

Selective Recognition and Extraction of the Uranyl Ion

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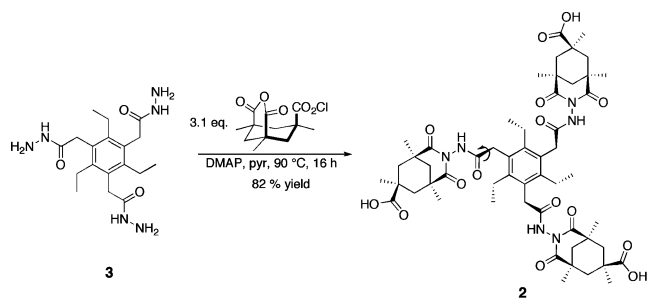
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Abstract: A tripodal receptor capable of extracting uranyl ion from aqueous solutions has been developed. At a uranyl concentration of 400 ppm, the developed ligand extracts ~59% of the uranyl ion into the organic phase. The new receptor features three carboxylates that converge on the uranyl ion through bidentate interactions. Solution studies reveal slow exchange of the carboxylates on the NMR time scale. The crystal structure of the complex shows that the carboxylates coordinate to uranyl ion while the amides hydrogen bond to one of the uranyl oxo-oxygen atoms. The hydrophobic coating of the ligand and its rigidity contribute to its ability to selectively extract uranyl ion from dilute aqueous solutions.

Recognition of the uranyl ion (UO_2^{2+}) is a long-standing goal for purposes of environmental remediation, metallurgical extraction, and water purification. Uranium is found in a variety of sources, both terrestrial and aqueous. Typical uranium ores contain deposits at ~1000 ppm. A more subtle source of uranium is coal ash, where it is found at 300 ppm.¹ The uranium present in aqueous environments exists naturally or as a contaminant. For instance, some Bavarian drinking water is polluted with uranium at 10 ppb, and contamination of the Dnieper River in Kiev has reached 11.5 ppm.² The Earth's oceans are a natural source where more than 99% of all global uranium resides. However, the low concentration of uranyl ion there (3 ppb)³ and the abundance of other cations call for chelating agents with high affinity and selectivity. We describe here a tripodal synthetic receptor that through its preorganization and hydrophobicity features, these attributes for the selective extraction of uranyl ion from water.

The linear geometry and characteristically short uranium–oxygen bonds of the uranyl ion limit the approach of complementary anions to the equator of the positively charged uranium center. In natural aqueous environments, the oxophilic uranyl ion is coordinated by three carbonate ligands.⁴ The small bite angle of carbonate/carboxylate allows for three ligands to be positioned around the metal, fully satisfying its coordination geometry. Complements to the uranyl ion's oxygen atoms can approach from many directions, as is apparent from the structures of uranyl–protein⁵ and uranyl–ligand^{6,7} complexes. Since the pioneering work of Raymond,⁸ few examples of uranyl ligands containing only carboxylates have been reported,^{9–11} even though it is the coordination motif preferred in nature. Here we present the rigid and preorganized tripodal carboxylate ligand **2**. The crystal structure of complex **1** (see Figure 2), the first structure involving binding of uranium by a tripodal ligand,¹² confirms the 1:1 stoichiometry of the complex and also indicates hydrogen bonding with the uranyl oxygens. This ligand extracts uranium from aqueous solutions into organic solutions with striking selectivity and produces a complex that shows unusual kinetic stability on the NMR time scale.

The new receptor is built from a rigid skeleton featuring three carboxylates that converge on the uranyl ion through bidentate interactions.¹³ We combined the triethylbenzene core with Kemp's triacid^{14,15} to minimize the internal rotations of the new ligand. The appropriate size, shape, and chemical complementarity was found in the use of hydrazine as the linker. Condensation of the known trihydrazide **3**¹⁶ with the Kemp anhydride acid chloride gave ligand **2** in good yield (Scheme 1). The planes of the imide and amide functions of **2** prefer to be perpendicular,^{17,18} and to avoid unfavorable steric and electronic clashes, the acid and the amide N–H are fixed near each other. The only remaining (freely rotating) single bonds in **2** are those indicated in the scheme. In one conformation, ligand **2** presents the three carboxyl groups well-positioned to satisfy the equatorial coordination geometry of the uranyl ion and simultaneously directs the three amide hydrogens toward a uranyl oxygen atom.

