

## Structural Insights into the Coordination and Extraction of Pb(II) by Disulfonamide Ligands Derived from *o*-Phenylenediamine

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The *o*-phenylenediamine-derived disulfonamide ligands **1** and **2** complex and efficiently extract Pb(II) from water into 1,2-dichloroethane via ion-exchange, in combination with 2,2'-bipyridine (97.5% and 95.0%, respectively, for 1:1 ligand-to-Pb ratios). The corresponding Pb(II)–sulfonamido binary complexes of ligands **1** and **2** (**3** and **4**, respectively), and ternary complexes with 2,2'-bipyridine (**5** and **6**, respectively), were isolated and characterized. <sup>1</sup>H NMR spectra of the organic phases after extraction show the formation of ternary Pb–sulfonamido–bipy complexes. X-ray characterization of **3**, **4**, and the ternary complex **5** consistently demonstrates four primary coordination sites and a stereochemically active lone pair on Pb. The X-ray structure of **3** shows a pseudo trigonal bipyramidal configuration on Pb, with the lone pair occupying one of the equatorial sites, and the formation of an unusual “hemidirected” coordination polymer via axial S=O–Pb coordination. The same axial S=O–Pb coordination pattern with two DMSO molecules is observed in the structure of **4**·[2(CH<sub>3</sub>)<sub>2</sub>SO], thus rationalizing the high solubility of the binary complexes in strongly coordinating solvents. In contrast, the X-ray structure of the ternary complex **5** reveals a distorted four-coordinate configuration with only weak S=O–Pb coordination leading to dimer formation, thus explaining its higher solubility in weakly coordinating solvents. FT-IR spectroscopy confirms the X-ray data, since the ligand  $\nu_{\text{S=O}}$  stretching frequencies shift to lower values in the binary Pb(II)–sulfonamido complexes and are again altered upon formation of the ternary Pb(II)–sulfonamido–bipy complexes, as would be expected for 2,2'-bipy complexation and hindered S=O–Pb coordination.

### Introduction

Lead exposure continues to be one of the most serious environmentally related threats to human health in the United States and worldwide.<sup>1</sup> Therefore, there is a strong need to design ligands that can complex Pb(II),<sup>2</sup> which is the most mobile form of lead in the environment, efficiently and selectively for Pb(II) extraction and transport<sup>3</sup> and for sensing applications.<sup>4</sup>

The design of selective ligands for Pb(II) should take into account its unique coordination chemistry.<sup>2,5</sup> Pb(II) complexes can adopt many different ligand geometries with coordination numbers as low as 2 and as high as 10.<sup>6</sup> The geometry of Pb(II) complexes is highly dependent on whether the lone electron pair of the metal is stereochemically

active.<sup>6,7</sup> For low coordination numbers (2–5), the lone pair is stereochemically active and the ligand-to-metal bonds are distributed unevenly around the metal center with an identifiable void (presumably the location of the lone pair) present

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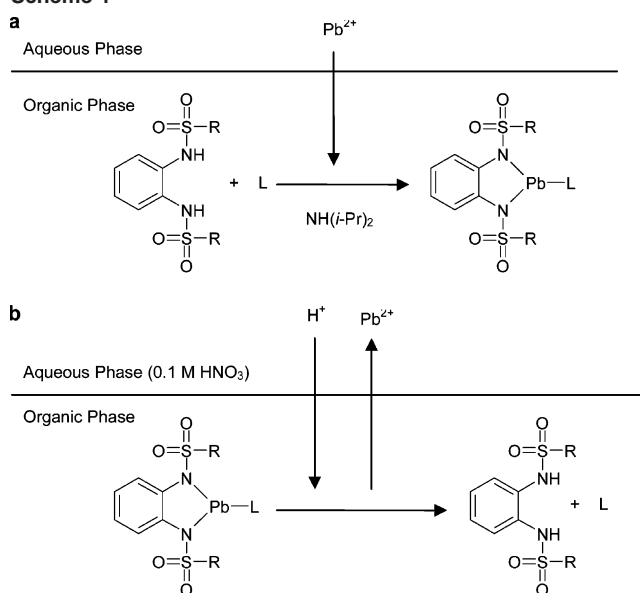
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in the coordination sphere, resulting in a “hemidirected” ligand environment.<sup>6</sup> On the other hand, complexes with high coordination numbers (9–10) adopt a holodirected geometry in which the ligands are distributed evenly throughout the coordination sphere with a stereochemically inactive lone pair. For intermediate coordination numbers (6–8), the stereochemical activity of the lone pair, and hence the geometry, depends strongly on the nature of the ligands and the donor atoms. In general, complexes with large, bulky ligands and with soft donors have a stereochemically inactive lone pair and holodirected geometries.<sup>6</sup>

Although numerous successful macrocyclic ligands for binding and extraction of Pb(II) have been reported in the literature,<sup>2a,8,9</sup> their synthesis is often time-consuming and expensive, making their large-scale application for extraction and detection of Pb(II) cost-prohibitive.<sup>10</sup> By contrast, the synthesis of ionizable chelates,<sup>11,12</sup> which can extract via an ion-exchange mechanism, is generally more straightforward. Moreover, chelates generally exhibit more favorable complexation–decomplexation kinetics<sup>13</sup> and offer great potential for combinatorial ligand strategies<sup>14</sup> due to their synthetic versatility.<sup>14</sup> Therefore, there is a strong interest in developing practical low-coordinate Pb(II) ion-exchangers that take advantage of the preference of Pb(II) for hemidirected geometries with a stereochemically active lone pair in order to enhance selectivity against other competing metals.

Recently, we reported that disulfonamide ionizable chelates derived from *o*-phenylenediamine can complex and efficiently extract Pb(II) via an ion-exchange mechanism.<sup>15,16</sup> Deprotonation of the sulfonamide ligand by an organic base results in the formation of a Pb(II) complex, and the metal

Scheme 1 <sup>a,b</sup>

<sup>a</sup> Complex formation results in extraction of Pb(II) into the organic phase (extraction stage). <sup>b</sup> Contact of the organic phase with dilute acid transfers the extracted metal to a second aqueous phase for analysis (stripping stage).

is extracted into the organic phase (Scheme 1a). A secondary coligand may be used to improve the solubility of the complex in the organic medium and the extraction selectivity. The metal can be isolated and the ligand recovered after extraction by contacting the organic phase with dilute aqueous acid (stripping stage), which results in decomplexation and transfer of the Pb(II) to a new aqueous phase (Scheme 1b). 2,2′-Bipyridine (2,2′-bipy) was used as a coligand for Pb(II) extraction by **1** and **2** due to the poor solubility of the binary Pb(II)–sulfonamido complexes in

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water-immiscible solvents.<sup>15</sup> Herein, we report in full on the coordination of Pb(II) by these extractants using X-ray crystallography, IR, and <sup>1</sup>H NMR. The X-ray structures of the binary complex **4** and the ternary complex **5**, which is formed during the extraction process, give us insight on coordination by solvent molecules and 2,2'-bipy. This structural data in combination with FT-IR spectroscopy elucidate the role of the 2,2'-bipy coligand during extraction.

