



## Novel lead(II) carboxylate– arsonate hybrids

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### ABSTRACT

Hydrothermal reactions of lead(II) acetate with phenylarsonic acid ( $\text{H}_2\text{L}^1$ ) (or 4-hydroxy-3-nitrophenylarsonic acid,  $\text{H}_3\text{L}^2$ ) and 5-sulfoisophthalic acid monosodium salt ( $\text{NaH}_2\text{SIP}$ ) (or 1,3,5-benzenetricarboxylic acid ( $\text{H}_3\text{BTC}$ )) as the second metal linkers afforded three novel mixed-ligand lead(II) carboxylate–arsonates, namely,  $\text{Pb}_5(\text{SIP})_2(\text{L}^1)_2(\text{H}_2\text{O})$  **1**,  $\text{Pb}_3(\text{SIP})(\text{L}^2)(\text{H}_2\text{O})$  **2** and  $\text{Pb}(\text{H}_2\text{L}^2)(\text{H}_2\text{BTC})$  **3**. The structure of **1** features a complicated 3D network composed of 2D double layers of lead(II) sulfoisophthalate bridged by 1D chains of lead(II) arsonates along *b*-axis, forming large tunnels along *b*-axis which are occupied by phenyl rings of the arsonate ligands. In **2**, the Pb(II) ions are bridged by  $\{\text{L}^2\}^{3-}$  anions into a 2D double layer whereas the interconnection of the Pb(II) ions via bridging and chelating SIP anions gave a 2D double layer. The cross-linkage of the above two building units leads to a complicated 3D network. In **3**, the interconnection of the Pb(II) ions via bridging  $\{\text{H}_2\text{L}^2\}^-$  and  $\{\text{H}_2\text{BTC}\}^-$  anions leads to a 1D double chain down *a*-axis. These 1D chains are further interconnected via hydrogen bonds among non-coordination carboxylate groups and arsonate oxygens into a 3D supramolecular architecture.

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### 1. Introduction

The chemistry of metal phosphonates has been an active research area in recent years due to its potential applications in the areas of catalysis, ion exchange, proton conductivity, intercalation chemistry, photochemistry and magnetic materials chemistry [1–4]. In order to design metal phosphonates with open-frameworks, a variety of functional groups such as amino acids, crown ethers, amino groups and carboxylates have been attached to the phosphonate groups [5–22]. Furthermore, the introduction of a second ligand such as 4,4'-bipy and oxalate anion has been proved to be an effective synthetic method, since these second metal linkers can act as pillars to link neighboring layers or be incorporated into the inorganic layer to form a new hybrid layered architecture [5–22]. Metal arsonates are expected to display a similar structural chemistry to those of metal phosphonates, but the larger ionic radius of As(V) could lead to some different architectures with different physical properties. So far, reports on metal arsonates are rather scarce [23–39]. A variety of polyoxometalate (POM) clusters of vanadium, molybdenum and tungsten have been reported [23–36], in which each arsonate group bridges with several metal centers as the phosphonate group in metal phosphonates containing POM clusters [20]. It is interesting that during the investigations of the V/O/PhAsO<sub>3</sub><sup>2-</sup> system the condensation of arsonate ligand gave a new hexadentate ligand,

$\{\text{Ph}_6\text{As}_6\text{O}_{14}\}^{4-}$ , in addition to the unusual  $\{\text{V}_2\text{O}_3\}^{4+}$  cluster [37], and the structure of another vanadium compound,  $\text{V}_2\text{O}_4(\text{PhAsO}_3\text{H})\cdot\text{H}_2\text{O}$ , features a vanadium oxide layer with the arsonate ligand hanging in the interlayer space [38]. In a gallium compound, two  $\text{PhAsO}_3^{2-}$  ligands were also condensed into a dimeric  $\{\text{Ph}_2\text{As}_2\text{O}_5\}^{2-}$  anion, which bridges with two Ga(III) ions and forms a four-member ring [39]. So far no lead(II) arsonates has been reported. As a logical expansion of our previous works on lead(II) phosphonates, we wish to design open frameworks of lead(II) arsonates by applying a second metal linker, such method has been found to be very effective to design 3D networks of lead(II) phosphonates [40–42]. We selected phenylarsonic acid ( $\text{H}_2\text{L}^1$ ) (or 4-hydroxy-3-nitrophenylarsonic acid with two additional function groups,  $\text{H}_3\text{L}^2$ ) as the arsonate ligand and 5-sulfoisophthalic acid monosodium salt ( $\text{NaH}_2\text{SIP}$ ) (or 1,3,5-benzenetricarboxylic acid ( $\text{H}_3\text{BTC}$ )) as the second metal linker. Hydrothermal reactions of the above two types of ligands with lead(II) acetate resulted in three novel lead(II) arsonates with novel 3D network structures or 3D supramolecular assembly, namely,  $\text{Pb}_5(\text{SIP})_2(\text{L}^1)_2(\text{H}_2\text{O})$  (**1**),  $\text{Pb}_3(\text{SIP})(\text{L}^2)(\text{H}_2\text{O})$  (**2**) and  $\text{Pb}(\text{H}_2\text{L}^2)(\text{H}_2\text{BTC})$  (**3**). Herein we report their syntheses, crystal structures and characterizations.

### 2. Experimental section

#### 2.1. Materials and methods

All chemicals were obtained from commercial sources and used without further purification. Elemental analyses were

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performed on a German Elementary Vario EL III instrument. The FT-IR spectra were recorded on a Nicolet Magna 750 FT-IR spectrometer using KBr pellets in the range of 4000–400 cm<sup>-1</sup>. Thermogravimetric analyses were carried out on a NETZSCH STA 449C unit at a heating rate of 10 °C/min under a nitrogen atmosphere. Photoluminescence analyses were performed on a Perkin-Elmer LS55 fluorescence spectrometer. X-ray powder diffraction (XRD) patterns (CuK $\alpha$ ) were collected on a XPERT-MPD  $\theta$ -2 $\theta$  diffractometer.

## 2.2. Synthesis of Pb<sub>5</sub>(SIP)<sub>2</sub>(L<sup>1</sup>)<sub>2</sub>(H<sub>2</sub>O) (**1**), Pb<sub>3</sub>(SIP)(L<sup>2</sup>)(H<sub>2</sub>O) (**2**) and Pb(H<sub>2</sub>L<sup>2</sup>)(H<sub>2</sub>BTC) (**3**)

