

Syntheses, Structures, and Characterizations of Four New Lead(II) 5-Sulfosalicylate Complexes with Both Chelating and Bridging Neutral Ligands

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Four structurally diverse complexes, $\{[\text{Pb}(\text{Hssal})(2,2'\text{-bipy})](4,4'\text{-bipy})_{0.5}\}_n$ (**1**), $[\text{Pb}_2(\text{Hssal})_2(2,2'\text{-bipy})_2(4,4'\text{-bipy})(\text{H}_2\text{O})_2]$ (**2**), $[\text{Pb}(\text{Hssal})(\text{phen})(4,4'\text{-bipy})_{0.5}]_n$ (**3**), and $[\text{Pb}(\text{Hssal})(2,2'\text{-bipy})(\text{bpe})_{0.5}]_n$ (**4**), have been synthesized and characterized by elemental analyses, IR, thermogravimetric analyses, fluorescent spectra, and single-crystal X-ray analyses, where Hssal^{2-} is doubly deprotonated 5-sulfosalicylate, 2,2'-bipy is 2,2'-bipyridine, phen is 1,10-phenanthroline, 4,4'-bipy is 4,4'-bipyridine, and bpe is *trans*-1,2-bis(4-pyridyl)ethylene. The structure of complex **1** possesses a one-dimensional ladderlike chain with guest 4,4'-bipy molecules, while the molecular structure of complex **2** is a dimeric species with a coordinating 4,4'-bipy ligand. Complex **3** consists of a one-dimensional ladderlike chain with monodentate 4,4'-bipyridine but somewhat different from that of complex **1**. Complex **4** is a two-dimensional layer structure. In **1–4**, all 5-sulfosalicylates are doubly deprotonated, and all carboxylate groups of Hssal^{2-} chelate to Pb^{II} ions; however, the coordination modes of sulfonyl groups are different: syn–syn bridging in **1**, noncoordinating in **2**, syn-skew bridging in **3**, and one-atom bridging in **4**. The noncoordinating mode of sulfonate in Pb^{II} complexes containing 5-sulfosalicylate is first reported in this presentation. The 4,4'-bipy ligands act as guest molecules in **1**, dimeric linkers in **2**, and monodentates in **3**. The π – π stacking interactions can be observed in complexes **1–3**, whereas there is no such interaction in complex **4**. The coordination spheres of Pb^{II} ions in **1–4** are controlled by three factors: the activity of a lone pair of electrons, weak Pb–O interactions, and π – π stacking interactions. The Pb^{II} lone pair in **4** is inactive, whereas in **1–3**, they are stereochemically active. The thermal stability and fluorescent property of complexes **1–4** are different from those of Pb^{II} complexes only containing chelating ligands, $[\text{Pb}(\text{Hssal})(2,2'\text{-bipy})(\text{DMF})]_n$ (**5**), and $[\text{Pb}(\text{Hssal})(2,2'\text{-bipy})(\text{H}_2\text{O})]_n$ (**6**), and $[\text{Pb}(\text{Hssal})(\text{phen})(\text{DMF})]_n$ (**7**).

Introduction

Lead is a heavy toxic metal found in critical life cycles as a result of its widespread use in the industry. The molecular mechanisms of lead toxicity are probably associated with several different types of proteins. Therefore, the mechanisms of Pb^{II} binding to zinc-binding domains have been extensively studied by using various techniques,¹ in these

investigations the Pb^{II} coordination chemistry, such as the lone pair of electrons, coordination number, and coordination geometry, plays an important role in the elucidation of interactions of Pb^{II} with zinc-binding domains. In addition, the study of Pb^{II} model complexes in biological systems² and removal of lead by chelating agents through coordination have been of crucial importance.³

On the other hand, the lead can exhibit a variable coordination number and geometry with or without a stereochemically active lone pair; therefore, structural diversities in lead complexes will inevitably occur. Coordination bonds and noncovalent interactions (such as hydrogen-

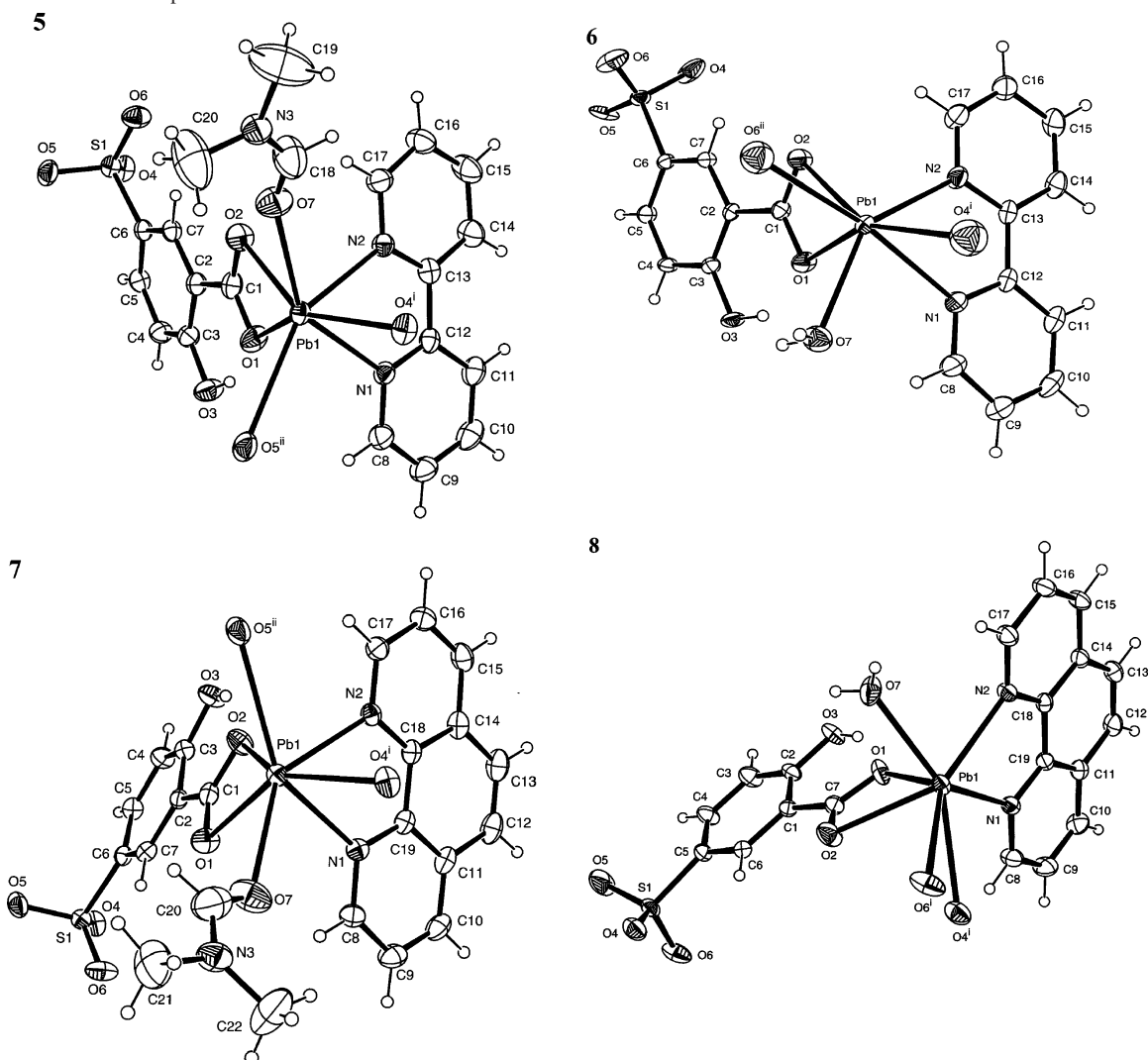
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Chart 1. Structures of Complexes 5–8



