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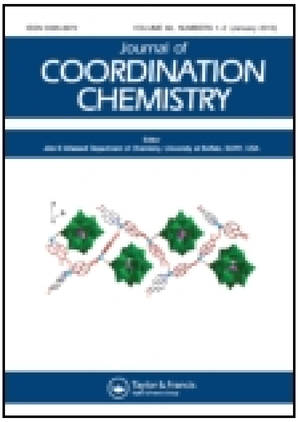

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Supramolecular assemblies of two piperazine metal-organic bismuth(III) derivatives: a new precursor for the preparation of bismuth(III) oxide bromide nano-structures

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Two $BiBr_3$ supramolecular complexes, $[Bi(2\text{-bpmp})Br_{2.06}Cl_{0.94}]$ (**1**) and $[Bi(4\text{-}H_2bpmp)Br_{4.29}Cl_{0.71}]\cdot H_2O$ (**2**) {2-bpmp = N,N′-bis(2-pyridylmethyl)piperazine and 4-bpmp = N,N′-bis(4-pyridylmethyl)piperazine}, were prepared by reaction of bismuth(III) chloride and potassium bromide with two nitrogen donor ligands under thermal gradient conditions using the branched tube method. Compounds **1** and **2** were structurally characterized by single-crystal X-ray diffraction. In monomeric **1,** bismuth is coordinated by two pyridyl and piperazine nitrogens of 2-bpmp, and by three halides. Compound **2** is also monomeric but is bonded to only one pyridyl nitrogen. In both compounds, extensive hydrogen-bonding interactions lead to supramolecular networks; in **2,** the hydrogen bonds are augmented by π–π stacking interactions. Thermal stabilities of both compounds were studied by thermal gravimetric and differential thermal analyses. Thermal decomposition of nanosized **1** and **2** in air produced BiOBr nanoparticles.

Keywords: Bismuth(III); N,N′-Bis(2-pyridylmethyl)piperazine; N,N′-Bis(4-pyridylmethyl)piperazine; Supramolecular complexes; Nanoparticles

Introduction

Metal-organic supramolecular compounds represent an important interface between synthetic chemistry and materials science. Interest has been focused on discrete supramolecular complexes and coordination polymers based on polydentate ligands owing to novel structural topologies and potential applications in sensing, catalysis, ion exchange, separations, or gas storage [1, 2]. Various molecular frameworks have been synthesized by direct chemical combination of selected basic components affected by variables, such as coordination geometry of metal cations, binding site of donating atoms, and the length and shape of spacers [1–4]. Features of counter-ions such as charge, size, geometry, and solvent template effects play roles in self-assembly of functional molecular complexes.

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In contrast to transition metal coordination polymers, formation of polymers with heavy metal ions such as bismuth(III) is surprisingly sparse [5–9] and this is even more true for supramolecular architectures based on Bi(III) [10–12]. Some Bi(III) complexes with spacer ligands such as $\{[Bi(SC_6F_5)_3(thf)(4,4'\text{-bipy})]\}\infty$ [13], $\{[Bi(SC_6F_5)_3(dmf)\{1,2\text{-bis}(4\text{-pyridyl})\text{ethane}\}]\}\infty$ [13], $\{[Bi(SC_6F_5)_3(thf)\{$*trans*$\text{-}1,2\text{-bis}(4\text{-pyridyl})\text{ethene}\}]\cdot thf\}\infty$ [13], $\{[Bi(SC_6F_5)_3\{2,4,6\text{-tris}(4\text{-pyridyl})\text{-}1,3,5\text{-triazine}\}]\}\infty$, $Bi(SC_6F_5)_3\{2,4,6\text{-tris}(2\text{-pyridyl})\text{-}1,3,5\text{-triazine}\}]$ [14], $[BiX_2Ph(4,4'\text{-bipy})]_n$ [12], and $[4,4'\text{-bipyH}]_n^{n-}[Bi(4,4'\text{-bipy})Br4]_n^{n-}$ [15] were recently reported.

