

Communications to the Editor

Synthesis of $[U(\text{Se}_2)_4]^{4-}$: The First Homoleptic Actinide/Polychalcogenide Complex

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Despite the extensive inventory of homoleptic metal/polychalcogenide complexes known, there are no examples of corresponding actinide complexes. The high oxophilicity of these metals precludes the use of solvents such as dimethylformamide commonly used to synthesize other metal/chalcogenide complexes. However, the molten salt synthetic technique has been well-demonstrated to provide a low-temperature route to new, meta-stable compounds, especially in ternary systems of alkali metal/transition-metal/chalcogenides.^{1,2} As part of our continuing effort to explore the utility of this technique (which does not require common organic solvents) and to extend polychalcogenide chemistry to actinides, we have examined the reactivity of uranium in these melts. We report here the facile synthesis of the potassium salt of $[U(\text{Se}_2)_4]^{4-}$, the first uranium polyselenide complex. Synthesized at 300 °C, K_4USe_8 is a molecular compound in which exist discrete anions of uranium coordinated to four $\eta^2\text{-Se}_2^{2-}$ ligands.³

K_4USe_8 has been synthesized from a mixture of 0.126 g (0.80 mmol) of K_2Se , 0.095 g (0.40 mmol) of U, and 0.257 g (3.25 mmol) of Se. These reagents were thoroughly mixed, sealed in an evacuated Pyrex ampule, and heated at 300 °C for 10 days (cooling 2 °C/h). Products were isolated by carefully washing away the polyselenide flux with dimethylformamide (DMF). K_4USe_8 has proven to be slightly soluble in DMF, however, and washing was continued only until the green/brown color of Se_2^{2-} solution was replaced by a slowly evolving brown/yellow color, indicating K_4USe_8 as the primary component in solution. Solubility is slow enough that yield as high as 53% has been achieved, with further optimization expected.

A single $[U(\text{Se}_2)_4]^{4-}$ anion is shown in Figure 1A. The uranium center sits on a crystallographic 2-fold axis, but the entire anion has a triangulated dodecahedral geometry and can hence be assigned a pseudo D_{2d} symmetry. A dodecahedral structure is characterized by the location of coordinating atoms at the corners of two trapezoids which lie orthogonal to each other; in $[U(\text{Se}_2)_4]^{4-}$ the Se-Se bonds form the nonparallel sides of their respective trapezoids. The $[U(\text{Se}_2)_4]^{4-}$ is distorted from an ideal dodecahedron in two respects. First, the bases of the Se trapezoids intersect at the U center, leaving the four basal seleniums in a

