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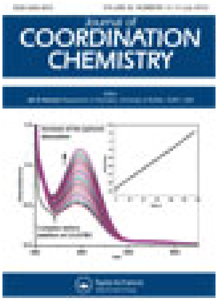

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Three coordination polymers built from planar tetranuclear clusters and 5-sulfoisophthalic acid

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Three coordination polymers built from planar tetranuclear clusters and 5-sulfoisophthalic acid

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Three coordination polymers built from planar tetranuclear clusters and H_3sip ligands, Pb_2Cl(sip)(bipy) (**1**), Pb_2Br(sip)(H_2O) (**2**), and $Ni_4(sip)_2(pyz)_2(H_2O)_8(OH)_2 \cdot 2H_2O$ (**3**) (H_3sip = 5-sulfoisophthalic acid, bipy = 2,2′-bipyridine, and pyz = pyrazine), have been hydrothermally synthesized and characterized by IR, TGA, and single-crystal X-ray diffraction. Compound **1** features a 2-D layer-like structure containing tetranuclear square $[Pb_4(SO_3)_2]$ clusters. Complex **2** has a 3-D open framework architecture constructed from tetranuclear cluster $[Pb_4Br_2(SO_3)_2]$ inorganic building blocks. The tetranuclear units, $[Ni_4(OH)_2(COO)_4]$, in **3** are interlinked through carboxylates and μ_2-pyz ligands to generate a 2-D layer structure. The connecting modes between tetranuclear clusters and organic ligands in the three compounds are discussed in this article. In the solid state at room temperature, yellow photoluminescence in **1** and **2** are observed.

Keywords: Hydrothermal syntheses; Planar tetranuclear clusters; 5-Sulfoisophthalic acid; Crystal structure; Photoluminescence

1. Introduction

Polynuclear metal complexes (clusters) derived from polydentate ligands receive attention because of their physicochemical properties [1–6] and relevance to active centers in biological systems [7–9]. Most polynuclear compounds have been prepared by self-assembly originating from multifunctional character of the ligands and labile coordination bonds, giving unpredictable structural motifs. This constitutes a "trial and error" method and the experience gained in each step is used to design new synthetic routes. Design and preparation of high-dimensional hybrid compounds self-assembled from polynuclear metal clusters remains a challenge in the material sciences.

Aromatic polycarboxylates containing sulfonic groups, such as 5-sulfoisophthalic acid (H_3sip), are potential multifunctional ligands due to their structural rigidity, chemical stability, and appropriate connectivity [10–13]. Although a large number of hybrid materials assembled from H_3sip and metal ions have been reported [14–17], the number of hybrid frameworks constructed from H_3sip and polynuclear metal

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clusters is limited [18–21]. Tetranuclear units among the polynuclear clusters include cubane-like [$Pb_4(\mu_3\text{-}OH)_2(COO)_2$], chair-structure [$Pb_4(\mu_3\text{-}OH)_2$], butterfly-like [$Pb_4(\mu_3\text{-}OH)_2$] and [$Ni_4F_2(COO)_4$], in which the carboxylate(hydroxyl)-bridged tetranuclear clusters feature distorted tetrahedral geometry [22–24]; hybrid compounds constructed from tetranuclear cluster units with planar geometry have been seldom reported. Two polymeric copper complexes formed from [$Cu_4(\mu_3\text{-}OH)(COO)_4$], in which the four copper ions are engaged by two μ_3-OH and four carboxylates of sip^{3-} to form a planar tetranuclear cluster, have been isolated by the Cao group [25].

To further understand the coordination chemistry of H_3sip, and its hybrid polymers built from polynuclear clusters, we use sip^{3-} to examine the coordination polymer chemistry of Pb^{2+} and Ni^{2+}, two 2-D coordination polymers, and one 3-D open framework complex built from H_3sip and planar tetranuclear clusters, $Pb_2Cl(sip)(bipy)$ (**1**), $Pb_2Br(sip)(H_2O)$ (**2**), and $Ni_4(sip)_2(pyz)_2(H_2O)_8(OH)_2{\cdot}2H_2O$ (**3**) (H_3sip = 5-sulfoisophthalic acid, bipy = 2,2′-bipyridine, pyz = pyrazine), will be presented with regard to its hydrothermal syntheses, crystal structures, characterizations, and photoluminescent properties. The basic building block in **1**, [$Pb_4(SO_3)_2$], with four Pb ions bridged by two sulfates of sip^{3-}, generate an unusual planar tetranuclear cluster, unusual in polynuclear complexes containing H_3sip.

2. Experimental

2.1. *Materials and methods*

All reagents were AR grade, commercially available and used without purification. IR spectra were recorded on a Perkin Elmer Spectrum 2000 FTIR spectrophotometer using KBr discs. C, H, and N elemental analyses were carried out on a Perkin Elmer elemental analyzer. The thermogravimetric analysis curve was obtained on a NETZSCH STA 449C thermogravimetric analyzer in flowing N_2 with a temperature ramp rate of $10^\circ C\,min^{-1}$. Excitation and emission spectra were obtained on an Edinburgh Instruments analyzer model FL920 spectrofluorometer.

2.2. *Preparation of $Pb_2Cl(sip)(bipy)$ (1)*

A mixture of $PbCl_2$ (0.4272 g, 1.5 mmol), NaH_2sip (0.2681 mg, 1 mmol), 2,2′-bipy (0.0157 g, 1 mmol), NaOH, (0.0482 g, 1.2 mmol) and water (15 mL) was placed in a 25 mL Teflon-lined stainless autoclave under autogenous pressure at 170°C for 4 days; colorless block-like crystals of **1** were obtained when the sample was cooled to room temperature at $5^\circ C\,h^{-1}$. The crystals were recovered by filtering, washed with distilled water, and dried in air (yield 58.6% based on Pb). Anal. Calcd for $C_{36}H_{22}Cl_2N_4O_{14}Pb_4S_2$ (1698.36): C, 25.44; H, 1.29; N, 3.30. Found: C, 25.32; H, 1.34; N, 3.39. IR spectrum (KBr pellet, cm^{-1}): 1757 s, 1654 s, 1600 s, 1592 ms, 1544 vs, 1477 s, 1490 s, 1361 s, 1312 m, 1241w, 1101 s, 1039 s, 1012 s, 923 m, 774 s, 720 ms, 644 ms, 609 s, 628 w, 452 w, 406 ms.

