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Binuclear Bi(III) halide complexes with 4,4`-ethylenepyridinium cations: luminescence tuning by reversible solvation

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Two new complexes based on 4,4`-ethylenepyridinium cation and binuclear Bi(III) anionic complexes, $(H_2bpe)_2[Bi_2X_{10}]\cdot 2H_2O$ (bpe = 1,2-bis(4-pyridyl)ethane) X = Cl (**1**), Br (**2**)) have been synthesized and characterized by X-ray diffractometry. In both cases, loss of solvent H_2O molecules affects the luminescent behavior, resulting in increase of intensity (ca. 5-fold). The desolvation is reversible, providing the potential use in the chemosensor systems.

Introduction

Anionic halide complexes of post-transition metals, in particular Bi(III), attracts a keen attention of researchers over the last decades.[1] Apart from fundamental problems and unresolved problems which are still present in this area of inorganic chemistry, such as rules and principles governing the formation of $\{Bi_aX_b\}^{n-}$ polynuclear structures,[2] it is based on a number of promising physical properties which these compounds reveal.[3-7] Most of research is focused on various optical features, for example, thermochromism, which seems to be common for iodobismuthates,[8-9] luminescence and photochromism. The last two properties are being studied especially extensively for complexes containing various viologen cations since 2007, when Guo et al. presented the first, reversibly photochromic hybrid of this type consisting of N,N`-dimethyl-4-4`-bipyridinium (methylviologen, MV) and $\{Bi_2Cl_8\}_n^{2n-}$ polymer anions.[10] Further studies have shown that this feature is common for this class and the key parameters may be tuned by varying the substituents on the N site of 4,4`-bipy; theoretical models of this affect have also been proposed.[11-14]

Very recently we reported the luminescent behavior of binuclear complex $(H_2(4,4\text{`-bipy}))_2[Bi_2Cl_{10}]$. We found that it is strongly affected by the solvate composition: if it contains two water molecules (this crystalline phase forms in a very good yield), it displays yellow luminescence (λ_{max} 530 nm), but after dehydration the maximum shifts to orange (λ_{max} 560 nm).[15] It may be proposed that the solvatochromism may be observed also among the other members of "aromatic cation-Bi(III) halide" hybrids. From another (chemical) point of view, one of the interesting features of the Bi(III) halide complexes is their ability to change the molecular structure upon solvation in solid state[16], as well as the evident tendency to undergo phase transitions[17], which should affect the physical properties, i.a. luminescence, making them attractive when targeting the development of sensors, i.a. chemosensors. To verify this hypothesis, we decided to expand the range of cations; moreover, we decided to switch away from the viologens in order to check if other, less studied pyridine derivatives may result in interesting luminescent behavior. Here we report the synthesis of two new Bi(III) halide complexes – $(H_2bpe)_2[Bi_2X_{10}]\cdot 2H_2O$ (X = Cl (**1**), Br (**2**); bpe = 1,2-bis(4-byridyl)ethane), their structure and luminescent behavior (solvatoluminescence).

Experimental

General procedures

All reagents were obtained from commercial sources and used as purchased. Elemental analysis was performed on Euro NA 3000 Elemental Analyzer (EuroVector).

Synthetic procedures

$(H_2bpe)_2[Bi_2Cl_{10}]\cdot 2H_2O$ (1). 100 mg (0.32 mmol) of $BiCl_3$ were dissolved in 4 ml of 2M HCl. Solution of bpe (59 mg, 0.32 mmol) in 4 ml of 2M HCl was added. After ca 1 minute, colourless crystals of **1**, suitable for X-ray diffractometry, start to appear; the process is complete in 4h. Yield 94%. For $C_{24}H_{32}N_4O_2Bi_2Cl_{10}$ calcd, %: C, 24.4; H, 2.73; N, 4.7; found, %: C, 24.5; H, 2.82; N, 4.8. IR (KBr, 4000-400 cm^{-1}): 3550 m, 3421 m, 3204 s, 3416 s, 3075 s, 2004 w, 1870 w, 1632 s, 1592 s, 1499 s, 1452 m, 1414 w, 1324 w, 1231 w, 1197 m, 1080 w, 1059 w, 1007 w, 952 w, 873 w, 818 s, 793 s, 612 w, 535 m, 478 w, 399 w. Phase purity has been confirmed by PXRD (see SI).

