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Reactions of Uranyl Thiolate Complexes with Molecular Oxygen: Syntheses and Crystal and Molecular Structures of the Uranyl Thiolate Peroxo Species $(HNEt_3)_2[(UO_2)_2(O_2)(SC_4N_2H_3)_4]$ and $(HNEt_3)[H(UO_2)_2(O_2)(SC_4N_2H_2Me)_4]\cdot Me_2CO\cdot 0.5Et_3N$ and of the Uranyl Thiolate Oxo Cluster $(HNEt_3)_2[(UO_2)_4(O)_2(SC_5NH_4)_6]\cdot Me_2CO$

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Although thiolate ligands have been used to separate heavy metal ions from dilute solution,[1] typical uranophilic ligands not unexpectedly contain oxygen and/or nitrogen donors with few examples of thiolate types.[2] In fact, structurally characterized compounds of the uranyl group with sulfur donor ligands in general are largely restricted to 1,1-dithio acid types[3] and thioether[4] and thione groups,[5] with a single reported example of a thiolate type in the mercaptopyridine *N*-oxide complex $[UO_2(ONC_5H_4S)_2(dmso)]$.[6] In the course of our investigations of the general coordination chemistry of thiopyrimidine and thiopyridine ligand types,[7] we have prepared solutions of uranyl thiolate complexes which upon exposure to atmospheric oxygen yield crystalline materials that have been identified as the unusual binuclear thiolate-ligated peroxo complexes $[HNEt_3]_2[(UO_2)_2(O_2)(SC_4N_2H_3)_4]$ (**1**) and $[HNEt_3][H(UO_2)_2(O_2)(SC_4N_2H_2Me)_4]\cdot Me_2CO\cdot 0.5Et_3N$ (**2**). While numerous peroxyuranates have been prepared,[8] only oxygen hetero ligands have been previously employed, and despite the enhanced complex stability endowed by such coligands,[8b] structural characterization of peroxyuranates has remained elusive.[8a] Furthermore, the syntheses of peroxyuranates have typically employed H_2O_2 as the source of peroxide,[8] rather than activation of molecular oxygen.[9,10] A final curious feature of the chemistry is the observation that employing the analogous mercaptopyridine ligand yields the unprecedented oxo-bridged tetranuclear species $[HNEt_3]_2[(UO_2)_4(O)_2(SC_5NH_4)_6]\cdot Me_2CO$ (**3**), rather than the peroxo complex.

The reaction of $UO_2(NO_3)_2\cdot 6H_2O$ with an excess of mercaptopyrimidine and triethylamine in ethanol in the presence of atmospheric oxygen yields yellow crystal of $[HNEt_3]_2[UO_2)_2(O_2)(SC_4N_2H_3)_4]$ (**1**).[11] When the analogous reaction is carried out using 2-mercapto-4-methylpyrimidine hydrochloride as ligand, the product obtained is $[HNEt_3][H(UO_2)_2(O_2)(SC_4N_2H_2Me)_4]\cdot Me_2CO\cdot 0.5Et_3N$ (**2**).[12] Whlie the reactions of the uranyl mercaptopyrimidine derivatives with molecular oxygen yield products wtih $\{UO_2\}^{2+}:O_2$ ratios of 2:1, substitution of pyridinethiol for mercaptopyrimidine in the preparation yields a tetranuclear species $[HNEt_3]_2[(UO_2)_4(O)_2(SC_5NH_4)_6]\cdot 2Me_2CO$ (**3**).[13] Measurements of the uptake of dioxygen gas at reduced temperature (0 °C) and constant pressure (1 atm), carried out as previously described,[14] confirmed these stoichiometries. The infrared spectra of **1**−**3** exhibit a sharp strong band in the 1015−1040 cm^{-1} region assigned to $\nu(C{-}S)$ and a pattern of additional ligand bands in the 1050−1500 cm^{-1} range. A strong absorbance characteristic of $\nu(U{=}O)$ for the uranyl group is observed in each case in the 800−905 cm^{-1} range, while **1** and **2** exhibit a medium-intensity feature at 804 cm^{-1} associated with $\nu(O{-}O)$,[8b] which is absent from the spectrum of **3**.

X-ray crystallographic studies of **1** and **2** reveal the first examples of peroxo-bridged diuranyl complexes.[15] As shown

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(11) Preparation of **1**: A solution of $UO_2(NO_3)_2\cdot 6H_2O$ (61 mg, 0.121 mmol) and mercaptopyrimidine (109 mg, 0.973 mmol) in ethanol (10 mL) was stirred for 1 h. After addition of NEt_3 (98 mg, 0.970 mmol) with stirring, the reaction mixture was filtered, and the filtrate was allowed to stand in the atmosphere for 1 week. Yellow crystals of **1** were collected in *ca.* 20% yield.

