

Short communication

New ligands for uranium complexation: A stable uranyl dimer bearing 2,6-diacetylpyridine dioxime



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ABSTRACT

The synthesis, characterization, and stability study of the first uranium complex bearing 2,6-diacetylpyridine dioxime (dapdoH₂) is reported. The dimeric complex [UO₂(dapdoH)Cl]₂ is stable in solution as shown by ESI-MS and NMR spectrometry, and its solid-state structure was further analyzed by X-ray crystallography, IR, Raman and luminescence studies.

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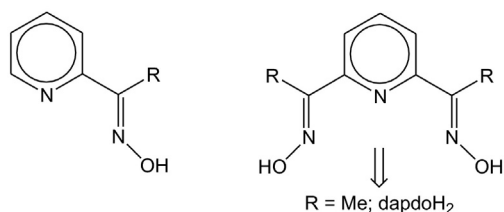
Actinide coordination complexes are under intense investigation for a number of reasons, including, but not limited to, a) the fundamental understanding of the coordination chemistry [1], b) nuclear waste applications [2], c) catalysis [3], and d) their unique magnetic properties [4]. Starting with the Manhattan project and into the perpetual nuclear power era, the need of uranium has been unceasing [5]. In seawater, uranium exists in ppb concentrations; estimates show that if 1% was extracted, the current U reserves would see a tenfold increase [6]. Both nuclear wastewater cleanup and uranium seawater sequestration pose multiple challenges for the design of extractant technologies. One of the most important requirements for a nuclear waste chelating agent is considerable stability in protic acid conditions [7]. Furthermore, in seawater the uranium concentration is typically 3.3 μg/L, which is up to six orders of magnitude smaller than other seawater cations [8]. Moreover, due to the high Ca²⁺, Mg²⁺, and CO₃²⁻ concentrations, uranium predominantly exists as the Ca₂[UO₂(CO₃)₃] neutral species, or the Mg[UO₂(CO₃)₃]²⁻ anion [9]. Therefore, it is important for a uranium extractant to be able to outcompete CO₃²⁻, accommodate the dilute uranium, and be selective for uranium over other seawater cations. As with any other extraction technology, it needs to be reusable, inexpensive, and active over a range of seawater temperatures and other conditions [10].

Polymeric amidoximes have dominated the literature as uranium sequestrants; they were initially suggested in the 1980s and later field tested, retrieving 1 kg of U from the Pacific Ocean over 3 years in the coast of Japan [11]. Oximes (>C=N—OH) are known to be strong α-nucleophiles and very effective ligands for binding to transition metal and lanthanide ions [12]. Upon deprotonation, the oximate group is capable of coordinating strongly to a variety of different metal ions, and especially with metals in high oxidation states, such as tri- and tetravalent, thus yielding both oligo- and polynuclear compounds [13]. As a result, oximate-based complexes with relatively stable structures can be obtained; however, this stability is heavily affected by the presence of R-substituents on the oxime functionality, which are able to participate in the formation of chelate ring(s). To that end, Perlepes and coworkers recently showed that 2-pyridyl monoximes (Scheme 1) are efficient ligands for binding hexavalent uranium via the formation of an 'unusual' three-membered O—N—U ring [14]; unfortunately, all the reported complexes were not stable in solution.

In order to tackle some of these problems and introduce a new class of oximate ligands, which are suitable for binding efficiently to actinides and potentially with high selectivity for their separation and recycling, we decided to explore the coordination chemistry of 2,6-diacetylpyridine dioxime (dapdoH₂, Scheme 1) with the uranyl cation (UO₂²⁺). The ligand dapdoH₂ can readily form two stable five-membered chelating rings using its pyridine and oximate N atoms. In addition, the oximate O atoms can presumably foster the formation of uranyl-bridged complexes with unprecedented structures. Therefore, the 1:1 reaction of UO₂(O₂CMe)₂·2H₂O and dapdoH₂ in solvent

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Scheme 1. General structural formulae of 2-pyridyl monoximes (left) and pyridine-2,6-dioximes (right; R = H, Me (dapdoH₂), Ph, etc.).