bonding and π - π stacking interactions), the metal-to-ligand molar ratio, the coordinative function of the ligands, the type of metal ions, the presence of solvent molecules, counterions, or organic guest molecules, and interactive information stored in the ligands should be taken into account in the process of the rational design and synthesis of metal coordination polymers.^{4–6} Therefore, careful selection of suitable polyfunctional organic ligands is helpful for constructing novel metal coordination polymers.^{7–9} To understand the Pb^{II} chemistry with polyfunctional chelating ligands, the 5-sul-

fosalicylic acid (H_3ssal) has been selected for synthesizing novel coordination polymers in our laboratory and other groups and five complexes based on the Pb^{II}/ H_3ssal /2,2'-bipyridine (2,2'-bipy) or 1,10-phenanthroline (phen) systems, namely, $[Pb(Hssal)(2,2'-bipy)(DMF)]_n$ (**5**), $[Pb(Hssal)(2,2'-bipy)(H_2O)]_n$ (**6**), $[Pb(Hssal)(phen)(DMF)]_n$ (**7**), $[Pb(Hssal)(phen)(H_2O)]_2$ (**8**), and $[Pb_3(ssal)_2(phen)_3]_n$ (**9**),^{10,11} have been synthesized (Chart 1), in which all contain neutral amine chelating ligands, i.e., 2,2'-bipy or phen. It is obvious that only one of these five complexes, **9**, has no solvent molecule, while each of the other four complexes has one solvent molecule (water or *N,N'*-dimethylformamide, DMF) occupying the coordination site. It can be predicted that if these sites were replaced by other neutral ligands, such as bridging ligands, resulting complexes will contain both chelating and bridging ligands and then the new architectures can be tuned or significantly changed by such strategies. Although a lot of transition-metal complexes with both chelating and

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bridging neutral ligands have been reported, only one Pb^{II} complex with two such ligands was published in our laboratory, [Pb₂(NO₃)₄(2,2'-bipy)₂(μ-4,4'-bipy)] (**10**; 4,4'-bipy = 4,4'-bipyridine).¹² Therefore, further exploration for the Pb^{II}/H₃ssal/2,2'-bipy, phen/4,4'-bipy, or *trans*-1,2-bis(4-pyridyl)ethylene (bpe) systems will provide abundant diverse structural complexes. Herein, we present syntheses, structures, properties, and weak interactions of four polymeric complexes, namely, {[Pb(Hssal)(2,2'-bipy)](4,4'-bipy)_{0.5}]_n} (**1**), [Pb₂(Hssal)₂(2,2'-bipy)₂(4,4'-bipy)(H₂O)₂] (**2**), [Pb(Hssal)(phen)(4,4'-bipy)_{0.5}]_n (**3**), and [Pb(Hssal)(2,2'-bipy)(bpe)_{0.5}]_n (**4**).

Experimental Section

Materials and Physical Measurements. All starting materials were obtained from commercial sources and were of reagent grade. C, H, and N elemental analyses were carried out on a Perkin-Elmer analyzer model 1110. The IR spectra were taken on a Nicolet Nexus 470 IR spectrophotometer as KBr pellets in the 400–4000 cm⁻¹ region. Thermogravimetric analyses were studied by a NETZSCH STA 409 in a N₂ atmosphere in the temperature range between room temperature and 800 °C at a heating rate of 10 °C min⁻¹ using Al₂O₃ crucibles. The photoluminescence study was carried out on a powdered sample in the solid state at room temperature using a Hitachi 850 spectrometer.

Preparation of {[Pb(Hssal)(2,2'-bipy)](4,4'-bipy)_{0.5}]_n} (1**).** A mixture of Pb(CH₃COO)₂·3H₂O (0.191 g, 0.50 mmol), 5-sulfosalicylic acid dihydrate (0.127 g, 0.50 mmol), 2,2'-bipy (0.078 g, 0.50 mmol), and 4,4'-bipy (0.076 g, 0.49 mmol) in a water/ethanol (3:1) solution (20 mL) was refluxed for 2 h and then filtered. A cottonlike solid was quickly precipitated without further filtration. One week later colorless block-shaped crystals of **1** started to form and a cottonlike solid gradually disappeared within 2 weeks. Yield: 71% based on a Pb^{II} salt. Anal. Calcd (found): C, 40.18 (40.20); H, 2.45 (2.29); N, 6.39 (6.41). IR (KBr pellet, cm⁻¹): 1630(m), 1589(s), 1572(s), 1489(m), 1475(w), 1448(m), 1438(s), 1387(w), 1375(w), 1315(w), 1306(w), 1212(s), 1173(s), 1126(m), 1083(w), 1034(s), 1010(m), 895(w), 823(m), 773(s), 758(w), 733(w), 675(m), 645(w), 601(m), 585(m), 540(w), 451(w), 420(w), 407(w).

Preparation of [Pb₂(Hssal)₂(2,2'-bipy)₂(4,4'-bipy)(H₂O)₂] (2**).** A mixture of Pb(CH₃COO)₂·3H₂O (0.191 g, 0.50 mmol), 5-sulfosalicylic acid dihydrate (0.127 g, 0.50 mmol), 2,2'-bipy (0.031 g, 0.20 mmol), and 4,4'-bipy (0.154 g, 0.99 mmol) in a water/ethanol/*N,N'*-dimethylformamide (DMF) (3:1:1) solution (20 mL) was refluxed for 2 h and then filtered. Colorless block-shaped crystals of **2** were obtained after 1 day. Yield: 75% based on a Pb^{II} salt. Anal. Calcd (found): C, 38.01 (38.09); H, 2.73 (2.60); N, 6.33 (6.07). IR (KBr pellet, cm⁻¹): 3318(s), 1603(s), 1592(s), 1557(s), 1474(m), 1442(s), 1377(m), 1356(w), 1315(w), 1292(m), 1254(m), 1211(s), 1181(s), 1156(m), 1122(m), 1075(m), 1024(s), 1015(m), 895(w), 840(w), 820(w), 796(w), 771(m), 733(w), 671(w), 648(w), 621(w), 586(m), 567(w), 413(w).