$(H_2bpe)_2[Bi_2Br_{10}]\cdot 2H_2O$ (2). The procedure was similar to those for **1**, with BiOBr (68 mg, 22 mmol) and corresponding amound of bpe (41 mg, 22 mmol) and 2M HBr (3 and 3 ml, respectively). Pale yellow crystals of **2** start to form almost immediately; the process is complete in 2h. Yield 96%. For $C_{24}H_{32}N_4O_2Bi_2Br_{10}$ calcd, %: C, 17.7; H, 1.98; N, 3.4; found, %: C, 17.9; H, 2.06; N, 3.5. IR (KBr, 4000-400 cm^{-1}): 3555 m, 3415 m, 3200 m, 3412 m, 3068 m, 1990 w, 1865 w, 1631 s, 1590 s, 1497 s, 1414 m, 1322 m, 1230 m, 1194 s, 1080 w, 1058 w, 1010 w, 869 w, 811 s, 784 s, 610 w, 532 w, 477 w. Phase purity has been confirmed by PXRD (see SI).

Dehydration/rehydration experiments. Samples of **1** and **2** were kept at 50°C for 4h. A small amount (10-20 mcl) of water has been added to samples of **1an** or **2an;** wet powders were kept for 2.5 h. In both cases, the absence/presence of solvate/non-aqueous phases was confirmed by PXRD.

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 from 280 to 420 nm and corrected for the spectral distribution of the lamp intensity using a photodiode reference detector. Emission spectra were recorded from 350 to 650 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 (370 nm).

X-ray diffractometry

Single-crystal X-ray diffraction data of **1** and **2** were collected on a Bruker-Nonius X8 Apex CCD diffractometer at 150(2) K using graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). The standard technique was used (combined φ and ω scans of narrow frames). Data reduction and multi-scan absorption were carried out using the SADABS.[18] The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package.[18] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of $[H_2bpe]^{2+}$ cations were located geometrically and refined as riding with fixed U_{iso} (1.2 of the parent atoms). Hydrogen atoms of lattice water molecules were located from difference Fourier maps and refined as riding with $U_{iso}(H) = 1.5U_{eq}(O)$ and O—H distances restrained to 0.89(2) Å. In compound **2** the water hydrogen atoms were modeled as disordered over three overlapping orientations with equal occupancies (0.67 per each H atom). Crystallographic data and selected refinement details are given in Table 1. Geometric parameters of the $[Bi_2Cl_{10}]^{4-}$ and $[Bi_2Br_{10}]^{4-}$ anions are listed in Table 1S (SI). Hydrogen-bonding parameters are summarized in Table 2S (SI). Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre under the reference numbers CCDC 1056757 and 1056758 for **1** and **2**, respectively, and may be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html.

XRD powder analysis was performed on Shimadzu XRD-7000 diffractometer (CuK-alpha radiation, Ni – filter, 5 – 60° 2θ range, 0.03° 2θ step, 1s per step, room temperature). Indexing of the diffraction patterns was carried out using single-crystal data.

Results and discussion

The complexes **1** and **2** were obtained from bpe and $BiCl_3$ or BiOBr dissolved in corresponding 2M HX acid. Although the general synthetic strategy for polynuclear halide complexes of Bi(III) is common-sense and simple (“cation + source of Bi + source of halide”), there is a number of key parameters (solvent, temperature etc.) which may be varied, resulting in anions of different structure and nuclearity.[2] There is no direct correlation between the initial stoichiometry and the composition of products; moreover, there often appears a tendency towards simultaneous formation of several compounds and the separation is often challenging.[19-24] However, the use of HX acids, i.a. concentrated, as solvents and sources of halide (in great excess in respect to Bi) usually results in anions of lower nuclearity, predominantly mononuclear $[BiX_6]^{3-}$ [25-29] and binuclear $[Bi_2X_{10}]^{4-}$.[14-15,30-31] Therefore, the fact that $[Bi_2X_{10}]^{4-}$ cations have formed under the reaction conditions is not exceptional.