2.3. *Preparation of $Pb_2Br(sip)(H_2O)$ (2)*

A mixture of $PbBr_2$ (0.5505 g, 1.5 mmol), NaH_2sip (0.2682 mg, 1 mmol), NaOH (0.0482 g, 1.2 mmol), and water (15 mL) was placed in a 25 mL Teflon-lined stainless steel autoclave under autogenous pressure at 170°C for 3 days; colorless block-like crystals of **2** were obtained when the sample was cooled to room temperature at 5°C h^{-1}. The crystals were recovered by filtering, washed with distilled water, and dried in air (yield 51.3% based on Pb). Anal. Calcd for $C_8H_5BrO_8Pb_2S$ (755.47): C, 12.71; H, 0.66. Found: C, 12.86; H, 0.71. IR spectrum (KBr pellet, cm^{-1}): 3517 ms, 3381 ms, 1769 s, 1658 s, 1603 ms, 1594 ms, 1554 vs, 1479 m, 1494 s, 1365 s, 1310 m, 1246w, 1100 s, 1038 ms, 1011 s, 920 m, 764 s, 715 ms, 650 ms, 601 ms, 634 w, 454 w, 401 ms.

2.4. *Preparation of $Ni_4(sip)_2(pyz)_2(H_2O)_8(OH)_2 \cdot 2H_2O$ (3)*

A mixture of $NiSO_4 \cdot 7H_2O$ (0.3943 g, 1.5 mmol), NaH_2sip (0.3433 mg, 1.2 mmol), pyrazine (0.1201 g, 1.5 mmol), NaOH (0.0601 g, 1.5 mmol), and water (15 mL) was placed in a 25 mL Teflon-lined autoclave under autogenous pressure at 165°C for 4 days and green block-like crystals of **3** were obtained when the sample was cooled to room temperature at 5°C h^{-1}. The crystals were recovered by filtering, washed with distilled water, and dried in air (yield 48.9% based on Ni). Anal. Calcd for $C_{20}H_{28}N_2Ni_4O_{26}S_2$ (1011.4): C, 23.73; H, 2.77; N, 2.77. Found: C, 23.54; H, 2.86; N, 2.81. IR spectrum (KBr pellet, cm^{-1}): 3511 s, 3369 ms, 2348 w, 1833 w, 1685 w, 1610 s, 1565 s, 1438 s, 1377 s, 1208 s, 1177 ms, 1126 w, 1105 ms, 1073 ms, 1048 s, 1073 w, 1001 ms, 925 w, 849 w, 771 ms, 722 w, 669 ws, 620 ms, 547 w, 493 w.

2.5. *Single-crystal structure determination*

Single crystals of **1**–**3** were mounted on a Rigaku Mercury CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 K. The intensity data sets were collected with the ω scan technique and reduced using CrystalClear software [26]. The structures were solved by direct methods and refined by full-matrix least-squares. Non-hydrogen atoms were located by difference Fourier map and subjected to anisotropic refinement. Hydrogen atoms were added according to theoretical models. All the calculations were performed by Siemens SHELXTL^{TM} version 5 package of crystallographic software [27]. The final difference Fourier maps for **1** and **2** show residual peaks of 3.79 e Å^{-3} (0.04 Å from Pb(2)) and holes of −4.02 e Å^{-3} (0.71 Å from Pb(2)), residual peaks of 3.23 e Å^{-3} (1.38 Å from Pb(1)) and holes of −3.22 e Å^{-3} (0.96 Å from Pb(1)), respectively, and the relatively higher residuals are mainly due to the absorption correction problems with the heavy Pb(II). Crystallographic data and structural refinements as well as the selected bond distances and angles for the three complexes are summarized in tables 1 and 2.

3. Results and discussion

3.1. *Crystal structure description of 1*

X-ray single-crystal analysis reveals that **1** features a 2-D layer-like architecture constructed from tetranuclear lead(II) motifs as a secondary building block. As depicted in figure 1, the asymmetric unit of **1** contains two crystallographically independent lead(II) ions, one sip^{3-}, one 2,2′-bipy and one chloride. Pb(1) is

Table 1. Crystal data and structure refinements for **1**, **2**, and **3**.

Complexes	**1**	**2**	**3**
Formula	$C_{36}H_{22}Cl_2N_4O_{14}Pb_4S_2$	$C_8H_5BrO_8Pb_2S$	$C_{20}H_{28}N_2Ni_4O_{26}S_2$
Molecular weight	1698.36	755.47	1011.40
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_1/c$	I mma
Unit cell dimensions (Å, °)			
a	14.099(3)	8.3883(17)	14.972(3)
b	11.153(2)	14.892(3)	17.087(3)
c	15.143(7)	12.354(4)	13.063(3)
β	118.81(2)	123.82(2)	
Volume (Å^3), Z	2086.4(11), 2	1282.1(6), 4	3341.9(12), 4
Calculated density (Mg m^{-3})	2.703	3.914	2.010
Absorption coefficient (mm^{-1})	16.390	29.541	2.451
$F(000)$	1544	1328	2056
Crystal size (mm^3)	0.26 × 0.25 × 0.17	0.35 × 0.29 × 0.25	0.46 × 0.24 × 0.20
θ range for data collection (°)	3.07–27.92	3.23–27.45	3.12–27.40
Limiting indices	$-18 \le h \le 18$,	$-10 \le h \le 10$,	$-16 \le h \le 19$,
	$-14 \le k \le 14$,	$-19 \le k \le 19$,	$-22 \le k \le 21$,
	$-19 \le l \le 19$	$-12 \le l \le 15$	$-16 \le l \le 16$
Reflections collected/unique (R_{int})	19,951	11,842	15,632
Independent reflection	4759 [R(int) = 0.0983]	2859 [R(int) = 0.0948]	2033 [R(int) = 0.0429]
Data/restraints/parameters	4759/12/281	2859/3/182	2033/6/160
Goodness-of-fit on F^2	1.037	1.033	1.087
Final R indices [I > 2δ(I)]	$R_1 = 0.0593$, $wR_2 = 0.1578$	$R_1 = 0.0498$, $wR_2 = 0.1288$	$R_1 = 0.0284$, $wR_2 = 0.0661$
Largest difference peak and hole (e Å^{-3})	3.791 and −4.024	3.233 and −3.221	0.636 and −0.490

Table 2. Selected bond lengths (Å) and angles (°) for **1**, **2**, and **3**.