Preparation of [Pb(Hssal)(phen)(4,4'-bipy)_{0.5}]_n (3**).** A mixture of Pb(CH₃COO)₂·3H₂O (0.191 g, 0.50 mmol), 5-sulfosalicylic acid dihydrate (0.127 g, 0.50 mmol), phen (0.020 g, 0.10 mmol), and 4,4'-bipy (0.154 g, 0.99 mmol) in a water/DMF (3:1) solution (20 mL) was refluxed for 2 h and filtered. Colorless block-shaped crystals of **3** were obtained after 1 day. Yield: 68% based on a

Pb^{II} salt. Anal. Calcd (found): C, 42.29 (42.29); H, 2.37 (2.34); N, 6.16 (6.16). IR (KBr pellet, cm⁻¹): 1619(m), 1577(s), 1518(m), 1474(m), 1445(s), 1430(m), 1412(w), 1372(w), 1336(m), 1297(m), 1256(s), 1238(s), 1155(s), 1136(s), 1119(m), 1102(m), 1072(m), 1035(w), 1016(s), 895(w), 855(m), 831(w), 819(m), 803(w), 783(w), 724(s), 669(s), 640(w), 617(w), 596(s), 586(m), 567(w), 534(w), 459(w), 418(w), 405(m).

Preparation of [Pb(Hssal)(2,2'-bipy)(bpe)_{0.5}]_n (4**).** A mixture of Pb(CH₃COO)₂·3H₂O (0.190 g, 0.50 mmol), 5-sulfosalicylic acid dihydrate (0.128 g, 0.50 mmol), 2,2'-bipy (0.077 g, 0.49 mmol), and *trans*-1,2-bis(4-pyridyl)ethylene (0.091 g, 0.50 mmol) in a water/ethanol/DMF (3:1:1) solution (25 mL) was refluxed for 2 h and filtered. The resulting solution was set aside for evaporation for 3 days, and pale-yellow needle crystals of **4** were obtained. Yield: 84% based on a Pb^{II} salt. Anal. Calcd (found): C, 41.19 (41.19); H, 2.55 (2.47); N, 6.27 (6.25). IR (KBr pellet, cm⁻¹): 1604(s), 1560(m), 1496(w), 1474(m), 1439(s), 1421(m), 1369(w), 1358(w), 1337(m), 1319(w), 1301(m), 1256(s), 1236(s), 1151(s), 1117(m), 1072(m), 1036(w), 1010(s), 979(w), 959(w), 897(w), 858(w), 821(m), 774(s), 732(w), 671(m), 646(w), 628(w), 596(m), 559(w), 544(w), 462(w), 420(w), 405(w).

X-ray Structure Determination. Data collection for complexes **1–4** was carried out by a Bruker SMART diffractometer equipped with a CCD area detector. The data were integrated by use of the SAINT program,¹³ and the intensities were corrected for Lorentz factor polarization and absorption. The four structures were solved by the Patterson method and successive Fourier syntheses. Full-matrix least-squares refinements on *F*² were carried out using the SHELXL-97 package.¹⁴ All H atoms bonded to C atoms were placed in calculated positions and refined as riding, with C–H = 0.93 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C). In **3**, the 4,4'-bipy ligand is heavily disordered, and the atoms were only isotropically refined. All of the programs used are included in the WinGX Suite with version 1.70.¹⁵ Detailed crystal data and structure refinements for **1–4** are listed in Table 1.

Results and Discussion

Synthesis. In our previously reported system of Pb^{II}/H₃ssal/2,2'-bipy, we have prepared two complexes with different topologies, **5** and **6**.¹⁰ Because the Pb^{II} ion has a versatile coordination number and varied coordination geometry, we introduced the bridging ligands such as 4,4'-bipy and bpe into the system of Pb^{II}/H₃ssal/2,2'-bipy, with two aims: one is to construct novel coordination polymers, and the other is to explore the effect of the neutral ligands on the network assembly. The 4,4'-bipy ligand in most of the metal complexes acts as a spacer ligand and forms one-, two-, or three-dimensional coordination polymers, whereas the 2,2'-bipy ligand only acts as a terminal chelating function. The reaction of 4,4'-bipy, Pb(CH₃COO)₂, H₃ssal, 2,2'-bipy, ethanol, and water under reflux led to the formation of complex **1**, in which 4,4'-bipy is a guest molecule. In order to obtain a coordinating 4,4'-bipy complex, we changed the molar ratio of Pb^{II}/H₃ssal/2,2'-bipy/4,4'-bipy from 1:1:1:1 to 5:5:2:10 in a water/ethanol solution, but only cottonlike solids

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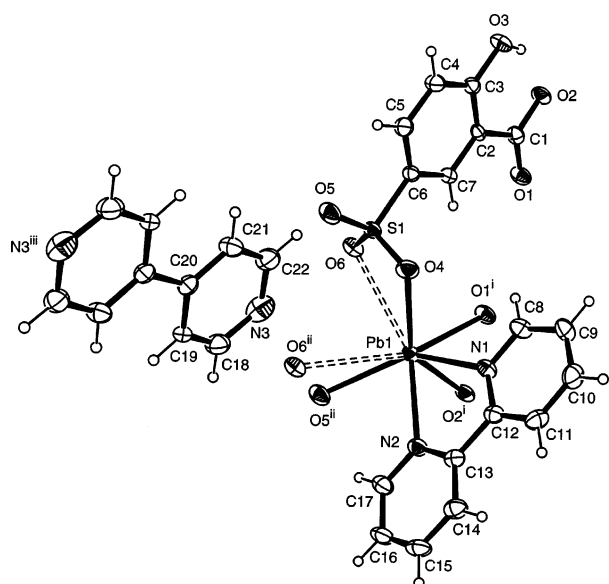
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Table 1. Crystallographic Data and Refinement Parameters for Complexes 1–4

complex	1	2	3	4
empirical formula	C ₂₂ H ₁₆ N ₃ O ₆ PbS	C ₄₂ H ₃₆ N ₆ O ₁₄ Pb ₂ S ₂	C ₂₄ H ₁₇ N ₃ O ₆ PbS	C ₂₃ H ₁₇ N ₃ O ₆ PbS
<i>M</i> _r	657.6	1351.3	682.66	670.65
cryst size (mm ³)	0.11 × 0.22 × 0.27	0.20 × 0.22 × 0.30	0.10 × 0.14 × 0.23	0.11 × 0.12 × 0.32
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 1̄	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	10.0888(5)	14.1956(8)	11.3325(11)	11.6713(7)
<i>b</i> (Å)	10.3628(5)	10.9841(7)	15.0546(15)	15.5691(10)
<i>c</i> (Å)	10.7442(6)	15.5903(9)	12.6712(13)	11.8091(8)
α (deg)	88.834(1)	90.00	90.00	90.00
β (deg)	88.418(1)	116.482(2)	91.369(1)	96.122(1)
γ (deg)	67.372(1)	90.00	90.00	90.00
<i>V</i> (Å ³)	1036.37(9)	2175.9(2)	2161.17(4)	2133.61(3)
<i>Z</i>	2	2	4	4
<i>D</i> _c (Mg·m ^{−3})	2.107	2.063	2.098	2.088
<i>μ</i> (mm ^{−1})	8.288	7.902	7.954	8.054
θ range	1.9–25.5	2.4–26.0	2.3–25.1	2.2–25.5
unique reflns	3820	4261	3711	3963
obsd reflns	3605	3798	2693	3476
no. of param	301	316	307	310
<i>F</i> (000)	630	1300	1312	1288
<i>T</i> (K)	295(2)	295(2)	295(2)	295(2)
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.034, 0.070	0.028, 0.064	0.064, 0.155	0.038, 0.067
<i>R</i> 1, <i>wR</i> 2 [all data]	0.032, 0.069	0.024, 0.062	0.042, 0.130	0.031, 0.064
GOF	1.111	1.081	0.997	1.021