The three compounds were synthesized in a similar procedure. A mixture of Pb(CH<sub>3</sub>COO)<sub>2</sub> · 3H<sub>2</sub>O (0.23 g, 0.6 mmol), H<sub>2</sub>L<sup>1</sup> (0.04 g, 0.2 mmol) or H<sub>3</sub>L<sup>2</sup> (0.05 g, 0.2 mmol), 5-sulfoisophalic acid monosodium salt (NaH<sub>2</sub>SIP) (0.11 g, 0.4 mmol) or H<sub>3</sub>BTC (0.08 g, 0.4 mmol) in 10 mL of deionized water, were put into a Parr Teflon-lined autoclave (23 mL), and heated at 180 °C for 5 days. The initial and final pH values of solution are 3.5 and 4.0 for **1** and **2**, and 2.5 and 3.0 for **3**, respectively. Crystals of compounds **1–3** were collected in a ca. 76% yield (based on L<sup>1</sup>, 0.15 g), 26% yield (based on Pb, 0.059 g), and 38% yield (based on L<sup>2</sup>, 0.052 g) respectively. Their purity has also confirmed by XRD powder diffraction (see Supporting Materials). Anal. Calcd. for C<sub>28</sub>H<sub>16</sub>O<sub>21</sub>S<sub>2</sub>As<sub>2</sub>Pb<sub>5</sub> (*M<sub>r</sub>* = 1938.32): C, 16.85; H, 2.04. Found: C, 17.35; H, 0.83. IR data (KBr, cm<sup>-1</sup>): 3434 (m), 1599 (m), 1523 (s), 1439 (m), 1363 (s), 1199 (s), 1109 (m), 1045 (m), 829 (m), 777 (m), 723 (m), 614 (m). Anal. Calcd. for C<sub>14</sub>H<sub>8</sub>NO<sub>14</sub>AsPb<sub>3</sub> (*M<sub>r</sub>* = 1142.76): C, 14.07; H, 1.61; N, 1.26. Found: C, 14.71; H, 0.71; N, 1.23. IR data (KBr, cm<sup>-1</sup>): 3434 (s), 1599 (s), 1523 (m), 1432 (m), 1355 (s), 1234 (m), 1168 (m), 1102 (w), 1035 (m), 795 (m), 718 (w), 618 (w). Anal. Calcd. for C<sub>15</sub>H<sub>10</sub>NO<sub>12</sub>AsPb (*M<sub>r</sub>* = 678.35): C, 26.16; H, 2.12; N, 2.03. Found: C, 26.56; H, 1.49; N, 2.06. IR data (KBr, cm<sup>-1</sup>): 3431 (m), 3283 (m), 3138 (m), 3071 (m), 1704 (vs), 1653 (m), 1612 (vs), 1528 (s), 1359 (m), 1247 (s), 1163 (m), 1091 (m), 909 (s), 895 (m), 838 (vs), 727 (m), 710 (m), 691 (m), 543 (m).

## 2.3. Single-crystal structure determination

Single crystals of compounds **1–3** were mounted on either a Rigaku Mercury CCD diffractometer (for **1** and **2**) or a Siemens Smart CCD (for **3**), both equipped with a graphite-monochromated MoK $\alpha$  radiation ( $\lambda$  = 0.71073 Å). Intensity data were collected by the narrow frame method at 293 K. The data sets were corrected for Lorentz and Polarization factors as well as for absorption by a multi-scan method (for **1** and **2**) or  $\psi$ -scan technique (for **3**) [43]. All three structures were solved by the direct methods and refined by full-matrix least-squares fitting on *F*<sup>2</sup> by SHELX-97 [44]. All non-hydrogen atoms except O(1w) atoms in **1** and **2** were refined with anisotropic thermal parameters. C(21), C(22), C(23), C(24), C(25), C(26), C(32), C(33), C(35) and C(36) of **1** are severely disordered and each has two orientations with an occupancy factor of 50% for each site. Hydrogen atoms excluding those for water molecules and those associated with the disordered phenyl rings of the arsonate ligands in compound **1** were located at geometrically calculated positions and refined with isotropical thermal parameters. Crystallographic data and structural refinements for compounds **1–3** are summarized in Table 1. Important bond lengths are listed in Table 2.

CCDC-666407-666409 (for **1–3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

## 3. Results and discussion

### 3.1. Structure description for Pb<sub>5</sub>(SIP)<sub>2</sub>(L<sup>1</sup>)<sub>2</sub>(H<sub>2</sub>O) (**1**)

The structure of **1** features a complicated 3D network. As shown in Fig. 1, there are five unique Pb(II) ions in its asymmetric unit. They display different coordinated geometries (Fig. 2) Pb(1) is five-coordinated by one sulfonate oxygen and four carboxylate oxygen atoms from four SIP anions. Pb(2) is five-coordinated by one sulfonate oxygen, three carboxylate oxygen atoms from three

**Table 1**  
Summary of crystal data and structure refinements for **1–3**

	<b>1</b>	<b>2</b>	<b>3</b>
Empirical formula	C <sub>28</sub> H <sub>16</sub> As <sub>2</sub> O <sub>21</sub> Pb <sub>5</sub> S <sub>2</sub>	C <sub>14</sub> H <sub>8</sub> AsNO <sub>14</sub> Pb <sub>3</sub> S	C <sub>15</sub> H <sub>10</sub> NO <sub>12</sub> AsPb
Formula weight	1938.32	1142.76	678.35
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	C2/c	P2 <sub>1</sub> /n	P-1
Crystal size (mm)	0.30 × 0.10 × 0.03	0.3 × 0.25 × 0.05	0.2 × 0.2 × 0.2
<i>a</i> (Å)	35.12(1)	11.1241(7)	5.126(1)
<i>b</i> (Å)	10.522(4)	10.5933(8)	11.8894(3)
<i>c</i> (Å)	22.847(9)	17.826(1)	14.8166(2)
$\alpha$ (deg)	90.000	90.000	98.83(1)
$\beta$ (deg)	118.251(1)	100.865(4)	94.60(1)
$\gamma$ (deg)	90.000	90.000	98.12(1)
<i>V</i> (Å <sup>3</sup> )	7435.9(4)	2062.9(3)	878.62(3)
<i>Z</i>	8	4	2
<i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	3.463	3.679	2.564
$\mu$ (mm <sup>-1</sup> )	24.532	26.19	11.54
<i>F</i> (000)	6880	2024	636.0
Reflections collected	28143	15508	4947
Unique reflections	8518 [ <i>R</i> <sub>int</sub> = 0.0607]	4710 [ <i>R</i> <sub>int</sub> = 0.0766]	3268 [ <i>R</i> <sub>int</sub> = 0.0921]
Observed data [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	7076	3584	3147
GOF on <i>F</i> <sup>2</sup>	0.995	0.946	1.199
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>a</sup>	0.0347, 0.0685	0.0430, 0.0964	0.0631, 0.1641
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.0459, 0.0730	0.0518, 0.0991	0.0655, 0.1661

<sup>a</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ,  $wR_2 = \{ \sum w[(F_o)^2 - (F_c)^2]^2 / \sum w(F_o)^2 \}^{1/2}$ .

