This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Binuclear Bi(III) halide complexes with 4,4'-ethylenepyridinium cations: luminescence tuning by reversible solvation

Sergey A. Adonin,*a,b Marianna E. Rakhmanova,∗a Anton I. Smolentsev,∗a,b Ilya V. Korolkov,a Maxim N. Sokolov,a,b and Vladimir P. Fedin*a,b

Two new complexes based on 4,4'-ethylenepyridinium cation and binuclear Bi(III) anionic complexes, (H₂bpe)₂[Bi₂X₁₀]·2H₂O (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 H₂O 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. 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 polynuclear structures, it is based on a number of promising physical properties which these compounds reveal. Most of research is focused on various optical features, for example, thermochromism, which seems to be common for iodobismuthates, 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 {Bi₂Cl₁₀}₂⁺ polymer anions. 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.

Very recently we reported the luminescent behavior of binuclear complex (H₂(4,4'-bipy))₂[Bi₂Cl₁₀]. 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 (λmax 530 nm), but after dehydration the maximum shifts to orange (λmax 560 nm). 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,

as well as the evident tendency to undergo phase transitions, which should affect the physical properties, i.e. 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 – (H₂bpe)₂[Bi₂X₁₀]·2H₂O (X = Cl (1), Br (2); bpe = 1,2-bis(4-hydridyl)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

(H₂bpe)₂[Bi₂Cl₁₀]·2H₂O (1). 100 mg (0.32 mmol) of BiCl₃ 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 C₂₆H₂₆N₂O₂Bi₂Cl₁₀ calcd, %: C, 24.4; H, 2.73; N, 4.7; found, %: C, 24.5; H, 2.82

IR (KBr, 4000-400 cm⁻¹): 3550 m, 3241 m, 3204 s, 3416 s, 3075 s, 3004 w, 1870 w, 1632 s, 1592 s, 1499 s, 1452 w, 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$_2$bpe)$_2$[Bi$_2$Br$_{10}$]$·$2H$_2$O (2). The procedure was similar to those for 1, with BiOBr (68 mg, 22 mmol) and corresponding amount of bpe (41 mg, 22 mmol) and 2M HBr (3 and 3 ml, respectively). Pale yellow crystals of 2 start to form almost immediately; the process is complete in 2h. Yield 96%. For C$_{24}$H$_{32}$N$_4$O$_2$Bi$_2$Br$_{10}$ calecd, %: 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, 1194 s, 1080 w, 1058 w, 1010 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 ml) 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 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 ($λ$ = 0.71073 Å). The standard technique was used (combined $φ$ and $ω$ scans using a photodiode reference detector. Emission spectra were recorded from 350 to 650 nm and corrected for the spherical correction spectra provided by the manufacturer. Additionally, the 1st and 2nd harmonic oscillations of the excitation source were blocked by edge filters (370 nm).

XRD powder analysis was performed on Shimadzu XRD-7000 diffractometer (CuKα 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. 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.

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$_6$]$^{1-}$, 25-29 and binuclear [Bi$_2$X$_{10}$]$^{4-}$, 14-15,30-31. Therefore, the fact that [Bi$_2$X$_{10}$]$^{4-}$ 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 $P1$ and $Z = 2$ and 1, respectively. Despite the same stoichiometry, they show significant differences in their lattice parameters and cannot be considered as isomorphous (Table 1). 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.
accordingly, it would be expected that both compounds share an overall similar structural arrangement composed of discrete ions \( \text{[H}_2\text{bpe}]^{2-} \) and \( \text{[Bi}_2\text{X}_10]^{4-} \), and lattice water molecules, which are held together by various types of hydrogen bonds, namely \( \text{O}--\text{H} \cdots \text{O}, \text{N}--\text{H} \cdots \text{O}, \text{O}--\text{H} \cdots \text{X}, \text{N}--\text{H} \cdots \text{X} \) and \( \text{C}--\text{H} \cdots \text{X} \). The geometric parameters of the \( \text{[H}_2\text{bpe}]^{2-} \) cations have normal values. However, they adopt quite different geometric in 1 and 2 as indicated by the angles between pyridine rings and between pyridine rings and \( \text{C}_3\text{H}_4 \) 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 \( \text{[H}_2\text{bpe}]^{2-} \) 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 \( \text{[H}_2\text{bpe}]^{2-} \) cations in 2 can be described as rather “flattened”.

The \( \text{[Bi}_2\text{X}_10]^{4-} \) anions show a typical dimeric structure consisting of two \( \text{Bi}_x \) edge-sharing octahedra; they are centrosymmetric with the inversion centers midway between the \( \text{Bi} \) atoms. The \( \text{Bi}--\text{Cl} \) and \( \text{Bi}--\text{Br} \) 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 \( \text{Cl}--\text{Bi}--\text{Cl} \) and \( \text{Br}--\text{Bi}--\text{Br} \) 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.

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 \( \text{O}--\text{H} \cdots \text{O}, \text{N}--\text{H} \cdots \text{O}, \text{O}--\text{H} \cdots \text{X} \) and \( \text{N}--\text{H} \cdots \text{X} \) 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 \( \text{C}--\text{H} \cdots \text{X} \) hydrogen bonds between aromatic (mostly) \( \text{H} \) atoms of the \( \text{[H}_2\text{bpe}]^{2-} \) cations and halogen atoms of the \( \text{[Bi}_2\text{X}_10]^{4-} \) anions (with \( \text{H}--\text{Cl} \) and \( \text{H}--\text{Br} \) distances of < 2.95 and 3.05 Å to be compared with the sums of the corresponding van der Waals radii). Finally, aromatic \( \pi--\pi \) stacking and \( \text{C}--\text{H} \cdots \pi \) interactions are observed, although their structural role in the relatively complex packing is not prominent.

![Figure 1. Hydrogen bonding patterns (dashed lines) between the \( \text{[H}_2\text{bpe}]^{2-} \) and \( \text{[Bi}_2\text{X}_10]^{4-} \) 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\cdots O, N--H\cdots O, O--H\cdots X and N--H\cdots 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.](image-url)
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 H2O 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 preferred 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 than 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”)\textsuperscript{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\textsuperscript{32-34} and various aromatic substrates.\textsuperscript{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 reported 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.

Acknowledgements
This work has been supported by Russian Science Foundation (Grant No. 14-23-00013).

Notes and references
\textsuperscript{a} Nikolaev Institute of Inorganic Chemistry, 3 Lavrentieva Av., 630090 Novosibirsk, Russia. E-mail: adonin@niic.nsc.ru
\textsuperscript{b} Novosibirsk State University, Pirogova St. 2, 630090 Novosibirsk, Russia

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/