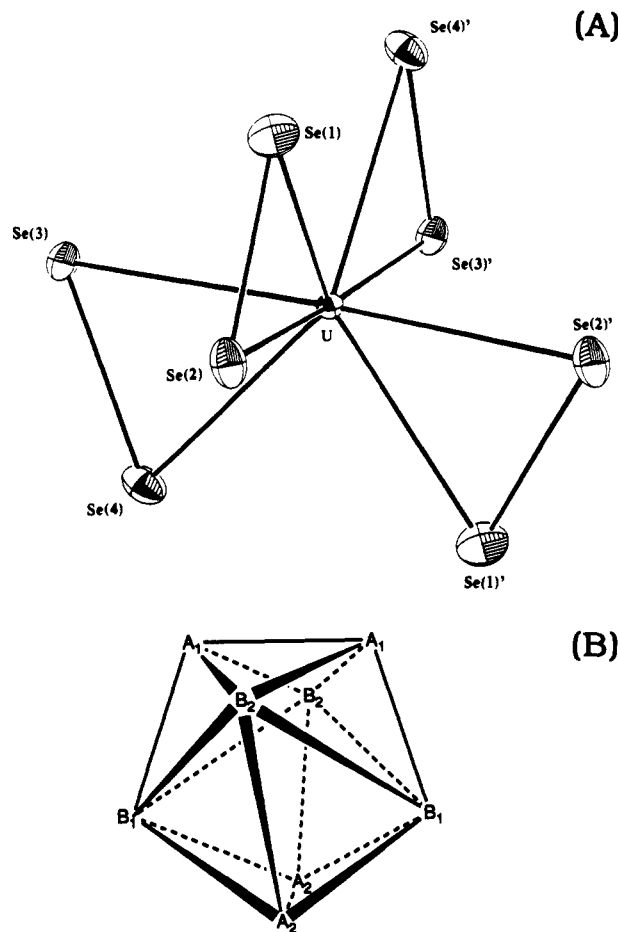


Figure 1. (A) ORTEP representation of $[U(\text{Se}_2)_4]^{4-}$. Selected bond distances (Å) are as follows: U-Se(1), 2.840 (3); U-Se(2), 2.903 (3); U-Se(3), 2.923 (3); U-Se(4), 2.920 (3); Se(1)-Se(2), 2.385 (4); Se(3)-Se(4), 2.401 (4). Selected bond angles (deg) are as follows: Se(1)-U-Se(2), 49.05 (8); Se(3)-U-Se(4), 48.54 (8); Se(4)-U-Se(1)', 79.95 (9); Se(3)-U-Se(2)', 177.51 (9); Se(2)-U-Se(3), 93.10 (8); Se(2)-U-Se(2)', 87.4 (1); Se(2)-U-Se(3)', 93.10 (8); Se(3)'-U-Se(3), 86.5 (1). The Se(2), Se(2)', Se(3), Se(3)', and U atoms lie no more than 0.063 Å from the same plane. (B) An ideal triangulated dodecahedron. The intersecting trapezoids are bounded by A_n , apex positions, and B_n , basal positions. In the case of $[U(\text{Se}_2)_4]^{4-}$ the center of the dodecahedron and the points B_1 , B_1' , B_2 , and B_2' lie in the same plane.

nearly square-planar arrangement; in an ideal dodecahedron the trapezoids slice further into each other. Secondly, the presence of the Se-Se bonds, although slightly elongated (2.38 and 2.40 Å), necessitates that the corresponding Se-U-Se angle be smaller than in an ideal dodecahedron (Se(1)-U-Se(2) angle, 49.05°; corresponding dodecahedron angle,⁴ 73.69°). Although without precedent in metal/chalcogenide systems, $[U(\text{Se}_2)_4]^{4-}$ is isostructural (but not isoelectronic) with the known peroxoanions $[\text{M}(\text{O}_2)_4]^{n-}$ (M = Cr^{5+} , V^{5+} , Nb^{5+} , Ta^{5+} , Mo^{6+} , W^{6+}). The potassium cations are located in two different sites. The first is coordinated by seven Se atoms in an irregular polyhedron (range of K(1)-Se distances, 3.475 (7)-3.190 (7) Å; av 3.357 Å), while the second is in a site coordinated by nine Se atoms, again in an

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(3) Crystals of K_4USe_8 are orthorhombic $Fdd2$ (No. 43) with $a = 17.331$ (4) Å, $b = 20.584$ (3) Å, $c = 8.811$ (3) Å, $V = 3143$ (1) Å³, $Z = 8$, $D_{\text{calc}} = 4.336$ g/cm³, $\mu = 291.703$, $2\theta_{\text{max}} = 50.00$; total data collected, 797; unique data, 797; data with $F_o^2 > 3\sigma(F_o^2)$, 647. Complete anisotropic refinement (60 variables) resulted in a final $R = 3.6\%$, $R_w = 4.7\%$. Single-crystal X-ray diffraction data were collected at 23 °C on a Rigaku AFC6 diffractometer (Mo $K\alpha$ radiation), and the structure was solved with the TEXSAN software package. An empirical absorption correction (DIFABS) was applied to all data. The space group's acentric nature necessitated refinement of both enantiomorphs of the unit cell, and the better of the two (0.6% lower R value) has been reported. Purity and identity were confirmed by comparison of product's X-ray powder pattern to one calculated from the appropriate structural parameters (see supplemental material).

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irregular polyhedron (range of K(2)–Se distances, 3.694 (8)–3.253 (7) Å; av 3.470 Å). We note that examples of molecular uranium/chalcogenide complexes are sparse. A fully characterized homoleptic uranium thiolate has been recently reported.⁶ Prior to this, most work has dealt with complexes of uranyl with various sulfur-containing ligands,⁷ including a complex containing a single $\eta^2\text{-S}_2^{2-}$.^{8,9}

The magnetic susceptibility of K_4USe_8 was measured as a function of temperature (5–250 K). Strong paramagnetic behavior, conforming to the Curie–Weiss law, is observed from approximately 120 K on up. Below this region, a transition is observed at approximately 90 K and is then followed by antiferromagnetic ordering which has a critical temperature of 65 K at the midpoint of a broad and shallow transition. The μ_{eff} at 300 K is 3.82 μ_{B} , consistent with an f^2 configuration where $L \neq 0$.¹⁰ The exhibited paramagnetic behavior of the compound at high temperatures renders difficult any ⁷⁷Se NMR study of this compound. Antiferromagnetic transitions of various degrees have been reported for the uranium compounds MU_8Q_{17} (M = Cr, V, Co, Fe, Ni) by Noel and Troc,¹¹ although their data are complicated by the presence of M^{2+} . Neither K^+ nor Se_2^{2-} would contribute to any magnetic phenomenon, so, barring any impurity, we are observing behavior based solely on U^{4+} .