Compound **1**			
Pb(1)–O(6)#1	2.544(10)	N(2)–Pb(1)–N(1)	63.3(5)
Pb(1)–N(2)	2.547(15)	O(6)#1–Pb(1)–O(2)	73.4(4)
Pb(1)–N(1)	2.596(16)	O(6)#1–Pb(1)–O(5)#2	108.2(4)
Pb(1)–O(2)	2.651(9)	N(2)–Pb(1)–O(5)#2	139.3(4)
Pb(1)–O(5)#2	2.678(10)	N(2)–Pb(1)–O(7)#1	86.1(5)
Pb(1)–O(7)#1	2.757(12)	O(2)–Pb(1)–O(7)#1	121.5(3)
Pb(2)–O(4)#3	2.400(11)	O(5)#2–Pb(1)–O(7)#1	71.1(3)
Pb(2)–O(1)	2.567(9)	O(4)#3–Pb(2)–O(1)	76.7(3)
Pb(2)–Cl(1)	2.581(5)	O(4)#3–Pb(2)–O(8)#4	151.7(3)
Pb(2)–O(8)#4	2.755(11)	O(1)–Pb(2)–O(8)#4	75.0(3)
Compound **2**			
Pb(1)–O(6)#1	2.403(12)	Pb(2)–O(1)#4	2.636(12)
Pb(1)–O(5)#2	2.511(11)	Pb(2)–O(7)#2	2.673(12)
Pb(1)–O(3)	2.595(13)	Pb(2)–O(8)	2.679(13)
Pb(1)–Br(1)	2.9442(18)	Pb(2)–Br(1)#5	3.109(2)
Pb(2)–O(4)#3	2.515(12)	Pb(2)–Br(1)	3.2003(19)
Pb(2)–O(2)	2.546(12)	Br(1)–Pb(2)#5	3.109(2)
O(6)#1–Pb(1)–O(5)#2	97.6(4)	O(1)#4–Pb(2)–O(8)	138.6(4)
O(6)#1–Pb(1)–O(3)	76.8(4)	O(7)#2–Pb(2)–O(8)	67.2(4)
O(5)#2–Pb(1)–O(3)	158.4(5)	O(4)#3–Pb(2)–Br(1)#5	81.0(3)
O(4)#3–Pb(2)–O(2)	68.7(4)	O(4)#3–Pb(2)–Br(1)	147.8(3)
O(2)–Pb(2)–O(1)#4	73.7(4)	O(2)–Pb(2)–Br(1)	83.1(3)
O(2)–Pb(2)–O(7)#2	144.7(3)	O(7)#2–Pb(2)–Br(1)	94.5(2)
O(1)#4–Pb(2)–O(7)#2	71.7(4)	O(8)–Pb(2)–Br(1)	113.5(3)
O(2)–Pb(2)–O(8)	145.3(4)	Br(1)#5–Pb(2)–Br(1)	76.96(5)
Compound **3**			
Ni(1)–O(3)	2.023(2)	O(3)–Ni(1)–O(2)#1	92.70(6)
Ni(1)–O(2)#1	2.0656(17)	O(3)–Ni(1)–O(1)	91.31(6)
Ni(1)–O(2)#2	2.0656(17)	O(2)#1–Ni(1)–O(1)	175.21(7)
Ni(1)–N(1)	2.091(3)	O(5)#1–Ni(2)–O(3)	95.15(7)
Ni(1)–O(1)	2.1149(18)	O(3)–Ni(2)–O(4)#1	177.83(7)
Ni(1)–O(1)#3	2.1149(18)	O(5)–Ni(2)–O(4)	86.82(7)
Ni(2)–O(5)#1	2.0672(15)	O(5)–Ni(2)–O(3)	87.95(7)
Ni(2)–O(3)#2	2.0751(14)	O(3)–Ni(2)–O(4)	94.60(6)
Ni(2)–O(4)#1	2.0968(18)	O(4)#1–Ni(2)–O(4)	86.30(10)

Symmetry codes: for **1**, #1: x, $-y-3/2$, $z-1/2$; #2: x, $y+1$, z; #3: x, $-y-3/2$, $z+1/2$; #4: $-x$, $-y-1$, $-z-1$; for **2**, #1: $-x,y-1/2,-z+1/2$; #2: $x+1$, y, $z+1$; #3: $-x,y+1/2$, $-z+1/2$; #4: $-x+1$, $-y$, $-z+1$; #5: $-x$, $-y$, $-z+1$; for **3**, #1: x, $-y+1$ $-z+2$; #2: $-x+2$, $-y+1$, $-z+2$; #3: $-x+2$, y, z.

surrounded by two nitrogen atoms of 2,2′-bipy and five oxygen atoms from four sip^{3-} with three from carboxylates (O(5 A), O(6C), and O(7C), symmetry code for A: x, $1+y$, z; and for C: x, $-1.5-y$, $-0.5+z$) and two from sulfates (O(2) and O(3B), B: $-x$, $-1-y$, $-1-z$). The seven-coordinate Pb(1) environment lies 1.35 Å above the plane defined by O(3B), O(5 A), O(6C), and O(7C), and N(1), N(2), and O(2) indicate a stereochemically active lone pair of electrons on Pb(1) [28]. Pb(1)–O distances range from 2.544(10) to 2.779(11) Å, in which the Pb(1)–O(3B) bond of 2.779(11) Å is slightly longer than the Pb(1)–O(7C) bond [2.758(13) Å]. Five-coordinate Pb(2) lies 0.22 Å above the plane defined by O(1), O(3B), O(4D), and O(7 A), while Cl(1) is 2.34 Å below the plane. The coordination sphere on Pb(2) is rather one-sided, indicating a stereochemically active lone pair of electrons on Pb(2). Pb(2)–O distances