Scheme 1. Synthesis of Uranyl Ligand **2**

The ^1H NMR spectrum of ligand **2** in MeOD (shown in Figure 1) indicates a time-averaged C_{3v} symmetry, the conformation expected as a result of the directing effects of the 1,3,5-triethylbenzene core.¹⁹ Treatment of **2** with uranyl nitrate or uranyl acetate and triethylamine (TEA) in MeOH at room temperature results in the quantitative formation of uranyl complex **1**. Upon complexation of uranyl ion, many of the signals in the NMR spectrum of **2** exhibit substantial shifts (Figure 1a,b). Most affected are the methylene protons, which are shifted ~0.5 ppm upfield from their positions for the deprotonated ligand.

When uranyl ion is added to a solution of **2** with no base present, the resulting proton NMR spectrum is broad and unresolved. Upon addition of base (TEA), the signals become sharp and resolved, matching those in the spectrum in Figure 1b. The sharp signals suggest that ligand **2** is in slow exchange with the complex on the NMR time scale, a feature that is unusual for carboxylate ligands bound to uranium.²⁰ In fact, when less than 1 equiv of uranyl ion is added to a basic solution of **2**, separate signals appear for uncomplexed deprotonated ligand (Figure 1a) and complex (Figure 1b) in solution [see the Supporting Information (SI)].

A strong base such as TEA is not needed in order to drive complex formation. For example, sodium acetate or pyridine are

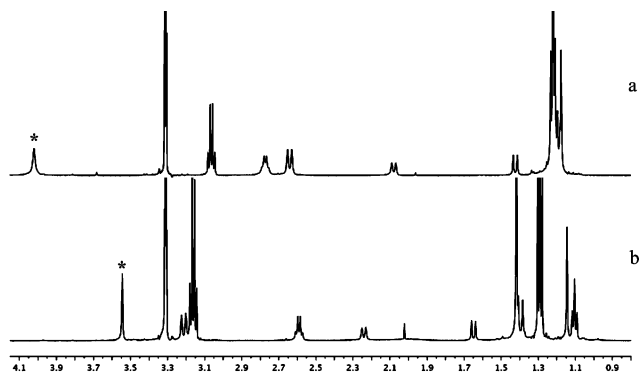


Figure 1. (a) ^1H NMR spectrum of uranyl ligand **2** with 3 equiv of TEA added. (b) ^1H NMR spectrum of uranyl ligand **2** with 3 equiv of TEA and 1 equiv of uranyl nitrate added. The asterisks label the methylene protons adjacent to the amide carbonyl.

sufficiently basic to produce complex **1** quantitatively. Slow diffusion of pentane into a pyridine solution of **2** and uranyl nitrate yielded pale-yellow single crystals suitable for X-ray diffraction.²¹ Ligand **2** and uranyl ion crystallize as the 1:1 complex **1** (Figure 2) with a nearby pyridinium ion to balance the charge.^{22,23}

As anticipated, the crystal structure reveals that the three alkyl carboxylates converge onto the uranium center, fully satisfying the hexacoordinate geometry of the uranyl ion. In addition, the three amide hydrogens near the inner uranyl oxo-oxygen atom produce secondary stabilizing interactions. These amide hydrogens are able to interact with the uranyl oxygen through three long hydrogen bonds with an average $\text{N}\cdots\text{O}$ distance of 3.5 Å. The solid-state structure of **1** confirms a two-component recognition motif by the new ligand.

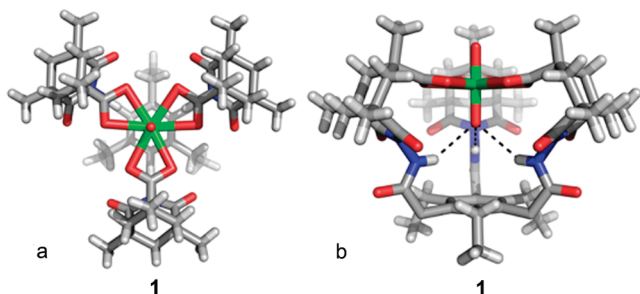


Figure 2. Views of the X-ray structure of uranyl complex **1**. The pyridinium counteranion and other solvent molecules have been removed for clarity. Carbon is colored gray, nitrogen blue, oxygen red, uranium green, and hydrogen white. (a) Top view of **1** showing the threefold symmetry. (b) Side view of **1** showing the amide H atoms directed toward the uranyl oxygen.