CH₂Cl₂ led to a yellow solution and the subsequent isolation of yellow plate-like crystals of the dinuclear uranyl compound [(UO₂)₂Cl₂(dapdoH)₂] (**1**) in 65% yield (see ESI). Complex **1** is the first actinide compound bearing a coordinated pyridine dioxime ligand. The coordinated Cl[−] ions resulted from the metal-ion assisted activation and cleavage of the C—Cl bond from the solvent CH₂Cl₂ [15]. This is a very interesting dehalogenation of CH₂Cl₂ with implications in biological and industrial catalysis [16]. Considering the fact that uranium recovery involves eluting the adsorbents with 1 N HCl or similar acid, the ligand is required to be stable under protic acidic conditions [17]. To that end, and in order to optimize the synthetic conditions for the isolation of **1**, we decided to perform the aforementioned reaction in the presence of equimolar amounts of HCl (1 M) and in solvent MeCN to exclude the possibility of Cl[−] delivery by the solvent. Indeed, complex **1** crystallized again albeit in higher yields (80%, see ESI).

Complex **1** crystallizes in the monoclinic space group *P*2₁/*n*. Its structure consists of dinuclear [(UO₂)₂Cl₂(dapdoH)₂] molecules (Fig. 1). There is a crystallographic inversion centre at the mid-point of the U^{VI}...U^{VI} axis. The U^{VI} atoms are doubly bridged by the diatomic oximate groups of two singly deprotonated η¹:η¹:η¹:η¹:μ dapdoH[−] ligands. Each dapdoH[−] ligand chelates one U^{VI} atom forming two five-membered U—N—C—C—N chelating rings, while its oximate oxygen atom (O8 and O8') is terminally bound to the other metal centre. The U(1)N(1)O(8)U(1') unit is not perfectly planar; its torsion angle is 33.2°. The deviations of atoms U1, N1, O8 and U1' from the U(1)N(1)O(8)U(1') best mean plane are 0.007, 0.058, 0.079 and 0.028 Å, respectively. The two uranyl oxygen atoms (O1 and O2) occupy the axial positions of each U^{VI} atom. A monodentate Cl[−] ion completes seven-coordination at each metal centre. Each U^{VI} atom possesses an almost ideal pentagonal bipyramidal geometry as confirmed by Continuous Shape Measures (CSHM) using the program SHAPE (CSHM = 1.35, Fig. S1, Table S1). The oximate N and O atoms, and the terminal Cl[−] ion, form the equatorial plane. The small bite angles of the dapdoH[−] chelates (N1—U1—N2 = 62.2° and N2—U1—N3 = 61.6°) are close to the ideal 72° of a pentagonal plane, thus inducing a small distortion to the ideal pentagonal bipyramid. It is also known that the small bite angles in five-membered chelating rings help to minimize the ring strain and enhance the kinetic stability of the overall system against ligand substitution reactions, which in turn is of vital importance for

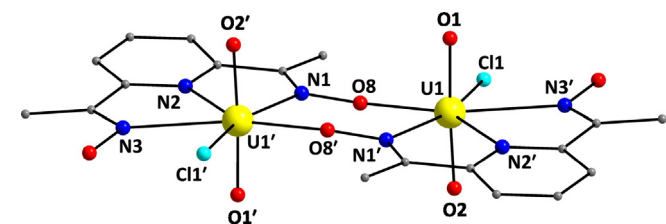


Fig. 1. Molecular structure of **1**. H atoms are omitted for clarity. Selected distances (Å) and angles (°): U1—O1 1.773(2), U1—O2 1.777(2), U1—O8 2.191(2), U1—N1' 2.519(3), U1—N2' 2.577(2), U1—N3' 2.598(3), U1—Cl1 2.708(1). Color scheme: U^{VI} yellow, O red, N blue, Cl cyan, C dark gray. Symmetry operation for the primed atoms: 1 − *x*, 1 − *y*, 1 − *z*. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

various applications, such as metal-ion recognition, catalysis, separation, etc.