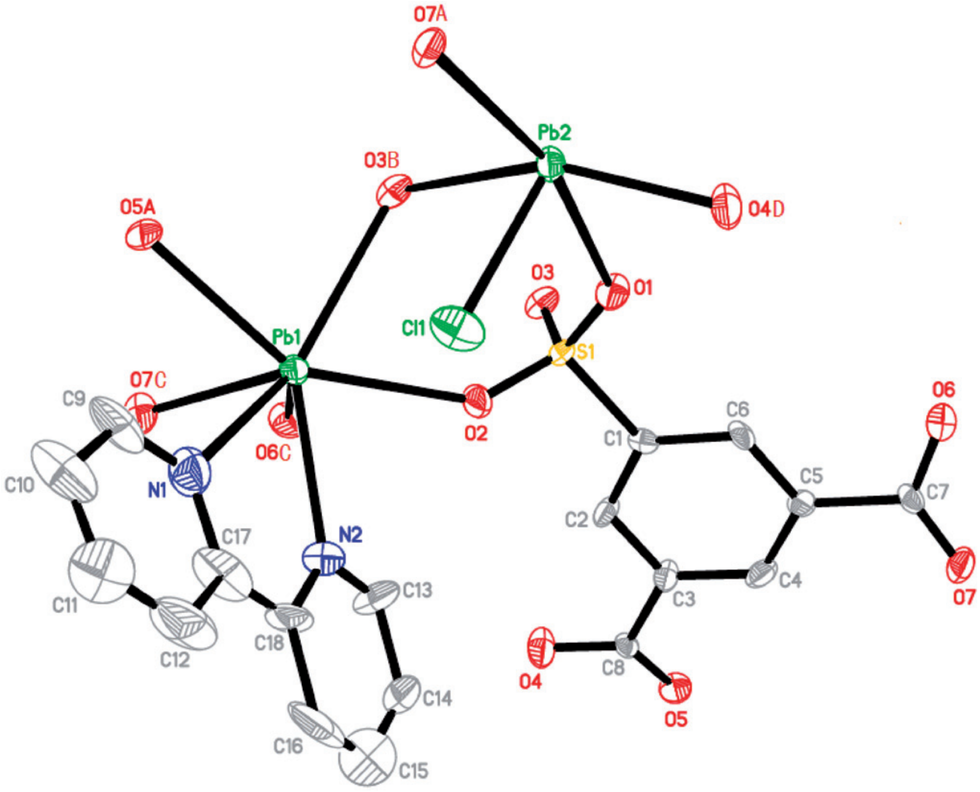


Figure 1. The molecular structure of **1**. All hydrogen atoms have been omitted for clarity.

[2.400(11)–2.850(12) Å] are similar to those in the seven-coordinate Pb(1). Pb–O bond lengths in **1** fall in the range of those previously reported [29].

As shown in figure 2, Pb1, Pb2, Pb1A, and Pb2A (A: $-x, -1-y, -1-z$) in the structure of **1** are linked by two sulfonates from different sip^{3-} ligands generating a planar Pb_4 cluster, in which the largest deviation of O(1), O(2), and O(3) of $-SO_3$ from the Pb(1), Pb(2), Pb(1 A), and Pb(2 A) plane is 1.7167, 1.7697, and 1.1411 Å, respectively. The Pb(1) $\cdots$ Pb(2) and Pb(1 A) $\cdots$ Pb(2) separations are 4.540(2) and 4.672(1) Å, respectively, and the Pb(1 A)–Pb(2)–Pb(1) and Pb(2)–Pb(1)–Pb(2 A) angles are 89.69(2) and 90.31(2)°, respectively. Such planar tetranuclear cluster $[Pb_4(SO_3)_2]$ core in **1** has not been previously observed although $[Pb_4(\mu_3\text{-}OH)_2]$ and $[Pb_4(\mu_3\text{-}OH)_2(COO)_2]$ tetranuclear units have been found in similar complexes [30–32].

As shown in scheme 1(a), the independent sip^{3-} in **1** exhibits an interesting coordinating mode, octadentate with the tetradentate sulfonate (two oxygen atoms bridging two metals and the third oxygen bridging two metals), one $\mu_2\text{–}\eta^2:\eta^1$ carboxylate (one oxygen bridging two metals, the other connecting one metal, and the carboxylate coordinating to two metals), and one bridging bidentate carboxylate (two oxygen atoms bridging two metals). Coordination of sulfonate is relatively weak [33], and one sulfonate linking four Pb's has been seldom observed. Such coordination with each sip^{3-} coordinated to eight metals is uncommon in compounds containing sip^{3-}.

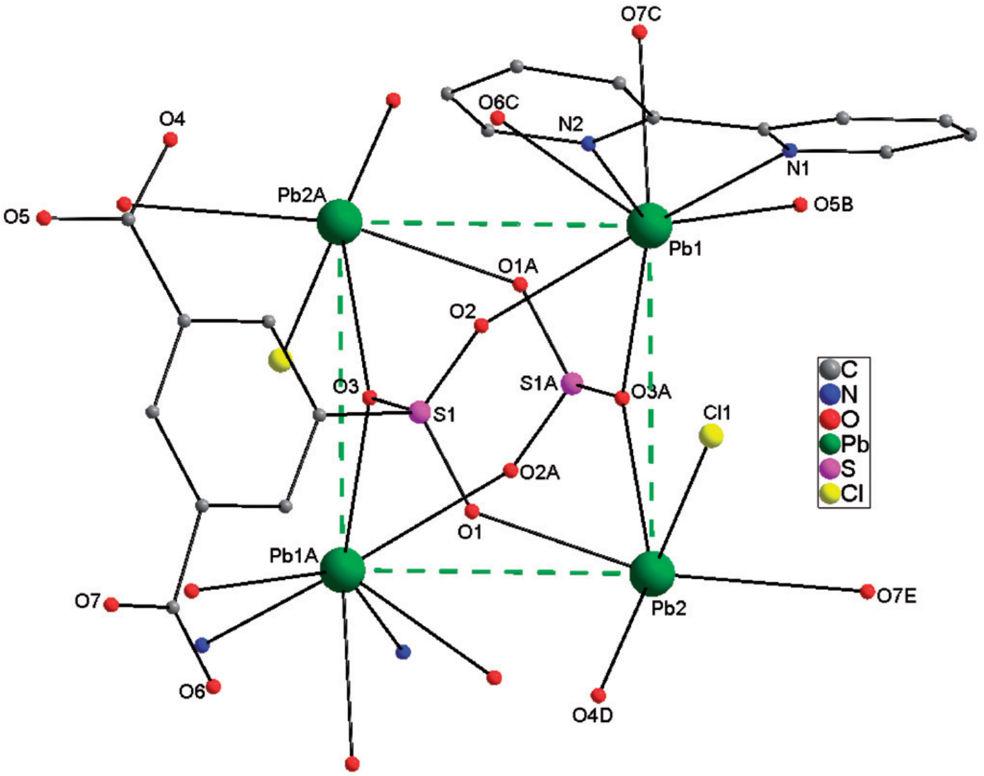
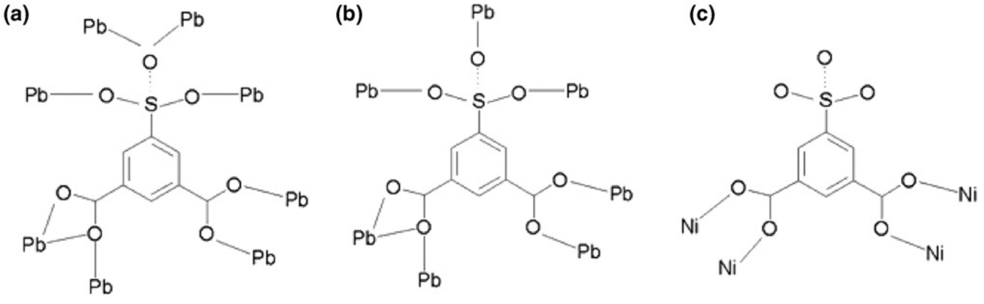