## Experimental Section

**Materials and Methods.** All materials (purchased from Aldrich Chemical Co., ACROS organics, or TCI) were standard reagent grade and were used without further purification, with the exception of 1,2-dichloroethane (DCE), which was distilled from CaH<sub>2</sub>. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on either a 400 or a 600 MHz Bruker NMR spectrometer and were referenced, using the residual solvent resonances. All chemical shifts,  $\delta$ , are reported in ppm. FT-IR spectra were recorded on a Nicolet Magna-IR 560 spectrometer. ICP-MS measurements were carried out on a Hewlett-Packard 4500 series plus or a Perkin-Elmer Elan-II DRC. Positive-mode electrospray ionization mass spectra were obtained on a Finnigan ThermoQuest LC-MS instrument using 0.01 mg/mL solutions directly infused to the MS chamber at a rate of 0.01 mL/min.

**N,N'-Diphenyl-1,2-benzenedisulfonamide (1).**<sup>17</sup> A solution of 1,2-phenylenediamine (2.01 g, 18.6 mmol) and pyridine (5.12 g, 64.7 mmol) in 75 mL of CH<sub>2</sub>Cl<sub>2</sub> was added dropwise to a solution of benzenesulfonyl chloride (6.56 g, 37.1 mmol) dissolved in 50 mL of CH<sub>2</sub>Cl<sub>2</sub>. The reaction mixture was stirred at room temperature for 22 h and was monitored by TLC (70:30, hexanes/EtOAc). The reaction mixture was diluted with an additional 200 mL of CH<sub>2</sub>Cl<sub>2</sub> and washed sequentially with 1M HCl, 1M NaHCO<sub>3</sub>, and H<sub>2</sub>O. The resulting organic phase was separated and dried by pouring it through a Na<sub>2</sub>SO<sub>4</sub> column. The volatiles were removed and the residue was recrystallized from MeOH/H<sub>2</sub>O to give 5.91 g of **1** (82%) as a white powder. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 20 °C): 7.66 (dd, 4H, *J* = 7.3 and 1.8 Hz), 7.54 (tt, 2H, *J* = 7.5 and 1.4 Hz), 7.41 (t, 4H, *J* = 7.8 Hz), 7.03 (dd, 2H, *J* = 6.0 and 3.5 Hz), 6.92 (dd, 2H, *J* = 5.9 and 3.6 Hz), 6.80 (s, 2H). <sup>13</sup>C-<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 20 °C): 140.06, 134.43, 132.31, 130.31, 128.57, 128.09, 126.6. FT-IR (KBr): N-H, 3276 and 3225 cm<sup>-1</sup>; S=O, 1336 and 1165 cm<sup>-1</sup>.

**N,N'-Di-(4-tert-butylbenzene)-1,2-benzenedisulfonamide (2).** The compound was synthesized in a method similar to that for **1**: 4-tert-butylbenzenesulfonyl chloride (2.17 g, 9.34 mmol) was dissolved in 20 mL of CH<sub>2</sub>Cl<sub>2</sub>, 1,2-Phenylenediamine (0.505 g, 4.67 mmol)/pyridine (1.30 mL, 1.19 g, 13.1 mmol) dissolved in 25 mL of CH<sub>2</sub>Cl<sub>2</sub> was added, and the mixture was stirred for 10.5 h. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexanes gave 2.01 g (86%) of **2** as

a white powder. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 20 °C): 7.60 (d, 4H, *J* = 8.5 Hz), 7.42 (d, 4H, *J* = 8.5 Hz), 7.02 (dd, 2H, *J* = 6.0 and 3.5 Hz), 6.96 (dd, 2H, *J* = 5.9 and 3.5 Hz), 6.73 (s br, 2H), 1.29 (s, 18H). <sup>13</sup>C-<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 20 °C): 157.73, 135.87, 131.18, 127.85, 127.72, 126.52, 126.43, 35.70, 31.52. FT-IR (KBr): N-H, 3316, 3272, and 3238 cm<sup>-1</sup>; S=O, 1337 and 1166 cm<sup>-1</sup>. Elemental anal. Calcd for C<sub>26</sub>H<sub>32</sub>N<sub>2</sub>S<sub>2</sub>O<sub>4</sub>: C, 62.37; H, 6.44; N, 5.60. Found: C, 61.98; H, 6.45; N, 5.50.

**Pb[1,2-C<sub>6</sub>H<sub>4</sub>(NSO<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>] (3).** A solution of Pb(NO<sub>3</sub>)<sub>2</sub> (0.853 g, 2.58 mmol) in 100 mL of MeOH was added dropwise to a solution of **1** (1.00 g, 2.56 mmol) and 2.2 equiv of NEt<sub>3</sub> (0.569 g, 5.63 mmol) in 400 mL of MeOH. After stirring for 1 h, the reaction mixture was added dropwise to an equal volume of H<sub>2</sub>O. After removal of most of the methanol, a white precipitate was collected, washed with CH<sub>2</sub>Cl<sub>2</sub>, and recrystallized from MeOH/H<sub>2</sub>O yielding 1.28 g of **3** (84%). <sup>1</sup>H NMR (CD<sub>3</sub>OD, 20 °C): 7.93 (dd, 4H, *J* = 6.0 and 2.1 Hz), 7.43 (m, 6H), 6.53 (dd, 2H, *J* = 6.0 and 3.5 Hz), 6.30 (dd, 2H, *J* = 6.0 and 3.5 Hz). <sup>13</sup>C-<sup>1</sup>H-NMR (CD<sub>3</sub>OD, 20 °C): 144.61, 141.37, 133.02, 130.00, 128.43, 121.26, 120.44. FT-IR (KBr): S=O, 1257 and 1129 cm<sup>-1</sup>. Elemental anal. Calcd for PbC<sub>18</sub>H<sub>14</sub>N<sub>2</sub>S<sub>2</sub>O<sub>4</sub>: C, 36.42; H, 2.38; N, 4.72. Found: C, 36.01; H, 2.58; N, 4.66.

**Pb[1,2-C<sub>6</sub>H<sub>4</sub>(NSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-*p*-Bu<sup>t</sup>)<sub>2</sub>] (4).** Synthesized in a method similar to that for **4**, from **2** (0.648 g, 1.29 mmol) and 2.2 equiv of NEt<sub>3</sub> (0.287 g, 2.85 mmol) dissolved in 80 mL of MeOH by the addition of Pb(NO<sub>3</sub>)<sub>2</sub> (0.429 g, 1.30 mmol) dissolved in 85 mL of MeOH. Yield: 0.913 g (95%). <sup>1</sup>H NMR (CD<sub>3</sub>OD, 20 °C): 7.84 (d, 4H, *J* = 8.6 Hz), 7.46 (d, 4H, *J* = 8.6 Hz), 6.56 (dd, 2H, *J* = 6.0 and 3.5 Hz), 6.33 (dd, 2H, *J* = 5.9 and 3.5 Hz), 1.22 (s, 18H). <sup>13</sup>C-<sup>1</sup>H-NMR (CD<sub>3</sub>OD, 20 °C): 155.80, 140.61, 140.43, 127.31, 125.96, 120.20, 119.44, 34.91, 30.50. FT-IR (KBr): S=O 1271 and 1138 cm<sup>-1</sup>. Elemental anal. Calcd for PbC<sub>26</sub>H<sub>30</sub>N<sub>2</sub>S<sub>2</sub>O<sub>4</sub>: C, 44.24; H, 4.28; N, 3.97. Found: C, 44.24; H, 4.50; N, 3.99.