Crystal structures. Compounds **1** and **2** both crystallize in the triclinic system with space group $P\bar{1}$ and $Z = 2$ and 1, respectively. Despite the same stoichiometry, they show significant differences in their lattice parameters and cannot be considered as isostructural (Table 1) *stricto sensu*. The asymmetric unit of **1** contains twice as many atoms as that of **2**, while the unit cell volumes are related in about the same manner.

Table 1. Crystal data, data collection and refinement parameters for **1** and **2**

Empirical formula	$C_{24}H_{32}Bi_2Cl_{10}N_4O_2$	$C_{24}H_{32}Bi_2Br_{10}N_4O_2$
Formula weight	1181.00	1625.60
Temperature (K)	150(2)	150(2)
Crystal size (mm^3)	0.22 × 0.15 × 0.12	0.18 × 0.12 × 0.10
Crystal system	Triclinic	Triclinic
Space group	$P\ -1$	$P\ -1$
Z	2	1
a (Å)	10.9907(6)	9.9694(4)
b (Å)	11.3474(6)	10.7558(5)
c (Å)	15.5308(8)	10.8145(5)
α (º)	78.4430(10)	63.2080(10)
β (º)	85.2330(10)	68.5300(10)
γ (º)	72.7580(10)	81.1380(10)
V (Å^3)	1811.81(17)	963.23(7)
$D_{\mathrm{calcd.}}$ (g cm^{-3})	2.165	2.802
μ (Mo Kα) (mm^{-1})	10.467	19.522
θ range (º)	1.34 – 27.48	2.12 – 27.68
h, k, l indices range	$-14 \le h \le 14$; $-14 \le k \le 14$; $-20 \le l \le 20$	$-12 \le h \le 12$; $-14 \le k \le 13$; $-13 \le l \le 14$
F(000)	1112	736
Reflections collected	47738	9717
Unique reflections	8297 ($R_{\mathrm{int}} = 0.0314$)	4444 ($R_{\mathrm{int}} = 0.0198$)
Observed reflections [$I > 2\sigma(I)$]	7517	3805
Parameters refined	391	199
$R[F^2 > 2\sigma(F^2)]$	$R_1 = 0.0137$ $wR_2 = 0.0336$	$R_1 = 0.0223$ $wR_2 = 0.0474$
$R(F^2)$ (all data)	$R_1 = 0.0166$ $wR_2 = 0.0347$	$R_1 = 0.0313$ $wR_2 = 0.0491$
GOOF on F^2	1.056	1.028
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.789, –0.705	1.918, –0.727

Accordingly, it would be expected that both compounds share an overall similar structural arrangement composed of discrete ions $[H_2bpe]^{2+}$ and $[Bi_2X_{10}]^{4-}$, and lattice water molecules, which are held together by various types of hydrogen bonds, namely O—H···O, N—H···O, O—H···X, N—H···X and C—H···X (Fig. 1). The geometric parameters of the $[H_2bpe]^{2+}$ cations have normal values. However, they adopt quite different geometries in **1** and **2** as indicated by the angles between pyridine rings and between pyridine rings and C_2H_4 moieties. While each pyridine ring is essentially planar, the dihedral angles between the rings are 20.57(6) and 27.08(6)° in **1** and 15.72(11)° in **2**, evidencing a twisted configuration of the $[H_2bpe]^{2+}$ cations. But the most notable difference is in the angles which define the rotation of the pyridine rings with respect to the ethane bridges. These angles are in the range 59.0(2) – 83.6(2)° in compound **1**, while in **2** they are remarkably lower – only 3.4(6) and 13.1(6)°. In general, the overall shape of $[H_2bpe]^{2+}$ cations in **2** can be described as rather "flattened".