In this article, we focus on the simple preparation of two bismuth(III) complexes based on piperazine derivatives, $[Bi(2\text{-bpmp})Br_{2.06}Cl_{0.94}]$ (**1**) and $[Bi(4\text{-}H_2bpmp)Br_{4.29}Cl_{0.71}]\cdot H_2O$ (**2**) {2-bpmp = N,N′-bis(2-pyridylmethyl)piperazine and 4-bpmp = N,N′-bis(4-pyridylmethyl)piperazine} (figure 1). The two nitrogen donors, 2-bpmp and 4-bpmp, have been selected, as they are capable of bridging and thus may be able to form polymeric structures. Recent investigations have addressed the use of these two ligands for the preparation of coordination polymers with other metal ions [16–20]. These studies demonstrated that these long conjugated flexible ligands are capable of coordinating transition metal centers via both terminal pyridyl and the piperazine nitrogens and are able to generate coordination polymers. Subtle changes in these conformationally flexible ligands as spacers and the relative orientations of nitrogens on pyridyl rings towards the piperazine spacer resulted in unusual building blocks, leading to polymeric motifs that have not been achieved using normal rigid bidentate organic ligands. Bi(III) has versatile coordination chemistry and can serve to link bridging ligands to form polymeric compounds with 2-bpmp and 4-bpmp. Attempts to isolate suitable single crystals of $[BiLBr_3]$ and $[BiLBr_3]$, L = 2-bpmp and 4-bpmp were not successful and **1** and **2** crystallized with two different halides, $[Bi(2\text{-bpmp})Br_{2.06}Cl_{0.94}]$ (**1**) and $[Bi(4\text{-}H_2bpmp)Br_{4.29}Cl_{0.71}]\cdot H_2O$ (**2**).

Materials and methods

Physical measurements

With the exception of 2-bpmp and 4-bpmp which were prepared according to literature procedures [16–20], all reagents and solvents for the synthesis and analysis were commercially available and used as received. IR spectra were recorded using a Perkin–Elmer 597 and a Nicolet 510P spectrophotometers. Microanalyses were carried out using a Heraeus CHN-O-Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. The thermal behavior was investigated with a PL-STA 1500 apparatus. Crystallographic measurements were made at 100(2) K using a Bruker AXS SMART APEX CCD diffractometer. The intensity data were collected using graphite-monochromated Mo-K_α radiation. The structures were solved by direct methods and refined by

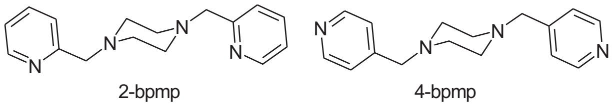

Figure 1. Organic nitrogen donor ligands used in the two bismuth(III) halide complexes.

full-matrix least-squares on F^2. Molecular structure plots were prepared using Mercury [21] and ORTEPIII [22].

In **1**, sites of all halides are occupied by both bromide and chloride which are disordered with each other. The occupancy of bromides are 0.552(3), 0.680(4), and 0.828(4), with the remainder being taken up by chloride. The anisotropic displacement parameters of overlapping Br and Cl were constrained to be identical.

In **2**, three halides show significant disorder of bromide with chloride with occupancy rates for Br3, Br4, and Br5 of 0.903(7), 0.804(7), and 0.585(8), respectively. Overlapping disordered halides were constrained to have identical ADPs. Water hydrogens were placed based on hydrogen bonding considerations using appropriate distance restraints.

Synthesis

To isolate single crystals of [Bi(2-bpmp)$Br_{2.06}Cl_{0.94}$] (**1**) and [Bi(4-H_2bpmp)$Br_{4.29}Cl_{0.71}$]·H_2O (**2**), 1 mmol of 2-bpmp and 4-bpmp and a mixture of 1 mmol of bismuth(III) chloride and 3 mmol of potassium bromide were placed in the main arm of a branched tube. Methanol was carefully added to fill both arms. The tube was sealed and the

Table 1. Crystal data and structure refinement for [Bi(2-bpmp)$Br_{2.06}Cl_{0.94}$] (**1**) and [Bi(4-H_2bpmp)$Br_{4.29}Cl_{0.71}$]·H_2O (**2**).

Identification code	**1**	**2**
Empirical formula	$C_{16}H_{20}BiBr_{2.06}Cl_{0.94}N_4$	$C_{16}H_{24}BiBr_{4.29}Cl_{0.71}N_4O$
Formula weight	675.26	847.60
Temperature	100(2)k	100(2)k
Wavelength	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$Pna2_1$
Unit cell dimensions	$a = 7.8760(4)$ Å	$a = 17.862(3)$ Å
	$b = 15.6282(9)$ Å	b = 8.3158(14) Å
	$c = 16.1089(9)$ Å	$c = 16.151(3)$ Å
	$\alpha = 90°$	$\alpha = 90°$
	$\beta = 99.4116(9)°$	$\beta = 90°$
	$\gamma = 90°$	$\gamma = 90°$
Volume	1956.12(19) $Å^3$	2399.1(7) $Å^3$
Z	4	4
Density (Calcd)	2.293 mg m^{-3}	2.347 mg m^{-3}
Absorption coefficient	13.355 mm^{-1}	14.676 mm^{-1}
Crystal size	0.40 × 0.11 × 0.08	0.12 × 0.1 × 0.04 mm
Theta range for data collection	2.56–31.22°	2.28–30.03°
Index ranges	$-10 \le h \le 10$	$-23 \le h \le 21$
	$-18 \le k \le 20$	$-11 \le k \le 11$
	$-21 \le l \le 20$	$-21 \le l \le 21$
Reflections collected	4856	5871
Independent reflections	4308	4092
Absorption correction	Multi-scan	Multi-scan
Max. and min. transmission	0.103 and 0.344	0.328 and 0.556
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4856/0/229	5871/7/257
Goodness of fit on F^2	1.018	1.023
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0270$	$R_1 = 0.0420$
	$wR_2 = 0.0641$	$wR_2 = 0.0702$
R Indices (all data)	$R_1 = 0.0319$	$R_1 = 0.0860$
	$wR_2 = 0.0657$	$wR_2 = 0.0817$
Largest diff. peak and hole	2.395 and −2.256 e × $Å^{-3}$	1.712 and −1.167 e × $Å^{-3}$