**Pb[1,2-C<sub>6</sub>H<sub>4</sub>(NSO<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>][2,2'-bipy] (5).** Compound **1** (0.264 g, 0.680 mmol), 1 equiv of 2,2'-bipy (0.106 g, 0.679 mmol), and 2.2 equiv of diisopropylamine (0.20 mL, 1.42 mmol) were dissolved in 45 mL of DCE. Pb(NO<sub>3</sub>)<sub>2</sub> (0.699 g, 2.11 mmol) was dissolved in 45 mL of H<sub>2</sub>O and added to the DCE solution. The two phases were contacted under vigorous stirring for 36 h at room temperature. The organic phase was separated and dried by pouring through a Na<sub>2</sub>SO<sub>4</sub> column. The DCE was removed under vacuum, and the isolated solid was washed many times with ether. The product was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexanes and dried under vacuum for 12 h at 40 °C. Yield: 0.204 g (40%). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 20 °C): 8.67 (ddd, 2H, *J* = 4.8, 1.0, and 0.8 Hz), 8.36 (td, 2H, *J* = 8.1 and 1.0 Hz), 8.00 (m, 4H), 7.94 (td, 2H, *J* = 7.7 and 1.8 Hz), 7.54 (m, 6H), 7.44 (ddd, 2H, *J* = 7.3, 4.8 and 1.3 Hz), 6.54 (dd, 2H, *J* = 6.0 and 3.5 Hz), 6.34 (dd, 2H, *J* = 6.0 and 3.5 Hz). <sup>13</sup>C-<sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, 20 °C): 155.50, 149.57, 143.57, 140.46, 137.65, 131.89, 129.10, 127.45, 124.51, 120.76, 119.68, 118.81. FT-IR (KBr): S=O 1261 and 1129 cm<sup>-1</sup>. ESI-MS (CH<sub>3</sub>OH): 751 (M+H<sup>+</sup>).

**Pb[1,2-C<sub>6</sub>H<sub>4</sub>(NSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-*p*-Bu<sup>t</sup>)<sub>2</sub>][2,2'-bipy] (6).** The compound was synthesized in a method similar to that for **5** from **2** (0.130 g, 0.260 mmol), 1 equiv of 2,2'-bipy (0.041 g, 0.260 mmol), and 2.3 equiv of diisopropylamine (0.08 mL, 0.56 mmol) dissolved in 30 mL of DCE contacted with Pb(NO<sub>3</sub>)<sub>2</sub> (0.435 g, 1.31 mmol) dissolved in 30 mL of H<sub>2</sub>O. Yield: 0.165 (74%). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 20 °C): 8.68 (d, 2H, *J* = 4.1 Hz), 8.37 (d, 2H, *J* = 8.0 Hz), 7.95 (td, 2H, *J* = 7.9 and 1.7 Hz), 7.92 (d, 4H, *J* = 8.5 Hz),

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7.55 (d, 4H,  $J = 8.5$  Hz), 7.46 (dd, 2H,  $J = 6.9$  and 5.1 Hz), 6.61 (dd, 2H,  $J = 5.8$  and 3.5 Hz), 6.38 (dd, 2H,  $J = 5.9$  and 3.4 Hz), (s, 18H).  $^{13}\text{C}\{-^1\text{H}\}$ -NMR (DMSO- $d_6$ , 20 °C): 155.99, 155.42, 150.15, 141.12, 141.05, 138.31, 127.89, 126.49, 125.15, 121.38, 120.26, 119.33, 35.58, 31.69. FT-IR (KBr): S=O 1267 and 1137  $\text{cm}^{-1}$ .

**Distribution Experiments (ICP–MS).** Typical ICP–MS experiments were performed as follows: All glassware was contacted with 8 M  $\text{HNO}_3$  overnight and then washed with water. The DCE was distilled and vigorously stirred with water for 1 h. A stock solution of ligand (0.15–3 mM), 2.2 equiv of  $\text{NH}(i\text{-Pr})_2$ , and 1 equiv of 2,2'-bipy was prepared in DCE. An appropriate amount of stock solution and DCE was used in preparing 800  $\mu\text{L}$  of organic phase samples. Stock solutions of  $\text{M}(\text{NO}_3)_2$  (3  $\mu\text{M}$  to 3 mM) were prepared. 800  $\mu\text{L}$  of the aqueous phases were subsequently prepared using appropriate amounts of the metal stock solution and equilibrated  $\text{H}_2\text{O}$ . The two phases were contacted for 12 h in a rotating wheel and then separated. For stripping, 500  $\mu\text{L}$  aliquots of the organic phases were contacted with 500  $\mu\text{L}$  of a 0.1 M  $\text{HNO}_3$  solution for 3 h. The source aqueous phases and stripped aqueous phases for each sample were diluted twice before the ICP–MS runs so that the final metal concentration before measurement did not exceed 125 ppb. A 2%  $\text{HNO}_3$  thallium internal standard solution was prepared and used for the dilution of the aqueous phases, as well as for the determination of a calibration curve. Internal standards solutions for Co, Ni, Cu, Cd, and Zn were prepared in the same fashion using Sc or In (for Cd). Calibration curves were determined with known metal ICP–MS standards (GFS Chemicals, Inc.) and a minimum of seven points ranging from 0 to 150 ppb. For Pb, the total isotopic counts for  $m/z$  of 206, 207, and 208 were measured for the calibration curve and samples. All samples were adjusted using a blank sample, which contained metal and DCE only. The distribution ratios were calculated from the corrected amounts of metal present in the two phases. All extraction experiments were performed in independent triplicate samples.

**X-ray Crystallography.** Single crystals of **3** were grown in 50:50 MeOH/ $\text{H}_2\text{O}$ . X-ray intensity data were collected at 100 K on an Enraf-Nonius, CAD4 diffractometer fitted with a 1.1 mm collimator and an Oxford Cryosystems 600 series low-temperature device. A pale yellow hexagonal plate, measuring  $0.40 \times 0.35 \times 0.16$   $\text{mm}^3$ , was mounted on the end of a glass fiber. A total of 7764 reflections were collected of which 3935 were independent ( $R_{\text{int}} = 0.036$ ). Data reduction was carried out using XCAD4, supplied by Klaus Harms. Bruker's SHELXTL (version 5.1, IRIX) was used for absorption correction, structure solution/refinement, and molecular graphics. A lamina absorption correction, based on a set of psi-scans was applied. All non-hydrogen atoms were refined anisotropically. Each H-atom was placed in a calculated position, refined using a riding model, and given an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of the atom to which it is attached. Full-matrix least-squares refinement against  $|F|^2$  of the quantity  $\sum w(F_o^2 - F_c^2)^2$  was used to adjust the refined parameter. Structural analysis was performed by Ton Speck's PLATON.

