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Binuclear Bismuth Halide Complexes (*N*-Me(2,2'-BipyH))$_2$[Bi$_2$X$_{10}$] (X = Cl, Br): Syntheses, Crystal Structures, and Optical Properties

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Abstract—Binuclear halide complexes (*N*-Me(2,2'-BipyH)$_2$[Bi$_2$X$_{10}$] (X = Cl (**I**), Br (**II**); 2,2'-Bipy = 2,2'-bipyridine) are synthesized by the reaction of solutions of [BiX$_6$]$^{3-}$ and (*N*-Me(2,2'-BipyH)(NO$_3$)$_2$ in 2 M HX. The structure of [Bi$_2$X$_{10}$]$^{4-}$ anions consists of octahedral fragments {BiX$_6$} linked by two μ_2-bridging halide ligands. The structures of the compounds are determined by X-ray diffraction analysis (CIF files CCDC 1455987 (**I**) and 1455988 (**II**)). The forbidden gap width E_g is determined for complex **II** from the diffuse reflectance spectrum.

Keywords: bismuth, halide complexes, binuclear complexes, crystal structure

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INTRODUCTION

Polynuclear halide complexes of bismuth(III) (polyhalide bismuthates) represent a very interesting field of coordination chemistry [1–4]. On the one hand, a variety of structural types is a bright feature of this class of compounds. The compounds containing both discrete anions with the number of Bi atoms from 2 to 8 [5–17] and polymer fragments (as a rule, one-dimensional [16–20]) are known nowadays. However, heterometallic complexes are known only for iodides [21–24]. On the other hand, in some cases, polyhalide bismuthates demonstrate the physical properties interesting from the viewpoint of developing novel materials, in particular, photochromism [25–27], luminescence, and solvatochromism. In the most part of cases, the optical properties of the polyhalide bismuthate complexes are governed, to a significant extent, by the nature of the organic cation. The photochromic properties are due to the use of various viologens (*N*-alkylated derivatives of 4,4'-bipyridine) as cations. The most outstanding results (maximum changes in color) were obtained for the complexes containing methyl viologen (*N*,*N*'-dimethyl-4,4'-bipyridinium). At the same time, halobismuthates containing 2,2'-bipyridine (2,2'-Bipy) derivatives are poorly studied. The tetranuclear chloride complex (H$_2$(2,2'-Bipy))$_4$[Bi$_4$Cl$_{20}$] [28, 29] and several iodine-containing polyhalide bismuthates bearing mono- or bisprotonated 2,2'-Bipy [28, 30] are known. In this work, we synthesized and characterized isostructural complexes containing *N*-methyl-2,2'-bipyridinium and binuclear anions [Bi$_2$X$_{10}$]$^{4-}$ (X = Cl (**I**), Br (**II**)).

EXPERIMENTAL

The syntheses were carried out in air. The starting AgNO$_3$, HBr, methyl iodide, 2,2'-bipyridine, BiCl$_3$, and BiOBr (reagent grade or analogous grade of purity) were purchased from commercial sources and used as received. *N*-Methyl-2,2'-pyridinium iodide was synthesized by the reaction of 2,2'-Bipy with methyl iodide (1 : 1) in dichloromethane [31], and its purity was checked by the ^{1}H NMR spectrum. Elemental analysis was carried out at the Analytical Laboratory of the Nikolaev Institute of Inorganic Chemistry (Siberian Branch, Russian Academy of Sciences) using a EuroEA 3000 CHN analyzer.