The ligand's interaction with the uranyl oxo-oxygen atoms was also corroborated using IR spectroscopy. The strong ν_3 antisymmetric stretch of the uranyl ion usually occurs at $\sim 920\text{ cm}^{-1}$,²⁴ while the ν_1 symmetric stretch is IR-inactive. However, hydrogen bonding to one of the oxo-oxygens of the uranyl ion removes the center of symmetry, so the ν_1 stretch becomes IR-active.⁸ The IR spectrum of complex **1** shows the strong ν_3 antisymmetric stretch of the uranyl ion at 902 cm^{-1} (see the SI). This stretch is revealing because it is inversely proportional to the donor strength of the equatorial ligands.²⁵ The medium band that appears at 842 cm^{-1} is the ν_1 stretch, which confirms the hydrogen-bonding interactions between the amide hydrogens and one of the oxo-oxygens.

The application of **2** as an agent for uranyl ion sequestration was investigated through liquid–liquid extractions. An aqueous

solution of uranyl nitrate (1.6 equiv) in acetate buffer (pH 5) was stirred with a chloroform solution of **2** (1 equiv), and the concentrations of uranium in each phase were determined before and after extraction with inductively coupled plasma–atomic emission spectroscopy (ICP–AES) (see the SI). The extraction experiments were run at a series of uranium concentrations: 400, 40, and 4 ppm. At 400 ppm, $59 \pm 9\%$ of **2** successfully extracted aqueous uranyl ion into the organic phase, and at 40 ppm, $29 \pm 9\%$ of **2** removed uranium from the aqueous phase.²⁶ At 4 ppm, no uranium was extracted. The uranium can be recovered from the ligand by adding 0.5 M HNO_3 (see the SI). The reported tripodal carboxylate ligands of Raymond did not extract uranyl ion at high concentrations of NaCl.^{8,27} In contrast, ligand **2** is highly selective for uranyl. The extraction of uranyl ion at 400 ppm was carried out in the presence of the six ions that dominate the chemistry of seawater: Cl^- , Na^+ , Mg^{2+} , Ca^{2+} , K^+ , and SO_4^{2-} .³ With these ions present at seawater concentrations, **2** showed no diminished function; again, $\sim 59\%$ of **2** extracted uranyl ion into the organic phase.

In summary, the new chelating ligand **2** has been synthesized to complex uranyl ion. The crystal structure of the complex shows that all three of the carboxylates coordinate to the uranyl ion while the hydrogens of the amides hydrogen bond to the inner uranyl oxo-oxygen atom. The hydrogen-bonding interaction was corroborated with IR spectroscopy. In solution, the complex is in slow exchange with the ligand, as shown by the sharp and resolved ^1H NMR signals. The hydrophobic coating of the ligand and its rigidity all contribute to its ability to extract uranyl ion out of dilute aqueous solutions without interference by other ions in seawater.

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Supporting Information Available: ^1H NMR, ^{13}C NMR, and mass spectra of all compounds; experimental details of ICP–AES analysis; single-crystal X-ray diffraction experimental procedures and data for complex **1**; and complete ref 2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (21) Crystal data for $[\text{C}_{10}\text{H}_{12}\text{N}_2]^+[\text{UO}_2(\text{C}_{59}\text{H}_{75}\text{N}_7\text{O}_{15})]^- \cdot 6\text{C}_5\text{H}_5\text{N}$: $\text{C}_{99}\text{H}_{112}\text{N}_{15}\text{O}_{17}\text{U}$; $M = 1945.99$; monoclinic; $C2/c$; $a = 40.971(19) \text{ \AA}$, $b = 21.705(8) \text{ \AA}$, $c = 19.145(7) \text{ \AA}$, $\alpha = 90.00^\circ$, $\beta = 112.144(9)^\circ$, $\gamma = 90.00^\circ$; $V = 15770(11) \text{ \AA}^3$; $Z = 8$; $\rho_{\text{calcd}} = 1.633 \text{ g mL}^{-1}$; $\mu(\text{Mo K}\alpha) = 2.144 \text{ mm}^{-1}$; $2\theta_{\text{max}} = 46.78^\circ$; $T = 100(2) \text{ K}$; 51633 reflns collected; $R_1 = 0.0910$ for 7130 reflns; $R_{\text{int}} = 0.1315$ (749 parameters) with $I > 2\sigma(I)$; $R_1 = 0.2345$, $wR_2 = 0.2629$; GOF = 1.058 for all 11401 data; CCDC 792943.
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