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Hybrid salts of binuclear Bi(III) halide complexes with 1,2-bis(pyridinium)ethane cation: synthesis, structure and luminescent behavior

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Abstract. Reactions between 1,2-bis(pyridinium)ethane bromide ((BPE)Br₂) and $[BiCl_6]^{3-}/[BiBr_6]^{3-}$ in HCl or HBr results in isostructural binuclear complexes (BPE)₂[Bi₂X₁₀] (X = Cl (1) and Br (2)) which were characterized by X-ray diffractometry, IR and Raman spectroscopy. Both complexes manifest orange-red luminescence in solid state.

Keywords: bismuth / halide complexes / luminescence / p-block metals / X-ray diffractometry

1. Introduction

One of the prominent features of many late and post-transition metals is their ability to form polynuclear halide complexes. This trend is especially remarkable in the case of bismuth in 3+ oxidation state: there is a great structural diversity of structural types, including discrete anions of various nuclearity (1 to 8) and coordination polymers (mostly one-dimensional) [1-9], as well as heterometallic derivatives. Apart from purely fundamental interest, this class of compounds demonstrates a number of interesting and promising physical properties such as ferroelasticity or semiconductivity [10-20], thermochromism [21-23], photochromism [24-28] etc.

Within the last decades, there appeared a number of studies focused on luminescent properties of polynuclear Bi(III) halides (polyhalidebismuthates, or PHB), but they remain relatively sporadic [29-31]. Generally, it can be noted that in the reported cases the major contribution to the luminescence is provided by the aromatic cations. It was shown that the role of anionic part is predominantly "structural": the crystal packing of PHB units may have a great influence on optical properties [1]. Very recently we have reported solvatochromic effect for $[Bi_2X_{10}]^{2^{-}}$ complexes containing H₂(4,4°-bipy) [32] or H₂bpe (H₂bpe = 4,4-ethylenebipyridinium) [33] cations; it was shown that the changes in solvate composition may influence the luminescent behavior, affecting both emission maxima [32] and intensities [33]. Aiming at

further expansion of the PHB-based luminescent complexes and search for new solvatochromic materials, we have decided to study the PHBs with the BPE cation. From the structural point of view, this pyridine-based cation is closely related to the 4,4-ethylenebipyridinium; however, it could be anticipated that the alkylation at nitrogen would affect its ability to form the NH···X contacts which are usual for the PHBs containing protonated polypyridines [32-35]. In present paper, we report the synthesis of two new Bi(III) halide complexes – (BPE)₂[Bi₂X₁₀] (X = Cl (1), Br (2)), their structures and the studies of their luminescence in solid state.

2. Experimental Section

All reagents, except of the (BPE) Br_2 , were obtained from commercial sources and used as purchased. (BPE) Br_2 was obtained according to the previously published procedure [36] by heating Py and 1,2-dibromoethane (2:1 molar ratio) in dry CH₃CN for 24 h. Elemental analysis was performed on a Euro NA 3000 Elemental Analyzer (EuroVector).

Synthesis of (BPE)₂[**Bi**₂**Cl**₁₀] (1). 100 mg (0.32 mmol) of BiCl₃ were dissolved in 5 ml of 2M HCl. Solution of (BPE)Br₂ (110 mg) in 5 ml of 2M HCl was added. White crystalline precipitate of 1 started to form immediately and the process completed within 6 h. Yield 86%. For C₂₄H₂₈N₄Bi₂Cl₁₀ calcd, %: C, 25.2; H, 2.5; N, 4.9; found, %: C, 25.4; H, 2.6; N, 5.1%. IR (4000-400 cm⁻¹, KBr): 3130 w, 3056 m, 3011 w, 2972 w, 1838 w, 1726 w, 1631 s, 1580 m, 1491 s, 1457 m, 1306 w, 1215 w, 1193 s, 1052 w, 953 w, 964 w, 775 s, 678 s, 495 m, 450 w.

Synthesis of $(BPE)_2[Bi_2Br_{10}]$ (2). The procedure was the same as for 1, using BiOBr instead of BiCl₃ and HBr instead of HCl. Precipitation of 2 begins immediately after the mixing and completes within 20-30 minutes. Yield 91%. For C₂₄H₂₈N₄Bi₂Br₁₀ calcd, %: C, 18.1, H, 1.8; N, 3.5; found, %; c, 18.2; H, 1.9; N, 3.7. IR (4000-400 cm⁻¹, KBr): 3126 w, 3052 m, 2963 w, 1830 w, 1721 w, 1628 s, 1578 m, 1488 s, 1453 m, 1317 w, 1189 s, 1954 w, 947 w, 858 w, 770 m, 674 s, 492 m, 447 w.