Synthesis of (*N*-Me(2,2'-BipyH)$_2$[Bi$_2$Cl$_{10}$] (I). *N*-Methyl-2,2'-pyridinium iodide (50 mg, 0.167 mmol) was dissolved in H$_2$O (5 mL), and AgNO$_3$ (30 mg, 0.176 mmol) was added with stirring. A precipitate of AgI was separated in 10 min. Several µL of 2 M HCl were added to the mother liquor, and the solution was repeatedly filtered in 10 min. Then concentrated HCl (1 mL) and a solution of BiCl$_3$ (54 mg, 0.171 mmol) in 2 M HCl (5 mL) were succes-

Table 1. Crystallographic parameters and details of diffraction experiments for complexes **I** and **II**

Parameter	**I**	**II**
FW	1116.91	1561.51
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pbca*	*Pbca*
a, Å	11.60580(17)	11.89483(16)
b, Å	14.75069(19)	15.37395(18)
c, Å	18.6287(3)	19.1288(3)
V, Å^3	3189.12(8)	3498.10(8)
Z	4	4
ρ_{calcd}, g/cm^3	2.326	2.965
μ, mm^{-1}	11.881	21.491
$F(000)$	2080	2800
Crystal size, mm	0.26 × 0.16 × 0.06	0.19 × 0.17 × 0.06
θ Range, deg	3.45–31.04	3.33–29.59
Range of indices *hkl*	$-17 \leqslant h \leqslant 17, -22 \leqslant k \leqslant 21, -27 \leqslant l \leqslant 22$	$-15 \leqslant h \leqslant 17, -19 \leqslant k \leqslant 22, -26 \leqslant l \leqslant 25$
N_{hkl} measured/independent	31914/4786	31883/4550
R_{int}	0.0920	0.0664
N_{hkl} with $I > 2\sigma(I)$	4017	3774
GOOF for F^2	1.032	1.101
R factors ($I > 2\sigma(I)$)	$R_1 = 0.0419$, $wR_2 = 0.1131$	$R_1 = 0.0363$, $wR_2 = 0.0898$
R factors (for all reflections)	$R_1 = 0.0512$, $wR_2 = 0.1207$	$R_1 = 0.0499$, $wR_2 = 0.0954$
$\Delta\rho_{max}/\rho_{min}$, e/Å^3	4.808/−3.104	3.374/−2.784

sively added. Large colorless crystals of compound **I** were formed within 3 days. The yield was 38%.

For $C_{22}H_{24}N_4Cl_{10}Bi_2$

anal. calcd., %:	C, 23.7;	H, 2.17;	N, 5.0.
Found, %:	C, 23.8;	H, 2.26;	N, 5.1.

Synthesis of (*N*-Me(2,2'-BipyH)$_2$[Bi$_2$Br$_{10}$] (II). The procedure was similar to the synthesis of compound **I** except for the use of HBr instead of HCl and of BiOBr (52 mg, 0.17 mmol) instead of $BiCl_3$. The crystals of compound **II** were formed within 1.5 days. The yield was 61%.

For $C_{22}H_{24}N_4Br_{10}Bi_2$

anal. calcd., %:	C, 16.9;	H, 1.55;	N, 3.6.
Found, %:	C, 17.0;	H, 1.61;	N, 3.8.

X-ray diffraction analysis. Diffraction data for single crystals of compounds **I** and **II** were obtained at 130 K on an Agilent Xcalibur automated diffractometer equipped with an Atlas S2 two-coordinate detector (graphite monochromator, $\lambda(\text{Mo}K_\alpha)$ = 0.71073 Å, ω scan mode). The integration, application of absorption correction, and determination of unit cell parameters were performed using the CrysAlisPro program package [32]. The structure was solved by a direct method and refined by full-matrix least squares in the anisotropic approximation except for hydrogen atoms (SHELX-2014) [33]. The positions of the hydrogen atoms of the organic cation were calculated geometrically and refined by the riding model. The X-ray diffraction analysis details and selected 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 (CIF files CCDC 1455987 (**I**) and 1455988 (**II**); https://summary.ccdc.cam.ac.uk/structure-summary-form) and are available from the authors.

The diffuse reflectance spectrum $R_d = f(\lambda)$ for compound **II** was measured on a Shimadzu UV-3101 PC spectrophotometer in the range of wavelengths λ from 240 to 800 nm (gap width 5 nm). The calibration accuracy of the wavelength axis was ±0.3 nm for the UV and visible ranges, and measurement inaccuracies related to the scattered light were 0.01%. The standard was $BaSO_4$.