**Table 2**  
Selected bond lengths (Å) for compounds **1–3**

<b>Compound 1</b>			
Pb(1)–O(6)	2.491(2)	Pb(1)–O(2)#1	2.558(2)
Pb(1)–O(8)	2.526(2)	Pb(1)–O(9)	2.562(2)
Pb(1)–O(4)#2	2.586(3)	Pb(2)–O(1)	2.403(1)
Pb(2)–O(10)	2.411(2)	Pb(2)–O(14)#3	2.524(2)
Pb(2)–O(2)	2.697(2)	Pb(2)–O(1W)	2.640(2)
Pb(3)–O(15)	2.240(2)	Pb(3)–O(3)	2.4233(15)
Pb(3)–O(17)#4	2.3767(18)	Pb(3)–O(19)	2.7406(16)
Pb(4)–O(18)#5	2.2694(17)	Pb(4)–O(20)	2.479(2)
Pb(4)–O(11)#6	2.4760(19)	Pb(4)–O(7)#3	2.6479(19)
Pb(4)–O(19)	2.7405(19)	Pb(5)–O(20)#5	2.4303(16)
Pb(5)–O(16)	2.298(2)	Pb(5)–O(17)#4	2.7148(14)
Pb(5)–O(19)	2.414(2)	As(1)–O(15)	1.6809(18)
As(1)–O(16)	1.6799(19)	As(1)–O(17)	1.687(2)
As(2)–O(18)	1.668(2)	As(2)–O(19)	1.6998(19)
As(2)–O(20)	1.683(2)	S(1)–O(5)	1.448(3)
S(1)–O(6)	1.444(2)	S(1)–O(7)	1.452(3)
S(2)–O(12)	1.455(3)	S(2)–O(13)	1.452(3)
S(2)–O(14)	1.471(3)		
<b>Compound 2</b>			
Pb(1)–O(2)	2.214(7)	Pb(1)–O(10)#1	2.521(8)
Pb(1)–O(11)	2.330(7)	Pb(1)–O(12)#2	2.566(7)
Pb(2)–O(7)#3	2.291(7)	Pb(2)–O(14)#4	2.457(7)
Pb(2)–O(1)	2.405(7)	Pb(2)–O(4)#3	2.561(8)
Pb(2)–O(3)#5	2.380(7)	Pb(2)–O(9)#6	2.685(8)
Pb(3)–O(3)#5	2.315(7)	Pb(3)–O(13)#7	2.446(7)
Pb(3)–O(1)	2.390(7)	Pb(3)–O(14)#7	2.742(6)
Pb(3)–O(1w)	2.866(7)	As(1)–O(3)	1.666(7)
As(1)–O(2)	1.680(8)	As(1)–O(1)	1.687(7)
S(1)–O(7)	1.433(8)	S(1)–O(8)	1.455(8)
S(1)–O(9)	1.439(8)		
<b>Compound 3</b>			
Pb(1)–O(12)#1	2.32(1)	Pb(1)–O(11)	2.67(1)
Pb(1)–O(11)#2	2.37(1)	Pb(1)–O(7)	2.72(1)
Pb(1)–O(6)	2.56(1)	As(1)–O(12)	1.64(1)
As(1)–O(11)	1.67(1)	As(1)–O(13)	1.73(1)
C(13)–O(8)	1.32(2)	C(13)–O(9)	1.22(2)
C(14)–O(4)	1.31(2)	C(14)–O(5)	1.25(2)
C(15)–O(6)	1.26(2)	C(15)–O(7)	1.27(2)
<b>Hydrogen bonds</b>			
O(4)···O(5)#3	2.60(2)	O(13)···O(9)#4	2.66(1)
O(3)···O(1)	2.58(2)		

Symmetry transformations used to generate equivalent atoms: for **1**: #1  $-x+3/2, -y+3/2, -z+1$ ; #2  $x, y+1, z$ ; #3  $x, y-1, z$ ; #4  $-x+1, -y, -z+1$ ; #5  $-x+1, -y-1, -z+1$ ; #6  $x, -y, z+1/2$ . For **2**: #1  $-x+1/2, y-1/2, -z+1/2$ ; #2  $-x+1, -y, -z+1$ ; #3  $-x+2, -y, -z+1$ ; #4  $x+1/2, -y+1/2, z-1/2$ ; #5  $-x+3/2, y+1/2, -z+1/2$ ; #6  $-x+3/2, y-1/2, -z+1/2$ ; #7  $-x+1, -y+1, -z+1$ . For **3**: #1  $x-1, y, z$ ; #2  $-x+1, -y, -z+1$ ; #3  $-x-1, -y+1, -z+2$ ; #4  $x+1, y, z-1$ .

SIP<sup>3-</sup> anions and an aqua ligand. Pb(4) is five-coordinated by one carboxylate oxygen, one sulfonate oxygen atom from two SIP<sup>3-</sup> anions and three arsonate oxygen atoms from two {L<sup>1</sup>}<sup>2-</sup> anions. The coordination geometry around Pb(1), Pb(2) and Pb(4) can be described as a severely distorted  $\psi$ -PbO<sub>5</sub> octahedron with one site occupied by the lone pair electrons. Pb(3) is four-coordinated by three arsonate oxygen atoms from three {L<sup>1</sup>}<sup>2-</sup> anions and one oxygen atom from a SIP<sup>3-</sup> anion. Pb(5) is also four-coordinated but by four arsonate oxygen atoms from four {L<sup>1</sup>}<sup>2-</sup> anions. The coordination geometry around Pb(3) and Pb(5) can be described as a severely distorted  $\psi$ -PbO<sub>4</sub> trigonal bipyramid with one site occupied by the lone pair electrons. The two phenylarsonate anions display two different coordination modes (Scheme 1a and b). The one containing As(1) atom is tetradentate and bridges with four lead(II) ions, O(17) is  $\mu_2$ -bridging whereas O(15) and O(16) are unidentate. The one containing As(2) atom is hexadentate and connects with six lead(II) ions: O(19) is  $\mu_3$ -bridging, O(20) is  $\mu_2$ -bridging whereas O(18) is unidentate. The two SIP<sup>3-</sup> anions also exhibit two different types of coordination modes (Scheme 1e and

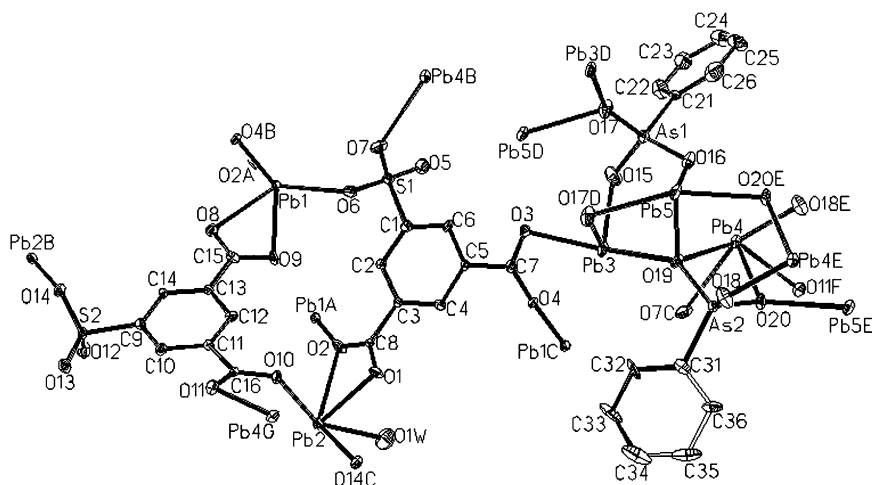
f). The SIP anion containing S(1) atom is pentadentate and connects with four lead(II) ions: one carboxylate group forms a bidentate chelation with one lead(II) ion and the other carboxylate group bridges with two Pb(II) ions (Scheme 1e). The SIP anion containing S(2) atom acts as a heptadentate ligand and bridges with six lead(II) ions, one carboxylate group is bidentate bridging whereas the other one is tridentate chelating and bridging. Two sulfonate oxygens are unidentate whereas the third one remains non-coordinated (Scheme 1f). Both types of coordination modes are different from that in Pb(BTS)(OH)(H<sub>2</sub>O) with a pillared layered structure, in which both carboxylate groups are tridentate chelating and bridging whereas the sulfonate group is bidentate bridging [45]. The Pb–O distances range from 2.240(2) to 2.741(2) Å (Table 2), which are comparable to those reported for other Pb(II) phosphonates and Pb(II) carboxylates [40–42].

The interconnection of Pb(3), Pb(4) and Pb(5) atoms by the bridging phenylarsonic ligands groups resulted in a 1D chains (Fig. 3a). The interconnection of the Pb(1), Pb(2), Pb(3) and Pb(4) atoms by bridging and chelating SIP anions leads to a 2D layer (Fig. 3b). It is reported that in lead(II) complex with BTS and 3-Pyridyl-CH<sub>2</sub>NH(CH<sub>2</sub>PO<sub>3</sub>H<sub>2</sub>)<sub>2</sub>, the lead(II) ions also form a 2D layer motif with BTS anions, whereas in the lead(II) complex with BTS and *N*-(phosphonomethyl)-*N*-methylglycine, the lead(II) ions are bridged by BTS anions into a 1D chain [46]. The cross-linkage of the above two building blocks afforded to a complicated 3D network with large tunnels along *b*-axis, the phenyl rings of the arsonate ligands are located at these tunnels (Fig. 4).

