

Stabilization of Uranyl Cations in Molten Sodium Polysulfide and Formation of the Novel Solid Oxysulfide $\text{Na}_4(\text{UO}_2)\text{Cu}_2\text{S}_4$

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Complex solid state oxysulfides are generally rare, and over the course of the last two decades they have been prepared by conventional high temperature reactions.^{1,2} Molten chalcogenide fluxes are now a proven approach to generate new, kinetically stable chalcogenide phases,³ but oxychalcogenides present a greater challenge. The major difficulty in attempting to synthesize new metal/oxychalcogenides from molten A_2Q_x fluxes is the high stability of the binary metal oxides. The use of relatively mild reaction temperatures (in solid state synthetic terms) of 250–600 °C, which has proven effective in the formation of kinetically stabilized compounds in so many systems, does not help to overcome the high lattice stability of the oxides.³ Hence in general, reactions in which oxygen has been included are likely to lead to the formation of separate oxide and chalcogenide phases, rather than to the desired phase. The examples of metal/oxychalcogenides from molten polychalcogenide fluxes which do exist ($\text{Ba}_6\text{Ti}_5\text{S}_{15}\text{O}$,⁴ $\text{Na}_{1.9}\text{Cu}_2\text{Se}_2\cdot\text{Cu}_2\text{O}$,⁵ and $\text{Na}_4(\text{UO}_2)(\text{S}_2)_3\cdot\text{Na}_2\text{S}_3$ ⁶) were discovered by accident rather than by design. In order to help insure the incorporation of oxide and chalcogenide into the same compound, the system must be given a thermodynamically stable alternative to phase separation. One way this can be done is through the use of very stable oxymetal cations such as the uranyl ($(\text{UO}_2)^{2+}$) which should prove to be a useful building block in molten A_2Q_x reactions. The formation of the oxymetal cation can be achieved through the use of an oxygen transfer reagent. Selenium dioxide was chosen as an oxygen source because it is convenient to manipulate in these closed tube reactions and it readily decomposes to liberate two O^{2-} anions as the highly oxidized Se^{4+} cations partially oxidize the surrounding polychalcogenide environment. The Se is in such small amounts, relative to the sulfides of the flux, that its incorporation into a resulting product would be unlikely. This approach led to the discovery of the new lamellar oxysulfide phase of $\text{Na}_4(\text{UO}_2)\text{Cu}_2\text{S}_4$.⁷ The synthesis of this compound represents a successful attempt to link uranyl cations into an extended solid state chalcogenide structure.⁸

The $\text{Na}_4(\text{UO}_2)\text{Cu}_2\text{S}_4$ is a layered material with corrugated layers made of uranyl cations and bridging $[\text{Cu}_4\text{S}_8]^{12-}$ clusters which bond to the equatorial planes of four separate $(\text{UO}_2)^{2+}$

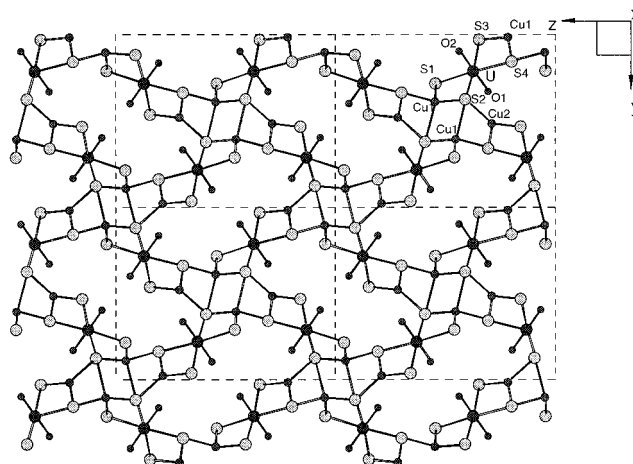


Figure 1. The view perpendicular to an anionic layer of $\text{Na}_4(\text{UO}_2)\text{Cu}_2\text{S}_4$.

units. The view perpendicular to the layers see Figure 1 reveals that the interconnections between $[\text{Cu}_4\text{S}_8]^{12-}$ and $(\text{UO}_2)^{2+}$ result in large cavities (6.4 by 9.3 Å) which are aligned from layer to layer, forming straight perpendicular channels through the lattice. The alkali cations of this structure reside within both the cavities and the intralayer grooves.