The $[Bi_2X_{10}]^{4-}$ anions show a typical dimeric structure consisting of two BiX_6 edge-sharing octahedra; they are centrosymmetric with the inversion centers midway between the Bi atoms. The Bi—Cl and Bi—Br bond lengths vary in the wide ranges 2.5650(5) – 2.9902(5) and 2.7279(4) – 3.0493(4) Å (longest values correspond to the bridging halogen atoms). The Cl–Bi–Cl and Br–Bi–Br *cis*- and *trans*-angles fall in the intervals 84.586(14) – 98.512(15) and 171.306(15) – 177.641(14)°, and 86.270(12) – 95.842(12) and 174.307(13) – 175.957(11)°, respectively (Table 1S). These geometrical data are in good accordance with previous results for similar materials.

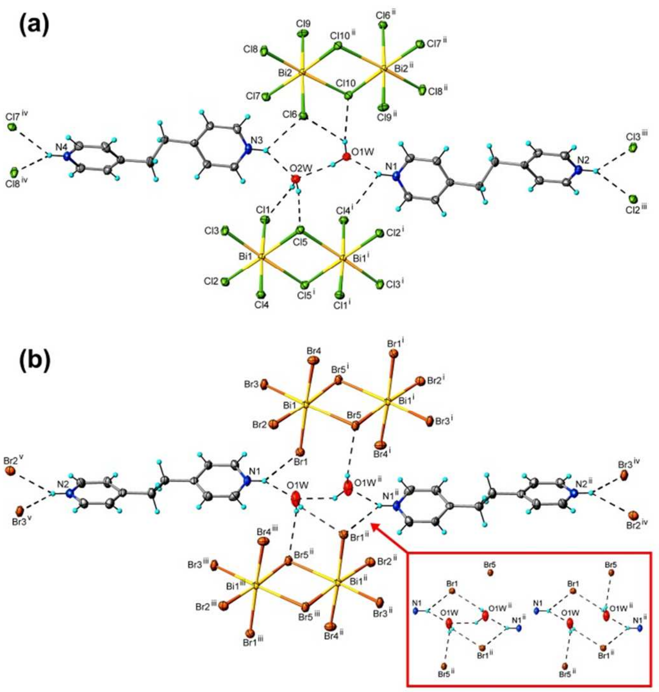

Figure 1. Hydrogen bonding patterns (dashed lines) between the $[H_2bpe]^{2+}$ and $[Bi_2X_{10}]^{4-}$ ions and lattice water molecules in **1** (a) and **2** (b). Alternative orientations of the water molecules in 2 are shown in the insert. For clarity, only the O—H···O, N—H···O, O—H···X and N—H···X bonds are shown. Thermal ellipsoids are drawn at the 50% probability level. Symmetry operations: a) (i) $1 - x, 2 - y, - z$; (ii) $2 - x, 1 - y, 1 - z$; (iii) $x, 1 + y, 1 + z$; (iv) $2 - x, - y, - z$; b) (i) $2 - x, - y, 1 - z$; (ii) $1 - x, - y, 1 - z$; (iii) $x - 1, y, z$; (iv) $x, y - 2, 1 + z$; (v) $1 - x, 2 - y, - z$.

Comprising a large number of potential hydrogen bond acceptors, the structures of **1** and **2** are determined by the interplay between hydrogen bonds of different strength. Indeed, in both compounds the relatively strong hydrogen bonds O—H···O, N—H···O, O—H···X and N—H···X cause the formation of layers extended parallel to the (2 1 –1) and (0 1 2) planes, respectively (Fig. 2, Table 2S). Neighboring layers are further linked into a three-dimensional framework *via* multiple weak C—H···X hydrogen bonds between aromatic (mostly) H atoms of the $[H_2bpe]^{2+}$ cations and halogen atoms of the $[Bi_2X_{10}]^{4-}$ anions (with H···Cl and H···Br distances of < 2.95 and 3.05 Å to be compared with the sums of the corresponding van der Waals radii). Finally, aromatic π–π stacking and C—H···π interactions are observed, although their structural role in the relatively complex packing is not prominent.