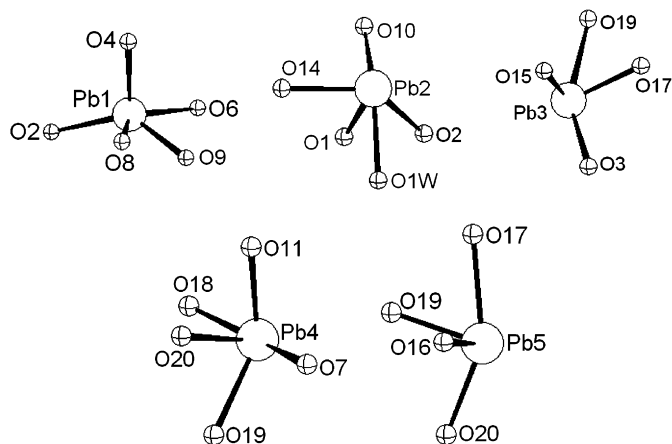
### 3.2. Structure description for Pb<sub>3</sub>(SIP)(L<sup>2</sup>)(H<sub>2</sub>O) (**2**)

As shown in Fig. 5, the formula unit of **2** contains three Pb(II) ions, one fully deprotonated {L<sup>2</sup>}<sup>3-</sup> anion, and one fully deprotonated SIP<sup>3-</sup> anion and one aqua ligand. The three unique Pb(II) ions exhibit different coordinated geometries (Fig. 6). Pb(1) is four-coordinated by one sulfonate and two carboxylate oxygen atoms from three SIP anions as well as an arsonate oxygen atom from a {L<sup>2</sup>}<sup>3-</sup> anion, its coordination geometry can be described as a  $\psi$ -PbO<sub>4</sub> trigonal bipyramid with one corner filled by the lone pair electrons. Pb(3) is four-coordinated by a bidentate chelating carboxylate group of a BTS<sup>3-</sup> anion, two arsonate oxygens from two {L<sup>2</sup>}<sup>3-</sup> anions and an aqua ligand, its coordination geometry can be described as a  $\psi$ -PbO<sub>4</sub> distorted square pyramid with the pyramidal site filled by the lone pair electrons (Fig. 6). Pb(2) is six-coordinated by one carboxylate and one sulfonate oxygen atoms from two SIP anions, two arsonate oxygen atoms, one nitro oxygen atom and one hydroxyl group from three {L<sup>2</sup>}<sup>3-</sup> anions in a severely distorted octahedral geometry. The Pb(3)–O(1w) distance of 2.866(7) Å is significantly longer than those of the remaining Pb–O bonds (2.214(7)–2.742(6) Å) (Table 2), hence it can be considered as a weak coordination bond. The {L<sup>2</sup>}<sup>3-</sup> anion is heptadentate and connects with six lead(II) ions: two arsonate oxygens are bidentate whereas the third one is unidentate, the hydroxyl group and one nitro oxygen form a six-member chelation ring with a lead(II) ion, the other nitro oxygen remains non-coordinated (Scheme 1c). The SIP<sup>3-</sup> anion is heptadentate and bridges with six lead(II) ions: one carboxylate group chelates bidentately with a Pb(II) ion and also bridges with another Pb(II) ion whereas the other carboxylate group bridges with two Pb(II) ions. The sulfonate group bridges with two Pb(II) ions by using two oxygen atoms and the third sulfonate oxygen atom remains non-coordinated (Scheme 1e). Such coordination mode has also been observed in **1**.

The interconnection of the lead(II) ions via bridging and chelating {L<sup>2</sup>}<sup>3-</sup> anions resulted in the formation of a (–202) layer (Fig. 7a). The interconnection of the Pb(II) ions via bridging



**Fig. 1.** ORTEP representation of the selected unit in compound **1**. The thermal ellipsoids are drawn at 50% probability level. Only one orientation was shown for the disordered carbon atoms of phenylarsonic acid ligands for clarity. Symmetry codes for the generated atoms: (a)  $-x+3/2, -y+3/2, -z+1$ ; (b)  $x, y+1, z$ ; (c)  $x, y-1, z$ ; (d)  $-x+1, -y, -z+1$ ; (e)  $-x+1, -y-1, -z+1$ ; (f)  $x, -y, z+1/2$ ; and (g)  $x, -y, z-1/2$ .



**Fig. 2.** Coordination geometries around the Pb(II) ions in compound **1**.

and chelating SIP anions leads to a  $(-101)$  Pb(II) carboxylate-sulfonate layer (Fig. 7b). The cross-linkage of the above two building units gave a complicated 3D network (Fig. 8). Such 3D network can also be viewed as the lead(II) arsonate-sulfonate inorganic layers passing  $1/4$  and  $3/4$  of  $c$ -axis being bridged by organic groups of the above two types of multi-dentate ligands. There are also  $\pi \cdots \pi$  interactions between neighboring phenyl rings of arsonate or BTS ligands. These phenyl rings are parallel to each other and have inter-ring distances of 3.448 and 3.644 Å, respectively. These  $\pi \cdots \pi$  interactions further stabilize the framework of the structure.

### 3.3. Structure description for $Pb(H_2L^2)(H_2BTC)$ (**3**)

The asymmetric unit of **3** contains one lead(II) ion, one doubly protonated  $\{H_2L^2\}^-$  anion and one doubly protonated  $\{H_2BTC\}^-$  anion. As shown in Fig. 9, the lead(II) is five-coordinated by a bidentate chelating carboxylate group of a  $\{H_2BTC\}^-$  anion and three arsonate oxygens from three  $\{H_2L^2\}^-$  anions. Its coordination geometry can be described as a severely distorted  $\psi$ -PbO<sub>5</sub> octahedron with the lone pair of the lead (II) ion occupying the sixth site. The Pb–O bond distances are in the range of 2.32(1)–2.72(1) Å (Table 2), which are comparable to those reported in compounds **1** and **2**. The arsonate ligand is doubly

protonated: the hydroxyl group and one oxygen atom of the arsonate group. Based on As–O distances, O(13) is most likely protonated. The  $\{H_2L^2\}^-$  anion is tridentate: the arsonate group bridges with three Pb(II) ions by using two oxygen atoms and the third oxygen atom remains non-coordinated. The nitro group and hydroxyl groups are also non-coordinated (Scheme 1d). The tricarboxylate ligand is also doubly protonated, O(4) and O(8) atoms are most likely protonated based on C–O distances (Table 2). The  $\{H_2BTC\}^-$  anion is bidentate chelating with a Pb(II) ion by using one carboxylate group, the other two protonated carboxylate groups remain non-coordinated (Scheme 1g). Such kind of coordination mode has also been reported in the layered mixed-ligand lead(II) complex containing both *N*-cyclohexylimino-bis(methylene-phosphonic acid) and BTC, in which additional neutral  $H_3BTC$  molecule act as the interlayer intercalated species [40]. In layered  $Pb_3(BTC)_2 \cdot H_2O$ , the BTC anions adopt three types of multi-dentate coordination modes in which all carboxylate groups are chelating and bridging [47].