were formed. However, in the mixed solvents of water/ethanol/DMF, the dimeric species with the coordinating 4,4'-bipy, complex **2**, was obtained. In the Pb^{II}/H₃ssal/phen/4,4'-bipy system, a change of the molar ratio of phen/4,4'-bipy from 1:1 to 1:10 gave the unique product, complex **3**. In the Pb^{II}/H₃ssal/2,2'-bipy/bpe system refluxed in ethanol/DMF/water, complex **4** was produced in a molar ratio of 1:1:1:0.5 or 5:5:2:10, indicating that the molar ratio of the reactants is not a key factor in the formation of complex **4**.

The syntheses of complexes **2**–**4** were achieved by adding the solvent DMF. However, the volume of DMF should be less than the volume of water used in the syntheses; otherwise, only complex **5** or **7** was obtained, indicating that the existence and volume control of DMF are the important factors for the formation of complexes with both chelating and bridging ligands.

**Figure 1.** ORTEP view (40% probability ellipsoids) of the asymmetric unit of complex **1** with the numbering scheme.

Complexes **1**, **3**, and **4** are solvent-free species, while all of complexes **5**–**8** incorporate a coordinating water or DMF, indicating that the bridging ligands can replace the sites occupied by solvents and then influence the assembly of the molecular structures.

Structure of 1. Single-crystal X-ray diffraction reveals that complex **1** consists of a one-dimensional ladderlike chain, constructed from Pb^{II} ions and 2,2'-bipy and Hssal^{2−} ligands, while the 4,4'-bipy ligand only acts as a guest molecule in the crystal packing. As shown in Figure 1, each Pb^{II} ion is eight-coordinated by two N atoms from one 2,2'-bipy ligand and six O atoms: two from a carboxylate group and four from two sulfonyl groups of two different Hssal^{2−} ligands (Table 2), in which six bond lengths are relatively shorter and two longer (dashed lines in Figure 1), termed as “primary” and “secondary” bonds, respectively.^{1b} Secondary bonds are always overlooked (for example, reexamination of [Pb(*i*-mnt)₂]₂^{4−} results in a new picture of the molecular structure),^{1b} while recently such bonds have been accepted as bonding.¹⁶

All bond distances of Pb–O(COO[−]) in **1** are in the typical range of 2.489(4)–2.516 (4) Å. However, the bond lengths Pb1–O6 = 3.144(4) Å and Pb1–O6ⁱⁱ = 3.128(4) Å are longer than the sum of the ionic radii but significantly shorter than the sum of the van der Waals radii (3.54 Å),¹⁷ which can be explained by the presence of an active lone pair in the proximity of the sulfonate O atoms.

The pioneering works on the Pb^{II} lone pair have produced valuable knowledge.^{18,19} A stereochemically active Pb^{II} lone pair of electrons has important effects on the property and

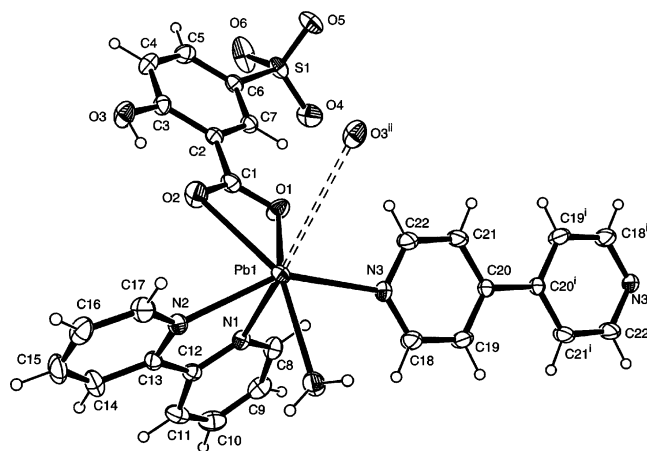
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Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes 1–4^a