Table 2. Selected bond lengths and bonds angles in complexes **I** and **II***

Bond	d, Å	Bond	d, Å
I			
Bi(1)–Cl(1)	2.5510(12)	Bi(1)–Cl(3)	2.6680(13)
Bi(1)–Cl(2)	2.8283(11)	Bi(1)–Cl(4)	2.6101(12)
Bi(1)–Cl(2)^i	2.9580(11)	Bi(1)–Cl(5)	2.7581(12)
II			
Bi(1)–Br(1)	2.6982(6)	Bi(1)–Br(4)	2.9669(6)
Bi(1)–Br(2)	2.8324(7)	Bi(1)–Br(4)^i	3.0872(6)
Bi(1)–Br(3)	2.8894(7)	Bi(1)–Br(5)	2.7547(6)
Angle	ω, deg	Angle	ω, deg
I			
Cl(1)Bi(1)Cl(2)	94.79(4)	Cl(3)Bi(1)Cl(5)	171.28(4)
Cl(1)Bi(1)Cl(2)^i	171.78(4)	Cl(4)Bi(1)Cl(2)^i	91.22(4)
Cl(1)Bi(1)Cl(3)	88.77(4)	Cl(4)Bi(1)Cl(2)	170.07(4)
Cl(1)Bi(1)Cl(4)	94.88(5)	Cl(4)Bi(1)Cl(3)	90.66(4)
Cl(1)Bi(1)Cl(5)	84.33(4)	Cl(4)Bi(1)Cl(5)	95.23(4)
Cl(2)Bi(1)Cl(2)^i	79.39(4)	Cl(5)Bi(1)Cl(2)	88.00(4)
Cl(3)Bi(1)Cl(2)	87.26(4)	Cl(5)Bi(1)Cl(2)^i	89.64(4)
Cl(3)Bi(1)Cl(2)^i	96.67(4)	Bi(1)Cl(2)Bi(1)^i	100.61(4)
II			
Br(1)Bi(1)Br(2)	88.315(19)	Br(3)Bi(1)Br(4)	88.669(19)
Br(1)Bi(1)Br(3)	84.587(19)	Br(3)Bi(1)Br(4)^i	89.152(18)
Br(1)Bi(1)Br(2)	88.315(19)	Br(3)Bi(1)Br(4)	88.669(19)
Br(1)Bi(1)Br(3)	84.587(19)	Br(3)Bi(1)Br(4)^i	89.152(18)
Br(1)Bi(1)Br(2)	88.315(19)	Br(3)Bi(1)Br(4)	88.669(19)
Br(1)Bi(1)Br(3)	84.587(19)	Br(3)Bi(1)Br(4)^i	89.152(18)
Br(1)Bi(1)Br(2)	88.315(19)	Br(3)Bi(1)Br(4)	88.669(19)
Br(1)Bi(1)Br(3)	84.587(19)	Br(3)Bi(1)Br(4)^i	89.152(18)

*Symmetry transformations used to generate equivalent atoms: ^{i} $-x, -y, -z + 1$.

RESULTS AND DISCUSSION

Binuclear complexes of various structures represent the most frequently met type of halobismuthates: their fraction among the structurally characterized compounds is more than 65% [2]. At the same time, $[Bi_2Cl_{10}]^{4-}$ anions are most abundant among the binuclear chloride complexes. Among bromide anions, $[Bi_2Br_{10}]^{4-}$ are met [34–36] approximately twofold more rarely than $[Bi_2Br_9]^{3-}$ [2, 37–41]. On the whole, the formation of polyhalide bismuthates with the relatively high ratio X : Bi = 5 is typical of reactions where aqueous solutions of hydrohalic acids are simultaneously used as a source of halide ion and solvent [2]. Low yields of the compounds and a comparatively slow formation of crystals of compounds **I** and **II** are very unusual and untypical of polyhalide bismuthates with large aromatic cations (for example, 95% for $(H_2(4,4'\text{-Bipy}))_2[Bi_2Cl_{10}] \cdot 2H_2O$) [2].

Attempts to obtain the polybromide complex by the reaction in a solution of Br_2 in HBr according to the principle described by us earlier [42] were unsuccessful (compound **II** identified by the X-ray diffraction data was formed in the synthesis).