X-ray crystallography. Diffraction data for single crystals of compounds **1** and **2** were obtained at 130 K on an automated Agilent Xcalibur diffractometer equipped with a CCD AtlasS2 detector (MoK α , graphite monochromator, ω -scans). Integration, absorption correction, and determination of unit cell parameters were performed using the CrysAlisPro program package [37]. The structures were solved by a direct method and refined by the full-matrix least squares technique in the anisotropic approximation (except hydrogen atoms) using the SHELX-97 (for **2**) and SHELX-2013 (for **1**) software packages [38]. Positions of hydrogen atoms of organic ligands were calculated geometrically and refined in the riding model. The crystallographic data and details of the structure refinements are summarized in Table 1. Selected bond distances and angles are listed in Tables 2–3. Crystallographic data have been deposited at the Cambridge

Crystallographic Data Centre under the reference numbers CCDC 1455367 and 1455368 for **1** and **2**, respectively, and may be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

Luminescence studies. Excitation and emission spectra were recorded with a Horiba Jobin Yvon Fluorolog 3 photoluminescence spectrometer equipped with a 450 W Xe lamp, an integration sphere, Czerny–Turner double grating (1200 grooves per mm) excitation and emission monochromators and an FL-1073 PMT detector. Excitation spectra were recorded in 350-570 nm range and corrected for the spectral distribution of the lamp intensity using a photodiode reference detector. Emission spectra were recorded from 500 to 900 nm and corrected for the spherical response of the monochromators and the detector using typical correction spectra provided by the manufacturer. Additionally, the 1st and 2nd harmonic oscillations of the excitation source were blocked by edge filters.

MA

Identification code	1	2
Empirical formula	CatHaoBiaChoNt	CatHaoBiaBrooNt
Empirical formula	C241128D12C1101V4	C241128D12D110114
Formula weight	1144.96	1589.56
Crystal system	Monoclinic	Monoclinic
Space group	<i>C</i> 2/ <i>c</i>	C2/c
<i>a</i> , Å	19.0866(3)	19.7959(7)
<i>b</i> , Å	9.84714(11)	9.9395(3)
<i>c</i> , Å	20.1054(3)	20.7937(10)
β, deg.	110.2129(16)	111.314(5)
<i>V</i> , Å ³	3546.06(9)	3811.6(2)
Ζ	4	4
$D(\text{calcd}), \text{g/cm}^3$	2.145	2.770
μ , mm ⁻¹	10.688	19.727
F(000)	2144	2864
Crystal size, mm	$0.45 \times 0.08 \times 0.08$	$0.15 \times 0.04 \times 0.02$
θ range for data collection, deg.	3.45-32.90	3.40–29.50
Index ranges	$-29 \le h \le 28, -14 \le k \le 15, \\ -29 \le l \le 29$	$-26 \le h \le 22, -13 \le k \le 13, \\ -17 \le l \le 27$
Reflections collected / independent	39346 / 6271	10805 / 4571
$R_{ m int}$	0.0283	0.0464
Reflections with $I > 2\sigma(I)$	5672	3262
Goodness-of-fit on F^2	1.067	0.905

Table 1. Crystal data and structure refinement for ${\bf 1}$ and ${\bf 2}.$

Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0323, wR_2 = 0.0923$	$R_1 = 0.0373, wR_2 = 0.0459$
<i>R</i> indices (all data)	$R_1 = 0.0368, wR_2 = 0.0947$	$R_1 = 0.0707, wR_2 = 0.0554$
Largest diff. peak / hole, $e/Å^3$	5.373 / -1.108	1.556 / -1.502