Figure 2. View of the tetranuclear-Pb cluster in **1**.



Scheme 1. The coordinated modes of the sip^{3-} in **1** (a), **2** (b), and **3** (c).

Tetranuclear clusters $[Pb_4(SO_3)_2]$ as secondary building blocks in **1** are interconnected through carboxylates of sip^{3-} (O7 and its symmetry atoms) into a 2-D (4,4)-honeycomb layer-like structure in the *bc* plane, as shown in figure 3. Each tetranuclear cluster is linked by four adjacent tetranuclear clusters in a corner-shared fashion. According to the classification scheme of Cheetham and Rao [34, 35], the hybrid framework can be classified on the basis of the dimensionality (n, m) of the inorganic (I) and organic (O) connectivity, defining a symbol I^nO^m. So the connectivity between tetranuclear cluster $[Pb_4(SO_3)_2]$ and ligands lead to the 2-D framework of **1** with the I^2O^0 type.

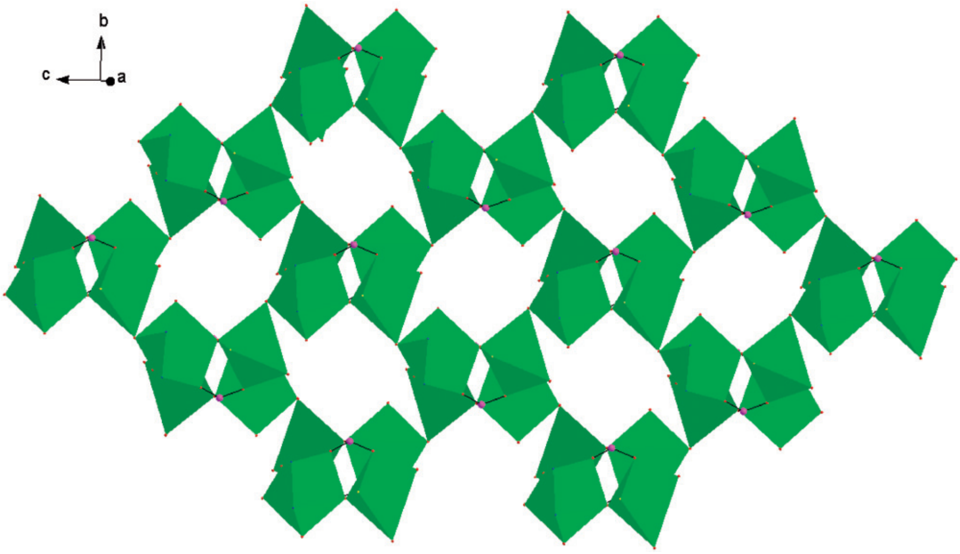


Figure 3. The 2-D layer-like architecture of **1** in the *bc* plane.

3.2. *Crystal structure description of 2*

X-ray single-crystal analysis reveals that **2** is a 3-D open framework architecture constructed from tetranuclear lead(II) motifs as secondary building blocks. As depicted in figure 4, the asymmetric unit of **2** contains two crystallographically independent lead(II) ions, one sip^{3-}, one coordinated water, and one bromide. In this centrosymmetric tetramer, Pb(1) shows distorted $[PbO_4Br]$ five-coordinate geometry, in which Pb(1) lies 0.40 Å above the plane defined by O(3), O(5C), and O(7E), while Br(1) and O(6E) are below the plane by 1.83 and 1.39 Å, respectively. The coordination sphere on Pb(1) is rather one-sided, indicating a stereochemically active lone pair of electrons on Pb(1). The Pb(2), on the other hand, is seven-coordinate bound to two Br^- (Pb–Br = 3.110(2)–3.200(2) Å) and five oxygen atoms, one from water (O8, Pb–O = 2.688(12) Å), two from sulfonates of two sip^{3-} (O(2) and O(1D), Pb–O = 2.546(11)–2.634(11) Å) and two from carboxylates of two sip (O(4B) and O(7C), Pb–O = 2.514(11)–2.674(11) Å).

As shown in figure 5, the four Pb^{2+} ions (Pb1, Pb2, Pb1A, and Pb2A, A: $-x$, $-y$, $1-z$) in **2** are interlinked by two bridging μ_3-Br and two sulfonates from different sip^{3-} ligands to form a planar parallelogram Pb_4 subunit, in which the largest deviation of Br(1) from the Pb(1), Pb(2), Pb(1A), and Pb(2A) plane is 1.055 Å. Pb(1) ··· Pb(2) and Pb(1) ··· Pb(2A) separations are 4.542(1) and 5.395(2) Å, respectively, and the Pb(2A)–Pb(1)–Pb(2) and Pb(1)–Pb(2)–Pb(1A) angles are 58.88(1)° and 121.12(2)°, respectively. Planar tetranuclear $[Pb_4Br_2(SO_3)_2]$ core in **2** has not been previously observed although $[Pb_4(\mu_3\text{-}OH)_2]$ and $[Pb_4(\mu_3\text{-}OH)_2(COO)_2]$ tetranuclear units have been found in similar complexes.

As shown in scheme 1(b), independent sip^{3-} in **2** exhibits different coordination from that of **1**, septa-dentate with two carboxylates identical to that of **1**, while the sulfonate in **2** is tridentate (three oxygen atoms bridge three metals).