The solid-state far-IR spectrum of K_4USe_8 shows three peaks: 261 cm^{-1} , which can be tentatively assigned to Se–Se stretching in the diselenides, and 167.6 and 153 cm^{-1} , which are presumably due to U–Se vibrations.

As mentioned before, K_4USe_8 is slowly soluble in DMF, and similar behavior has been found with ethylenediamine. The compound was insoluble in neat acetonitrile, even with the addition of $[(\text{Bu})_4\text{N}]^+$; however, it was successfully dissolved in solutions of either 15C5 or 18C6 crown ethers or 2,2,2-cryptand in CH_3CN .

In all solvents the solutions of K_4USe_8 gave brown/yellow colors of various hues which were stable, by UV/vis, out to 3 days. The DMF and CH_3CN /complexant solutions gave similar UV/vis spectra: one broad plateau at 400–430 nm for DMF and at 390–430 nm for the CH_3CN /complexant. After decomposition the solutions revert to brown/green in color, and their UV/vis spectra show the features of a polyselenide solution (peaks at 400 and 640 nm for DMF 417 and 560 nm for CH_3CN). Such a decomposition takes place in all solvents tested upon exposure to air as well as simply upon standing, due to the high oxophilicity of U(IV), making distilled and degassed solvents a requirement. In ethylenediamine solutions of K_4USe_8 , UV/vis shows peaks at 346, 404, 492, and 807 nm, while a polyselenide/ethylenediamine

solution shows peaks at 408, 560, and 805 nm. Although clearly not a simple Se_x^{2-} solution, the presence of several peaks in the ethylenediamine solution indicates a significantly stronger solvent interaction with the anion than in either DMF or CH_3CN .

With preliminary indications that $[\text{U}(\text{Se}_2)_4]^{4-}$ may have appreciable stability in certain solvents, the possibility of using it as a starting material for further chemistry becomes intriguing. Potentially the $[\text{U}(\text{Se}_2)_4]^{4-}$ could be used as starting material for convenient entry into the unexplored U/Se chemistry or act as a ligand for other metals. The Se_2^{2-} units could present sites for facile redox chemistry and reactivity with organic molecules and organometallic compounds.

Acknowledgment. We thank Mr. Ju-Hsiou Liao for his help in X-ray data collection and the calculation for the sample's powder pattern. The NSF is gratefully acknowledged for support. Financial support is also acknowledged from the Center for Fundamental Materials Research at Michigan State University and the P. T. Barnum Memorial Circus Clown's Widows and Orphans Fund.

Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, bond distances and angles of all atoms, and calculated and observed powder patterns (5 pages); listings of calculated and observed structure factors (6 pages). Ordering information is given on any current masthead page.

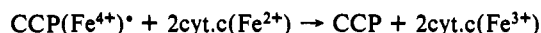
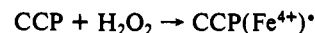
Crystal Structure and Preliminary Functional Analysis of the Cytochrome *c* Peroxidase His175Gln Proximal Ligand Mutant

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Cytochrome *c* peroxidase (CCP) catalyzes the peroxide-dependent oxidation of cytochrome *c* in the following multistep reaction:¹



H_2O_2 oxidizes CCP to an intermediate state termed compound I which consists of a ferryl (Fe^{4+}) iron and an amino acid(s) centered free radical denoted by the dot (*) in the above scheme. Central to the peroxidase mechanism are the invariant distal side residues, His52 and Arg48, which work in concert to stabilize the charge separation required in the heterolytic fission of the peroxide O–O bond.^{2,3}

Less clear is the precise role of the proximal ligand. The function of the proximal ligand may be in regulating the iron redox potential, stabilizing the ferryl intermediate of compound I, assisting in cleavage of the peroxide O–O bond, and/or simply

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