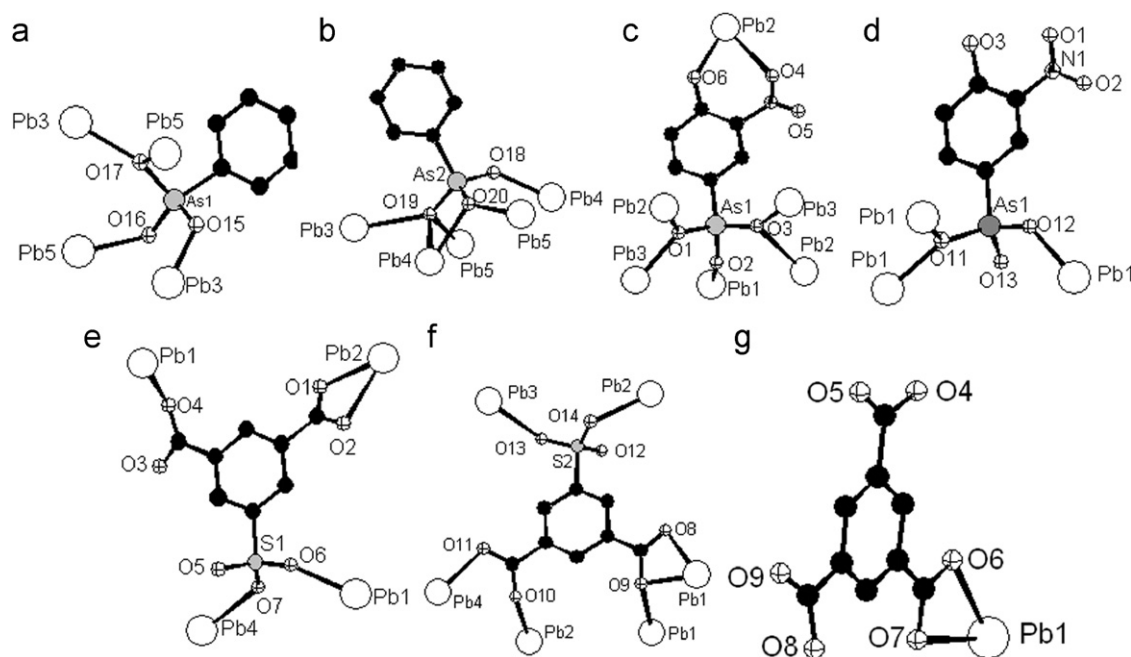
The interconnection of the Pb(II) ions via bridging arsonate groups of the  $\{H_2L^2\}^-$  anions leads to a 1D double chain along  $b$ -axis (Fig. 10). The  $\{H_2BTC\}^-$  anions are hanging on the above chains. Within the 1D chain, hydrogen bonds are formed between hydroxyl groups and nitro groups of the arsonate ligands (O(3)–H(7b)  $\cdots$  O(1)) (Fig. 10). The O  $\cdots$  O separate is 2.58(2) Å and the hydrogen bond angle is 139.5°. These 1D chains are further interlinked via hydrogen bonds among non-coordination carboxylate groups and non-coordinate arsonate oxygens into a 3D supramolecular assembly (Fig. 11). The O(4)  $\cdots$  O(5) (symmetry operator:  $-x-1, -y+1, -z+2$ ) and O(13)  $\cdots$  O(9) (symmetry operator:  $x+1, y, z-1$ ) separations are 2.60(2) and 2.66(1) Å (Table 2), respectively and the corresponding hydrogen bond angles are 174.4° and 178.8°, respectively. Hence the 3D supramolecular assembly of **3** is expected to be quite stable due to these strong hydrogen bonds.

The measured XRD powder patterns of compounds **1–3** match with the ones simulated from their single crystal structure data, thus all three compounds can be obtained as single phases (See Supporting Materials).

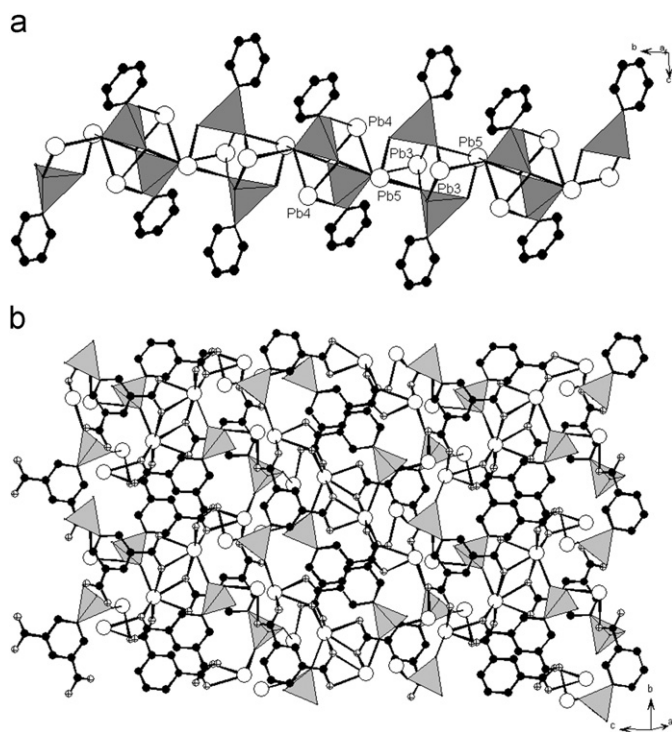
### 3.4. IR, luminescence properties and TGA studies for compound **1–3**

The FT-IR spectra of all of the three compounds show the typical  $\nu(As=O)$  [33] stretching vibration bands ( $1109\text{ cm}^{-1}$  for **1**,  $1101\text{ cm}^{-1}$  for **2** and  $1091\text{ cm}^{-1}$  for **3**). Compounds **1** and **2** exhibit



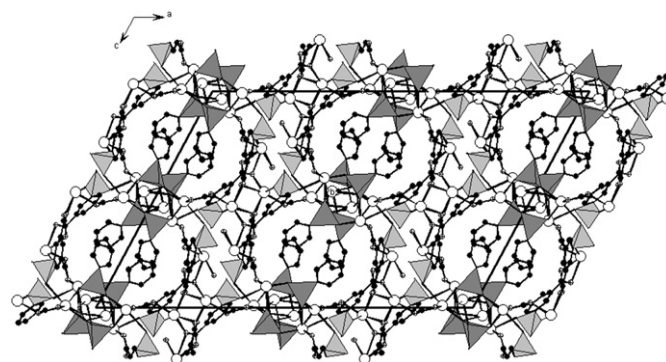


**Scheme 1.** Coordination modes of  $H_2L^1$ ,  $H_3L^2$ ,  $NaH_2SIP$ ,  $H_3BTC$  ligands in compounds **1–3**.



**Fig. 3.** 1D chains of lead(II) arsonate along  $b$ -axis (a) and a double 2D layer of Pb(II) carboxylate-sulfonate in **1**. The  $CaSO_3$  and  $CSO_3$  tetrahedra are shaded in medium and light gray, respectively. Pb, C and O atoms are represented by open, black and crossed circles, respectively.