Single crystals of **4**·[2(CH<sub>3</sub>)<sub>2</sub>SO] and **5**·[1.5(CH<sub>3</sub>)<sub>2</sub>CO] were grown in 50:50 DMSO/ $\text{H}_2\text{O}$  and via slow evaporation of acetone, respectively. The X-ray intensity data were measured at 300 K on a Bruker SMART 1000 CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube ( $\lambda = 0.71073$  Å) operated at 2000 W of power. For **4**·[2(CH<sub>3</sub>)<sub>2</sub>SO], a colorless block of approximate dimensions  $0.11 \times 0.08 \times 0.03$   $\text{mm}^3$  cemented onto a quartz fiber with epoxy glue was used for the crystallographic

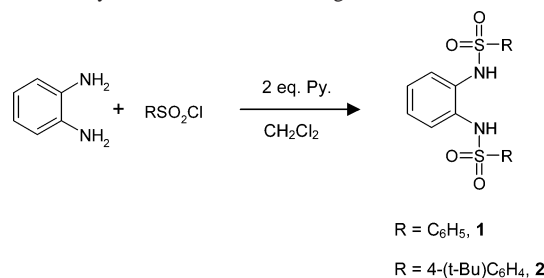
**Table 1.** Crystallographic Data for **3**, **4**·[2(CH<sub>3</sub>)<sub>2</sub>SO], and **5**·[1.5(CH<sub>3</sub>)<sub>2</sub>CO]

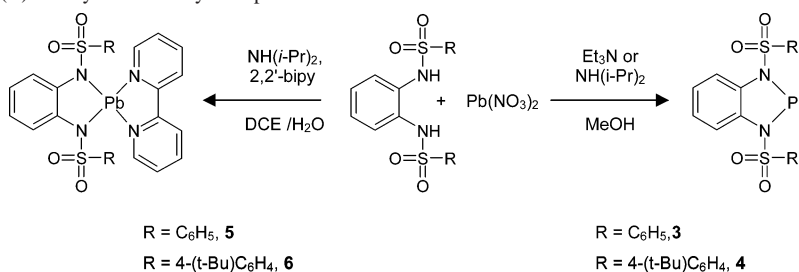
	<b>3</b>	<b>4</b> ·[2(CH <sub>3</sub> ) <sub>2</sub> SO]	<b>5</b> ·[1.5(CH <sub>3</sub> ) <sub>2</sub> CO]
formula	C <sub>18</sub> H <sub>14</sub> N <sub>2</sub> O <sub>4</sub> PbS <sub>2</sub>	C <sub>30</sub> H <sub>36</sub> N <sub>2</sub> O <sub>6</sub> PbS <sub>4</sub>	C <sub>32.50</sub> H <sub>31</sub> N <sub>4</sub> O <sub>5.50</sub> PbS <sub>2</sub>
formula weight	593.6	856.04	836.92
crystal system	monoclinic	monoclinic	monoclinic
crystal size (mm <sup>3</sup> )	0.40 × 0.35	0.11 × 0.08 × 0.03	0.40 × 0.25 × 0.21
space group	$P2_1/n$	$P2_1/n$	$C2/c$
<i>a</i> , Å	9.8201(15)	10.4577(19)	19.4207(11)
<i>b</i> , Å	19.358(3)	13.246(3)	13.4855(8)
<i>c</i> , Å	9.8553(12)	25.935(9)	25.6477(14)
$\alpha$ , deg	90	90	
$\beta$ , deg	99.828(10)	92.566(16)	95.1590(10)
$\gamma$ , deg	90	90	
<i>V</i> (Å <sup>3</sup> )	1846.0(5)	3589.1(16)	6689.9(7)
<i>Z</i>	4	4	8
<i>T</i> , °C	−173	27	27
$\lambda$ , Å	0.71073	0.71073	0.71073
<i>D<sub>c</sub></i> , g cm <sup>−3</sup>	2.14	1.584	1.662
<i>R</i> 1 <sup>a</sup>	0.028	0.042	0.036
w <i>R</i> 2 <sup>b</sup>	0.075	0.067	0.078

$$^a R1 = \frac{|\sum |F_o| - |F_c||}{\sum |F_o|}, \text{ based on } I > 2\sigma_I. \quad ^b wR2 = \sqrt{\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2}}$$

analysis, and the detector was placed at a distance of 4.997 cm away from the crystal. For **5**·[1.5(CH<sub>3</sub>)<sub>2</sub>CO], a yellowish block of approximate dimensions  $0.40 \times 0.35 \times 0.21$   $\text{mm}^3$  was mounted in a 0.3 mm capillary, which was filled with mother liquor. The capillary was sealed with epoxy glue, and the detector was placed at a distance of 5.020 cm away from the crystal. Data were measured using omega scans of 0.3° per frame for 5 s such that a hemisphere was collected. A total of 1271 frames were collected with a final resolution of 0.75 Å. No decay was indicated by the recollection of the first 50 frames at the end of data collection. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm, which also corrects for the Lorentz and polarization effects. Absorption corrections were applied using SADABS supplied by George Sheldrick. With the use of the Bruker SHELXTL (version 5.1) software, the structure of **4**·[2(CH<sub>3</sub>)<sub>2</sub>SO] was solved and refined in the space group  $P2_1/n$ . The structure of **5**·[1.5(CH<sub>3</sub>)<sub>2</sub>CO] was solved and refined in the space group  $C2/c$ . For **4**·[2(CH<sub>3</sub>)<sub>2</sub>SO], the asymmetric unit contains one independent molecule with two DMSO molecules coordinating to Pb. Both S atoms in DMSO, C28, C29, and C30 (methyl groups in DMSO) are disordered over two positions (54% and 46%) and were refined with occupancy. For **5**·[1.5(CH<sub>3</sub>)<sub>2</sub>CO], the asymmetric unit contains one independent molecule, one and half acetone molecules, which are not involved in the coordination. For both structures, all non-hydrogen atoms were derived from the direct method solution. With all non-hydrogen atoms being anisotropic and all hydrogen atoms being isotropic, the structures were refined to convergence by a least-squares method on  $F^2$ , using SHELXL-93, incorporated in SHELXTL.PC V 5.03. The results are summarized in Table 1.

**Scheme 2.** Synthesis of Sulfonamide Ligands



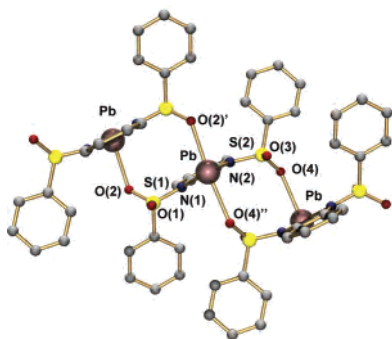
**Scheme 3.** Synthesis of Pb(II) Binary and Ternary Complexes

## Results and Discussion

**Synthesis of Ligands and Complexes.** The aryldisulfonamide ligands **1** and **2** were synthesized by a modification of previously reported procedures (Scheme 2).<sup>17</sup> The one-step synthesis is carried out in good yields by reacting two equiv of the corresponding arylsulfonyl chloride with *o*-phenylenediamine in the presence of two equiv of pyridine.

Binary complexes **3** and **4** were prepared in MeOH by reacting the ligand with  $\text{Pb}(\text{NO}_3)_2$  in the presence of  $\text{Et}_3\text{N}$  or  $\text{NH}(i\text{-Pr})_2$  (Scheme 3). By contrast, ternary complexes **5** and **6** were prepared using a two-phase method in which the ligand, 2,2'-bipy, and the base are all dissolved in 1,2-dichloroethane (DCE) (Scheme 3). The organic layer is then contacted with an aqueous solution of the  $\text{Pb}(\text{NO}_3)_2$ , and the Pb(II) complex is isolated from the organic phase.