(12) Preparation of **2**: After a solution of $UO_2(NO_3)_2\cdot 6H_2O$ (61 mg, 0.121 mmol) and 2-mercapto-4-methylpyrimidine hydrochloride (108 mg, 0.973 mmol) in acetone was stirred for 1 h, NEt_3 (200 mg, 1.95 mmol) was added with stirring. After the resultant reaction mixture was filtered, yellow crystals of **2** were collected in *ca* 45% yield.

(13) Preparation of **3**: A mixture of $UO_2\ (NO_3)_2\cdot 6H_2O$ (61 mg, 0.121 mmol) and mercaptopyridine (108 mg, 0.973 mmol) in acetone (10 mL) was stirred for 0.5 h, whereupon NEt_3 (49 mg, 0.485 mmol) was added, resulting in a deep red solution. Upon 2 days of standing, brilliant red crystals of **3** were collected in *ca.* 40% yield.

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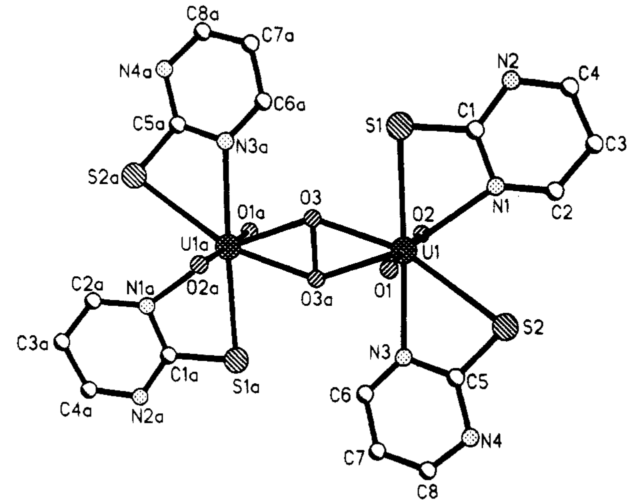

Figure 1. View of the structure of $[(UO_2)_2(O)_2(SC_4N_2H_3)_4]^{2-}$ (**1a**), showing the atom-labeling scheme. Selected bond lengths (Å) and angles (deg): U−O_t, 1.77(1); U−O3, 2.32(1); U1−S1, 2.917(5); U1−S2, 2.929(5); U1−N1, 2.62(1); U1−N3, 2.54(1); O3−O3A, 1.46(3); S1−U1−N1, 55.2(3); S2−U1−N3, 55.3(2); S1−U1−N3, 173.3(3).

in Figure 1, the structure of the molecular anion of 1, $[(UO_2)_2(O_2)(SC_4N_2H_3)_4]^{2-}$ (**1a**), consists of two $[(UO_2)(SC_4N_2H_3)_2]^0$ units bridged by O_2^{2-} in the planar side-on μ-η^2-η^2-peroxo coordination mode. Consequently, each uranium site effectively displays distorted hexagonal bipyramidal geometry with nearly coplanar equatorial rings and collinear axial $(UO_2)^{2+}$ groups. In contrast, the structure of the molecular anion $[H(UO_2)_2(O_2)(SC_4N_2H_2Me)_4]^-$ (**2a**) reveals the significant structural consequences of protonation (Figure 2 of supplementary material). The uranyl groups are bridged by a bent μ-η^2-η^2-peroxo linkage with an angle of 141.0° between the equatorial planes and an O1···O3 distance of 3.29 Å. While the structure of 2a did not reveal the site of protonation, the close approach of the uranyl oxygens suggests hydrogen bonding between O1 and O3 as a consequence of protonation at this site.

As shown in Figure 3, the X-ray investigations of 3[16] reveals that the molecular anion is the tetranuclear $[(UO_2)_4(O)_2(SC_5NH_4)_6]^{2-}$ (**3a**). The central core consists of the binuclear $\{(UO_2)_2(\mu\text{-}O)_2(SC_5NH_4)_2\}$ unit, in which the equatorial planes of the two uranyl groups are essentially coplanar. Each U1 uranyl unit of this central core is bridged through the μ_3-O1 oxo group to the second U1 site and to one of the exterior U2 sites and by a μ-O2 oxo group of the exterior U2 uranyl grouping in a long−short U1···O2 = U2 linkage. The equatorial planes of the exterior uranyl sites are thus normal to the plane of the central core, while the axial uranyl oxo groups lie in the central plane to produce an unusual tetranuclear planar $\{U_4O_2(\mu_3\text{-}O)_2(\mu\text{-}O)_2\}$ grouping. The equatorial plane of the central U1 site is defined by the sulfur and nitrogen donors of one pyridinethiolate and three groups to provide $\{UO_3SN\}$ coordination, while the exterior U2 site possesses an equatorial plane defined by sulfur and nitrogen donors from two pyridinethiolate ligand and a bridging oxo group to yield $\{UOS_2N_2\}$ coordination.