Complex 1			
Pb1–O1 ⁱ	2.516(4)	Pb1–O2 ⁱ	2.489(4)
Pb1–O4	2.687(4)	Pb1–O5 ⁱⁱ	2.915(5)
Pb1–O6	3.144(4)	Pb1–O6 ⁱⁱ	3.128(4)
Pb1–N1	2.496(5)	Pb1–N2	2.591(5)
O1 ⁱ –Pb1–O2 ⁱ	52.39(12)	O1 ⁱ –Pb1–O4	89.58(13)
O1 ⁱ –Pb1–O5 ⁱⁱ	126.69(12)	O1 ⁱ –Pb1–O6 ⁱⁱ	158.30(13)
O1 ⁱ –Pb1–N1	76.15(14)	O1 ⁱ –Pb1–N2	121.09(14)
O2 ⁱ –Pb1–O4	141.16(13)	O2 ⁱ –Pb1–O5 ⁱⁱ	91.59(13)
O2 ⁱ –Pb1–O6 ⁱⁱ	136.43(12)	O2 ⁱ –Pb1–N1	86.10(15)
O2 ⁱ –Pb1–N2	82.56(14)	O4–Pb1–O5 ⁱⁱ	121.76(13)
O4–Pb1–O6 ⁱⁱ	81.76(12)	O4–Pb1–N1	75.91(14)
O4–Pb1–N2	117.53(14)	O5 ⁱⁱ –Pb1–O6 ⁱⁱ	46.96(10)
O5 ⁱⁱ –Pb1–N1	147.31(14)	O5 ⁱⁱ –Pb1–N2	83.81(14)
O6 ⁱⁱ –Pb1–N1	120.26(13)	O6 ⁱⁱ –Pb1–N2	80.41(13)
N1–Pb1–N2	63.54(15)		
Complex 2			
Pb1–O1	2.503(3)	Pb1–O2	2.714(3)
Pb1–O7	2.560(3)	Pb1–N1	2.451(3)
Pb1–N2	2.536(3)	Pb1–N3	2.627(3)
O1–Pb1–O2	49.85(9)	O1–Pb1–O7	140.63(11)
O1–Pb1–N1	77.46(10)	O1–Pb1–N2	114.67(10)
O1–Pb1–N3	74.87(10)	O2–Pb1–O7	151.74(9)
O2–Pb1–N1	86.39(10)	O2–Pb1–N2	75.01(9)
O2–Pb1–N3	124.61(9)	O7–Pb1–N1	74.85(10)
O7–Pb1–N2	78.01(10)	O7–Pb1–N3	75.21(11)
N1–Pb1–N2	65.59(9)	N1–Pb1–N3	84.70(9)
N2–Pb1–N3	144.24(10)		
Complex 3			
Pb1–O1	2.657(8)	Pb1–O2	2.474(8)
Pb1–O4 ⁱ	2.688(7)	Pb1–O5 ⁱⁱ	2.803(8)
Pb1–O5 ⁱⁱⁱ	3.384(9)	Pb1–N1	2.506(8)
Pb1–N2	2.449(9)	Pb1–N3	2.821(16)
O1–Pb1–O2	50.2(2)	O1–Pb1–O4 ⁱ	144.1(3)
O1–Pb1–O5 ⁱⁱⁱ	112.3(3)	O1–Pb1–N1	114.3(3)
O1–Pb1–N2	76.2(3)	O1–Pb1–N3	81.1(4)
O2–Pb1–O4 ⁱ	147.4(2)	O2–Pb1–O5 ⁱⁱ	75.8(3)
O2–Pb1–N1	75.4(3)	O2–Pb1–N2	87.0(3)
O2–Pb1–N3	131.3(4)	O4 ⁱ –Pb1–O5 ⁱⁱ	103.6(3)
O4 ⁱ –Pb1–N1	72.4(3)	O4 ⁱ –Pb1–N2	75.3(2)
O4 ⁱ –Pb1–N3	74.3(4)	O5 ⁱⁱ –Pb1–N1	80.3(3)
O5 ⁱⁱ –Pb1–N2	145.1(3)	O5 ⁱⁱ –Pb1–N3	130.8(4)
N1–Pb1–N2	65.9(3)	N1–Pb1–N3	139.1(4)
N2–Pb1–N3	83.2(4)		
Complex 4			
Pb1–O1	2.432(4)	Pb1–O2	2.610(4)
Pb1–O5 ⁱ	2.967(4)	Pb1–O5 ⁱⁱ	2.917(4)
Pb1–N1	2.520(4)	Pb1–N2	2.444(4)
Pb1–N3	2.773(5)		
O1–Pb1–O2	51.65(12)	O1–Pb1–O5 ⁱ	82.12(13)
O1–Pb1–O5 ⁱⁱ	152.13(12)	O1–Pb1–N1	75.17(13)
O1–Pb1–N2	86.78(14)	O1–Pb1–N3	129.56(13)
O2–Pb1–O5 ⁱ	115.39(11)	O2–Pb1–O5 ⁱⁱ	151.98(12)
O2–Pb1–N1	115.49(13)	O2–Pb1–N2	76.53(13)
O2–Pb1–N3	77.92(13)	O5 ⁱ –Pb1–O5 ⁱⁱ	89.11(11)
O5 ⁱ –Pb1–N1	85.69(13)	O5 ⁱ –Pb1–N2	151.10(13)
O5 ⁱ –Pb1–N3	126.90(13)	O5 ⁱⁱ –Pb1–N1	77.84(13)
O5 ⁱⁱ –Pb1–N2	88.39(13)	O5 ⁱⁱ –Pb1–N3	76.31(13)
N1–Pb1–N2	65.65(14)	N1–Pb1–N3	137.34(14)
N2–Pb1–N3	80.24(14)		

^a Symmetry codes for **1**: i, 1 – x, 1 – y, 2 – z; ii, 1 – x, 1 – y, 1 – z. Symmetry codes for **3**: i, –1 + x, y, z; ii, 1 – x, –y, 1 – z; iii, –x, 1 – y, 1 – z. Symmetry codes for **4**: i, –x, –y, 2 – z; ii, 1 + x, y, z; iii, 1 – x, 1 – y, 2 – z.

structure of its complexes. If the Pb^{II} lone pair has no steric effects, which was termed as an inactive lone pair or

**Figure 2.** ORTEP diagram of the asymmetric unit of complex **2**. The thermal ellipsoids are drawn at 40% probability.

holodirected,¹⁸ all of the Pb–L bonds likely have similar lengths. In addition, the presence of an active lone pair leads to very long Pb–L bonds at the site occupied by the lone pair, a shortening of the Pb–L bond lengths opposite to the position of the lone pair, and a lengthening of those adjacent to this site.¹⁹

It has been observed that Pb–N bond lengths fall in the range of 2.62–2.88 Å for complexes with an inactive lone pair.²⁰ The Pb–N distances in **1** are shorter and locate in the site opposite to the lone pair. In addition, these Pb–N distances fall well within the ranges usually observed in Pb^{II} complexes containing a 2,2'-bipy ligand with an active lone pair.²¹ Therefore, the presence of an active lone pair is further confirmed.

Moreover, the weak interactions between Pb^{II} ions and N atoms of 4,4'-bipy may be accepted because the distance of Pb–N_{4,4'-bipy} is 3.555(6) Å, which is similar to the sum of the van der Waals radii (3.57 Å).¹⁷ If the 4,4'-bipy ligand were accepted as a weak bridging linker, the one-dimensional ladderlike chain of **1** should be extended into the two-dimensional network, in which the connection of Pb···4,4'-bipy···Pb is not linear with the Pb···Pb distance of 12.304 Å, which is slightly longer than that of **10** but similar to that of complex **2**.

Structure of 2. Determination of the structure of **2** by X-ray crystallography showed the complex in the solid state to be a dimeric species, similar to **10**. As shown in Figure 2, each Pb^{II} ion is chelated by two N atoms of one 2,2'-bipy ligand with Pb–N bond distances of 2.451(3) and 2.536(3) Å, one N atom of the 4,4'-bipy ligand with a Pb–N distance of 2.627(3) Å, which is much shorter than that of **10**, two O atoms from one carboxyl group of the Hssal²⁻ ligand with Pb–O distances of 2.503(3) and 2.714(3) Å, and one O atom from the water molecule with a Pb–O distance of 2.560(3) Å (Table 2), slightly shorter than that in **6**, resulting in a six-coordinate geometry with a PbN₃O₃ chromophore. The two pyridyl rings of the 4,4'-bipy ligand are completely

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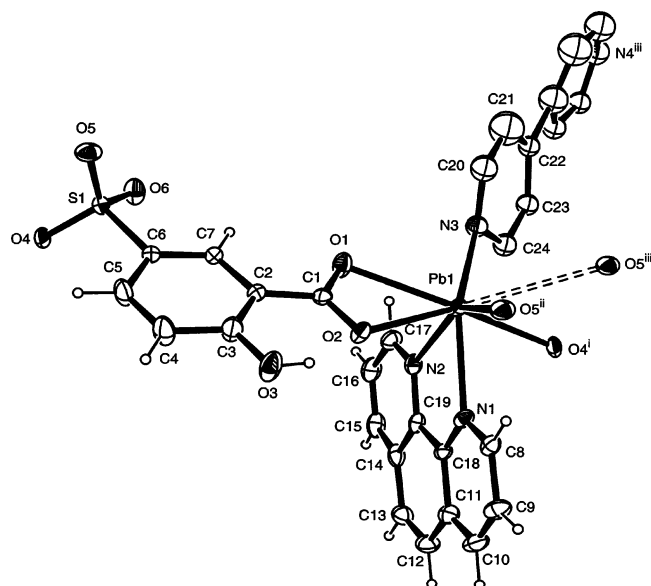


Figure 3. ORTEP view of the asymmetric unit of complex **3**. The thermal ellipsoids are drawn at 30% probability.

coplanar because one of the two pyridyl rings is imposed by symmetry. In complex **2**, the 4,4'-bipy ligand bridges two Pb^{II} ions rather than noncoordinating in **1**, with a separation of Pb...Pb = 12.2977(6) Å, similar to that in [PbCl₂(4,4'-bipy)]_n (12.303 Å)²² but shorter than that in **10** (12.631 Å).