**X-ray Crystallography.** The X-ray crystal structure of **3** (Figure 1) indicates that the Pb(II) is coordinated to two



**Figure 1.** PLUTO representation of the extended structure of **3**, showing the formation of a coordination polymer. Hydrogen atoms have been omitted for clarity.

sulfonamide nitrogen atoms of the deprotonated ligand, as well as by two oxygen atoms from neighboring complexes, resulting in the formation of an unusual coordination polymer with a hemidirected geometry.<sup>18</sup> A pseudo trigonal bipyramidal (tbp) configuration is observed, in which the equatorial positions are occupied by the Pb–N bonds and the lone pair. The axial positions are occupied by the Pb–O bonds responsible for the formation of the coordination polymer. Interestingly, in all previous studies of metals bound to *N,N'*-1,2-arenebis(benzenesulfonamide) ligands, the ligand

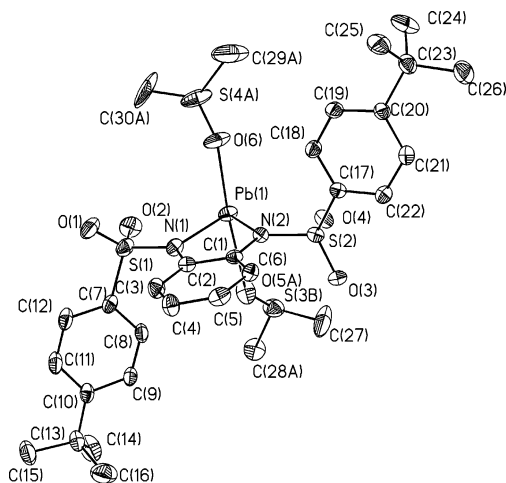
**Table 2.** Selected Bond Distances (Å) and Angles (deg) for **3**, **4**·[2(CH<sub>3</sub>)<sub>2</sub>SO], and **5**·[1.5(CH<sub>3</sub>)<sub>2</sub>CO]

<b>3</b>			
Pb–N(1)	2.296(4)	Pb···S(2)	3.314(1)
Pb–N(2)	2.329(4)	S(1)–O(1)	1.445(4)
Pb–O(2)'	2.599(4)	S(1)–O(2)	1.458(4)
Pb–O(4)''	2.524(3)	S(1)–N(1)	1.571(4)
Pb···O(1)	2.869(4)	S(2)–O(3)	1.448(4)
Pb···O(3)	3.043(3)	S(2)–O(4)	1.459(4)
Pb···S(1)	3.221(1)	S(2)–N(2)	1.569(4)
N(1)–Pb–N(2)	68.4(1)	N(2)–Pb–O(1)	120.4(1)
N(1)–Pb–O(1)	53.7(1)	N(2)–Pb–O(2)'	89.6(1)
N(1)–Pb–O(2)'	95.0(1)	N(2)–Pb–O(3)	51.2(1)
N(1)–Pb–O(3)	119.5(1)	N(2)–Pb–O(4)''	92.5(1)
N(1)–Pb–O(4)''	81.5(1)	O(2)'–Pb–O(4)''	175.0(1)
<b>4</b> ·[2(CH <sub>3</sub> ) <sub>2</sub> SO]			
Pb(1)–N(1)	2.326(6)	S(2)–O(3)	1.442(4)
Pb(1)–N(2)	2.321(4)	S(2)–O(4)	1.448(4)
Pb(1)–O(6)	2.521(5)	S(1)–N(1)	1.581(5)
Pb(1)–O(5A)	2.53(3)	S(2)–N(2)	1.591(5)
S(1)–O(1)	1.458(5)	S(4A)–O(6)	1.518(9)
S(1)–O(2)	1.452(5)	S(3B)–O(5A)	1.51(2)
N(1)–Pb(1)–N(2)	68.38(18)	N(1)–Pb(1)–O(5A)	83.2(7)
N(1)–Pb(1)–O(6)	88.29(19)	N(2)–Pb(1)–O(5A)	81.7(6)
N(2)–Pb(1)–O(6)	80.90(16)	O(6)–Pb(1)–O(5A)	162.5(6)
<b>5</b> ·[1.5(CH <sub>3</sub> ) <sub>2</sub> CO]			
Pb(1)–N(1)	2.411(5)	N(2)–S(1)	1.578(4)
Pb(1)–N(2)	2.338(5)	O(1)–S(1)	1.437(5)
Pb(1)–N(3)	2.568(5)	O(2)–S(1)	1.431(5)
Pb(1)–N(4)	2.651(5)	O(3)–S(2)	1.445(4)
N(1)–S(2)	1.565(4)	O(4)–S(2)	1.462(4)
N(1)–Pb(1)–N(2)	67.34(16)	N(2)–Pb(1)–N(4)	86.92(16)
N(2)–Pb(1)–N(3)	100.85(17)	N(1)–Pb(1)–N(4)	130.10(14)
N(1)–Pb(1)–N(3)	80.72(16)	N(3)–Pb(1)–N(4)	62.38(15)

simply coordinates to the metal in a bidentate fashion through the two nitrogen atoms, and no polymeric structure is formed.<sup>19</sup> The relatively short Pb–N bond lengths (2.296(4) and 2.329(4) Å) (Table 2) are consistent with the observation that Pb–N bonds opposite the location of the stereochemically active lone pair tend to be shorter in length than the average value.<sup>2a,6</sup> The distances between the Pb and the O atoms in the axial positions (2.524(3) and 2.599(3) Å) are within the range for Pb–O covalent bonds (ranging from 2.46 to 2.96 Å).<sup>20,21</sup> Longer distances are observed between Pb and the two sulfonyl oxygen atoms of the coordinated sulfonamide O(1) (2.869(4) Å) and O(3) (3.043(3) Å).

(18) For other Pb(II) coordination polymers see: (a) Harrowfield, J.; Miyamae, H.; Skelton, B. W.; Soudi, A. A.; White, A. H. *Aust. J. Chem.* **1996**, *49*, 1165. (b) Mann, K. L. V.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D. *Polyhedron* **1999**, *18*, 721. (c) Meng, X.; Song, Y.; Hou, H.; Fan, Y.; Zhu, Y. *Inorg. Chem.* **2003**, *42*, 1306. (d) Shi, Y.; Li, L.; Li, Y.; Tai, X.; Xue Z.; You, X. *Polyhedron* **2003**, *22*, 917.

(19) (a) Evans, C.; Henderson, W.; Nicholson, B. K. *Inorg. Chim. Acta* **2001**, *314*, 42. (b) Cheng, P.-H.; Cheng, H.-Y.; Lin, C.-C.; Peng, S. M. *Inorg. Chim. Acta* **1990**, *169*, 19. (c) Cheng, H.-Y.; Cheng, P.-H.; Lee, C.-F.; Peng, S. M. *Inorg. Chim. Acta* **1991**, *181*, 145.  
 (20) Holloway C. E.; Melnik, M. *Main Group Met. Chem.* **1997**, *20*, 399.  
 (21) Based on a search of the Cambridge Structural Database (CSD) for all Pb(II)–(NS(O)<sub>2</sub>C) fragments containing a Pb–O bond. Allen, F. H. *Acta Crystallogr.* **2002**, *B58*, 380. CSD reference codes FUYDOS, IGIGEK, IGIGIO, TEZMIU, and XAQNAE were found.