Table 2. Bond lengths (Å) and angles (°) for **1** and **2**.

1		**2**	
Bi(1)–N(3)	2.544(3)	Bi(1)–N(1)	2.658(8)
Bi(1)–N(1)	2.556(3)	Bi(1)–Br(3)	2.8526(18)
Bi(1)–N(2)	2.584(3)	Bi(1)–Br(2)	2.7009(14)
Bi(1)–N(4)	2.590(3)	Bi(1)–Br(4)	3.077(2)
Bi(1)–Cl(1)	2.627(15)	Bi(1)–Br(5)	2.796(10)
Bi(1)–Cl(3)	2.77(4)	Bi(1)–Cl(3)	2.56(4)
Bi(1)–Br(1)	2.789(4)	Bi(1)–Cl(4)	2.62(4)
Bi(1)–Br(2)	2.876(5)	Bi(1)–Cl(5)	2.62(4)
Bi(1)–Cl(2)	2.88(3)	Cl(3)–Bi(1)–Cl(5)	169.0(15)
Bi(1)–Br(3)	2.893(3)	Cl(3)–Bi(1)–N(1)	91.3(10)
N(3)–Bi (1)–N(1)	117.33(11)	Br(3)–Bi(1)–Br(4)	96.26(6)
N(3)–Bi(1)–N(2)	58.06(11)	Cl(4)–Bi(1)–Br(4)	7.1(5)
N(1)–Bi(1)–N(2)	65.05(11)	Br(5)–Bi(1)–Br(4)	83.0(2)
N(3)–Bi(1)–N(4)	65.44(11)	Br(1)–Bi(1)–Br(4)	94.64(5)
N(1)–Bi(1)–N(4)	176.36(11)	Br(2)–Bi(1)–Br(4)	170.52(5)
N(2)–Bi(1)–N(4)	116.30(11)	N(1)–Bi(1)–Br(4)	84.71(18)
N(3)–Bi(1)–Cl(1)	102.5(4)	Cl(5)–Bi(1)–Br(4)	85.6(9)
N(1)–Bi(1)–Cl(1)	93.0(4)	Cl(3)–Bi(1)–Br(4)	83.5(12)
N(2)–Bi(1)–Cl(1)	81.7(3)	Cl(4)–Bi(1)–Br(3)	102.4(5)
N(4)–Bi(1)–Cl(1)	84.0(4)	Br(5)–Bi(1)–Br(3)	171.4(2)
N(3)–Bi(1)–Cl(3)	147.9(8)	Br(1)–Bi(1)–Br(3)	92.33(5)
N(1)–Bi(1)–Cl(3)	89.5(9)	Br(2)–Bi(1)–Br(3)	91.50(5)
N(2)–Bi(1)–Cl(3)	153.4(9)	N(1)–Bi(1)–Br(3)	84.4(2)
N(4)–Bi(1)–Cl(3)	88.7(9)	Cl(5)–Bi(1)–Br(3)	172.9(9)
Cl(1)–Bi(1)–Cl(3)	92.7(9)	Cl(3)–Bi(1)–Br(3)	15.2(13)
N(3)–Bi(1)–Br(1)	101.29(13)	Cl(5)–Bi(1)–N(1)	89.0(9)
N(1)–Bi(1)–Br(1)	90.76(13)	Br(5)–Bi(1)–Cl(4)	77.4(6)
N(2)–Bi(1)–Br(1)	78.49(13)	Br(1)–Bi(1)–Cl(4)	90.9(6)
N(4)–Bi(1)–Br(1)	86.29(13)	Br(2)–Bi(1)–C(l4)	166.0(6)
Cl(1)–Bi(1)–Br(1)	3.4(4)	N(1)–Bi(1)–Cl(4)	88.8(6)
Cl(3)–Bi(1)–Br(1)	95.2(8)	Cl(5)–Bi(1)–Cl(4)	79.9(11)
N(3)–Bi(1)–Br(2)	80.25(11)	Cl(3)–Bi(1)–Cl(4)	89.1(13)
N(1)–Bi(1)–Br(2)	86.09(11)	Br(1)–Bi(1)–Br(5)	96.2(2)
N(2)–Bi(1)–Br(2)	100.19(10)	Br(2)–Bi(1)–Br(5)	88.5(2)
N(4)–Bi(1)–Br(2)	96.85(11)	N(1)–Bi(1)–Br(5)	87.1(3)
Cl(1)–Bi(1)–Br(2)	177.2(4)	Cl(5)–Bi(1)–Br(5)	3.1(11)
Cl(3)–Bi(1)–Br(2)	84.7(8)	Cl(3)–Bi(1)–Br(5)	166.5(12)
Br(1)–Bi(1)–Br(2)	176.86(13)	Br(2)–Bi(1)–Br(1)	90.46(4)
N(3)–Bi(1)–Cl(2)	77.9(5)	N(1)–Bi(1)–Br(1)	176.55(19)
N(1)–Bi(1)–Cl(2)	84.6(5)	Cl(5)–Bi(1)–Br(1)	94.4(9)
N(2)–Bi(1)–Cl(2)	96.4(3)	Cl(3)–Bi(1)–Br(1)	85.2(9)
N(4)–Bi(1)–Cl(2)	98.5(5)	N(1)–Bi(1)–Br(2)	90.66(18)
Cl(1)–Bi(1)–Cl(2)	177.4(6)	Cl(5)–Bi(1)–Br(2)	86.1(9)
Cl(3)–Bi(1)–Cl(2)	88.2(9)	Cl(3)–Bi(1)–Br(2)	104.9(12)
Br(1)–Bi(1)–Cl(2)	174.2(4)		
Br(2)–Bi(1)–Cl(2)	3.8(4)		
N(3)–Bi(1)–Br(3)	150.09(10)		
N(1)–Bi(1)–Br(3)	88.46(10)		
N(2)–Bi(1)–Br(3)	151.66(10)		
N(4)–Bi(1)–Br(3)	89.55(10)		
Cl(1)–Bi(1)–Br(3)	90.2(4)		
Cl(3)–Bi(1)–Br(3)	2.7(8)		
Br(1)–Bi(1)–Br(3)	92.69(12)		
Br(2)–Bi(1)–Br(3)	87.17(8)		
Cl(2)–Bi(1)–Br(3)	90.6(4)		