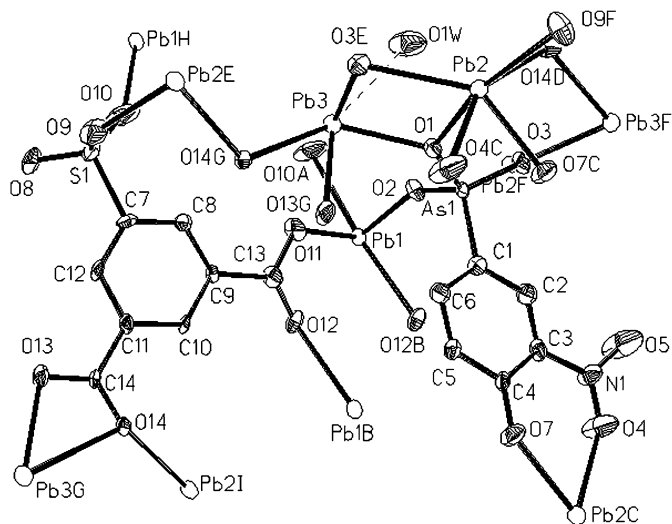
broad, strong absorptions centered at  $3434\text{ cm}^{-1}$  for both **1** and **2**, occurring because of the existence of water molecules in the structures. The absorptions in the region  $1000\text{--}1200\text{ cm}^{-1}$  for **1** and **2** are typical of the sulfonate group. The strong absorption bands at  $1199$  and  $1168\text{ cm}^{-1}$  for compounds **1** and **2**, respectively, are because of the  $\nu_{s-o}$  stretching [48]. The IR spectrum of **1** shows the typical asymmetric ( $1523\text{ cm}^{-1}$ ) and symmetric ( $1439$  and  $1363\text{ cm}^{-1}$ ). And the compounds **2** and **3** also exhibit strong bands



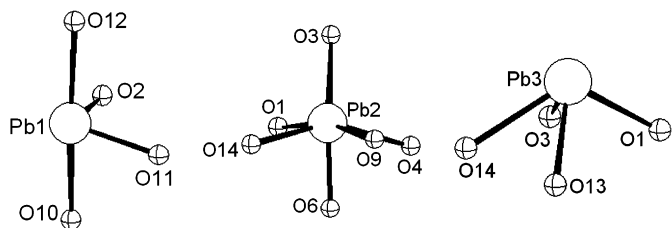
**Fig. 4.** View of the structure of compound **1** down the  $b$ -axis. The  $CaSO_3$  and  $CSO_3$  tetrahedra are shaded in medium and light gray, respectively. Pb, C and O atoms are represented by open, black and crossed circles, respectively.

at  $1523\text{ cm}^{-1}$ , and  $1432$  and  $1355\text{ cm}^{-1}$  for compound **2**, at  $1704\text{ cm}^{-1}$ , and  $1612$  and  $1528\text{ cm}^{-1}$  for compound **3**, respectively, correspond to the asymmetric and symmetric stretching bands of the carboxylate groups [48].

Photoluminescent properties of  $s^2$ -metal complexes are not well studied as compared with those of  $d^{10}$ -metal complexes, although there are reports on the photoluminescent properties of lead-containing materials [49,50]. The solid-state luminescence properties of compounds **1–3** as well as two free arsonate ligands and two second metal linkers were investigated at room temperature. The free phenylarsonic acid ligand exhibits two fluorescent emission bands at  $\lambda_{\text{max}} = 323, 368\text{ nm}$  upon excitation at  $242\text{ nm}$  whereas the 5-sulfoisophthalic acid monosodium salt ( $NaH_2SIP$ ) ligand displays a fluorescent emission band at  $\lambda_{\text{max}} = 327\text{ nm}$  upon excitation at  $260\text{ nm}$  [51]. Compound **1** displays two strong broad emission bands at  $\lambda_{\text{max}} = 376, 414\text{ nm}$  ( $\lambda_{\text{ex}} = 237\text{ nm}$ ) upon complexation of both  $L^1$  ligands and SIP ligands with the Pb(II) ions. The free 4-hydroxy-3-nitrophenylarsonic acid ligand displays a fluorescent emission band at  $\lambda_{\text{max}} = 421\text{ nm}$  with a shoulder at  $482\text{ nm}$  upon excitation at  $237\text{ nm}$  (Fig. 12a). Compound **2** displays a strong fluorescent emission band at  $\lambda_{\text{max}} = 356\text{ nm}$  ( $\lambda_{\text{ex}} = 213\text{ nm}$ ) upon complexation of the  $L^2$  ligands



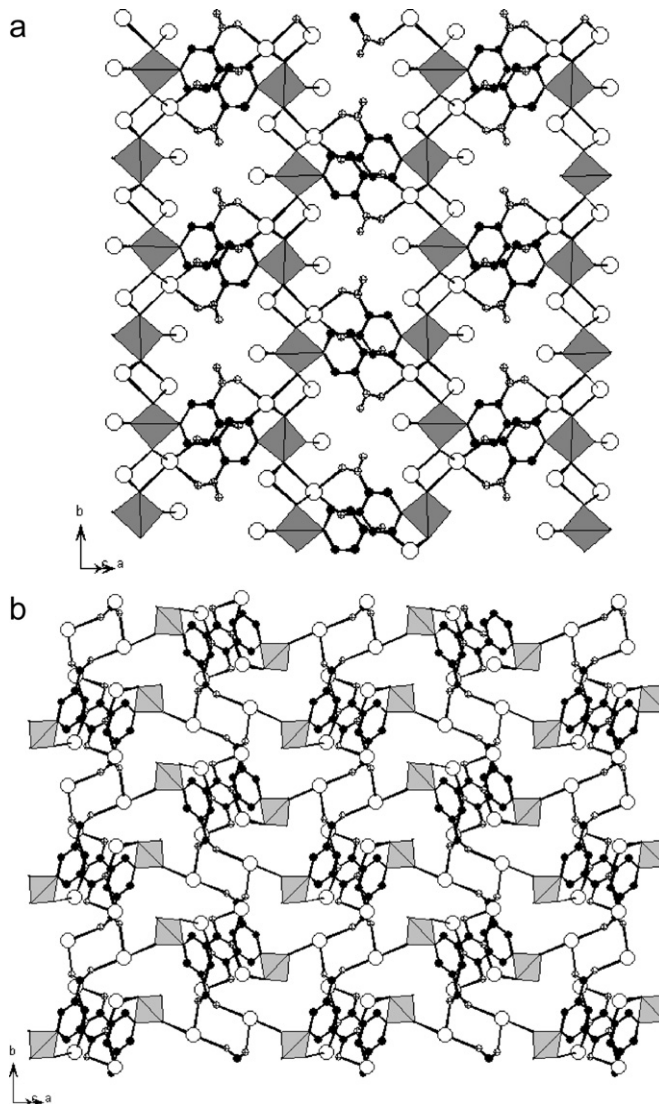
**Fig. 5.** ORTEP representation of the selected unit of compound **2**. Thermal ellipsoids are drawn at 50% probability level. Symmetry codes for the generated atoms: (a)  $-x+1/2, y-1/2, -z+1/2$ ; (b)  $-x+1, -y, -z+1$ ; (c)  $-x+2, -y, -z+1$ ; (d)  $x+1/2, -y+1/2, z-1/2$ ; (e)  $-x+3/2, y+1/2, -z+1/2$ ; (f)  $-x+3/2, y-1/2, -z+1/2$ ; (g)  $-x+1, -y+1, -z+1$ ; (h)  $1/2-x, 1/2+y, 1/2-z$ ; and (i)  $x-1/2, -y+1/2, z+1/2$ .