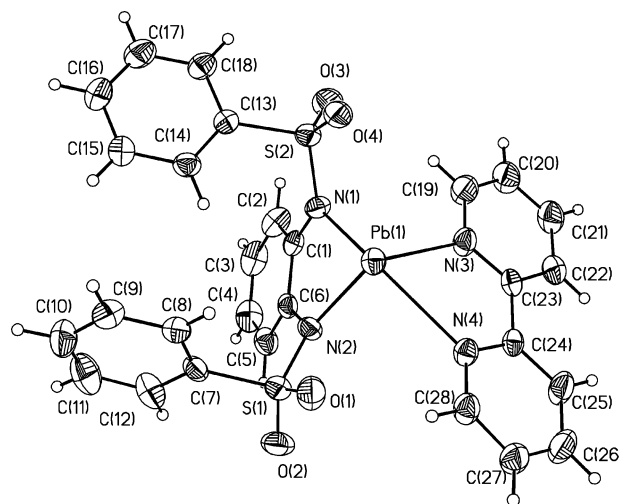


**Figure 2.** ORTEP plot of  $4 \cdot [2(\text{CH}_3)_2\text{SO}]$  (30% probability ellipsoids). For clarity, the hydrogen atoms have been omitted.

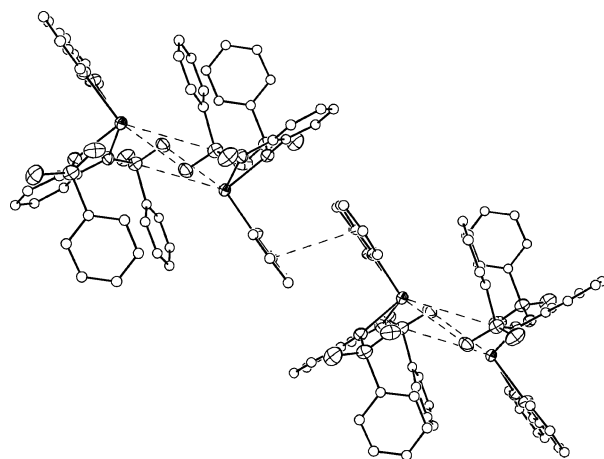
Further examination of the vacancy in the coordination sphere reveals that the space is partially filled by two aromatic rings from neighboring molecules (symmetry equivalents of the sulfonyl phenyl rings). While weak  $\text{Pb}-\pi$  interactions are fairly common, the shortest  $\text{Pb}-\text{C}$  distances reported here ( $\text{C}(14)$  3.695(6) Å,  $\text{C}(23)$  3.786(5) Å,  $\text{C}(24)$  3.724(5) Å) are generally longer than those typically observed in the literature,<sup>22</sup> suggesting that if any  $\text{Pb}-\pi$  interactions are present they are very weak. This observation is consistent with the presence of a stereochemically active lone pair in the vacant site.

The X-ray crystal structure of  $4 \cdot [2(\text{CH}_3)_2\text{SO}]$  (Figure 2) shows that the  $\text{Pb}(\text{II})$  is coordinated to two sulfonamide nitrogen atoms of ligand as well as two molecules of DMSO. Although the  $\text{O}-\text{Pb}-\text{O}$  angle ( $162.5(6)^\circ$ ) is smaller than in **3** ( $175.0(1)^\circ$ ), the geometry is also hemidirected and assumes a pseudo *tbp* configuration in which the lone pair occupies the vacant axial site. Similar to **3**, relatively short  $\text{Pb}-\text{N}$  (2.321(4) and 2.326(6) Å) distances are observed. The distances between the  $\text{Pb}$  and the two  $\text{O}$  atoms of the DMSO molecules (2.521(5) and 2.53(3) Å) are also comparable to the  $\text{Pb}-\text{O}$  distances for complex **3**.

In the same fashion as **3** and **4**, the X-ray crystal structure of ternary complex **5** (Figure 3) shows a four-coordinate metal center with a hemidirected geometry and a stereochemically active lone pair. However, slightly longer  $\text{Pb}-\text{N}$  bond distances (2.388(5) and 2.411(5) Å) than in **3** and **4** are observed between the sulfonamide ligand and the metal (Table 2). In addition, the  $\text{Pb}(\text{II})$  is also coordinated to the nitrogen atoms of the 2,2'-bipy. The distances between the metal center and the 2,2'-bipy nitrogen atoms are significantly larger (2.568(5) and 2.651(5) Å) than those observed for the sulfonamide nitrogen atoms and are also slightly larger than those observed before for  $\text{PbI}_2(2,2'\text{-bipy})$ .<sup>23</sup> However, the distances are similar to those reported for a related  $\text{Pb}(\text{II})$ -sulfonamide-2,2'-bipy complex.<sup>12a</sup>



**Figure 3.** ORTEP representation of the ternary complex **5** (30% probability ellipsoids).



**Figure 4.** Packing diagram of **5**, showing the formation a dimer. The packing is enhanced by  $\pi-\pi$  interactions between two bipyridine molecules. Hydrogen atoms have been omitted for clarity.

In contrast to complexes **3** and **4**, where coordination to neighboring molecules is strong, complex **5** exhibits only weak interactions with neighboring molecules as shown by the rather long  $\text{Pb}-\text{O}$  and  $\text{Pb}-\text{S}$  distances (3.238 and 4.034 Å, respectively). Nevertheless, as shown in Figure 4, the interaction between neighboring molecules results in the formation of a dimer, and the crystal packing is further enhanced by  $\pi-\pi$  interactions involving the 2,2'-bipy molecules (the center-to-center distance between the two 2,2'-bipy molecules is 2.696 Å). Further examination of the packing diagram (Figure 4), shows that the  $\text{Pb}-\text{N}$  bonds between the 2,2'-bipy and the metal center are closer to the lone pair (presumably located in the large vacancy in the coordination sphere) than the  $\text{Pb}-\text{N}$  bonds of the sulfonamide ligand. This observation correlates well with previous studies which show that ligands close to the lone pair exhibit longer  $\text{Pb}-\text{N}$  bond lengths than those away from the lone pair.<sup>2a,6</sup>

Comparison of the bond lengths in **3**, **4**, and **5** with those for the free ligand, **1**,<sup>24</sup> shows that the  $\text{S}-\text{N}$  bonds are

(22) (a) Edelmann, F. T.; Buijink, J.-K. F.; Brooker, S. A.; Herbst-Irmer, R.; Kilimann, U.; Bohnen, F. M. *Inorg. Chem.* **2000**, *39*, 6134 and references therein. (b) No, K. H.; Kim, J. S.; Shon, O. J.; Yang, S. H.; Suh, I. H.; Kim, J. G.; Bartsch, R. A.; Kim, J. Y. *J. Org. Chem.* **2001**, *66*, 5976.