The $[\text{Cu}_4\text{S}_8]^{12-}$ cluster, highlighted in Figure 2A, is exceptional with an unusual combination of copper atoms in two different coordination environments. The Cu(1) atom is surrounded by a tetrahedron of sulfur atoms and shares one of its edges with a neighboring Cu(2)-centered trigonal plane. A second edge on the tetrahedron is shared with another Cu(1) centered tetrahedron across a crystallographic inversion symmetry, generating the entire $[\text{Cu}_4\text{S}_8]$ cluster. The Cu–S bond distances about the trigonal planar Cu(2) are comparable to those seen in similar environment (2.245 Å in CsCuTeS_3 ⁸), but the tetrahedral Cu(1) has a bit more variety with two short bonds (2.280(3) and 2.271(3) Å), one average bond (2.446(3) Å), and

(7) Reproducible, high yield synthesis of $\text{Na}_4(\text{UO}_2)\text{Cu}_2\text{S}_4$ is achieved by the reaction of 0.078 g (1.0 mmol) of Na_2S , 0.016 g (0.25 mmol) of Cu, 0.030 g (0.126 mmol) of U, 0.014 g (0.126 mmol) of SeO_2 , and 0.048 g (1.5 mmol) of S. The reagents were thoroughly mixed in an N_2 filled glovebox and loaded into a Pyrex tube. The tubes were removed from the box and evacuated on a Schlenk line to $<3 \times 10^{-3}$ and flame sealed. The reactants were heated at 400 °C for 2 days and cooled to 200 °C at 4 °C/h, followed by quenching to 50 °C. Excess polysulfide flux was removed by washing twice with DMF, once with degassed water (which was left in contact with the sample for only 10 min), and then rinsed several times with degassed DMF until the solvent remains clear, signaling complete polysulfide removal. The sample was then dried under vacuum. The remaining material is dark blue to black chunky crystals of $\text{Na}_4(\text{UO}_2)\text{Cu}_2\text{S}_4$ with a very small amount of white, apparently amorphous, powder. Yield is ~65%, based on U. The identity of the phase was confirmed by comparing the product's powder X-ray diffraction pattern against one calculated using X-ray single crystal data. The phase is insoluble in methanol, DMF, and water and appears stable in air for extended periods.

(8) (a) Crystals of $\text{Na}_4(\text{UO}_2)\text{Cu}_2\text{S}_4$ belong to the space group $P2_1/c$ with $a = 6.693(4)$ Å, $b = 10.656(7)$ Å, $c = 13.722(6)$ Å, $b = 97.81(4)$, $V = 969.7(9)$ Å³, $Z = 4$. Single Crystal X-ray Diffraction Intensity data were collected using a Rigaku AFC6S four-circle automated diffractometer equipped with a graphite crystal monochromator (Mo $\text{K}\alpha$ rad). An ω - 2θ scan mode was used ($2\theta_{\text{max}} = 60^\circ$). The stability of the crystal was monitored with three standard reflections whose intensities were checked every 150 reflections, and unless noted, no crystal decay was detected. Data collected: 3199, unique: 2821, data present ($F_o^2 > 3\sigma(F_o^2)$): 1980. An empirical absorption correction based on ψ scans was applied to all data during initial stages of refinement. No. of variables 118. An empirical DIFABS^{8b} correction was applied after full isotropic refinement, after which full anisotropic refinement was performed. The structures were solved by direct methods using SHELXS-86 software,^{8c} and full matrix least squares refinement was performed using the TEXSAN software package.^{8d} Final $R/R_w = 3.5/4.0\%$. (b) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158–166. (c) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Doddard, R., Eds.; Oxford University Press: Oxford, England, 1985; pp 175–189. (d) Gilmore G. J. *Appl. Crystallogr.* **1984**, *17*, 42–46.

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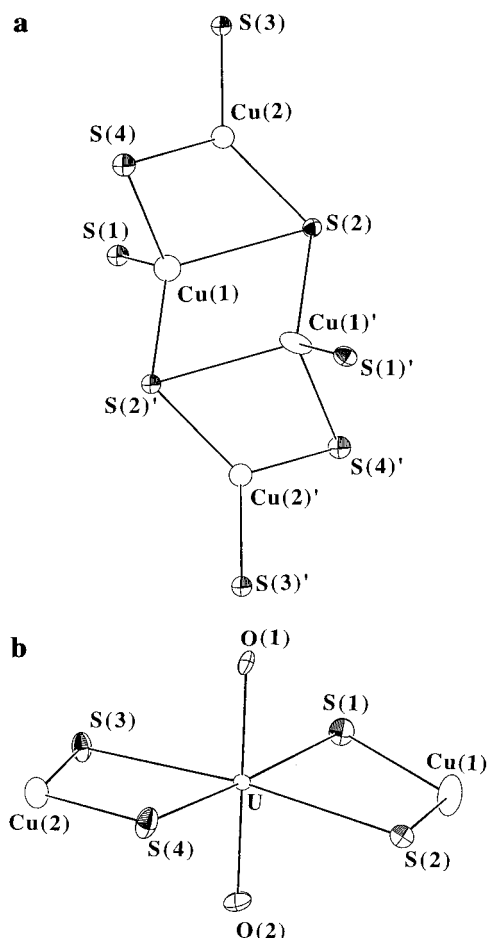