**Fig. 6.** Coordination geometries around the lead(II) ions in compound **2**.

and SIP ligands with the Pb(II) ions. The H<sub>3</sub>BTC exhibits a fluorescent emission band at  $\lambda_{\text{max}} = 355$  nm upon excitation at 260 nm (Fig. 12b). Compound **3** displays a strong fluorescent emission band at  $\lambda_{\text{max}} = 418$  nm ( $\lambda_{\text{ex}} = 237$  nm) and a weak fluorescent emission band at  $\lambda_{\text{max}} = 481$  nm ( $\lambda_{\text{ex}} = 237$  nm) upon complexation of the L<sup>2</sup> ligands and H<sub>2</sub>BTC ligands with the Pb<sup>II</sup> ions (Fig. 12c). These emission bands are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT) in nature, but rather can be attributed to an intraligand emission state [40–42].

The TGA curves of compound **1** exhibit two main steps of weight losses (Fig. 13). The first weight loss began at 100 °C and completed at 238 °C, which corresponds to the loss of an aqua ligand per formula unit, the weight loss of 0.94% is in good agreement with the calculated value of 0.93% (Fig. 13). The second step covering a temperature range of 412–554 °C corresponds to the combustion of SIP and phenylarsonic ligands. The total observed weight loss at 500 °C is 31.8%. If we assume the final residues are Pb<sub>3</sub>(AsO<sub>3</sub>)<sub>2</sub> and PbO in a molar ratio of 1:2, the calculated total weight loss is 32.3%. The TGA curves of compound **2** shows one main continuous step of weight losses. The weight loss began at 253 °C and completed at 491 °C, which corresponds to the combustion of SIP and phenylarsonic ligands. The final products are assumed to be Pb<sub>3</sub>(AsO<sub>3</sub>)<sub>2</sub> and PbO in a 1:3 molar ratio. The total observed weight loss at 700 °C is 27.9% is close to the calculated value (32.7%). The TGA curves of compound **3** shows one main step of weight losses. The weight loss began at 272 °C and completed at 529 °C, which corresponds to combustion of tricarboxylate and 3-nitro-4-hydroxyl-phenylarsonic ligands.



**Fig. 7.** A  $(-202)$  2D double layer of lead arsonate (a) and a  $(-101)$  2D layer of lead(II) carboxylate-sulfonate in **2** (b). The AsO<sub>3</sub> and SO<sub>3</sub> tetrahedra are shaded in medium and light gray, respectively. Pb, C and O atoms are represented by open, black and crossed circles, respectively.

The final residues are assumed to be Pb<sub>3</sub>(AsO<sub>3</sub>)<sub>2</sub> and As<sub>2</sub>O<sub>3</sub> in a 2:1 molar ratio. The total observed weight loss of 55.6% at 700 °C is close to the calculated one (52.6%) [23,24,49,52].

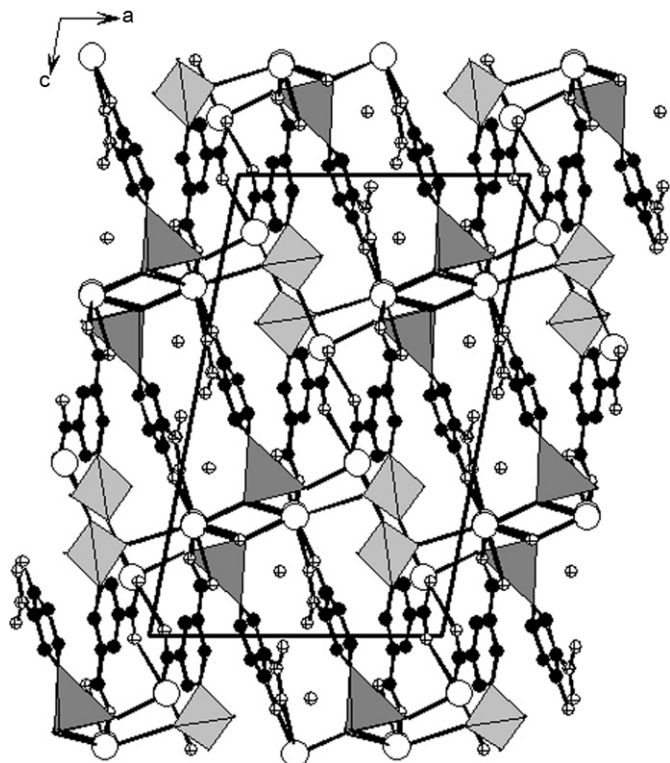
#### 4. Conclusion

In summary, hydrothermal reactions of Pb(II) acetate with H<sub>2</sub>L<sup>1</sup> or H<sub>3</sub>L<sup>2</sup> and 5-sulfoisophalic acid monosodium salt (NaH<sub>2</sub>SIP) or 1,3,5-benzenetricarboxylic acid (H<sub>3</sub>BTC) as the second metal linker afforded three new Pb(II) carboxylate-arsenate hybrids. The substitute groups on the arsonate ligands have strong effects on the structures of resultant compounds when they provide additional coordination atoms. Furthermore the nature of the second ligand with the metal ion is also very important. Results of our studies indicate that inorganic-organic hybrids of metal arsonates with various types of structures can be developed by using the same technique applied in the metal phosphonate systems. It is believed that a wide range of other new metal arsonates such as luminescent lanthanide arsonates and transition

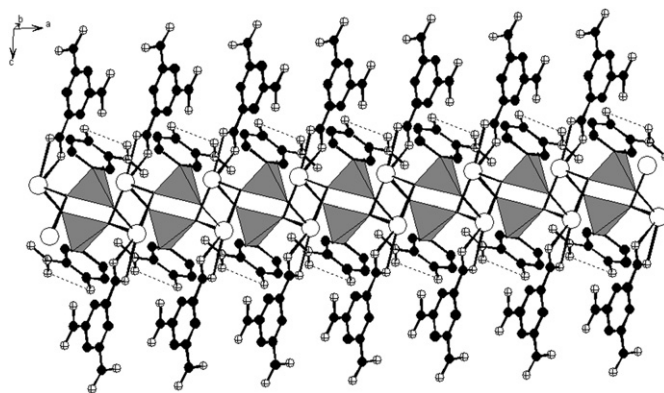
metal arsonates can be obtained by using such synthetic technique and currently we are exploring these possibilities.

### Acknowledgments

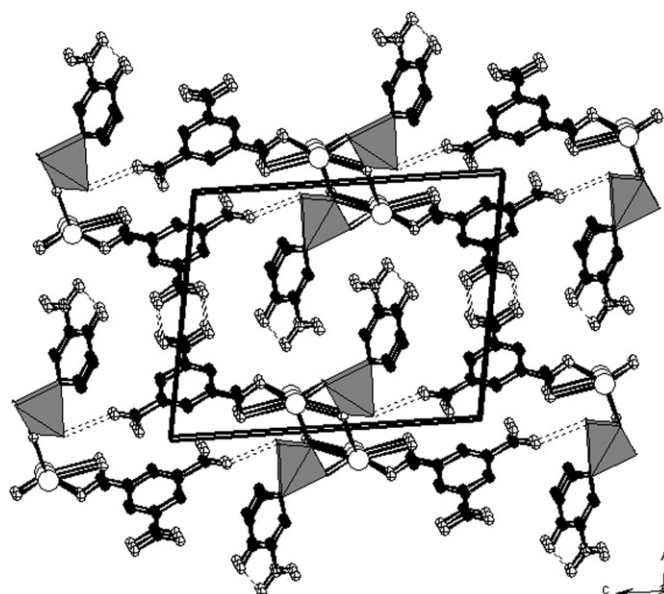
This work was supported by the National Natural Science Foundation of China (Nos. 20371047), the NSF of Fujian Province (E0610034), Key Project of the Chinese Academy of Sciences (No. KJXC2-YW-H01) and 973 Program (No. 2006CB932903).