The lone pair of electrons likely leaves space for the donor atoms of ligands around the Pb^{II} ion in **2**. The secondary bond of Pb–O3ⁱⁱ (−*x* + 1, −*y*, −*z* + 1) with a distance of 3.508(3) Å (dashed lines in Figure 2) and shorter Pb–N_{2,2'-bipy} opposite to the O3ⁱⁱ indicate the presence of an active lone pair. In addition, the [Pb₂(2,2'-bipy)₂(4,4'-bipy)(Hssal)₂·(H₂O)₂] complex contains water molecules coordinated to the Pb^{II} centers. The water O atoms form O–H...O hydrogen bonds with sulfonyl O atoms of the Hssal^{2−} ligands and extend the structure of **2** into a three-dimensional hydrogen-bonding architecture, which can enhance the solid stability of the crystal packing.

Structure of 3. Determination of the structure of **3** by X-ray crystallography showed the complex in the solid state to be a one-dimensional ladderlike chain, constructed from Pb^{II} ions and phen, 4,4'-bipy, and Hssal^{2−} ligands. As shown in Figure 3, each Pb^{II} ion adopts a seven-coordinate geometry, involving two N atoms from one phen ligand, one N atom from one 4,4'-bipy ligand, and four O atoms [two from a carboxylate group and two from two sulfonyl groups] (Table 2). The average distance of Pb–N_{phen} in **3** is 2.478–(9) Å, much shorter than those of Pb^{II} complexes containing phen.²³ The 4,4'-bipy ligand is monodentate to the Pb^{II} ion with a Pb–N_{4,4'-bipy} bond distance of 2.821(16) Å, which is much longer than that in **2** but similar to that in **10**. The carboxyl group of each Hssal^{2−} ligand chelates to the Pb^{II} ion with bond distances of 2.474(8) and 2.657(8) Å, while

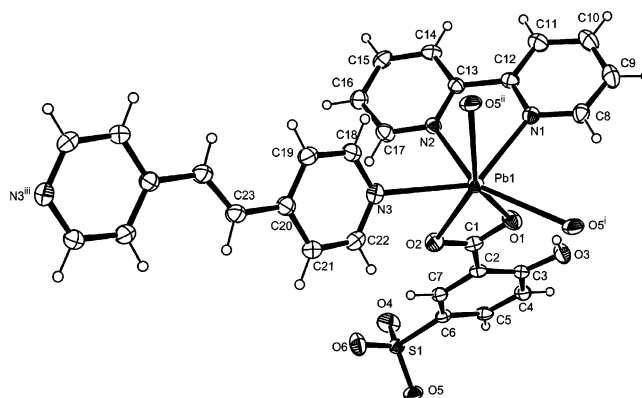


Figure 4. ORTEP view of the asymmetric unit of complex **4**. The thermal ellipsoids are drawn at 40% probability.

the sulfonate group is bidentately coordinated to the Pb^{II} ion through two O atoms with bond distances of 2.688(7) and 2.803(8) Å.

The arrangement of the phen, 4,4'-bipy, and Hssal^{2−} ligands suggests a gap or hole in the coordination geometry around the Pb^{II} ion [O4ⁱ–Pb1–O5ⁱⁱ 103.6(3)°], occupied possibly by a configurationally active lone pair of electrons on the Pb^{II} ion. In addition, analysis of the coordination geometry around the Pb^{II} ion indicates that there is a secondary bond, Pb–O5ⁱⁱⁱ (*x* − 1, *y*, *z*) (dashed lines in Figure 3) with a bond distance of 3.384(9) Å, which is close to the sum of the van der Waals radii.

Structure of 4. Single-crystal X-ray diffraction analysis reveals that the Pb^{II} ion in **4** is coordinated by four O (O1, O2, O5ⁱ, and O5ⁱⁱ) atoms from three symmetrical Hssal^{2−} groups, two N (N1 and N2) atoms from one 2,2'-bipy ligand, and the other N (N3) atom from bridging bpe ligand, resulting in a seven-coordinate complex with a PbN₃O₄ chromophore, as shown in Figure 4. The complex crystallizes in the monoclinic space group *P*2₁/*n* and consists of Pb^{II} ions bridged by both bpe and Hssal^{2−} ligands, thus forming a two-dimensional infinite framework. Each Hssal^{2−} anion contacts three Pb^{II} ions through carboxyl and sulfonyl groups. The carboxyl group chelates to the Pb^{II} ion with a typical Pb–O distance range, 2.432(4)–2.610(4) Å (Table 2). The sulfonyl group is coordinated to two Pb^{II} ions through one O atom with bond distances of 2.917(4) and 2.967(4) Å, leading to the formation of the ladderlike chain by [Pb(Hssal)] units. The Pb–N_{bpe} bond distance [Pb1–N3 = 2.773(5) Å] is much longer than that of {[Pb(μ-OAc)(μ-bpe)](ClO₄)_n}_n²⁴ but shorter than that of [Pb(μ-SCN)₂(μ-bpe)_{1.5}]_n.²⁴

In complex **4**, the arrangement of 2,2'-bipy, bpe, and Hssal^{2−} ligands does not suggest a gap or hole in the coordination geometry around the Pb^{II} ion, indicating that the lone pair of electrons on Pb^{II} is probably inactive in this complex.

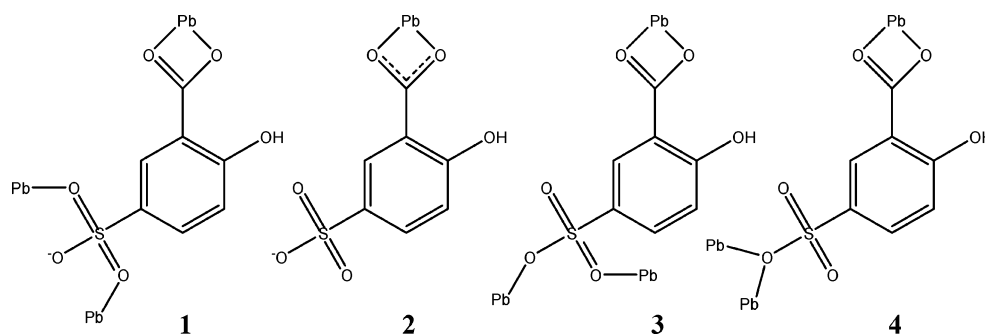
Coordination Modes of 5-Sulfosalicylates in Complexes 1–4. The H₃ssal ligands in complexes **1–4** only lose two H atoms for carboxyl and sulfonyl groups, while the H atom of the phenolic hydroxyl remains. The coordination modes of Hssal^{2−} ligands in **1–4** are illustrated in Chart 2.

