^iBi(1)Cl(3)$	84.31(4)	Bi(2)Cl(3)Bi(1)	171.13(4)
$Cl(3)Bi(2)Cl(3)^{ii}$	180.0		

* The coordinates of the dependent atoms were obtained by the following symmetry procedures: ^{i} $-x + 1, y, -z + 1/2$; ^{ii} $-x + 1, -y + 1, -z + 1$.

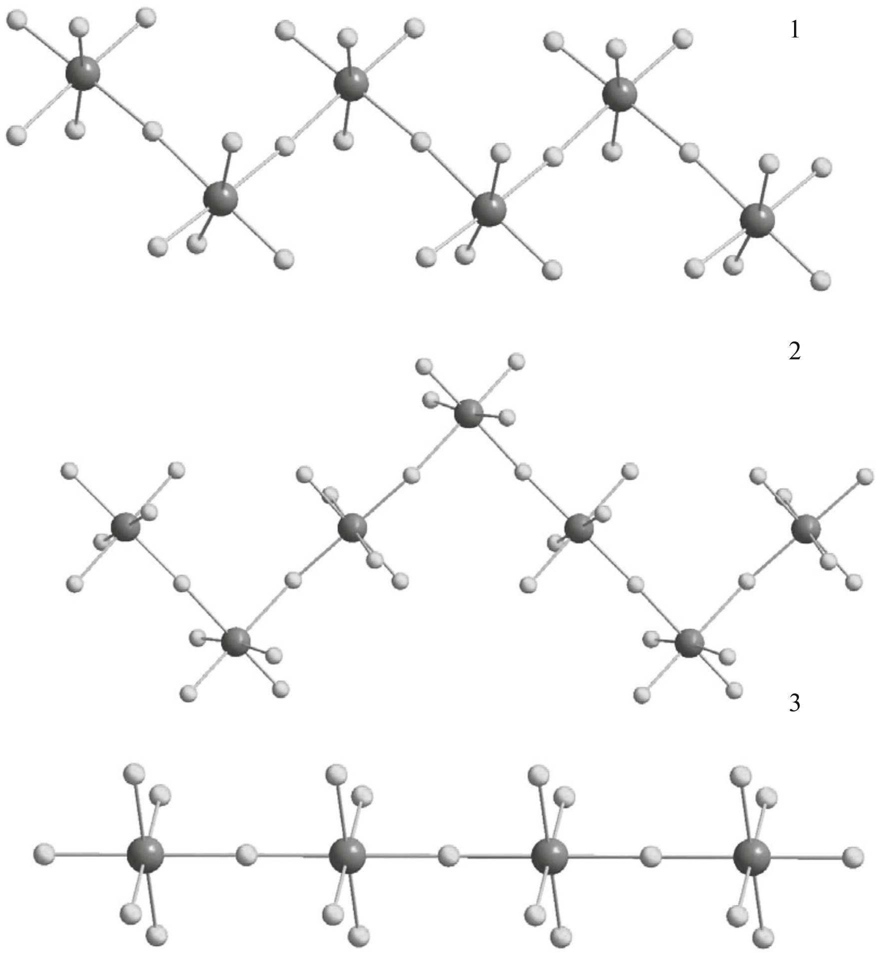

Fig. 1. Isomers of polymer chlorobismuthate anions $\{[BiCl_5]^{2-}\}_n$ of type 1–3.

correspond to the formula $\{[BiCl_5]^{2-}\}_n$ (Fig. 1). In the case of compound **I**, an isomer of the second type is formed, and the possibility of its existence has been discovered rather recently for a single example [33]. The independent part of structure **I** contains two Bi(III) cations in the octahedral coordination environment of the chlorine atoms (Fig. 2). The Bi(1) atom lies on the rotational axis 2, whereas Bi(2) occupies the inversion center. The Bi–Cl bond lengths (2.5970(10)–2.9753(9) Å, average 2.74(13) Å) are in the range characteristic of polyhalide bismuthates and are close to the values found for *n*-heptylenediammonium salt $\{[BiCl_5]^{2-}\}_n$ (2.55–2.97 Å) [33]. The octahedral fragments $\{BiCl_6\}$ in structure **I** are linked by common vertices into zigzag chains along the crystallographic axis *z* (Fig. 3). The chains are parallel to each other with a shift by half a translation along the diagonal *xy*.

