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Synthesis and Structural Characterization of a Uranyl(VI) Complex Possessing Unsupported Unidentate Thiolate Ligands

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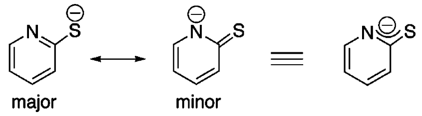
The synthesis and structural characterization of the first example of a uranyl(VI) complex possessing unsupported unidentate thiolate ligands, $UO_2(S\text{-}2,6\text{-}Cl_2C_6H_3)_2L_2$ (**2b**, L = *N*,*N*-diisobutylisopropylamide), are reported. Isolation of **2b** as a stable mononuclear complex is provided by the alkyl substituents of the organic amide ligands, which offer enhanced solubility, electron-releasing properties, and steric protection to help saturate the uranyl(VI) coordination sphere.

The uranyl(VI) ion is perhaps the most extensively studied unit in actinide chemistry, not only in the context of its chemical behavior under a variety of environmental conditions but also because of the unique structure and bonding of the linear O=U=O dioxo group and the photochemical and redox properties of this species.[1] However, because of the hard nature of the high-valent metal, the vast majority of uranyl(VI) complexes are coordinated in the equatorial plane by weak-field ligands comprising hard O, N, and halide donors. For example, among the softer halides, only recently have isolable uranyl iodide complexes been reported,[2−4] stabilized by neutral adducts such as tetrahydrofuran (THF), pyridine, and phosphine oxides within the uranyl(VI) coordination sphere to surmount the inherently weak U−I bonds.

Similarly, thiolate ligands are an important facet in coordination chemistry for a number of metals in a variety of oxidation states, but in striking contrast to the maturation of uranyl(VI) alkoxide chemistry,[5−8] the only structurally characterized thiolate complexes are represented by a few derivatives containing chelating pyridine-2-thiolate ligands. In these complexes, the ligands are anchored by the harder pyridine donors and possess a measure of resonance stabilization (Chart 1)[9] analogous to that of related dithiocarbamate ligands,[10] as suggested by the relatively short U−N and long U−S bond distances observed in the solid-state structures.[11,12]

Chart 1



Our interest in isolating a uranyl thiolate complex resides in testing the resilience of the uranyl(VI) ion with respect to reduction of the high-valent metal center in the presence of soft donor equatorial ligands and because cysteine thiolates have been implicated in uranium toxicity.[13] Herein we report the first structurally characterized example of a uranyl(VI) complex possessing unsupported (i.e., unidentate) thiolate ligands. This complex is made isolable through the electron-withdrawing chloride substituents of the thiolate ligand combined with the steric bulk, electron donation, and solubility provided by the neutral organic amide ligands.

Addition of a THF solution of the thiolate salt NaS-2,6-$Cl_2C_6H_3$ to the yellow uranyl(VI) chloride precursor $UO_2Cl_2L_2$ (**1**)[14] produces the air-sensitive uranyl thiolate complex $UO_2(S\text{-}2,6\text{-}Cl_2C_6H_3)_2L_2$ (**2**) as red crystals in high yield after workup in CH_2Cl_2/hexanes (Scheme 1). Exposing a solution of **2** to air liberates the amide ligand and generates the free

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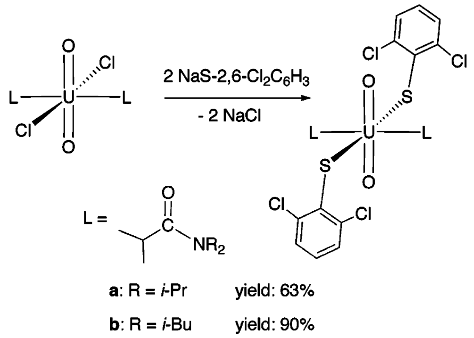
Scheme 1



thiol HS-2,6-$Cl_2C_6H_3$, as measured by ^{1}H NMR spectroscopy, along with an insoluble yellow uranium-containing compound.

Single crystals of **2b** suitable for X-ray crystallography were obtained by layering hexanes over a CH_2Cl_2 solution. A thermal ellipsoid drawing of **2b** is shown in Figure 1.[15]

An all-trans octahedral coordination geometry is observed for the uranium center in the solid-state structure of **2b**, consisting of trans oxo ligands O(3) and O(4), trans thiolate donors S(1) and S(2), and the carbonyl oxygen atoms O(1) and O(2) belonging to the trans amide ligands. The O(3)−U(1)−O(4) bond angle of 178.96(9)°, together with the U(1)−O(3) and U(1)−O(4) bond distances of 1.772(2) and 1.775(2) Å, respectively, are all typical for the trans dioxo uranyl unit. Similarly, the $\nu_{U=O}$ stretch of 912 cm^{-1} is relatively unchanged with respect to the precursor dichloride complex (924 cm^{-1}).[14] The U(1)−S(1) and U(1)−S(2) bond distances of 2.7143(7) and 2.7325(8) Å, respectively, are shorter than the corresponding U−S bond distances of 2.805(6) and 2.813(8) Å reported for $[UO_2(o\text{-}C_5H_4NS)(NO_3)_2]^-$ and $[UO_2(o\text{-}C_5H_4NS\text{-}3\text{-}SiMe_3)(NO_3)_2]^-$, respectively,[12] which as mentioned above possess chelating pyridine-2-thiolate ligands. The U−S bond distances in **2b** are comparable to those found in U(IV) complexes containing terminal thiolate ligands.[16,17]

The acute bond angles about the sulfur atoms [U(1)−S(1)−C(1) = 106.1(1)°; U(1)−S(2)−C(7) = 111.2(1)°] are typical of metal thiolate complexes and contrast with the much larger bond angles generally observed in alkoxide complexes,[8] reflecting the greater degree of π bonding in the latter. Shallow torsion angles of 5.9(1)° and 7.5(1)° exist between the uranyl unit and the ipso carbon atoms C(1) and C(7), respectively, of the aryl rings belonging to the trans thiolate ligands, with the rings staggered in an anti conformation. Given the steric flexibility provided by the octahedral uranium coordination environment, this geometry perhaps aligns the sulfur 3p orbitals for orbital interactions involving the amide ligands and the uranyl unit (see below).