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Chart 2



In complex **1**, a ladderlike chain was formed where the separation of $\text{Pb}\cdots\text{Pb}$ by sulfonate is 5.1235(5) Å, which is slightly longer than those in **5** and **6**. Moreover, the separations of $\text{Pb}\cdots\text{Pb}$ by Hssal^{2-} ligands in the ladderlike chain are 8.2685(6) and 10.7442(6) Å, which are much shorter than those in **5** and **6**. In **2**, the carboxylate group also chelates to one metal ion, while the sulfonate group is noncoordinating. To the best of our knowledge, in Pb^{II} complexes the sulfonate groups usually coordinate to the metal. In complex **3**, each Hssal^{2-} ligand performs a chelating-bridging coordination mode; therefore, a ladderlike chain was formed in which the separation of $\text{Pb}\cdots\text{Pb}$ by sulfonate is 4.7828(8) Å and is slightly shorter than that in **5**. Moreover, the separations of $\text{Pb}\cdots\text{Pb}$ by Hssal^{2-} ligands in the ladderlike chain are 8.5136(10) and 11.3325(11) Å, similar to those in **5**. In complexes **1** and **3**, each Hssal^{2-} ligand chelates to one Pb^{II} ion and bridges two Pb^{II} ions, but in **1** the sulfonate is a syn-syn bridging mode while in **3** the sulfonate acts as a syn-skew mode. In **4**, the Hssal^{2-} ligand is in a chelating and one-atom-bridging coordination mode: the carboxylate group chelates to one metal ion, and the sulfonate group coordinates to two metal atoms only using one O atom, which is rare in Pb^{II} complexes containing sulfonate groups. The $\text{Pb}\cdots\text{Pb}$ separation by sulfonates in the Pb_2O_4 planar unit is 4.1930(4) Å, while the $\text{Pb}\cdots\text{Pb}$ distances separated by Hssal^{2-} ligands are 8.6784(6) and 11.6713(7) Å. The individual polymeric chains of $[\text{Pb}(\text{Hssal})]$ units are almost parallel to each other and further bridged by bidentate bridging bpe ligands, resulting in a two-dimensional framework in which the $\text{Pb}\cdots\text{Pb}$ distance separated by bpe is 14.7303(10) Å.

Extended Frameworks of the $[\text{Pb}(\text{Hssal})]$ Building Blocks in Complexes 1–8. In these four new complexes, together with our previously reported four, **1–8**, all contain $[\text{Pb}(\text{Hssal})]$ building blocks. Because of the different coordination modes of Hssal^{2-} , these eight $[\text{Pb}(\text{Hssal})]_n$ units display variable frameworks depicted in Figure 5. Units of $[\text{Pb}(\text{Hssal})]$ in **1**, **3–5**, and **7** consist of one-dimensional frameworks, in which the frameworks of **3**, **5**, and **7** are similar. The motif of $[\text{Pb}(\text{Hssal})]$ in **2** is a monomer. Blocks of $[\text{Pb}(\text{Hssal})]$ in **6** consist of a two-dimensional framework, while in **8** $[\text{Pb}(\text{Hssal})]$ components afford a dimeric species. Therefore, the building blocks of $[\text{Pb}(\text{Hssal})]$ in **1–8** exhibit six frameworks, i.e., one monomer, one dimer, three one-dimensional chains, and one two-dimensional layer, clearly

indicating that neutral bridging ligands can regulate the assembly of frameworks.

Weak Interactions in Complexes 1–4. There are strong π – π interactions occurring between rings of symmetry-related 2,2'-bipy ligands from adjacent chains in **1**, with centroid-to-centroid distances of 3.662(4) Å for rings N1/C8–C12 and N2ⁱ/C13ⁱ–C17ⁱ (symmetry code i: $1 - x, 1 - y, 1 - z$) and 3.645(11) Å for rings N2/C20–C24 and N3ⁱⁱ/C30ⁱⁱ–C34ⁱⁱ (symmetry code ii: $x, -1 + y, z$). In complex **2**, the weak π – π stack interactions exist between rings of the 4,4'-bipy and Hssal^{2-} ligands, with a centroid-to-centroid distance of 3.920(2) Å, and the dihedral angle between the two rings is 2.7(2)°. There are very strong π – π interactions occurring between rings of symmetry-related phen ligands from adjacent chains in **3**, with a centroid-to-centroid distance of 3.4452(8) Å for rings C11–C14/C18,C19 and C11ⁱⁱⁱ–C14ⁱⁱⁱ/C18ⁱⁱⁱ,C19ⁱⁱⁱ (symmetry code iii: $-x, -y, -z$). However, there is no π – π stacking interactions in **4** because of the too long spacer of bpe for the formation of the π – π interactions.

Characterizations

IR Spectroscopy. In the spectra of complexes **1–4**, both COOH and SO₃H characteristic peaks near 1680 cm^{−1} are absent, indicating that these functional groups are deprotonated. In the region where $\nu(\text{O}=\text{H})$ phenoxo deformation occurs, two absorption bands are observed at 1475 and 1438 cm^{−1} for **1**, 1474 and 1442 cm^{−1} for **2**, 1474 and 1445 cm^{−1} for **3**, and 1474 and 1439 cm^{−1} for **4**. Therefore, these four complexes contain the Hssal^{2-} ligands, i.e., doubly deprotonated 5-sulfosalicylate. The IR spectra of **1–4** show typical asymmetric and symmetric carboxylate stretching bands at 1572 and 1387 cm^{−1} for **1**, 1557 and 1377 cm^{−1} for **2**, 1577 and 1372 cm^{−1} for **3**, and 1560 and 1369 cm^{−1} for **4**. The characteristic vibrations of $\nu_{\text{as}}(\text{SO}_3^-)$ in **1–4** are at 1212, 1173, and 1126 cm^{−1} in **1**, 1211, 1181, and 1122 cm^{−1} in **2**, 1238, 1155, and 1136 cm^{−1} in **3**, and 1236, 1151, and 1117 cm^{−1} in **4**, whereas the $\nu_{\text{s}}(\text{SO}_3)$ absorptions are at 1034 cm^{−1} in **1**, 1024 in **2**, 1016 cm^{−1} in **3**, and 1010 cm^{−1} in **4**.