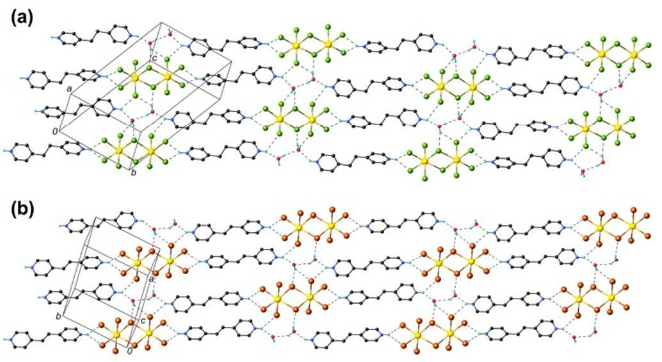

Figure 2. Projections of the layer onto the a) (2 1 –1) plane in **1** and b) (0 1 2) plane in **2**. H atoms not involved in hydrogen bonding (dashed lines) are omitted for clarity. C—H···X hydrogen bonds are not shown.

In both **1** and **2**, solvate water molecules can be eliminated by drying *in vacuo* and/or by gentle heating. According to the PXRD data, this results in new crystalline phases (**1an** and **2an**, see Experimental). Unfortunately, the dehydration does not proceed in a single crystal-to-single crystal way; attempts to obtain single crystals of the anhydrous phases by keeping those of **1** and **2** in dry air resulted in their destruction, giving the corresponding fatal distortion of diffraction patterns. However, according to the PXRD data, the loss of solvate H_2O is *reversible*: addition of water results in re-appearance of PXRD patterns correspond to pure **1** and **2**, respectively (Fig. 3, see Experimental for details). Peak intensity of freshly prepared **1** and **2** and those obtained by rehydration may vary due to preffered orientation.

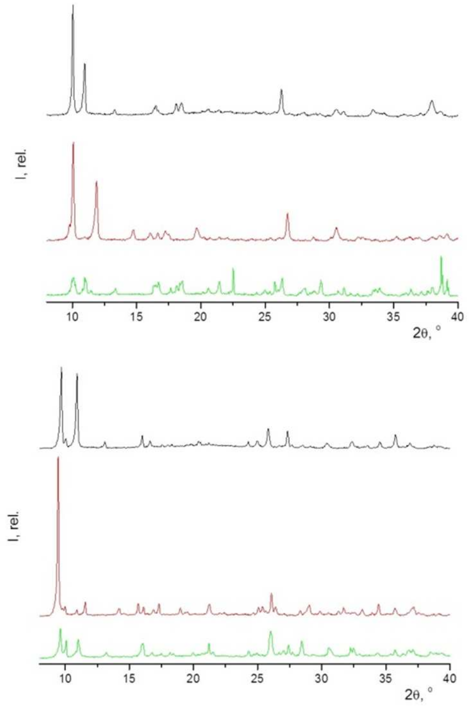

Figure 3. Diffraction patterns of **1** (above) and **2** (below) series. Green: **1** and **2**, red: **1an** and **2an**, black: rehydrated **1an** and **2an**.

All complexes show blue-green luminescence in the solid state at room temperature. The excitation spectra (Fig. 4) of **1an** display a broad band with two maxima: at ca. 360 nm and at ca. 395 nm. Other complexes (**1**, **2,** and **2an**) display a broad band with a maximum at ca. 360 nm. Taking these data into account, the 360 nm wavelength was chosen for recording of emission spectra.