(23) Zhu, H.; Xu, Y.; Yu, Z.; Wu, Q.; Fun, H.; You, X. *Polyhedron* **1999**, *18*, 3491.

significantly shorter (averaging 1.57 Å in **3** and 1.64 Å in **1**) when the ligand is bound to Pb(II). However, a corresponding lengthening of the S=O bond cannot always be observed based on the standard uncertainties in the crystallographic data. Such lengthening is expected based on the observed decrease of the S=O stretching frequency in the IR (vide infra).

The coordination of Pb(II) to the oxygen atoms of neighboring molecules or DMSO in complexes **3** and **4** explains why the binary Pb–sulfonamide complexes are poorly soluble in relatively less polar solvents such as DCE, yet soluble in more polar, highly coordinating solvents, such as CH<sub>3</sub>OH and DMSO. By contrast, in the ternary complex **5**, the coordination of 2,2'-bipy significantly interferes with self-association through Pb–O=S bonding, thus increasing the solubility in less polar solvents.

**IR Studies.** The changes in the FT-IR stretching frequencies upon complexation complement the information obtained from the X-ray structures. The IR data of binary complexes **3** and **4** show a significant decrease in the stretching frequencies of the S=O bonds as compared to their corresponding ligands. The lower frequency implies that the S=O bonds weaken upon complexation and correlates well with the X-ray crystal structure of **3** which shows that the sulfonamide oxygens are coordinated to Pb(II) centers of neighboring molecules, forming a coordination polymer. Interestingly, the S=O frequency of ternary complex **5** is slightly larger than that of the corresponding binary complex **3**. This is unexpected considering the electron-donating ability of the 2,2'-bipy ligand, which should actually decrease the S=O stretching frequency even further. These observations suggest that the addition of the 2,2'-bipy disrupts the self-association via S=O–Pb coordination, thus slightly strengthening the S=O bond, and increasing its stretching frequency. This interference with S=O–Pb coordination by 2,2'-bipy is indicated in the X-ray crystal structure and also by the higher solubility of **5** compared to that of **3** in noncoordinating solvents. The balance of electronic effects and hindered S=O–Pb coordination after the complexation of 2,2'-bipy is somewhat altered for the *t*-Bu-substituted analogues **6** and **4**, leading only to a very slight change to the opposite direction upon complexation. For the free ligands (Table 3), the N–H infrared stretching frequency varies significantly between solution and film. In solution, the N–H stretch appears at higher frequencies as compared to those from the KBr or thin-film measurements. The lower frequency of the N–H stretch in the solid state is indicative of a higher degree of self-association between the sulfonamide molecules as a result of hydrogen bonding. Addition of 2.2 equiv of NH(*i*-Pr)<sub>2</sub> to a ligand solution causes a significant decrease in the intensity of the N–H peak.

**<sup>1</sup>H NMR Studies.** Ligands **1** and **2** were shown to extract Pb(II) from water into DCE by ion-exchange at the liquid–liquid interphase when used in synergistic combinations with 2,2'-bipy, by forming the ternary complexes **5**

**Table 3.** IR Frequencies (cm<sup>-1</sup>) of the N–H and S=O Bonds of **1–6**<sup>a</sup>

	N–H	S=O	type of IR
<b>1</b>	3276, 3225	1336, 1165	KBr
<b>1</b>	3253	1336, 1165	film
<b>1</b>	3331	1331, 1170	solution
<b>1</b>	3332 <sup>b</sup>	1330, 1164	solution + NH( <i>i</i> -Pr) <sub>2</sub>
<b>2</b>	3316, 3272, 3238	1337, 1166	KBr
<b>2</b>	3255	1330, 1165	film
<b>2</b>	3333	1340, 1165	solution
<b>2</b>	3333 <sup>b</sup>	1337, 1166	solution + NH( <i>i</i> -Pr) <sub>2</sub>
C <sub>6</sub> H <sub>5</sub> NHSO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	3206	1332, 1158	KBr
C <sub>6</sub> H <sub>5</sub> NHSO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	3257	1332, 1153	film
C <sub>6</sub> H <sub>5</sub> NHSO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	3349, 3257	1348, 1165	solution
C <sub>6</sub> H <sub>5</sub> NHSO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	3352 <sup>b</sup>	1348, 1168	solution + NH( <i>i</i> -Pr) <sub>2</sub>
<b>3</b>	none	1257, 1129	KBr
<b>4</b>	none	1271, 1138	KBr
<b>5</b>	none	1261, 1129	KBr
<b>6</b>	none	1267, 1137	KBr

<sup>a</sup> For reference, the data of model compound C<sub>6</sub>H<sub>5</sub>NHSO<sub>2</sub>C<sub>6</sub>H<sub>5</sub> is also included. <sup>b</sup> The intensity of the N–H peak decreases significantly upon addition of the base.

and **6**. Attempts to extract Pb(II) in the absence of 2,2'-bipy were hindered by the low solubility of the binary complexes **3** and **4** in DCE. The <sup>1</sup>H NMR spectrum of the organic phase after extraction of Pb(II) by **1** exhibits resonances for both the ternary complex and the free ligand. Furthermore, it is apparent that the ligand and the complex are in slow exchange on the NMR time scale, because after extraction there are two different sets of peaks for the two species. To determine whether there is fast exchange between complex **5** and free 2,2'-bipy molecules in solution, 2,2'-bipy was added to a solution of isolated **5**. The fact that only one set of peaks is observed for the four 2,2'-bipy resonances, and that the chemical shifts are different than those observed for free 2,2'-bipy and **5**, clearly indicate that the free and coordinated 2,2'-bipy are in fast exchange on the NMR time scale. A control dilution experiment of 2,2'-bipy gave no changes in the <sup>1</sup>H NMR spectrum.

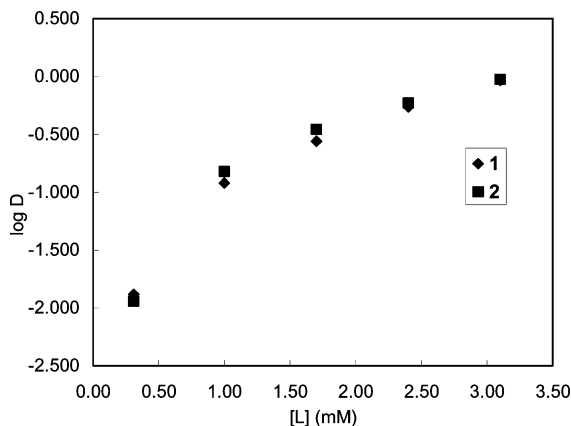
With the use of the following protocol, it is possible to indirectly determine the distribution ratio for Pb(II) (defined as  $D_{\text{Pb}} = [\text{Pb}^{2+}]_{\text{org}}/[\text{Pb}^{2+}]_{\text{aq}}$ , where org and aq refer to the concentrations in the organic and aqueous phases, after extraction, respectively) from the <sup>1</sup>H NMR data. Equation 1 relates  $D_{\text{Pb}}$  to the concentration of the ternary complex ( $[\text{Pb}(\text{L})(2,2'\text{-bipy})]_{\text{org}}$ ) and the initial concentration of Pb(II) ( $[\text{Pb}^{2+}]_i$ ).

$$D_{\text{Pb}} = [\text{Pb}(\text{L})(2,2'\text{-bipy})]_{\text{org}}/[\text{Pb}^{2+}]_i - [\text{Pb}(\text{L})(2,2'\text{-bipy})] \quad (1)$$