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Bi(1)–Cl(1)	2.6044(9)	Bi(1)–Cl(4)	2.7025(9)
Bi(1)–Cl(2)	2.7013(9)	Bi(1)-Cl(6)	2.9365(8)
Bi(1)–Cl(3)	2.6345(9)	Bi(1)–Cl(5)	2.9969(8)
Angle	ω, deg.	Angle	ω, deg.
Cl(1)–Bi(1)–Cl(2)	87.87(3)	Cl(3)–Bi(1)–Cl(4)	87.68(3)
Cl(1)-Bi(1)-Cl(3)	94.32(3)	Cl(3)-Bi(1)-Cl(6)	175.78(3)
Cl(1)-Bi(1)-Cl(4)	90.55(3)	Cl(3)-Bi(1)-Cl(5)	92.51(3)
Cl(1)-Bi(1)-Cl(6)	88.75(3)	Cl(4)-Bi(1)-Cl(6)	89.40(2)
Cl(1)-Bi(1)-Cl(5)	172.24(2)	Cl(4)-Bi(1)-Cl(5)	93.41(2)
Cl(2)-Bi(1)-Cl(4)	176.41(3)	Cl(6)-Bi(1)-Cl(5)	84.62(2)
Cl(2)-Bi(1)-Cl(6)	93.79(2)	Bi(1) ⁱ -Cl(6)-Bi(1)	96.66(3)
Cl(2)-Bi(1)-Cl(5)	88.54(2)	$Bi(1)^{i}-Cl(5)-Bi(1)$	94.10(3)
Cl(3)–Bi(1)–Cl(2)	89.23(3)		

Table 2. Selected bond lengths and angles for **1**.

Symmetry transformations used to generate equivalent atoms: i) -x + 1, y, $-z + \frac{1}{2}$.

RCCE

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Bi(1)–Br(1)	3.0211(7)	Bi(1)-Br(4)	2.7462(8)
Bi(1)–Br(2)	3.0803(7)	Bi(1)–Br(5)	2.8407(8)
Bi(1)–Br(3)	2.7230(7)	Bi(1)–Br(6)	2.8342(8)
Angle	ω, deg.	Angle	ω, deg.
Br(1)–Bi(1)–Br(2)	84.361(19)	Br(4)–Bi(1)–Br(6)	87.89(2)
Br(3)–Bi(1)–Br(2)	171.25(2)	Br(5)-Bi(1)-Br(1)	93.375(18)
Br(3)–Bi(1)–Br(1)	88.14(2)	Br(5)-Bi(1)-Br(2)	87.294(17)
Br(3)-Bi(1)-Br(4)	95.38(2)	Br(6)-Bi(1)-Br(1)	89.534(16)
Br(3)–Bi(1)–Br(5)	88.64(2)	Br(6)-Bi(1)-Br(5)	176.99(3)
Br(3)–Bi(1)–Br(6)	90.69(2)	Br(6)-Bi(1)-Br(2)	93.758(17)
Br(4)-Bi(1)-Br(1)	175.66(2)	$\operatorname{Bi}(1)^{i}$ -Br(1)-Bi(1)	96.87(3)
Br(4)-Bi(1)-Br(2)	92.32(2)	$Bi(1)$ – $Br(2)$ – $Bi(1)^i$	94.41(3)
Br(4)–Bi(1)–Br(5)	89.25(2)		

Table 3. Selected bond lengths and angles for 2.

Symmetry transformations used to generate equivalent atoms: i) -x + 1, y, $-z + \frac{1}{2}$.

Results and discussion

Synthesis of 1 and 2. The major part of PHBs reported to date is synthesized by a straightforward approach: "cation + source of halide ion + source of Bi(III)" [1]. In some cases, cation may be prepared *in situ* (for example, by protonation of corresponding base [32-34] or N-alkylation of polypyridyl [26-27]). The source of Bi depends on the nature of the solvent: if synthesis is carried out in a hydrohalic acid as medium, it may be Bi(III) oxide/ohyhalide/carbonate etc, resulting in $[BiX_6]^{3-}$ after dissolution. In general, there is usually no direct correlation between the initial stoichiometry and the composition of the products. However, the use of HCl, HBr or HI as a medium, providing also an excess of corresponding halide anions in solution, commonly results in complexes with higher X/Bi ratio (4 to 5.5) than

organic solvents. In can be noted also that the binuclear halobismuthates, especially $[Bi_2X_9]^{3-}$ and $[Bi_2X_{10}]^{4-}$, are the most widespread PHBs appearing in solid state [1]. Therefore, the formation of $[Bi_2X_{10}]^{4-}$ anionic moieties in **1** and **2** was rather expectable.