ligand-containing arm was immersed in an oil bath at 60 °C, while the other arm was kept at an ambient temperature. After 7–10 days, colorless crystals of **1** and **2** that deposited in the cooler arm were isolated. The single crystals were filtered off, washed with acetone and ether, and air dried.

Product 1. d.p. = 210 °C. Found: C, 28.50; H, 2.80; N, 8.40%. Calcd for $C_{16}H_{20}BiBr_{2.06}Cl_{0.94}N_4$: C, 28.43; H, 2.96; N, 8.29%. IR (cm^{-1}, KBr) bands: 439m, 630w, 772s, 797s, 1004s, 1081s, 1288m, 1438vs, 1589s, 2900s and 3025w.

Product 2. d.p. = 260 °C. Found: C, 22.50; H, 2.10; N, 6.50%. Calcd for $C_{16}H_{24}BiBr_{4.29}Cl_{0.71}N_4O$: C, 22.18; H, 2.77; N, 6.47%. IR (cm^{-1}, KBr) bands: 408w, 493w, 786m, 1016s, 1214m, 1364m, 1416s, 1490w, 1627s, 2765s, 2935vs and 3435s.

Results and discussion

Reaction of 2-bpdb and 4-bpmp with a mixture of bismuth(III) chloride and potassium bromide provided crystalline materials of $[Bi(2\text{-}bpmp)Br_{2.06}Cl_{0.94}]$ (**1**) and $[Bi(4\text{-}H_2bpmp)Br_{4.29}Cl_{0.71}]\cdot H_2O$ (**2**), respectively. IR spectra of these compounds show absorptions for 2-bpmp and 4-bpmp such as typical pyridyl vibrations at 1400–1580 cm^{-1}, and the elemental analysis data agree well with the numbers expected for the formulas.

