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Pb(II) Coordination and Synergistic Ion-Exchange Extraction by Combinations of Sulfonamide Chelates and 2,2′-Bipyridine

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The disulfonamide ligands 1,2-$C_6H_4(NH_2SO_2C_6H_5)_2$ (**1**) and 1,2-$C_6H_4(NH_2SO_2C_6H_4$-*p*-$Bu^t)_2$ (**2**), which are readily available in good yields from *o*-phenylenediamine and the corresponding sulfonyl chlorides, efficiently extract Pb(II) from water into 1,2-dichloroethane when used in synergistic combinations with 2,2′-bipyridine via an ion-exchange mechanism. The extraction was shown to proceed via the formation of a ternary Pb-sulfamido-2,2′-bipyridine complex. The X-ray crystal structure of the binary Pb-sulfamido complex **3** shows a coordination polymer with a stereochemically active lone pair on Pb formed by S═O—Pb axial coordination.

The selective complexation,[1] extraction,[2] and sensing[3] of toxic heavy metal cations, such as Pb(II), Cd(II), and Hg(II), is exceedingly important because of their economic, environmental, and biological roles.[4] Lead is still the most commonly encountered toxic metal pollutant in the environment, and therefore, there is a need for exploiting the unique coordination chemistry of Pb(II)[5] for the development of practical ligands as extractants, lead-poisoning treatment agents, and sensors.[6] Numerous examples of coordination and extraction of Pb(II) by macrocycles[7] have been reported. Ionizable chelates,[8] which extract metals via ion exchange, present potential advantages, including versatility, synthetic ease, and favorable complexation—decomplexation kinetics.[9] Notwithstanding the strong interest in Pb(II) coordination chemistry, there is yet to be discovered a practical Pb(II) ion-exchange extractant that would take advantage of the preference of Pb(II) in lower coordination numbers for irregular "hemi-directed"[10] coordination geometries with a stereochemically active lone pair.[5a] Herein, we report efficient synergistic Pb(II) ion-exchange extraction, from water into 1,2-dichloroethane (DCE), by combinations of 2,2′-bipyridine (bipy) and simple ionizable disulfonamides derived from *o*-phenylenediamine. The ternary Pb(II)-bipy-sulfamido complex was identified by ^{1}H NMR in the organic phase after extraction.

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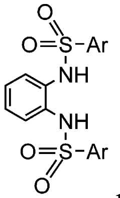
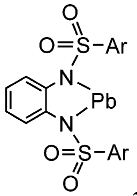
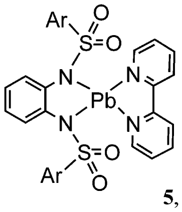
The X-ray crystal structure of the binary Pb(II)-sulfamido complex shows a hemidirected[10] geometry on Pb with a stereochemically active lone pair. A polymeric network is formed in the solid state via axial coordination of the S═O oxygen atoms to Pb.



1, 2



3, 4



5, 6

Ar = C_6H_5- (**1**, **3**, **5**), Ar = *p*-Bu^t-C_6H_4- (**2**, **4**, **6**)

The aryl sulfonamide ligands 1,2-$C_6H_4(NH_2SO_2C_6H_5)_2$ (**1**) and 1,2-$C_6H_4(NH_2SO_2C_6H_4$-*p*-$\mathrm{Bu}^t)_2$ (**2**) are readily available in good yields from *o*-phenylenediamine and the corresponding sulfonyl chlorides.[11] They are soluble in relatively less polar organic solvents, such as DCE, and they are weakly acidic (typical $\mathrm{p}K_a$ values range between 7.9 and 8.5),[12] thus being able to form complexes under mildly basic conditions. Despite these advantages, only a few examples of Pb(II) coordination by sulfonamides involving *N*-sulfonyl amino acids with one ionizable SO_2NH group have been reported.[13] In these cases, higher coordination numbers are observed with a monodentate coordination through the carboxylate oxygen or a *N*,*O*-bidentate coordination.

The Pb(II) complexes Pb[1,2-$C_6H_4(NSO_2C_6H_5)_2$] (**3**) and Pb[1,2-$C_6H_4(NSO_2C_6H_4$-*p*-$\mathrm{Bu}^t)_2$] (**4**) were synthesized from ligands **1** and **2**, respectively, by adding NH(*i*-Pr)$_2$ and Pb(NO$_3$)$_2$ in MeOH at room temperature. The X-ray crystal structure of **3**[14] (Figure 1 and Table 1) shows Pb(II) coordination to the sulfonamide ligand via two short[13,15] Pb−N bonds and to two neighboring sulfonamide complexes as well, giving a coordination polymer with a hemidirected geometry on Pb.[10] Because of its relatively large size and its strongly ionic nature, the coordination environment of Pb(II) tends to be complex, and polymeric structures[16] typically exhibit higher coordination numbers. Curiously, in all previously reported structures of metals bound to a *N*,*N′*-1,2-arenebis(benzenesulfonamide), the ligand simply coordinates to the metal in a bidentate fashion through the two nitrogen atoms, and no polymeric structure is formed.[17]