Although the concentration of the ternary complex cannot be directly determined by <sup>1</sup>H NMR, the ratio of ternary complex to free ligand can be determined from the integration ratio (defined as  $\Omega = [\text{Pb}(\text{L})(2,2'\text{-bipy})]_{\text{org}}/[\text{L}]_{\text{org}}$ ) of the central aromatic peaks from the complex to the ones from the free ligand. Substituting  $\Omega$  into (1) and defining  $\Theta$  as the ratio of the initial concentrations of Pb(II) to ligand ( $[\text{Pb}^{2+}]_i/[\text{L}]_i$ ) gives eq 2.

$$D_{\text{Pb}} = \Omega[\text{L}]_{\text{org}}/\Theta[\text{L}]_i - \Omega[\text{L}]_{\text{org}} \quad (2)$$

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**Figure 5.** Extraction of Pb(II) by **1** and **2** in the presence of 1.0 equiv of 2,2'-bipy and 2.2 equiv of NH(*i*-Pr)<sub>2</sub>. The distribution ratio *D* is defined as  $[Pb^{2+}]_{org}/[Pb^{2+}]_{aq}$ .  $[Pb]$  is constant at 6.30 mM (error in concentration is <5%).

Using the fact that  $[L]_i$  is equal to the sum of  $[Pb(L)(2,2'-bipy)]_{org}$  and  $[L]_{org}$  and substituting into (2) gives (3), which can be further simplified to (4).

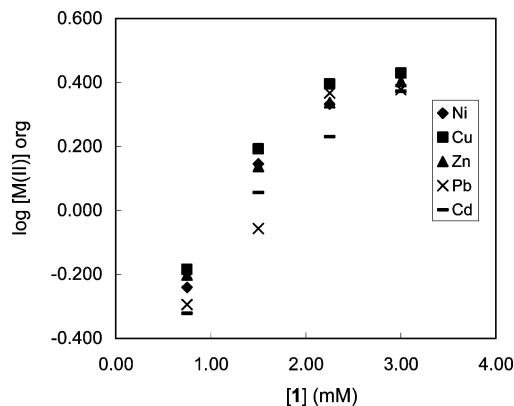
$$D_{Pb} = \frac{\Omega[L]_{org}}{\Theta([Pb(L)(2,2'-bipy)]_{org} + [L]_{org})} - \frac{\Omega[L]_{org}}{\Theta} \quad (3)$$

$$D_{Pb} = \frac{\Omega}{\Theta(\Omega + 1)} - \Omega \quad (4)$$

Substitution of the actual values of  $\Omega$  and  $\Theta$  gave a  $D_{Pb}$  of 61.26 for an initial Pb (II) concentration of 4.079 mM and a ligand concentration of 5.301 mM.

**Distribution Experiments (ICP–MS).** Extraction of Pb(II) by ligands **1** and **2** was also studied using ICP–MS. For extraction of Pb(II), aqueous phases containing Pb(NO<sub>3</sub>)<sub>2</sub> (0.15–6.30 mM) were contacted with DCE containing **1** or **2** (0–5 mM), 2.2 equiv of NH(*i*-Pr)<sub>2</sub>, and 1.0 equiv of 2,2'-bipy. Subsequently, the organic phases were stripped with 0.1 M HNO<sub>3</sub>. The concentration of Pb(II) at both the source aqueous phase and the stripping phase was determined by ICP–MS, allowing direct determination of the distribution ratios. The synergistic extraction of Pb(II) for a 1:1 ratio of ligand to Pb(II) was found to be as high as 97.5% for **2** and 95.0% for **1** (Figure 5). Double stripping of the organic phase showed no significant decrease in the distribution ratios obtained. Control experiments, using 2,2'-bipy only, NH(*i*-Pr)<sub>2</sub> only ligand only, as well as combinations of those in pairs, demonstrated that all components are necessary for the Pb(II) extraction. Further control experiments demonstrated the HNO<sub>3</sub> used for stripping does not react with either **1** or **2** and that both **1** and **2** are recoverable after extraction (>97% measured by <sup>1</sup>H NMR with 4,4'-dimethylbiphenyl as internal standard). The pH of the aqueous phase after contact was measured at 7.0 (±0.2). The control aniline derivative (C<sub>6</sub>H<sub>5</sub>NHSO<sub>2</sub>C<sub>6</sub>H<sub>5</sub>) did not extract under any conditions, indicating the need for coordination through the two chelating nitrogens for extraction. This synergistic system, showed 420 (for **1**) and 430 (for **2**) times higher extraction than 18-crown-6 (18C6) or combinations of 18C6 and 2,2'-bipy.

Further distribution studies were performed with other divalent metals. A plot of  $\log [M(II)]_{org}$  vs  $[L]_i$  for M(II) =



**Figure 6.** Extraction of M(NO<sub>3</sub>)<sub>2</sub> by **1** in the presence of 1.0 equiv of 2,2'-bipy and 2.2 equiv of NH(*i*-Pr)<sub>2</sub>. M(II) was kept constant at 2.70 mM.

Pb(II), Cd(II), Zn(II), Cu(II), and Ni(II) (Figure 6) shows that at a metal concentration of 2.70 mM and ligand concentration of 3.00 mM the extraction efficiency increases as follows: Cd(II) < Ni(II) < Pb(II) < Zn(II) < Cu(II). The higher *D* values of Zn(II) and Cu(II) over Pb(II) are likely attributed to stronger complexation of Zn(II) and Cu(II) to 2,2'-bipy.<sup>12c,d</sup> Such a conclusion is supported by the fact that the analogous *o*-phenylenediamine-derived dansylamide has been shown to selectively extract Pb(II) without the need for a coligand addition via the formation of the binary complex.<sup>16</sup>

## Conclusions

In conclusion, the simple sulfonamide ion-exchangers **1** and **2** can coordinate Pb(II), resulting in the formation of binary complexes **3** and **4**. X-ray crystallography shows that the metal center of these complexes can also accommodate coordination by either neighboring sulfonamide molecules, forming a coordination polymer, or by solvent molecules. These observations compare well with the tendency of Pb(II) to recruit additional ligand or solvent molecules in order to achieve desired coordination patterns. Self-association through S=O–Pb coordination explains why complexes **3** and **4** exhibit low solubility in weakly coordinating solvents, limiting their application to extraction. By contrast, ternary complex **5** is only weakly coordinated by neighboring molecules and is far more soluble in less polar solvents. Apparently, the addition of 2,2'-bipy disrupts the coordination of the metal center by additional molecules. As demonstrated by both <sup>1</sup>H NMR and ICP–MS studies, the enhanced solubility of ternary complexes **5** and **6** allows the efficient extraction of Pb(II) from water into DCE, albeit with no selectivity against Cu(II) and Zn(II). Future work will focus on the effects that changes of the peripheral sulfonamide groups may have on the ability of the metal to recruit additional molecules into the coordination sphere. Improving the solubility and extraction properties of the metal–ligand binary complexes, without the need for a coligand addition, could potentially lead to selective Pb(II) extraction.



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**Supporting Information Available:** Crystal data for complexes **3**, **4**, and **5**; partial  $^1\text{H}$  NMR spectra of ligands, complexes, and the organic phase after extraction. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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