The dissolution of initially precipitating crystals of complex **I** with the evaporation of the mother liquor

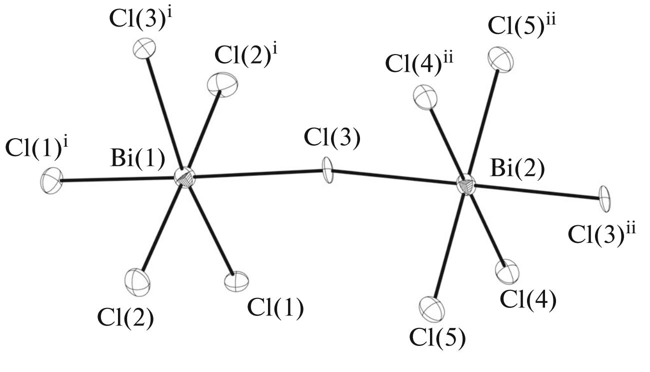

Fig. 2. Coordination environment of the bismuth atoms in structure **I** (ellipsoids of 50% probability). The coordinates of the dependent atoms were obtained by the following symmetry procedures: ^{i} $1 - x, y, 1/2 - z$; ^{ii} $1 - x, 1 - y, 1 - z$.

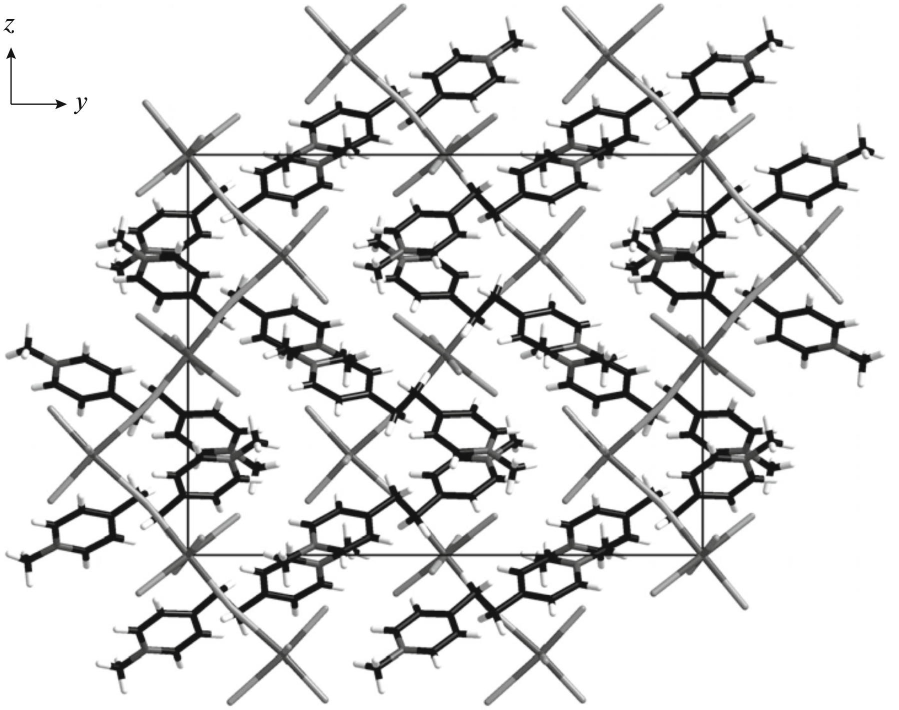

Fig. 3. Crystal packing for structure **I** (projection onto the plane *yz*).

(and, as a consequence, with an increase in the HCl concentration) is rather unusual. As a rule, complexes formed in similar reactions, especially those with large organic cations, are very poorly soluble even under the conditions of halide ion excess.

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