The crystals of compounds **I** and **II** are isostructural. The independent part contains one Bi^{3+} cation in the octahedral coordination environment of six halide ligands (Cl^- or Br^-). Two BiX_4^- fragments are linked by two bridging halide ligands (μ-Cl or μ-Br) to form binuclear anionic complex $[Bi_2(\mu\text{-}X)_2X_8]^{4-}$ (X = Cl and Br for compounds **I** and **II**, respectively) (Fig. 1). The Bi–Cl (terminal) distances range from 2.5510(12) to 2.7581(12) Å, and other ranges are as fol-

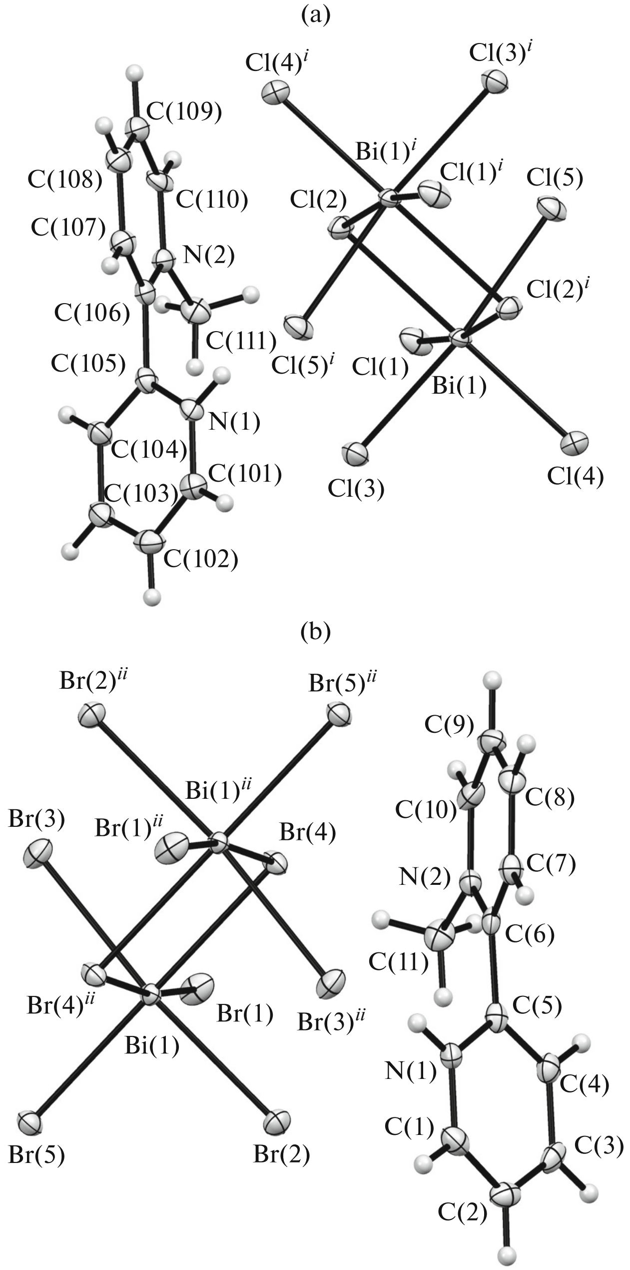

Fig. 1. Structures of the cation and anion in complexes (a) **I** and (b) **II**. Ellipsoids of 50% probability. Symmetry transformations used to generate equivalent atoms: ^{i} $-x$, $-y$, $1-z$; ^{ii} $1-x$, $-y$, $1-z$.

lows: Bi–Cl (bridging) 2.8283(11) and 2.9580(11), Bi–Br (terminal) 2.6982(6)–2.8894(7), and Bi–Br (bridging) 2.9669(6) and 3.0872(6) Å. The $[Bi_2(\mu\text{-}X)_2X_8]^{4-}$ anions are centrosymmetric. The organic cations are arranged in the general positions. The packing of the cations and anions is shown in Fig. 2. The complex anions form layers parallel to the *xz* plane, and the organic cations are arranged between them. The interactions between the components of the structure are van der Waals only.