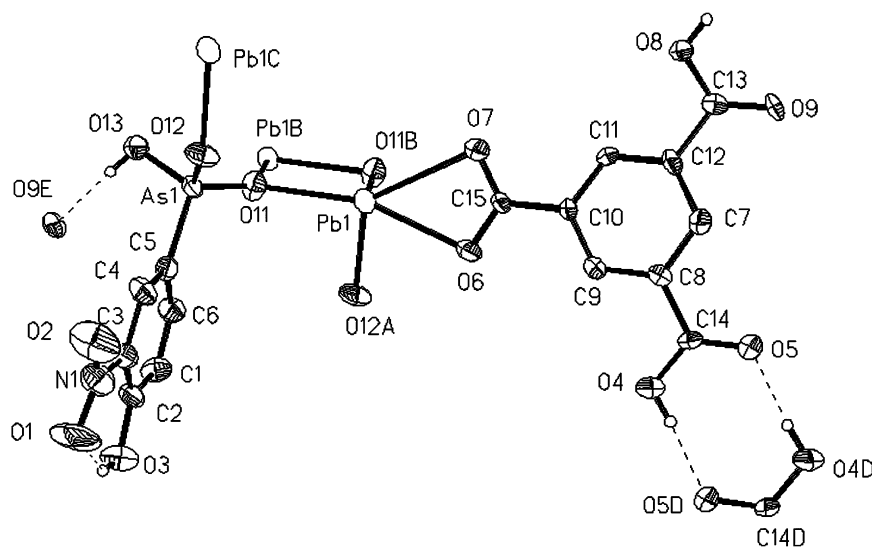
**Fig. 8.** View of the structure of compound **2** down the *b*-axis. The  $\text{CASO}_3$  and  $\text{CSO}_3$  tetrahedra are shaded in medium and light gray, respectively. Pb, C and O atoms are represented by open, black and crossed circles, respectively.



**Fig. 10.** A 1D lead(II) carboxylate-arsenate double chain in compound **3** along the *a*-axis. The  $\text{CASO}_3$  are shaded in gray. Pb, C, and O atoms are represented by open, black and crossed circles, respectively.



**Fig. 11.** View of the structure of compound **3** down the *a*-axis. The  $\text{CASO}_3$  are shaded in pink. Pb, C, and O atoms are represented by open, black and crossed circles, respectively.



**Fig. 9.** ORTEP representation of the selected unit of compound **3**. Thermal ellipsoids are drawn at 50% probability. Symmetry codes for the generated atoms: (a)  $x-1, y, z$ ; (b)  $-x+1, -y, -z+1$ ; (c)  $x+1, y, z$ ; (d)  $-x-1, -y+1, -z+2$ ; (e)  $x+1, y, z-1$ . Hydrogen bonds are drawn as dashed lines.

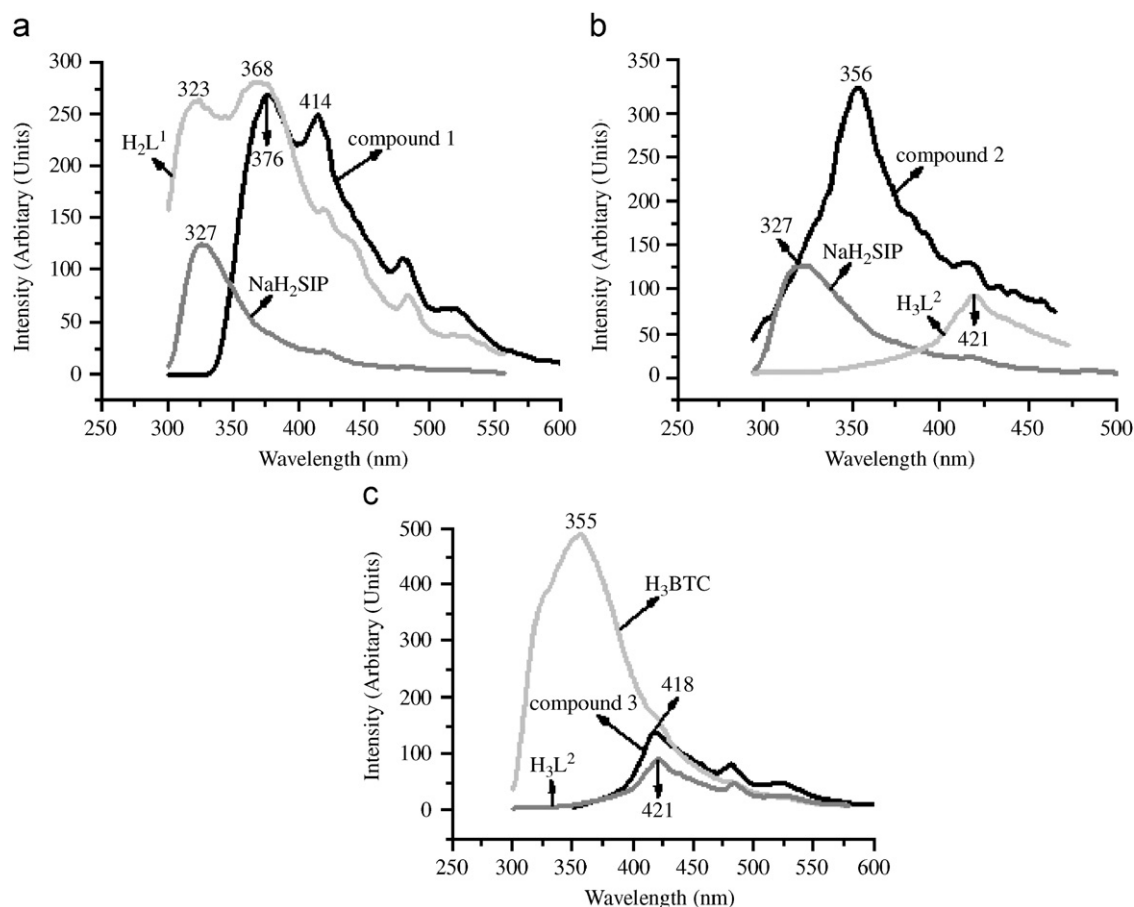


Fig. 12. Solid-state emission spectra of compounds **1** (a), **2** (b) and **3** (c).

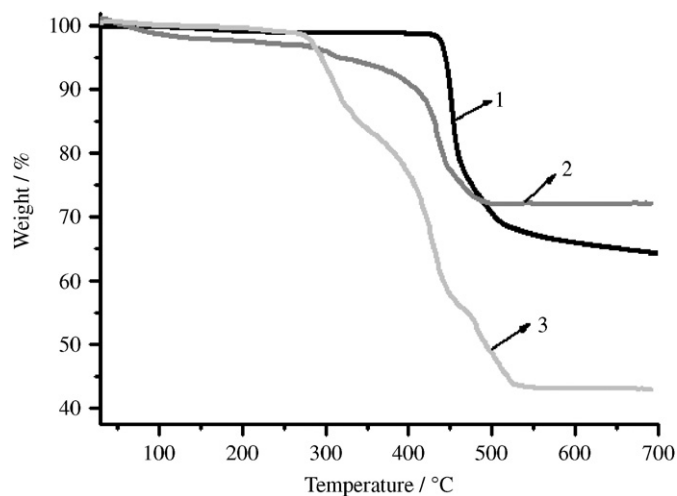


Fig. 13. TGA curves of compounds **1**–**3**.

#### Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jssc.2008.03.002](https://doi.org/10.1016/j.jssc.2008.03.002).

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