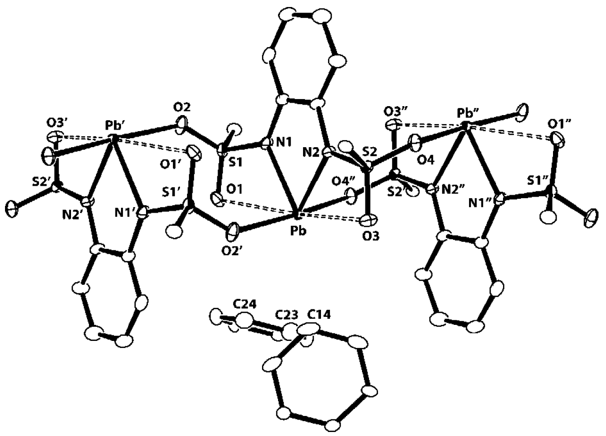


Figure 1. ORTEP representation (50% probability ellipsoids) of the extended structure of **3**. For clarity, hydrogen atoms and all but the ipso carbon atoms on the sulfonyl phenyl rings have been omitted.

Table 1. Selected Bond Distances (Å) and Angles (deg) for **3**

	distance (Å)		angle (deg)
Pb−N(1)	2.296(4)	N(1)−Pb−N(2)	68.4(1)
Pb−N(2)	2.329(4)	N(1)−Pb−O(1)	53.7(1)
Pb−O(2)′	2.599(4)	N(1)−Pb−O(2)′	95.0(1)
Pb−O(4)″	2.524(3)	N(1)−Pb−O(3)	119.5(1)
Pb···O(1)	2.869(4)	N(1)−Pb−O(4)″	81.5(1)
Pb···O(3)	3.043(3)	N(2)−Pb−O(1)	120.4(1)
Pb···S(1)	3.221(1)	N(2)−Pb−O(2)′	89.6(1)
Pb···S(2)	3.314(1)	N(2)−Pb−O(3)	51.2(1)
S═O$_{(\mathrm{avg})}$	1.45	N(2)−Pb−O(4)″	92.5(1)
S−N$_{(\mathrm{avg})}$	1.57	O(2)′−Pb−O(4)″	175.0(1)

The lead cation forms short bonds to both nitrogen atoms of a single disulfonamide ligand [2.296(4) and 2.329(4) Å]. These bonds are slightly shorter than those reported for related Pb(II)-sulfonamide complexes.[13] Pb(II) also forms short bonds to the two “axial” oxygen atoms on two neighboring sulfonamide groups [2.524(3) and 2.599(3) Å, O(2)′−Pb−O(4)″ angle = 175.0°]. It is through these bonds that the structure forms a polymer as illustrated in Figure 1. These Pb−O distances are comparable to those previously observed for related complexes (ranging from 2.46 to 2.96 Å).[15,18] Longer distances are observed between Pb and the other two sulfonyl oxygen atoms O(1) [2.869(4) Å] and O(3) [3.043(3) Å]. These bonds, though weak, close a Pb−N−S−O four-membered ring and draw the sulfur atoms close enough to the lead cation that some Pb−S bonding interactions might also be taking place. Chelation of a sulfonamide to Pb(II) through both its N and O atoms has been previously reported.[19]

All of the coordination around Pb takes place in one hemisphere, leaving most of the other hemisphere apparently

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(14) Crystal structure for **3**: monoclinic, space group $P2_1/n$, $a = 9.8201(15)$ Å, $b = 19.358(3)$ Å, $c = 9.8553(12)$ Å, $\beta = 99.828(10)°$, $V = 1846.0(5)$ Å^3, temperature = 100(2) K, $Z = 4$, $D_{\mathrm{calc}} = 2.14$ g/cm^3, $\mu = 9.393$ mm^{-1}, reflections collected = 7764, independent reflections = 3935 ($R_{\mathrm{int}} = 0.036$), R1 ($I > 2\sigma_I$) = 0.028, wR2 (all data) = 0.075 at 100 K.

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unoccupied. This is likely the location of the “lead(II) lone pair”.[10] Further examination of this space reveals that it is filled, although somewhat awkwardly, with two phenyl rings (symmetry equivalents of the sulfonyl phenyl rings). The fit is termed awkward because neither one forms an η^6 interaction with Pb. If Pb−π interactions are present, they are very weak, as the three closest carbon atoms [C(14), 3.695(6) Å; C(23), 3.786(5) Å; C(24), 3.724(5) Å] are beyond the sum of the ionic radius of Pb(II) (1.5 Å for high coordination numbers)[20] and the van der Waals radius of carbon (1.70 Å).[21] Although weak lead−arene interactions are fairly common, the lead−carbon distances reported here are generally longer than typically observed.[10c,22]

Comparison of the bond lengths in **3** with those in the free ligand **1** shows that the S−N bonds are significantly shorter (averaging 1.64 Å in **1**)[23] when the ligand is bound to Pb(II). However, a corresponding lengthening of the S=O bond cannot always be observed because of 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 spectrum from 1336 cm^{-1} (in **1**) to 1257 cm^{-1} (in **3**).