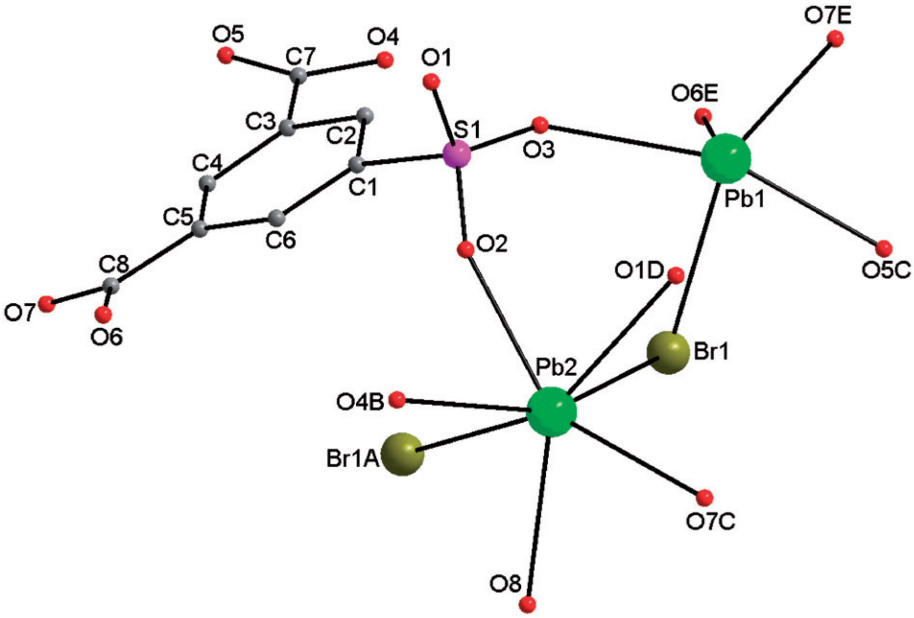


Figure 4. The molecular structure of **2**. All hydrogen atoms have been omitted for clarity.

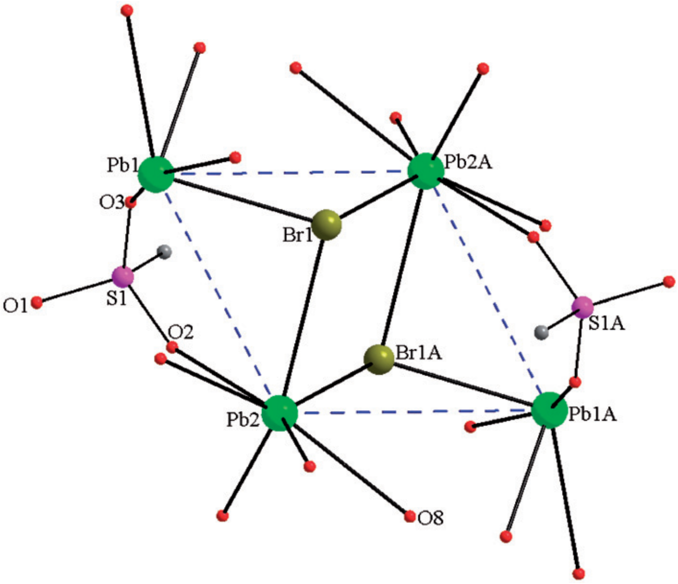


Figure 5. View of the tetranuclear inorganic cluster in **2**.

The tetranuclear [$Pb_4Br_2(SO_3)_2$] as secondary building blocks in **2** are interconnected through adjacent sulfonates into a 1-D chain-like structure along the *a*-axis (figure 6), further interconnected *via* carboxylates to form a 3-D open framework, as shown in figure 7. Unlike **1**, the connectivity between tetranuclear [$Pb_4Br_2(SO_3)_2$] and ligands lead to a 3-D framework of **2** with the I^1O^2 type.

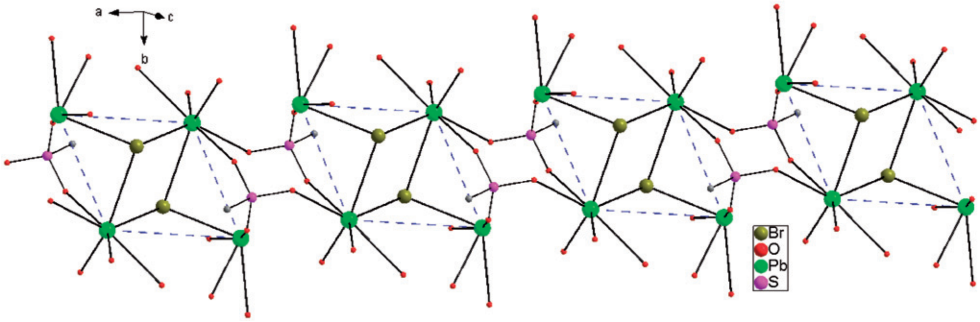


Figure 6. The 1-D chain of **2** along the *a*-axis.

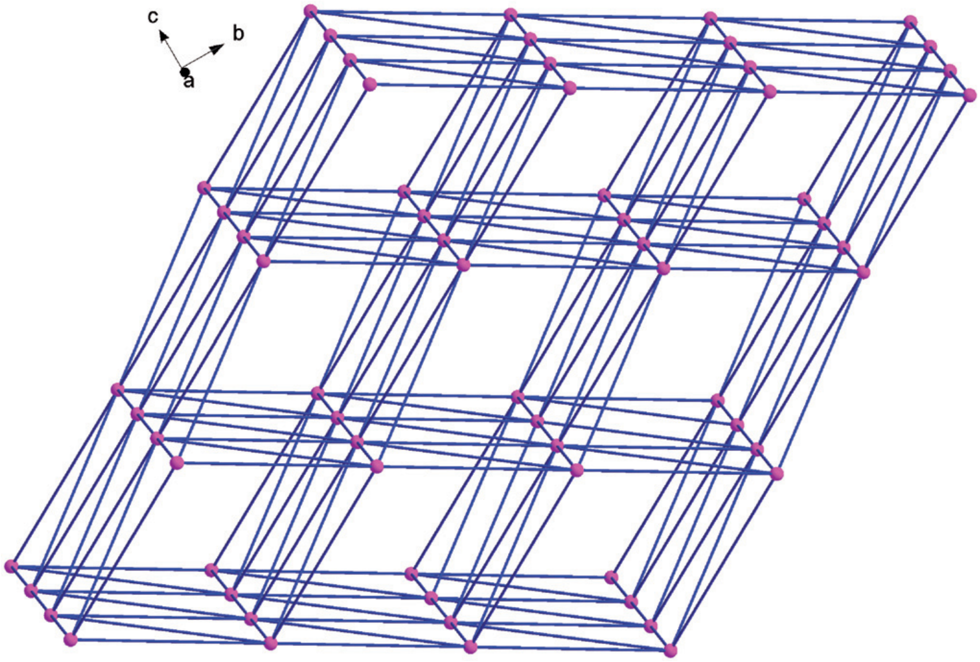


Figure 7. The topology structure for **2**.