Figure 2. (A) The $[\text{Cu}_4\text{S}_8]^{12-}$ cluster present in the structure of $\text{Na}_4(\text{UO}_2)\text{Cu}_2\text{S}_4$ and (B) The immediate coordination environment around the U atoms.

one quite long bond (2.624(4) Å). In the tetrahedral Cu environment of α - and β - KCuS_4 the range of Cu–S bond distances is 2.298–2.378 Å.¹⁰ The $[\text{Cu}_4\text{S}_8]$ cluster also exhibits short Cu–Cu distances, shown in Figure 2B as dashed lines. The

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Cu(1)–Cu(1') distance is 2.674(4) Å and that of Cu(1)–Cu(2) is even shorter at 2.503(2) Å, less than one of the Cu–S bonds. Although short Cu–Cu contacts, resulting from d^{10} – d^{10} interactions,¹¹ are seen in many compounds, these distances in $\text{Na}_4(\text{UO}_2)\text{Cu}_2\text{S}_4$ are exceptionally short and indicate a slightly stronger interaction than is usually observed.

The $(\text{UO}_2)^{2+}$ fragments are bonded around the $[\text{Cu}_4\text{S}_8]^{12-}$ clusters at four points, two at edge-sharing connections to $[\text{CuS}_4]$ tetrahedra and two more edge-sharing bridges to $[\text{CuS}_3]$ trigonal planes. Each uranyl cation ends up with only four sulfur atoms in the equatorial plane, forming nearly perfect octahedral angles about the central U^{6+} atom with the oxygen atoms in the axial positions, Figure 2B. There is only one crystallographically unique uranyl cation in the structure, and its connections alternate such that on one side is a bridge to a $[\text{CuS}_3]$ fragment and trans from it is a bridge to a $[\text{CuS}_4]$ fragment. The U–O and U–S bond distances are normal.

The U–Cu distances are unusually short in this compound and deserve special comment. The U–Cu(1) distance is 3.137 Å and is only slightly longer than the bonds seen in UCu_5 (2.92 and 3.05 Å),¹² but the U–Cu(2) distance (3.065 Å) is in the range of the intermetallic values. It would seem that there is at least a partial bonding interaction occurring between the U and some of the Cu atoms in this compound perhaps via electron donation from a fully occupied Cu^+ d^{10} orbital to empty U^{6+} f or d orbitals.

$\text{Na}_4(\text{UO}_2)\text{Cu}_2\text{S}_4$ shows total absorbance in its optical diffuse reflectance spectrum (500–2500 nm) which indicates that this valence precise compound is a semiconductor with a band gap <0.5 eV. Given that $\text{S}^{2-} \rightarrow \text{U}^{6+}$ and $\text{S}^{2-} \rightarrow \text{Cu}^+$ charge transfer transitions normally occur at energies >1.2 eV, as, for example, in $\text{Cs}_4(\text{UO}_2)(\text{S}_2)_2$ ⁶ and Cu_2S ,¹³ the very low energy absorption in $\text{Na}_4(\text{UO}_2)\text{Cu}_2\text{S}_4$ could be due to charge transfer excitations from filled d-levels of Cu^+ to the empty f-levels of U^{6+} .

The results presented here clearly suggest the uranyl cation to be a chemically compatible and robust building block in molten A_2Q_x fluxes. Not only does the synthesis of $\text{Na}_4(\text{UO}_2)\text{Cu}_2\text{S}_4$ call for a further examination of $(\text{UO}_2)^{2+}$ chemistry in other A_2Q_x congeners but also gives a strong indication that other oxymetal cations such as $(\text{TiO})^{2+}$, $(\text{VO})^{2+}$, $(\text{MoO})^{3+}$, and $(\text{WO})^{3+}$ could be stable in A_2Q_x fluxes as well.

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Supporting Information Available: Tables of fractional atomic coordinates, anisotropic thermal parameters, and bonds distances and angles for $\text{Na}_4(\text{UO}_2)\text{Cu}_2\text{S}_4$ (6 pages). See any current masthead page for ordering and Internet access instructions.

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