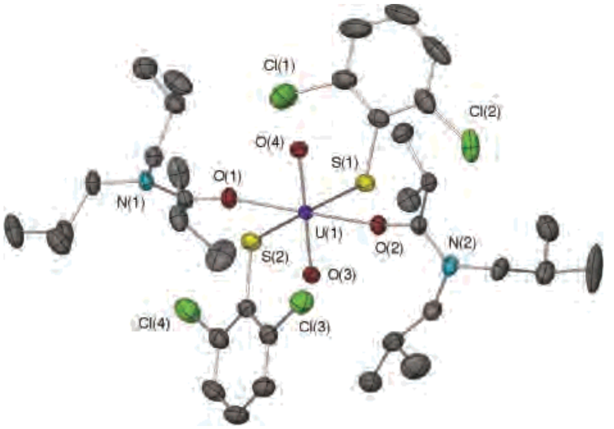


Figure 1. Thermal ellipsoid drawing of **2b**, showing thermal ellipsoids at 50% probability. Selected bond distances (Å) and bond angles (deg): U(1)−O(1), 2.3475(19); U(1)−O(2), 2.3245(18); U(1)−O(3), 1.7716(18); U(1)−O(4), 1.7746(17); U(1)−S(1), 2.7143(7); U(1)−S(2), 2.7325(8); O(1)−C(13), 1.262(3); O(2)−C(25), 1.265(3); O(1)−U(1)−O(2), 176.22(7); O(3)−U(1)−O(4), 178.96(9); S(1)−U(1)−S(2), 175.91(2); U(1)−O(1)−C(13), 167.83(18); U(1)−O(2)−C(25), 172.01(18).

The bonding parameters of the amide ligands suggest that these neutral donors are donating significant electron density to the uranium center, evidently to compensate for the low coordination number [uranyl(VI) complexes commonly accommodate five equatorial ligands][1] and the electronic mismatch of the uranyl(VI) center with the weaker coordination of the soft thiolate donors. For example, the U(1)−O(1) and U(1)−O(2) bond distances of 2.348(2) and 2.325(2) Å, respectively, are shorter than those normally observed for uranylamide complexes (usually between 2.36 and 2.40 Å),[18] and the U(1)−O(1)−C(13) and U(1)−O(1)−C(25) bond angles of 167.8(2)° and 172.0(2)°, respectively, are considerably wider compared to typical literature values (ranging between 135 and 160°).[19,20] Further, the amide moiety comprising the nitrogen atom N(2) and the carbonyl atoms O(2) and C(25) is coplanar with the uranyl unit. It is not known whether this geometry is a coincidence of steric factors or whether it optimizes electron donation from the conjugated π system within the amide group to the uranyl(VI) ion and whether the geometry adopted by the thiolate ligands contributes to this effect. Nevertheless, together with the pronounced weakening of the carbonyl unit signified by the lower energy $\nu_{C=O}$ stretch of 1562 cm^{-1} from that of the free amide (1645 cm^{-1}),[21] the structural data obtained from **2b** indicate that the neutral amides serve as suitable hard donors to help stabilize these uranyl(VI) thiolate complexes.

Isolation of **2** is likely also aided by the increased solubility and steric protection afforded by the alkyl substituents of the neutral ancillary amide ligands, offering synthetic advantages over other neutral (i.e., THF) donors. For example, our attempts to prepare analogous uranyl(VI)

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(15) Crystallographic data for **2b**: $C_{36}H_{56}Cl_4N_2O_4S_2U$, fw = 1024.78, monoclinic, $P2_1/n$, a = 16.8244(14) Å, b = 15.2484(12) Å, c = 17.1435(14) Å, β = 98.7500(10)°, V = 4346.9(6) Å^3, Z = 4, λ = 0.710 73 Å, ρ_{calc} = 1.566 g/cm^3, μ = 4.133 mm^{-1}, R1 = 0.0221, wR2 = 0.0511, GOF = 1.041.

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(20) A trend relating short U−O bond distances with wider U−O−C bond angles has recently been noted in structurally characterized uranylamide complexes.[18]

(21) A similar red shift is noted for **2a** to 1570 cm^{-1} from 1640 cm^{-1} for the free ligand.

thiolate complexes from $[UO_2Cl_2(THF)_2]_2$ have been thwarted by low solubility of the reaction products. Contrasting the solid-state structures of aryloxide and thiolate derivatives possessing the same phenyl substituents further illustrates the differing influences of the neutral ligands. In contrast to **2b**, a *dimeric* structure with bridging aryloxide ligands is observed for $[UO_2(O\text{-}2,6\text{-}Cl_2C_6H_3)(THF)_2]_2$. Given that reduced steric congestion provided by longer M−S bonds leads to a *greater* tendency for thiolate ligands to bridge compared to analogous alkoxide groups, it appears that the amide ligands in **2b** are responsible for saturating a mononuclear species. With the ability to tune the steric properties and solubility by varying the alkyl substituents of the organic amides, we are further investigating the synthetic versatility of these ancillary ligands in uranyl(VI) chemistry.

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Supporting Information Available: Synthetic procedures and spectroscopic data for **2** (Table S1 and Figures S1 and S2) and X-ray crystallographic file in CIF format for **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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