3.3. *Crystal structure description of 3*

As shown in figure 8, in **3** there are two crystallographically unique Ni centers, half of pyz, half of sip^{3-}, and one hydroxyl in the independent molecule. The three sulfonate oxygen atoms in sip^{3-} are disordered over two sites with occupancy of 0.50 and 0.50. Two crystallographically independent six-coordinate nickels are present, both adopting slightly distorted octahedral geometry with somewhat different coordination. Ni1 is bound to two oxygen atoms (O(2) and O(2A)) from the chelating carboxylate of two different sip^{3-} ligands and two coordinating water molecules (O(1) and O(1A)) in the equatorial plane, the remaining two coordination sites are filled by one μ_3-OH group

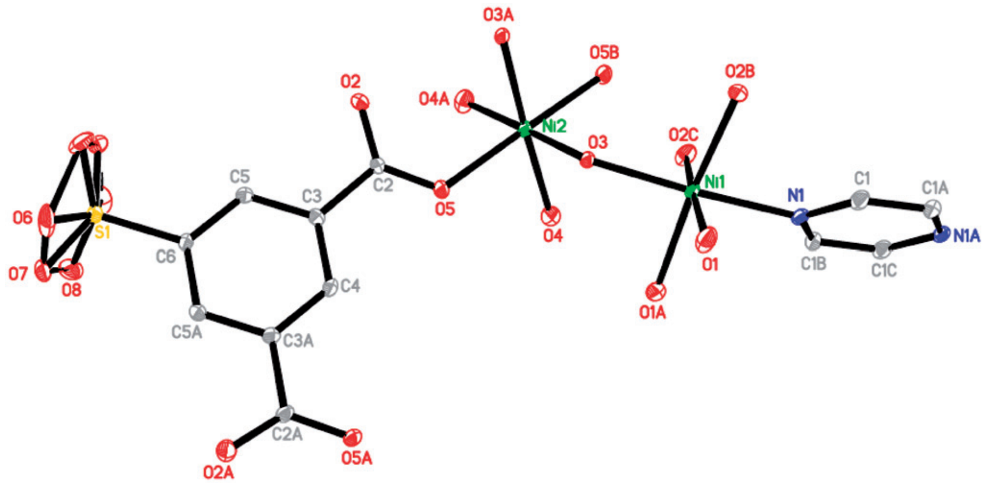


Figure 8. The molecular structure of **3**. All hydrogen atoms and lattice water molecules have been omitted for clarity.

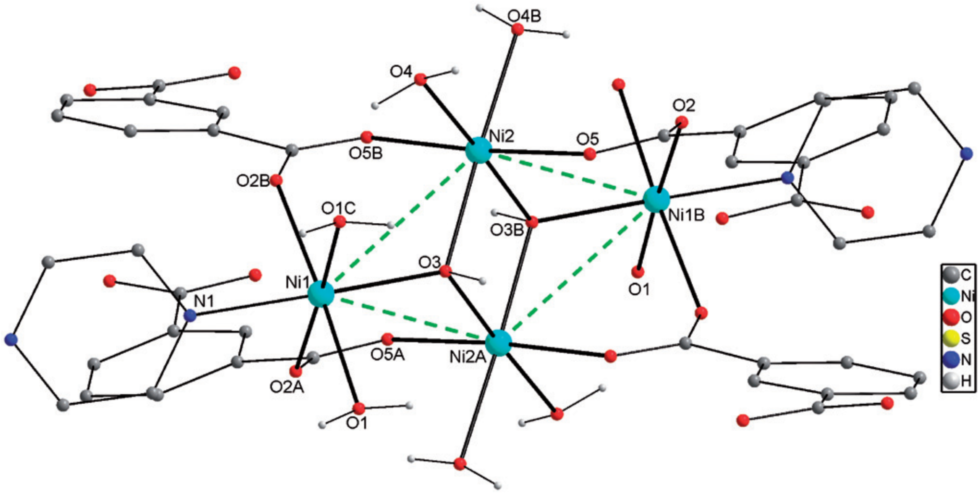


Figure 9. View of the tetranuclear-Ni cluster in **3**. The sulfonates and hydrogen atoms bound to carbons have been omitted for clarity.

(O3) and one pyz nitrogen in axial positions. Ni2 is coordinated to two oxygen atoms (O5 and O5) from chelating carboxylates of two different sip^{3-} ligands, one μ_3-OH (O3), and one coordinated water (O(4)) in the equatorial plane, and to one water (O4) and another μ_3-OH (O(3)) in axial positions.

In **3**, four nickels are arranged by two μ_3-OH and four carboxylate groups of sip^{3-} to a planar tetranuclear nickel unit, $[Ni_4(\mu_3\text{-}OH)_2(COO)_4]$, which sits on a crystallographic twofold axis that passes through the Ni2 and Ni2A, as shown in figure 9. The four nickels are in a plane and the largest deviation of the two μ_3-bridging hydroxyl groups from the Ni(1), Ni(2), Ni(1B), and Ni(2B) plane is 0.6011 Å. The distance between Ni(2)