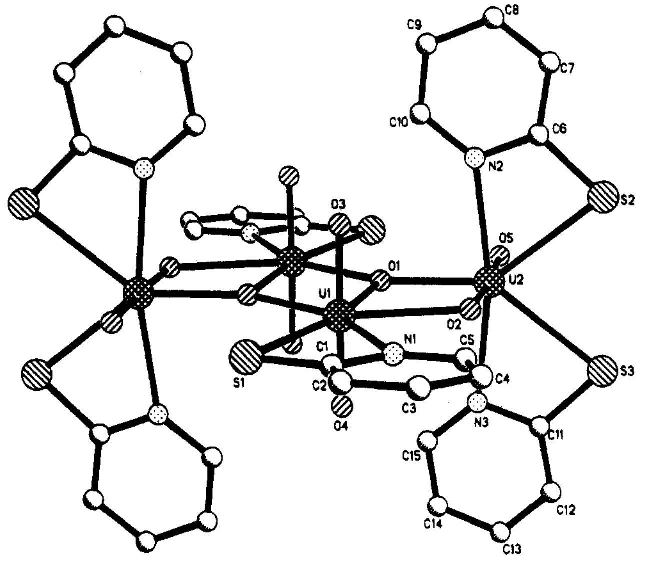

Figure 3. View of the structure of $[(UO_2)_4(O)_2(SC_5NH_4)_6]^{2-}$ (**3a**). Selected bond lengths (Å) and angles (deg): U1−O1, 2.356(7); U1−O2, 2.488(7); U1−O3, 1.780(8); U1−O4, 1.781(8); U1−S1, 2.868(3); U1−N1, 2.537(9); U1−O1A, 2.265(7); U2−O1, 2.157(7); U2−O2, 1.838(7); U2−O5, 1.771(7); U2−S1, 2.855(4); U2−S3, 2.845(4); U2−N2, 2.505(11); U2−N3, 2.510(10); O1−U1−O1A, 72.9(3); S2−U2−S3, 76.0(1); N2−U2−N3, 168.1(3).

The isolation of complexes **1**−**3** reveals the facility of oxygen activation by solutions of the appropriate uranyl thiolates. While the reactivity of the uranyl thiolates toward O_2 reflects the oxophilicity of the $(UO_2)^{2+}$ group and a preference for hard bases as ligands, the isolation of uranyl−peroxo species by direct activation of molecular oxygen is unusual, as previously cited examples of uranyl−peroxo species have invariably been prepared by reaction with H_2O_2 or alkyl peroxides.[8] Furthermore, the identity of the thiolate ligand dramatically influences the course of the reaction of the uranyl thiolate precursors with dioxygen, such that the uranyl pyrimidinethiolates react with a UO_2^{2+}:O_2 stoichiometry of 2:1 to yield the two-electron-reduced peroxo species, while the uranyl pyridinethiolate reaction results in a four-electron reduction and O−O cleavage to yield the oxo products, with a UO_2^{2+}:O_2 reaction ratio of 4:1. While 1:1 adducts $[(UO_2)(SN)_2O_2]^{2-}$ are probable intermediates, we have yet to detect or isolate such species.

We are currently studying further aspects of the stoichiometry of oxygen uptake by manometry. Since uranyl−peroxo species are known to effect the oxidation of olefins,[17] the effectiveness of the uranyl−thiolate−peroxo species in the oxymethalation of alkenes is also being investigated.

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Supplementary Material Available: Fully labeled structural diagrams and tables of experimental conditions for the X-ray studies, atomic positional parameters, bond lengths and angles, anisotropic temperature factors, calculated hydrogen atom positions, and IR data for **1**−**3** and Figure 2 comparing the structures of **1a** and **2a** (25 pages). Ordering information is given on any current masthead page.

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(15) Crystal data for $C_{28}H_{44}N_{10}O_6S_4U_2$ (**1**): monoclinic $P2_1/c$, $a = 11.356(2)$ Å, $b = 15.649(3)$ Å, $c = 12.290(2)$ Å, $\beta = 115.67(3)°$, $V = 1968.5(10)$ Å^3, $Z = 2$, $D_{calc} = 2.060$ g cm^{-3}; structure solution and refinement based on 1761 reflections (Mo Kα, $\lambda = 0.710\,73$ Å; $I_o \geq 3\sigma(I_o)$) converged at $R = 0.0437$. Crystal data for $C_{32}H_{42}N_{9.5}O_7S_4U_2$ (**2**): orthorhombic $Iba2$, $a = 27.950(6)$ Å, $b = 15.588(3)$ Å, $c = 20.820(4)$ Å, $V = 9071(3)$ Å^3, $Z = 8$, $D_{calc} = 1.869$ g cm^{-3}; 1974 reflections, $R = 0.0548$.

(16) Crystal data for $C_{40}H_{48}N_8O_{12}S_6U_4$ (**3**): monoclinic $P2_1/n$, $a = 9.412(2)$ Å, $b = 27.197(5)$ Å, $c = 12.726(3)$ Å, $\beta = 103.63(3)°$, $V = 3165.8(16)$ Å^3, $Z = 2$, $D_{calc} = 1.249$ g cm^{-3}; 3320 reflections, $R = 0.0378$.

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