The sulfonamides **1** or **2** were shown to extract Pb(II) from water into DCE via ion exchange, when used in synergistic combinations with 2,2′-bipy, by forming the mixed-ligand ternary complexes **5** and **6**. The coordination of 2,2′-bipy presumably interferes with the S=O−Pb coordination observed in the crystal structure of **3**, dramatically enhancing the solubility of **5** in DCE. The extraction of Pb(II) from $Pb(NO_3)_2$ (aq) into DCE was investigated using **1** or **2** together with 1 equiv of 2,2′-bipy and 2.2 equiv of NH(*i*-Pr)$_2$. The distribution ratios $D_{Pb} = [Pb]_o/[Pb]_{aq}$ were determined by inductively coupled plasma mass spectrometry (ICP-MS) of the aqueous phases after extraction (for $[Pb]_{aq}$) and after stripping of the organic phases with 0.1 M HNO_3 (for $[Pb]_o$). The synergistic system gave Pb(II) extraction as high as 97.5% (for $[Pb(II)]_t/[\mathbf{2}]_t = 1.0$) and 95.0% (for $[Pb(II)]_t/[\mathbf{1}]_t = 1.0$). Double stripping of the organic phases showed no increase in the values of D_{Pb}. Control experiments, using **1** or **2** only, 2,2′-bipy only, diisopropylamine only, or these compounds in pairs, demonstrated that the presence of all three components in the organic phase is essential for Pb(II) extraction. **1** and **2** were recoverable after extraction (>97% measured by ^1H NMR spectroscopy with 4,4′-dimethylbiphenyl as an internal standard). The pH of the aqueous phase after contact was measured at 7.0 (±0.2). The monosulfonamide analogue $C_6H_5SO_2NHC_6H_5$ did not extract at all under the extraction conditions. The NMR spectra of the organic phases after extraction using **1** and **2** are consistent with $Pb[1,2\text{-}C_6H_4(NSO_2C_6H_5)_2][2,2'\text{-bipy}]$ (**5**) and $Pb[1,2\text{-}C_6H_4(NSO_2C_6H_4\text{-}p\text{-}Bu^t)_2][2,2'\text{-bipy}]$ (**6**), respectively, being present. These ternary complexes[24] were also isolated by reacting **3** or **4** with 2,2′-bipy. NMR titration of **5** with increasing amounts of **1** or 2,2′-bipy showed slow exchange with sulfonamide **1** and fast exchange with bipy.

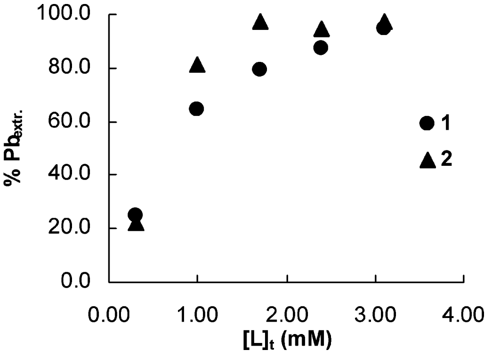

Figure 2. Percent Pb extracted (defined as $[Pb]_{org}/[L]_t) \times 100\%$) vs $[L]_t$ for **1** and **2**. $[Pb]_t$ is constant at 6.30 mM. (Error in concentration is <5%).

The extraction of Pb(II) by **1** and **2** was investigated for different ligand concentrations (Figure 2), as well as in comparison with 18-crown-6 (18C6), using a stable initial $[Pb(II)]_t$ of 6.30 mM. The sulfonamide/2,2′-bipy combinations gave distribution ratios of $D_{Pb}(\mathbf{1}) = 0.926$ and $D_{Pb}(\mathbf{2}) = 0.941$ for $[L]_t/[Pb]_t = 0.492$, which correspond to 97.8% and 98.6% Pb extraction, respectively. This was 420 (for **1**) and 430 times (for **2**) higher extraction than 18C6 or combinations of 18C6 and bipy under the same conditions. Ligands **1** and **2** were also very effective in the extraction of micromolar Pb(II) concentrations from water into DCE. With initial conditions of $[L]_t = 3.30$ mM, $[2,2'\text{-bipy}]_t = 3.30$ mM, $[NH(i\text{-}Pr)_2]_t = 7.26$ mM, $[Pb(II)]_t$ between 3 and 300 μM, and $[L]_t/[Pb(II)]_t$ between 8.89 and 970, ligand **1** extracted between 98.4% and 98.8% of Pb, and ligand **2** extracted between 99.5% and 100%.

In conclusion, synergistic extraction of Pb(II) from water into DCE was demonstrated by synergistic combinations of 2,2′-bipy and simple sulfonamide ion exchangers. The sulfonamide-Pb(II) complex **3** was shown to have a hemidirected geometry on Pb with a stereochemically active lone pair and with axial S=O−Pb coordination resulting in a polymeric network in the solid state. These results set the stage for using analogous sulfonamide chelates for extraction of Pb(II) and other toxic metals, elucidating aspects of selectivity, and determining the extraction mechanism involved.

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Supporting Information Available: Crystal data, synthesis and characterization information, and details on distribution experiments. This material is available free of charge via the Internet at http://www.pubs.acs.org.

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