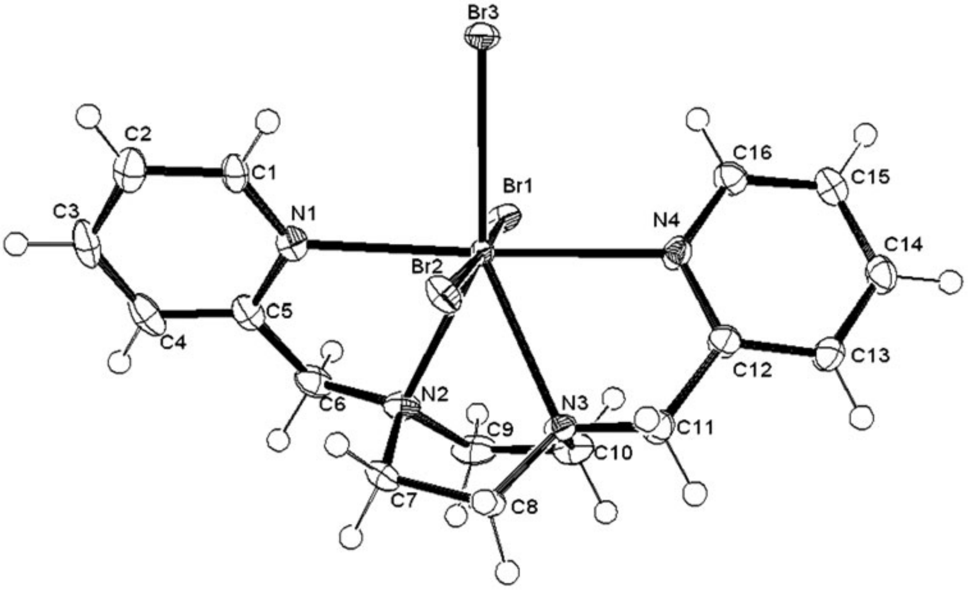

Figure 2. X-ray crystal structure showing the linking of 2-bpmp in $[Bi(2\text{-}bpmp)Br_{2.06}Cl_{0.94}]$ (**1**) (30% thermal displacement ellipsoids). The minor chlorides are omitted for clarity.

The solid-state structures of both complexes were determined by single-crystal X-ray diffraction analysis (tables 1 and 2 and figures 2–5). The structure of **1** shows monomeric units (figure 2). The halides are disordered among bromide and chloride with occupancies in favor of bromide of 0.552(3), 0.680(4), and 0.828(4). Bismuth ions are linked by four nitrogens of 2-bpmp and by three halides, thus forming a seven-coordinate complex with a Hal_3N_4 array of donor atoms. The aromatic rings of coordinated 2-bpmp are parallel and π–π stacking is observed between individual pyridyl rings. The distance between the centers is 3.813(1) Å (figure 3(a)). Hydrogens of py rings are also involved in C–H···Br interactions, acting as weak hydrogen-bond donors towards Br^- (figure 3(a)). Consequently, the monomeric structure is grown by weak hydrogen bonds and π–π stacking interactions into a 3-D network (figure 3(b)).