The optical absorbance in relative units was calculated from the diffuse reflectance spectra using the classical Kubelka–Munk (KM) function

$$\mathrm{KM} = F(R_d) = (1 - R_d)^2/(2R_d),$$

where F is the representation of the spectrum in the KM coordinates, R_d is the reflectance of the sample, and $F(R_d)$ is directly proportional to the absorption coefficient, i.e., $h\nu F(R_d)^2 = A(h\nu - E_g)$. The optical forbidden gap width (E_g) is determined from the edge

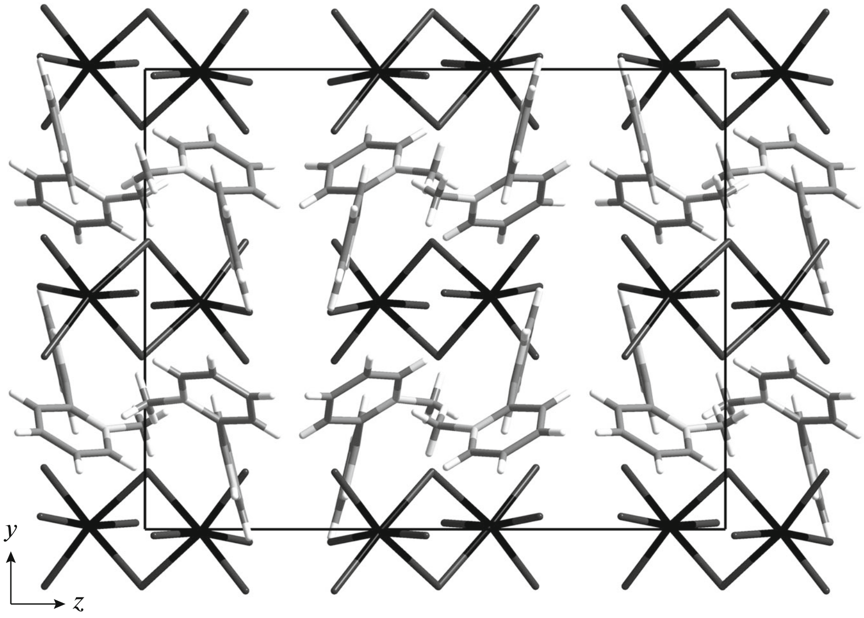

Fig. 2. Packing of the cations and anions in crystal of compound **I**.

of the fundamental absorption band by plotting the dependence of $h\nu$ from $(h\nu F(R_d))$. The tangent to the inflection point of the plot crosses the horizontal axis $h\nu$ and gives the value of the forbidden gap: for **II**, E_g = 2.71 eV (Fig. 3). This value is expectedly higher than that for the most part of iodine-containing polyhalide bismuthates (2.19–1.93 eV [23]; for BiI_3, 1.73 eV [43]), although is comparable with the values observed for the complexes containing mononuclear $[BiI_6]^{3-}$ anions [7].

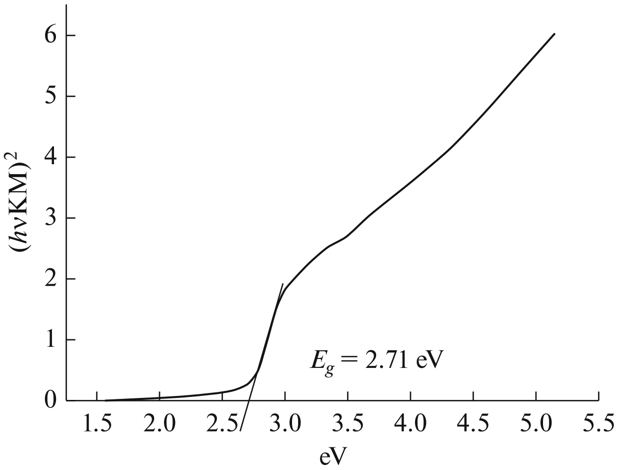

Fig. 3. Dependence of $(h\nu KM)^2$ on the incident radiation energy for complex **II**.

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