The U^{VI} and donor atoms in the equatorial plane are almost coplanar. The U...U distance is 4.891(2) Å and the O=U=O angle is 174.6(1)°. All the U—N, U—O and U=O bonds are strong and within the expected range for this class of complexes. The U—Cl distance is relatively long (2.708(1) Å) and it falls into the expected range for similar Cl[−]-bound U^{VI} compounds [18]. The crystal structure of complex **1** is stabilized by two symmetry-related, intermolecular hydrogen bonds between the unbound —OH groups of the dapdoH[−] ligands and the Cl[−] groups of neighboring dinuclear molecules. These interactions serve to link adjacent dimers in the crystal into 1D H-bonded chains, which run along the crystallographic *a* axis (Fig. S2). Although there are many dinuclear uranyl complexes reported in the literature, with a wide variety of bridging groups ranging from oxido, peroxido and halides to carboxylate [19], amino and sulfides, complex **1** is the only oximate-bridged {(UO₂)₂(μ-NO)₂} species reported to date.

In addition to single-crystal X-ray crystallography and CHN elemental analyses (see ESI), complex **1** was characterized by a variety of complementary spectroscopic and physicochemical techniques in both the solid-state and in solution. The IR spectrum (Fig. S3) reveals the presence of a strong band at 901 cm^{−1} assigned to the IR-active antisymmetric stretching vibration of the *trans*-{O = U = O}²⁺ group (*v*₃) [20]. The remaining bands were attributed to the aromatic group and oximate functionalities of dapdoH[−]. The Raman-active uranyl symmetric stretch (*v*₁) is observed at 850 cm^{−1} in the Raman spectrum of **1** (Fig. S4) [21]. The luminescent properties of U^{VI} are of great interest due to potential applications, including sensing of small molecules and photocatalysis. However, not all uranyl compounds possess luminescent properties, and the mechanisms of the emission from uranyl compounds are often difficult to rationalize. Therefore the introduction of an appropriate organic ligand for the sensitization of the uranyl emission remains a challenging task [22]. Solid-state luminescent studies were performed at room temperature and under the exact same conditions for the ligand dapdoH₂, the benchmark compound UO₂(O₂CMe)₂·2H₂O, and complex **1**. The organic ligand shows a violet-blue broad emission at 420 nm, upon maximum excitation at 352 nm (Fig. S5), which is diminished in the emission spectrum of **1**. The latter spectrum shows characteristic “five-finger” sharp peaks of uranyl materials (upon excitation at 300 nm) which are located at 460, 479, 499, 520, and 543 nm (Fig. 2). These emission peaks are generally assigned to the symmetric and antisymmetric vibrational modes of the uranyl group and they particularly correspond to the electronic and vibronic transitions of S₁₁ → S₀₀, S₁₀ → S_{0*v*'} (*v* = 0–3), respectively [23]. The peaks are also blue-shifted with respect to the UO₂(O₂CMe)₂·2H₂O starting material,

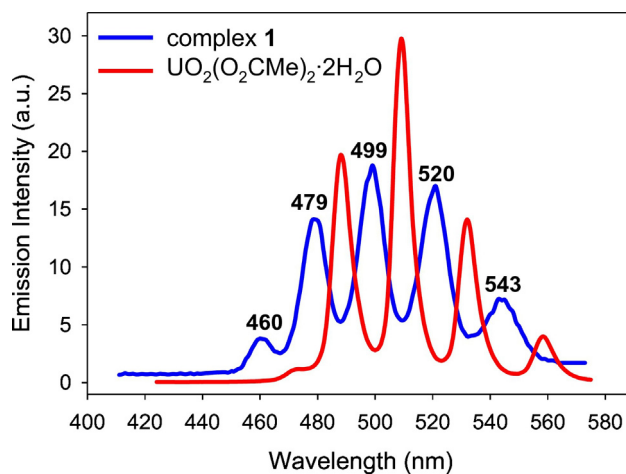


Fig. 2. Solid-state emission spectra of complex **1** (blue line) and UO₂(O₂CMe)₂·2H₂O (red line) at room temperature (λ_{ex} = 300 nm). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

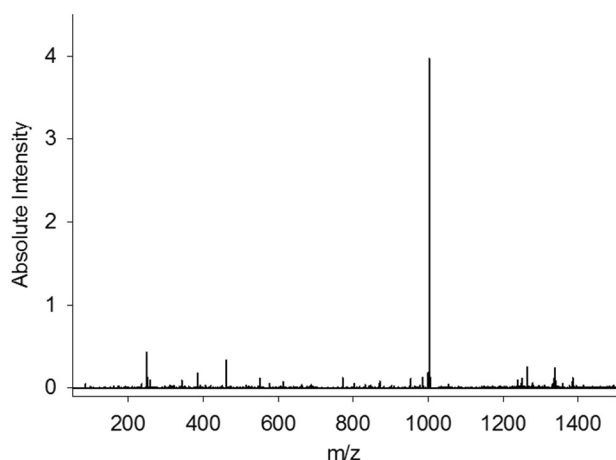


Fig. 3. Negative ion ESI mass spectrum of **1** in DMSO/MeCN.