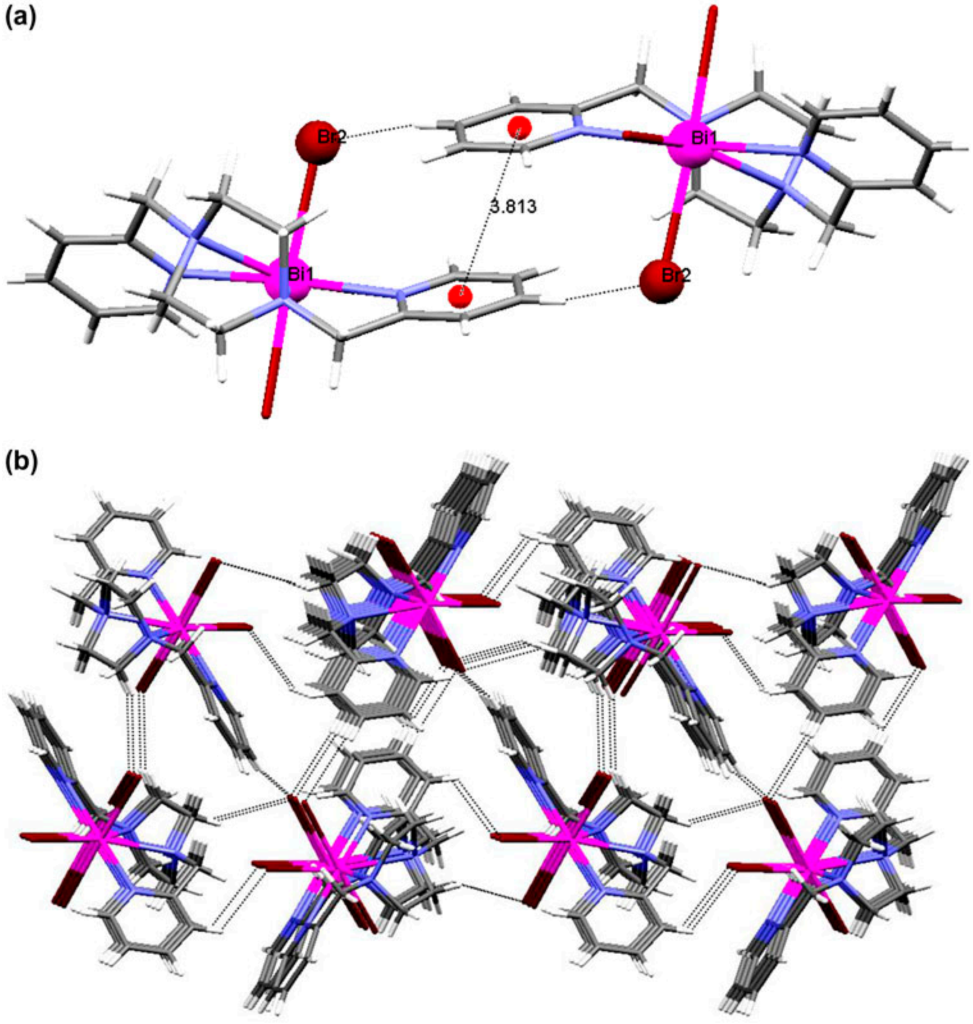

Figure 3. (a) Display of the C–H···Br and π–π stacking interactions and (b) the 3-D supramolecular structure in $[Bi(2\text{-bpmp})Br_{2.06}Cl_{0.94}]$ (**1**).

The molecular structure of **2** consists of a [Bi(4-H_2bpmp)$Br_{4.29}Cl_{0.71}$] unit and one lattice H_2O (figure 4). In **2**, three of the halides show significant disorder of bromide with chloride with occupancy rates for Br of 0.903(7), 0.804(7), and 0.585(8) for Br3, Br4, and Br5, respectively, with the actual composition of **2** being [Bi(4-H_2bpmp) $Br_{4.29}Cl_{0.71}$]·H_2O. The complex is monomeric and monometallic. The ligand is coordinated to only one bismuth via a pyridyl and 2-bpmp is protonated to yield H_2bpmp^{2+}. The coordination number of Bi in this compound is six with a distorted octahedral coordination environment. The molecules of **2** are linked by N-H···O_{water} and N–H···Br hydrogen bonds (figure 5). Consequently, the monomeric structure is grown by the

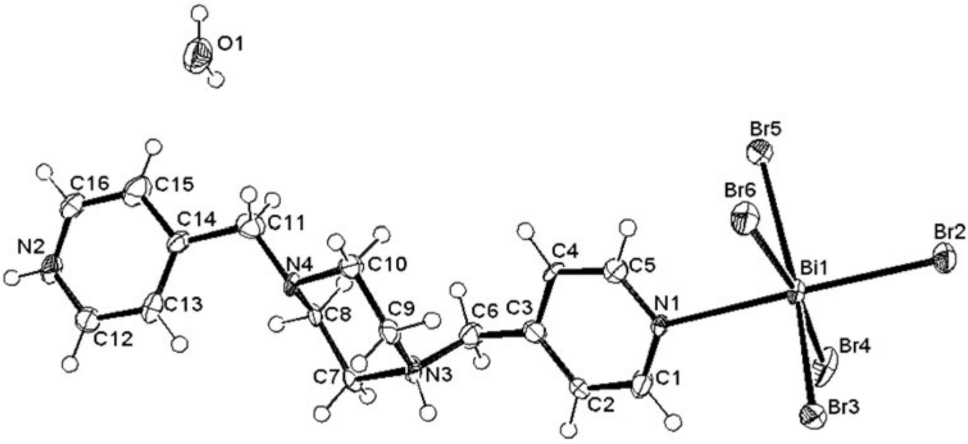

Figure 4. X-ray crystal structure of [Bi(4-H_2bpmp)$Br_{4.29}Cl_{0.71}$]·H_2O (**2**) (30% thermal displacement ellipsoids). Minor chlorides are omitted for clarity.