Thermal Stability Behavior. Thermal analysis of complex **1** shows that weight loss starts at 168 °C, and in the range 168–208 °C, the total loss of 12.6% corresponds to the release of 4,4'-bipy (calculated 11.9%). Complex **2** is stable up to 169 °C, and in the temperature range 169–238 °C, the total weight loss is 13.3%, corresponding to the release

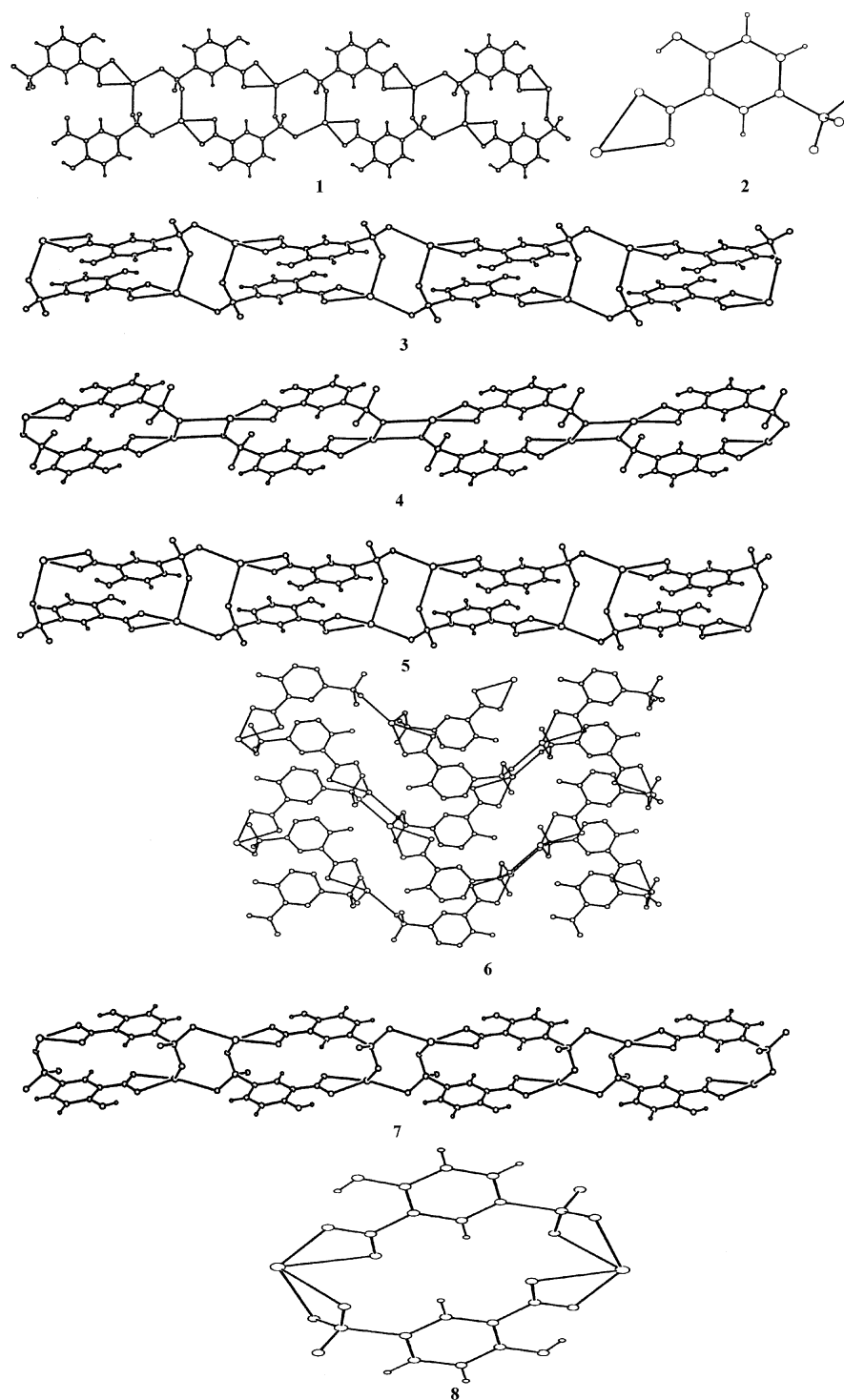


Figure 5. Eight frameworks constructed from $[\text{Pb}(\text{Hssal})]$ blocks in complexes **1–8**.

of water and 4,4'-bipy (calculated 14.2%). Complex **3** starts to lose weight at 272 °C, and in the temperature range 272–402 °C, the total weight loss is 41.5% (two-step departure of ligands without a clear platform), corresponding to the release of 4,4'-bipy and phen (calculated 37.8%). Complex **4** starts to lose weight at 270 °C, and in the temperature range 270–314 °C, the total weight loss is 42.3% (one-step departure of ligands), which corresponds to the release of bpe and 2,2'-bipy (calculated 36.9%).

Upon comparison to compounds **1–4**, we found that compounds **3** and **4** are more stable than compounds **1** and **2** because the latter contain guest 4,4'-bipy and water molecules, respectively. Compared to compounds **5–7** (without considering the release of solvent molecules), compounds **1–4** are systematically less stable, indicating that the bonds of Pb–N formed by bridging ligands are weaker than those of Pb–N formed by chelating ligands.

Fluorescence. The solid-state fluorescent spectra of complexes **1–4** at room temperature ($\lambda_{\text{ex}} = 220$ nm) show similar properties. The emission spectra are at 422, 440, 452, and 470 nm for **1**, at 412, 429, 453, and 470 nm for **2**, at 416, 439, 454, and 470 nm for **3**, and at 410, 423, 453, and 470 nm for **4**. The maximum emissions occur at 470 nm for complexes **1–4**, which are red-shifted about 20 nm compared to those of the free H_3ssal ligand (450 nm). Such large red shifts may likely be caused by the coordination of Hssal^{2-} or an interaction between ligands perturbed by Pb^{II} . The complexes **1–4** exhibit multiple peaks due to three ligands (one H_2ssal^- and two neutral ligands) contained in the complexes. Complexes **5–7** only with chelating ligands exhibit the strongest peaks at 408, 470, and 407 nm, respectively, indicating that bridging ligands and solvents largely influence the positions and strengths of peaks. Moreover, the coexistence of chelating and bridging ligands in complexes **1–4** leads to the ligand-to-ligand charge transfer.²⁵

Conclusion

In summary, four novel Pb^{II} complexes have been synthesized by the self-assembly of Pb^{II} ions and H_3ssal and chelating and bridging neutral ligands. (1) Assemblies of four complexes generate four types of diverse frameworks: two one-dimensional chains, a dimeric species, and a two-dimensional layer network. These diverse structures are largely controlled by the coordination modes of the Hssal^{2-} ligands, solvents, chelating ligands, coordination modes, and

spacer lengths of the bridging ligands. (2) All coordination modes of the Hssal^{2-} ligands in **1–4** are different. The 4,4'-bipy ligands in **1–3** act as noncoordinating guests in **1**, dimeric bridges in **2**, and monodentates in **3**. The bpe ligand in **4** acts as a polymeric linker. (3) The coordination spheres of Pb^{II} ions in **1–4** are controlled by three factors: the activity of a lone pair of electrons, weak Pb–O interactions and $\pi\text{--}\pi$ stacking interactions. The Pb^{II} lone pairs in **1–3** are stereochemically active, whereas in **4**, the lone pair is inactive. The aromatic–aromatic interactions can be found in complexes **1–3**, while no such interaction occurs in complex **4**. (4) Diverse structures of complexes **1–4** with both chelating and bridging neutral ligands lead to less thermal stability than those of Pb^{II} complexes only containing chelating ligands previously reported in our laboratory. Moreover, their fluorescent properties are also different from those of complexes **5–7**. Hence, the diverse product slate clearly illustrates that different novel structures can be designed and prepared by the combination of reactants, solvents, molar ratios, and neutral ligands (chelating and bridging), and the diverse structures lead to different functional properties, which is of great benefit for the design and control of the assembled frameworks for specific usage.

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Supporting Information Available: X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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