Inorganica Chimica Acta 450 (2016) 232–235

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Research paper

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

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ARTICLE INFO

Article history:
Received 24 February 2016
Received in revised form 6 May 2016
Accepted 4 June 2016
Available online 6 June 2016

Keywords:
Bismuth
Halide complexes
Luminescence
p-Block metals
X-ray diffractometry

ABSTRACT

Reactions between 1,2-bis(pyridinium)ethane bromide ((BPE)Br_2) and $[BiCl_6]^{3-}$/$[BiBr_6]^{3-}$ in HCl or HBr results in isostructural binuclear complexes $(BPE)_2[Bi_2X_{10}]$ (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.

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 (1–8) 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 H_2(4,4′-bipy) [32] or H_2bpe (H_2bpe = 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 – $(BPE)_2[Bi_2X_{10}]$ (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 M ratio) in dry CH_3CN for 24 h. Elemental analysis was performed on a Euro NA 3000 Elemental Analyzer (EuroVector).

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http://dx.doi.org/10.1016/j.ica.2016.06.010
0020-1693/

2.1. Synthesis of $(BPE)_2[Bi_2Cl_{10}]$ (**1**)

100 mg (0.32 mmol) of $BiCl_3$ were dissolved in 5 ml of 2 M HCl. Solution of $(BPE)Br_2$ (110 mg) in 5 ml of 2 M HCl was added. White crystalline precipitate of **1** started to form immediately and the process completed within 6 h. Yield 86%. For $C_{24}H_{28}N_4Bi_2Cl_{10}$ 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.

2.2. Synthesis of $(BPE)_2[Bi_2Br_{10}]$ (**2**)

The procedure was the same as for **1**, using BiOBr instead of $BiCl_3$ and HBr instead of HCl. Precipitation of **2** begins immediately after the mixing and completes within 20–30 min. Yield 91%. For $C_{24}H_{28}N_4Bi_2Br_{10}$ 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.

2.3. 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 (Mo Kα, 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 and 3.

Table 1
Crystal data and structure refinement for **1** and **2**.

Identification code	1	2
Empirical formula	$C_{24}H_{28}Bi_2Cl_{10}N_4$	$C_{24}H_{28}Bi_2Br_{10}N_4$
Formula weight	1144.96	1589.56
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*
a, Å	19.0866(3)	19.7959(7)
b, Å	9.84714(11)	9.9395(3)
c, Å	20.1054(3)	20.7937(10)
β, °	110.2129(16)	111.314(5)
V, Å^3	3546.06(9)	3811.6(2)
Z	4	4
D(calcd), g/cm^3	2.145	2.770
μ, mm^{-1}	10.688	19.727
F(000)	2144	2864
Crystal size, mm	0.45 × 0.08 × 0.08	0.15 × 0.04 × 0.02
θ range for data collection, °	3.45–32.90	3.40–29.50
Index ranges	$-29 \leqslant h \leqslant 28$, $-14 \leqslant k \leqslant 15$, $-29 \leqslant l \leqslant 29$	$-26 \leqslant h \leqslant 22$, $-13 \leqslant k \leqslant 13$, $-17 \leqslant l \leqslant 27$
Reflections collected/ independent	39346/6271	10805/4571
R_{int}	0.0283	0.0464
Reflections with $I > 2\sigma(I)$	5672	3262
Goodness-of-fit on F^2	1.067	0.905
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0323$, $wR_2 = 0.0923$	$R_1 = 0.0373$, $wR_2 = 0.0459$
R 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

2.4. 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.

3. Results and discussion

3.1. 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 (4–5.5) 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.

3.2. 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 $[Bi_2(\mu\text{-}X)_2X_8]^{4-}$ (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

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

Bond	*d*, Å	Bond	*d*, 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, °	Angle	ω, °
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)		

Symmetry transformations used to generate equivalent atoms: (i) $-x+1$, y, $-z+1/2$.