Structures of 1 and 2. The structure of chloro- (1) and bromobismuthate (2) anions $[Bi_2X_{10}]^{4-}$ is similar to those found in related compounds [32-34, 39-43]. Structures **1** and **2** are isostructural. The asymmetric unit contains one Bi^{3+} cation. The Bi cation has octahedral coordination environment provided by six halides (Cl⁻ or Br⁻). Two cations are interconnected *via* two bridging halide ligands (μ -Cl resp. μ -Br) to form binuclear $[Bi_2(\mu-X)_2X_8]^{4-}$ (X = Cl and Br for **1** and **2**, respectively) anion (Fig. 1). Bi–Cl(terminal) distances are in range 2.6044(9)–2.7025(9) Å, and Bi–Cl(bridging) distances range from 2.9365(8) Å to 2.9969(8) Å. Bi–Br(terminal) distances are in range 2.7230(7)–2.8407(8) Å and Bi–Br(bridging) distances are in range 3.0211(7) Å and 3.0803(7) Å, following the same trend. The centers of $[Bi_2(\mu-X)_2X_8]^{4-}$ anions occupy special positions 4*e* (0, *y*, ¹/₄; 0, *-y*, ³/₄; ¹/₂, *y* + ¹/₂, ¹/₂ – *y*, ³/₄), two bridging halogenide ligands (Cl(5) and Cl(6) in **1**, Br(1) and Br(2) in **2**) are situated on two-fold rotation axis. The organic cations occupy general positions. Fig. 2 shows crystal packing in the structure **1**. All the discrete constituents in the structures **1** and **2** are interconnected *via* van der Waals interactions.



Fig. 1. Structure of cation and anion in 1 (*a*) and 2 (*b*). Symmetry transformations used to generate equivalent atoms: i) -x + 1, y, $-z + \frac{1}{2}$.



Fig. 2. Crystal packing in 1 (H atoms are omitted).

Luminescence studies and Raman spectra. The compounds 1 and 2 manifest orange-red luminescence in the solid state at room temperature, the excitation and emission spectra of are displayed in Fig. 3. The excitation maximum for both compounds is about 480 nm. Taking into account these data, the excitation wavelength 480 nm was used for recording of the emission spectra. The powders of 1 and 2 exhibit orange-red photoluminescence (PL) with a broad emission with maxima at ca. 590 nm (Fig. 3).



Fig. 3. Excitation and emission spectra of the compounds 1 (black) and 2 (red)

Comparing these data with those reported earlier [32-34], several interesting observations can be made. As in the previous studies, the luminescence intensity for bromide complexes is generally lower than for the chloride analogues (this fact was also noted by Mercier et al. [44]). However, the extent of this difference varies very strongly, depending on the nature of cation: for **1** and **2**, it is comparable with $(H_2bpe)_2[Bi_2Cl_{10}]$ and $(H_2bpe)_2[Bi_2Br_{10}]$ ($H_2bpe = 4,4$ `-ethylenepyridinium) [33], but it is not so dramatic as in the $(H_2bpe)_2[Bi_2X_{10}]$ (X = Cl, Br) $(H_2bpe = 4,4$ `vinylenepyridinium) pair [34] or $(H_2(4,4$ `-bipy))_2[Bi_2Br_{10}] [45], where the luminescence of bromide complex is very weak.

The Raman spectra (see SI) of **1** and **2** are similar to those reported earlier for the other halobismuthate [46] and other p-block metal halide complexes [47-48]: the 150-310 cm⁻¹ area is responsible for Bi-X stretching vibrations.

4. Conclusions

To conclude, two new complexes based on 1,2-bis(pyridinium) cations and binuclear $[Bi_2X_{10}]^{4-}$ anions have been presented. Both complexes are luminescent, and the difference between the chloride (1) and bromide (2) complexes is less pronounced than in some previous examples; this fact may be of interest for further theoretical studies.

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Acceleration



Two organic-inorganic hybrids based on Bi(III) halide complexes; $(BPE)_2[Bi_2X_{10}]$ (X = Cl, Br) (BPE = 1,2-bis(pyridinium)ethane) have been prepared. Both complexes display orange-red luminescence; its intensity is higher for chloride complex than for bromide

-Two hybrid binuclear complexes (BPE)₂[Bi₂X₁₀] (X = Cl, Br) were synthesized

-Luminescent behavior was studied

Acceleration