suggesting the presence of a different coordination environment around the UO_2^{2+} cation as a result of its complexation with the dapdoH^- chelate and the Cl^- ion.

In order to probe the stability of **1** in solution, negative ion electrospray ionization (ESI) mass spectrometry (MS) studies were conducted in DMSO/MeCN. The strong intensity peak at 1002 m/z (Fig. 3) nicely reproduces the dinuclear $\{(\text{UO}_2)(\text{dapdo})\}_2$ core with the volatile coordinated Cl^- ions being replaced by a DMSO [$\text{M-DMSO} = 1002.59\text{ m/z}$] solvate molecule. In support of this assignment is the excellent match between the acquired isotopic patterns of the experimental and theoretically calculated distributions (Fig. S6), thus allowing us to confirm the structural integrity of the uranyl-dioximate core of **1** in solution.

In addition to the ESI-MS results, the ^1H NMR spectrum of **1** in $\text{DMSO-}d_6$ revealed the presence of various shifted signals when compared to the ^1H NMR of the free dapdoH_2 (Fig. 4). This indicates coordination of the dioxime ligand to the diamagnetic metal center which further supports the stability of the dinuclear $\{(\text{UO}_2)(\text{dapdo})\}_2$ core in solution. The peaks at around 11.7, 7.9, and 2.4 ppm in the ^1H NMR spectrum of **1** correspond to the NO-H, pyridine-H (py-3(5)H and py-4H) and CH_3 groups of the coordinated dapdoH^- ligand, respectively [24]. A detailed discussion of the ^1H NMR chemical shifts is provided in the ESI.

In conclusion, we have herein reported our first results from the employment of pyridyl dioximes in a very active field of research, the

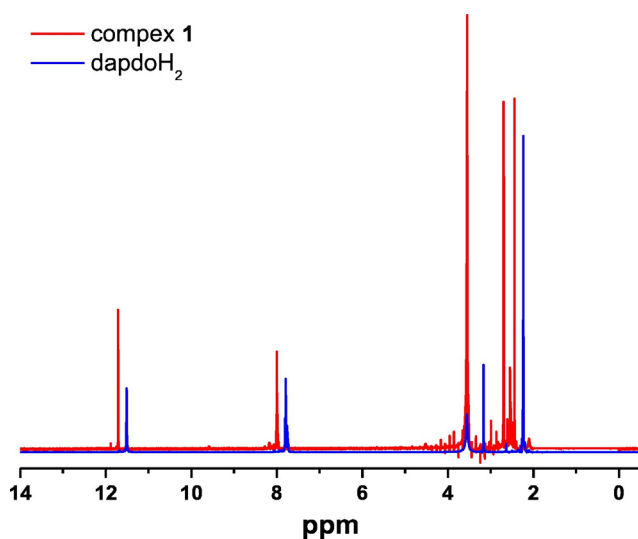


Fig. 4. ^1H NMR spectra of complex **1** and free dapdoH_2 in $\text{DMSO-}d_6$.

coordination chemistry of actinides and particularly the advancement of knowledge for the complexation of U^{VI} . The pronounced stability of $\{(\text{UO}_2)_2\text{Cl}_2(\text{dapdoH})_2\}$ in both solid-state and solution will allow us to further explore the kinetic and catalytic properties, as well as explore the selectivity of dapdoH_2 and related dioximate ligands over vanadyl and other transition metal ions which behave as competitors for uranyl in seawater conditions.

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Appendix A. Supplementary material

Electronic Supplementary Information (ESI) available: Complete synthetic and crystallographic discussion, structural figures, and spectroscopic and analytical data. CCDC-1505966 (**1**). Supplementary data associated with this article can be found in the online version, at doi: 10.1016/j.inoche.2017.01.021.

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