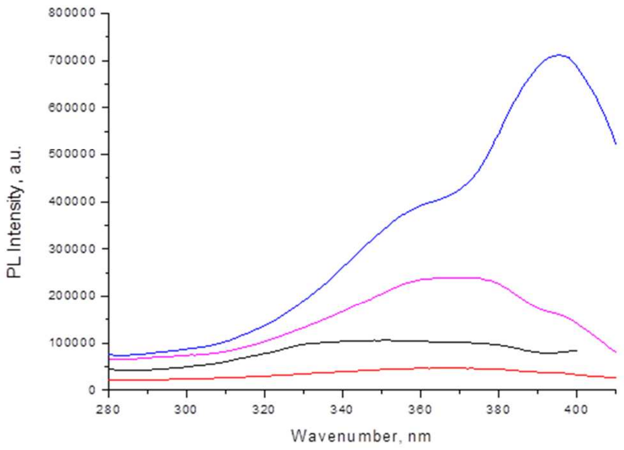

Figure 4. Excitation spectra of **1** (black), **1an** (blue), **2** (red) and **2an** (cyan)

The white powder of **1an** exhibits bright blue-green photoluminescence (PL) with a broad emission band with two maxima: ca. 420 nm and ca. 450 nm. (Fig. 5), while the luminescence of **1** is relatively weak. The yellow powder of **2an** exhibits good PL properties, in contrast to **2**. When excited at 360 nm, both emit blue-green light, with similarly shaped emission spectra with two maxima: ca. 420 nm and ca. 450 nm. (Fig. 5).

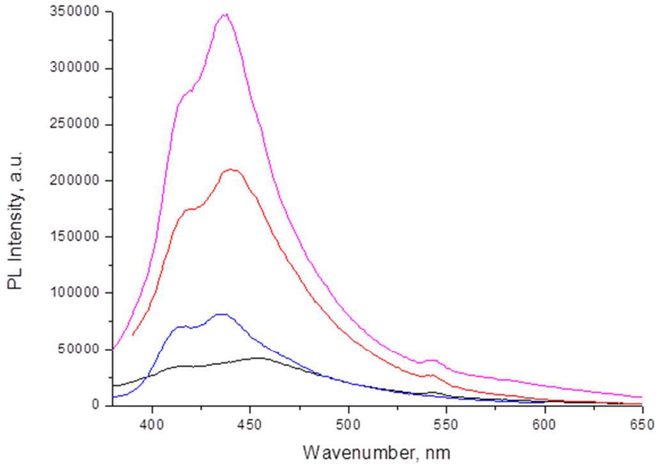

Figure 5. Emission spectra of **1** (blue), **1an** (violet), **2** (black) and **2an** (red)

Therefore, it can be concluded that dehydration of **1** and **2** strongly increases the intensity of luminescence. Interestingly, the intensity is generally higher for the chloride complexes then for the bromides, and this observation completely agrees with those made by Mercier et al. for viologen-based complexes ("this clearly shows that changing the halide has an influence only on the luminescence intensity")[11]. Probably, there is no general correlation applicable for the whole panoply of polynuclear Bi(III) halides, but it may appear in some particular cases. Anyway, additional studies in this field, allowing the collection of extended statistics, are required.

Solvatochromism is a well-known phenomenon, appearing in diverse classes of compounds, in particular, in metal-organic frameworks[32-34] and various aromatic substrates.[35] Discovery of this effect in the post-transition metal halides provides the opportunities of their further use in development of new materials.

Conclusions

Two new Bi(III) halide complexes with 4,4`-ethylenepyridinium cations have been prepared and characterized. The compounds demonstrate very promising luminescent features which surpass those reporetd for a number of viologen derivatives. A strong impact of solvate composition on these properties and reversibility of solvation in these systems allow us proposing the perspectives of their use in design of advanced chemosensors. We hope that these fact will inspire further research in this field, including variation of aromatic cations used in combination with Bi(III) halides, thus resulting in new, continually improving hybrid materials.

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Notes and references

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Electronic Supplementary Information (ESI) available: Tables of bond lengths and angles in **1** and **2,** thermogravimetry data for **1** and **2**. See DOI: 10.1039/b000000x/

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