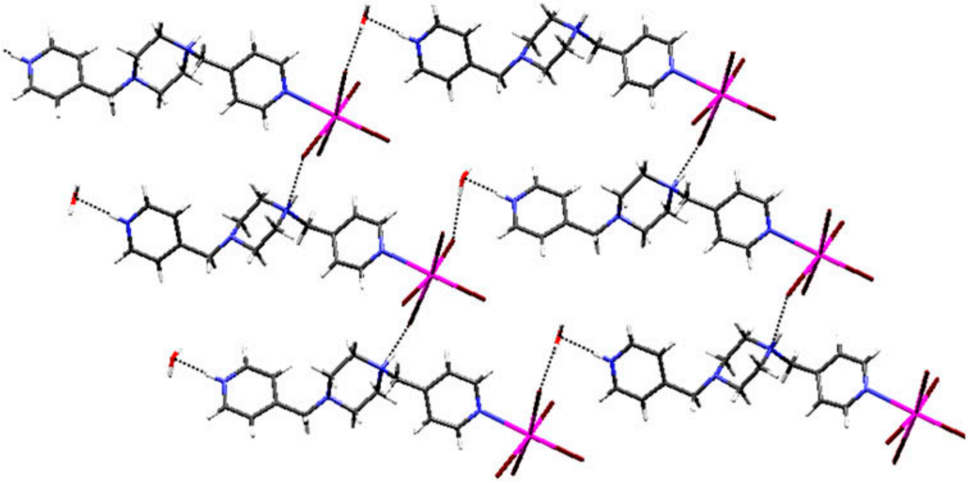

Figure 5. The 2-D supramolecular structure generated via N–H···O_{water} and N–H···Br interactions in [Bi(4-H_2bpmp)$Br_{4.29}Cl_{0.71}$]·H_2O (**2**).

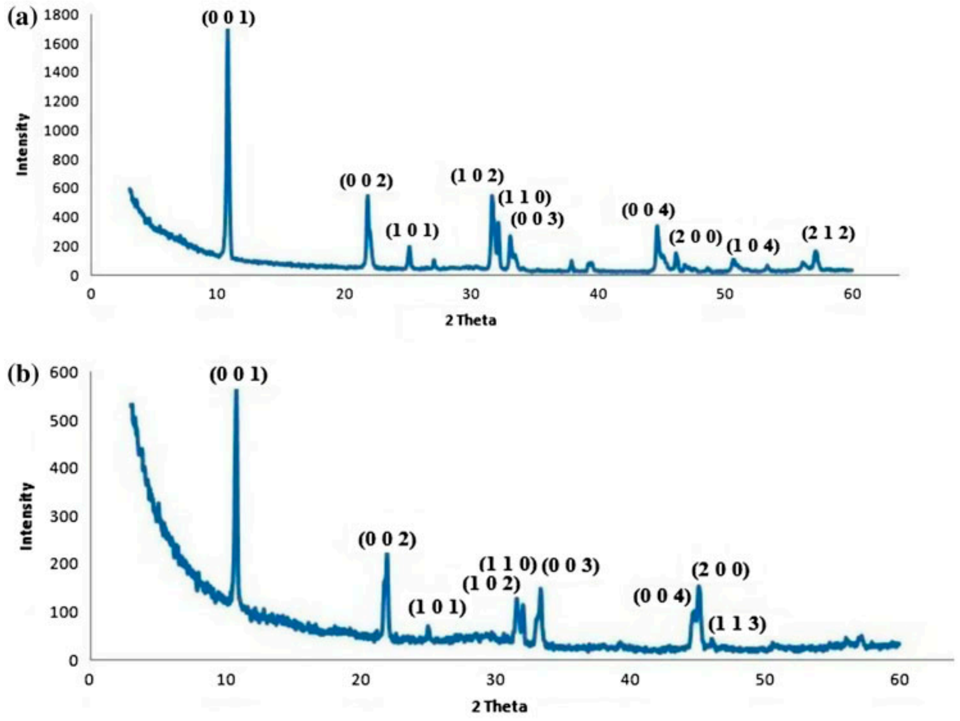

Figure 6. (a) XRD patterns of BiOBr nanostructures prepared by calcinations of **1** under air and (b) XRD patterns of BiOBr nanostructures prepared by calcinations of **2** under air.

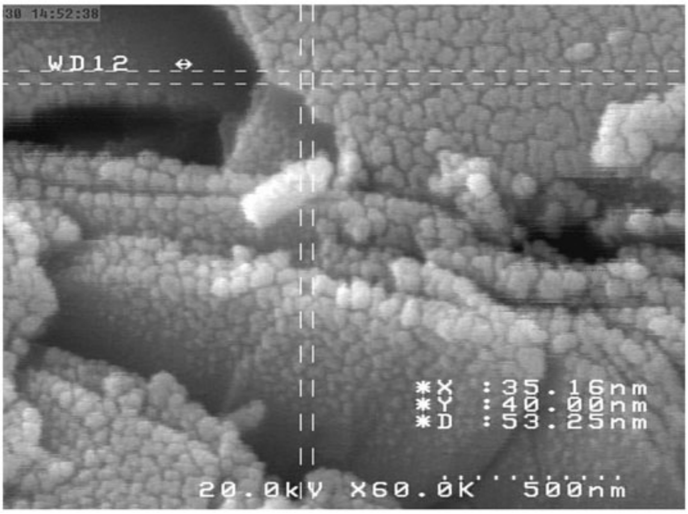

Figure 7. SEM photographs of BiOBr nanostructures (produced by calcination of **1** under air).