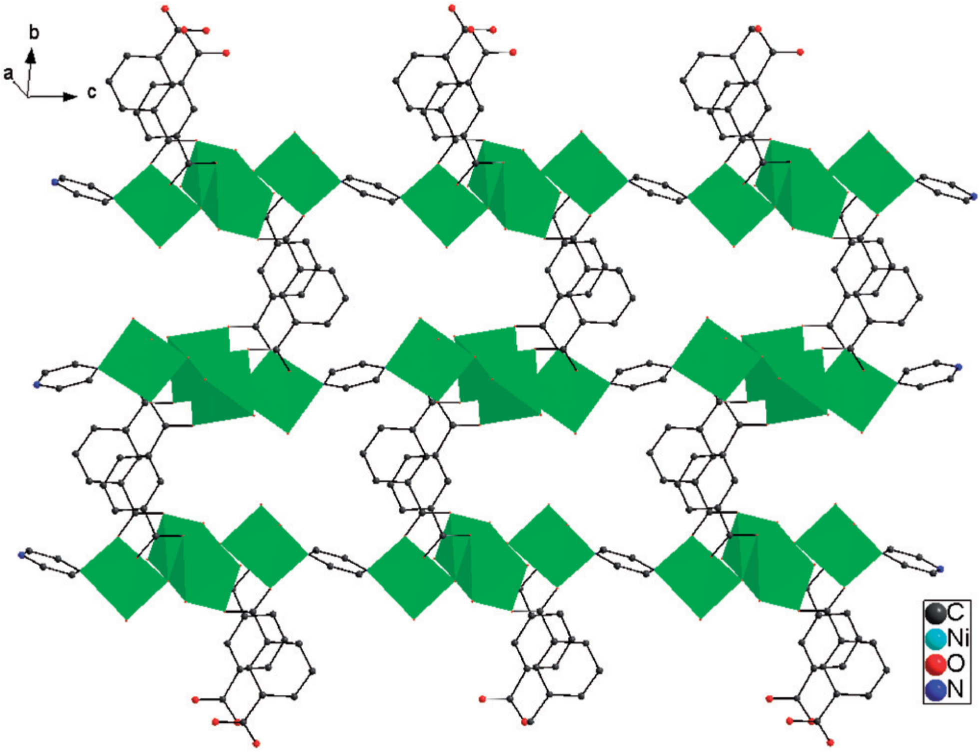


Figure 10. The 2-D layer structure for **3** in the *bc* plane. The uncoordinated sulfonates have been omitted for clarity.

and Ni(2A) is 3.070 Å, whereas the distance between Ni(2) and Ni(1) bridged by carboxylate is 3.542 Å. The angles of the adjacent three metals are different from those of **1**, that is, the angles of Ni(1)–Ni(2)–Ni(1B) and Ni(2)–Ni(1B)–Ni(2A) are 128.63 and 51.37°, respectively. Comparing the Ni_4 cluster in **3** with the Pb_4 cluster in **1**, the former adopts parallelogram configuration while the latter is approximately square.

Each sip^{3-} in **3** is connected to four Ni^{2+} ions through two bidentate carboxylates, as shown in scheme 1(c), and thereby is a μ_4 bridging ligand, not observed in previously reported sip^{3-} complexes. The deprotonated sulfonate does not participate in coordination, different from that in **1**, but balances the charge of the compound. Compound **3** is a rare example concerning Ni complex constructed from H_3sip with such coordination.

X-ray diffraction reveals that **3** possesses a 2-D layer structure constructed from planar tetranuclear Ni_4 building units, as shown in figure 10. Each tetranuclear nickel unit is interlinked through two pyz ligands to form a 1-D chain along the *c* axis, which further connects with each other by two carboxylates of sip^{3-} to finish a 2-D layer-like framework. Different from **1**, the connectivity between $[Ni_4(\mu_3\text{-}OH)_2(COO)_4]$ units and ligands lead to a 2-D framework of **3** with the I^0O^2 type. Compared with the similar 2-D compound $[Ni(2,2'\text{-bpy})(5\text{-npa})(bpe)_{0.5}(H_2O)]_n$ [36], **3** has two different characteristics, (1) the secondary building unit in the 2-D layer in **3** is tetranuclear Ni_4, while that in the former is mononuclear and (2) in **3**, the Ni_4 unit is a four-connected node and four-membered rings are connected by pyz and sip^{3-} forming a 2-D layer-like structure, while the Ni(II) is a three-connected node and six-membered rings are connected by bpe and 5-npa forming a 2-D wave-like sheet in the former compound.

3.4. *TGA properties of 1–3*

Thermal-gravimetric analysis (TGA) determined the thermal stability of **1**–**3**, as shown in the "Supplementary material." Compound **1** is stable to 210°C and initial weight loss of 22.16% below 440°C is assigned to the decomposition of 2,2′-bipy and Cl (Calcd 22.57%). Compound **2** is stable to 300°C with an initial weight loss of 13.78% below 390°C assigned to the decomposition of Br and coordinated water (Calcd 12.96%). For **3**, the first weight loss from 132°C to 195°C (18.21%) corresponds to the loss of coordinated and uncoordinated water molecules (Calcd 17.79%). The second weight loss from 410°C to 545°C was caused by the pyrolysis of sip^{3-} and μ_2-pyz resulting in a residue of $Ni(OH)_2$ (Found 36.79%; Calcd 36.65%).

3.5. *Luminescence of 1 and 2*

In the solid state, **1** and **2** show emission bands at 590 nm ($\lambda_{ex} = 412$ nm) and 594 nm ($\lambda_{ex} = 405$ nm), respectively, as shown in the "Supplementary material." Since free H_3sip exhibits photoluminescence at 355 nm, the yellow emission bands at 590 and 594 nm in **1** and **2**, respectively, may be attributed to the formation of $[Pb_4(SO_3)_2]$ and $[Pb_4Br_2(SO_3)_2]$ clusters and/or to ligand-to-metal charge transfer (LMCT). Compounds **1** and **2** are thermally stable and insoluble in common solvents, suggesting that the two coordination polymers could be significant in photoactive materials.

4. Conclusion

We prepared three hybrid coordination complexes constructed from different planar tetranuclear inorganic cluster subunits and H_3sip, $Pb_2Cl(sip)(bipy)$ (**1**), $Pb_2Br(sip)(H_2O)$ (**2**), and $Ni_4(sip)_2(pyz)_2(H_2O)_8(OH)_2{\cdot}2H_2O$ (**3**). The 2-D layer-like complexes **1** and **3**, and 3-D framework of **2** are constructed from planar tetranuclear units $[Pb_4(SO_3)_2]$, $[Ni_4(\mu_3\text{-}OH)_2(COO)_4]$, and $[Pb_4Br_2(SO_3)_2]$, respectively. The connectivity between tetranuclear cluster units and organic ligands leads to 2-D or 3-D framework of **1**–**3** with the I^2O^0, I^1O^2 and I^0O^2 types, respectively. The tetranuclear cluster $[Pb_4(SO_3)_2]$ as secondary building blocks in **1** is uncommon. The three compounds feature high thermal stability, and **1** and **2** show yellow photoluminescence emission bands at 590 nm ($\lambda_{ex} = 412$ nm) and 594 nm ($\lambda_{ex} = 405$ nm), respectively, in the solid state. Further study of magnetic properties and other metal ions is underway.

Acknowledgments

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