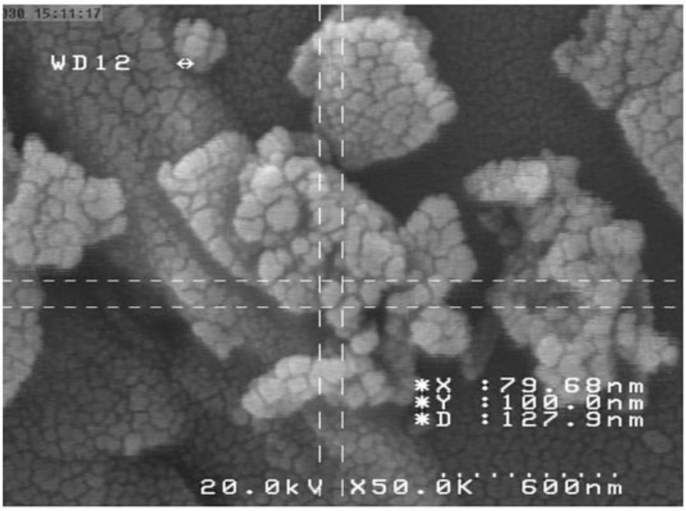

Figure 8. SEM photographs of BiOBr nanoparticles (produced by calcination of **2** under air).

weak hydrogen bonds into a 3-D network (figure 5). The XRD patterns simulated from single-crystal X-ray data of **1** and **2** and experimental powders are shown in Supplementary material. Supramolecular compounds generated from hydrogen bonding between protonated ligands have been reported [16, 23–25].

Thermogravimetric analysis

To examine the thermal stabilities of **1** and **2**, thermal gravimetric (TG) and differential thermal analyses (DTA) were carried out between 30 and 700 °C in a static atmosphere of nitrogen. Compound **1** is stable to 182 °C. It starts to decompose at about 182 °C and **1** decomposes in three steps until the final decomposition product $BiBr_{2.06}Cl_{0.94}$ (mass loss of 59.80%, Calcd 60.26%) is formed at 580 °C. The DTA curve displays an exothermic peak at 272 °C (Supplementary material) due to the decomposition of N,N′-bis (2-pyridylmethyl)piperazine (2-bpmp). The TG curve of **2** indicates that this compound is stable to 195 °C at which the removal of H_2O and $4\text{-}H_2bpmp^{2-}$ occurs (mass loss of 36.90%, Calcd 36.00%) and the decomposition is finished at 560 °C with two exothermic peaks at 344 and 478 °C (Supplementary material). The final decomposition product is suggested to be BiOBr (mass loss of 26.80%, Calcd 27.48%). In both **1** and **2,** the final product is BiOBr.

Thermal decomposition of the nanosized particles of **1** and **2** in air produced BiOBr nanoparticles, as established by their powder XRD patterns (figure 6(a) and (b)). Figures 7 and 8 show SEM images of BiOBr nanostructures from calcination of **1** and **2** under air. The morphology of **1** is a cluster of aggregated slabs and is not homogeneous with particles in the range of 35 nm. The morphology of **2** is large bulk particles with high agglomeration of 70 nm. The nanoparticles show a high degree of crystalline with sharp and well-defined peaks in the XRD pattern and JCPDS Card No. 09-0393 for BiOBr. Our work represents examples of coordination polymers used as precursors for the preparation of BiOBr nanoparticles [26–32].

Conclusions

Two bismuth(III) complexes with N,N′-bis(2-pyridylmethyl)piperazine (2-bpmp) and N,N′-bis(4-pyridylmethyl)piperazine (4-bpmp), [Bi(2-bpmp)$Br_{2.06}Cl_{0.94}$] (**1**) and [Bi(4-H_2bpmp)$Br_{4.29}Cl_{0.71}$]·H_2O (**2**) have been synthesized using the branched tube method. In assembly of **1** and **2**, factors such as metal, anions, solvent, and metal/ligand ratio are kept constant and the only variable parameter is the place of one of the donors in 2-bpmp and 4-bpmp. Coordination of the two ligands is quite different and the compounds are structurally diverse, but both showing monomeric structures. In **1**, 2-bpmp is not bridged but is only coordinated via four nitrogens. In **2**, 2-bpmp is protonated, similar to $[4,4'\text{-bipyH}]_n^{n-}$[Bi(4,4′-bipy)Br4$]_n^{n-}$ [13], to yield H_2bpmp^{2+}, only rarely seen for metal coordination polymers with this type of ligands [14–18]. Bi^{+3} may be the node of choice when one wants to prepare supramolecular compounds that contain protonated pyridyl ligands. Thermal decomposition of nanosized particles of **1** and **2** in air produced BiOBr nanoparticles.

Supplementary material

Crystallographic data for the structures reported in the article have been deposited with the Cambridge Crystallographic Data Centre as Supplementary publication no CCDC 699800 and 699799 for **1** and **2**, respectively. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44 1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

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