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Synthesis and Structure of the $[(UO_2)S_4]^{6-}$ Anion: A Cation-Stabilized Uranyl Sulfide

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Supporting Information

ABSTRACT: The new uranyl sulfide anion $[(UO_2)S_4]^{6-}$ has been synthesized and characterized as a cation-stabilized anion in the compound $Na_2Ba_2(UO_2)S_4$. This compound was synthesized at 873 K from the solid-state reaction of uranium, Na_2O_2, BaS, and sulfur. The coordination about the U^{6+} center in $[(UO_2)S_4]^{6-}$ is square bipyramidal with the uranyl O atoms 180° apart and four equatorial S atoms. The Na^+ and Ba^{2+} cations form interactions with the uranyl O atoms. Despite the inherent difficulties involved in the synthesis of complex uranium oxysulfides, it is demonstrated that under the right reaction conditions the UO_2^{2+} species can be produced in situ and result in totally new chalcogen derivatives.

Inorganic compounds and minerals containing U^{6+} as the uranyl ion (UO_2^{2+}) have been the subject of extensive research.[1,2] Despite the diversity of known uranyl compounds, only four compounds are known in which one or more disulfide (S_2^{2-}) groups are attached[3−5] and only one is known[6] in which sulfide (S^{2-}) ligands are attached to the linear UO_2^{2+} group. That compound, $Na_4(UO_2)Cu_2S_4$, has a sheetlike structure in which there are U−S−Cu bridges.

In general, the solid-state synthesis of complex uranium oxysulfides is very difficult because of the high stability of the binary uranium oxides and chalcogenides as well as of UOS. We demonstrate here that, by control of the reaction conditions, the choice of an appropriate oxygen-transfer agent, and the selection of cations, it has been possible to synthesize the novel uranyl sulfide $Na_2Ba_2(UO_2)S_4$.

Uranium powder (0.030 g, 0.126 mmol), Na_2O_2 (0.0196 g, 0.252 mmol), sulfur (0.0121g, 0.378 mmol), and BaS (0.030 g, 0.177 mmol) were loaded into a carbon-coated fused-silica tube in an argon-filled glovebox, and then the tube was flame-sealed at 10^{-4} Torr. ^{238}U powder was obtained through the hydridization of uranium turnings (IBI Laboratories) followed by decomposition of the hydride under vacuum.[7] The reaction tube was placed in a computer-controlled furnace, heated to 873 K in 12 h, held there for 96 h, cooled to 573 K over 150 h, and finally cooled to 298 K in 55 h. The reaction afforded black prisms of $Na_2Ba_2(UO_2)S_4$ in about 50 wt % yield. These were manually separated from excess flux. The crystals are stable under polyisobutylene oil, but they decompose upon prolonged exposure to air. Elemental analysis of the product using an Hitachi S-3400 scanning electron microscope revealed the presence of sodium, barium, uranium, oxygen, and sulfur in the approximate ratio 2:2:1:2:4.

Single-crystal X-ray diffraction data were collected at 100 K on an APEXII CCD diffractometer equipped with graphite-monochromatized Mo $K\alpha$ radiation.[8] The crystal-to-detector distance was 60 mm; the exposure time was 10 s/frame. Data reduction and structure solution and refinement were carried out by procedures standard in this laboratory.[9] Details are given in Table 1 and the Supporting Information.

Table 1. Crystallographic Data for $Na_2Ba_2(UO_2)S_4$

compound	$Na_2Ba_2(UO_2)S_4$
space group	$P\bar{1}$
a/Å	6.3325(2)
b/Å	6.7148(2)
c/Å	6.7530(2)
V/Å^3	252.14(1)
α/deg	81.235(1)
β/deg	67.101(1)
γ/deg	72.542(1)
$R(F)$ $[I > 2\sigma(I)]^a$	0.0134
$R_w(F_o^2)^b$	0.0354

$^a R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ for $F_o^2 > 2\sigma(F_o^2)$. $^b R_w(F_o^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum wF_o^4\}^{1/2}$ for all data. $w^{-1} = \sigma^2(F_o^2) + (0.0161F_o^2)^2$ for $F_o^2 \geq 0$; $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 < 0$.

Raman measurements of $Na_2Ba_2(UO_2)S_4$ were acquired using the inverted microscope setup previously reported.[9] A 20× objective was used to focus laser light onto the crystal surface and collect scattered light, which was then dispersed by a 1200 groove/mm grating onto a back-illuminated LN_2-cooled charge coupled device (Spec10:400BR, Princeton Instruments).

$Na_2Ba_2(UO_2)S_4$ charge balances as a U^{6+} compound. The compound crystallizes with one formula unit in the triclinic space group $P\bar{1}$. The structure (Figure 1) comprises isolated centrosymmetric $[(UO_2)S_4]^{6-}$ anions that are surrounded by Na^+ and Ba^{2+} cations. The coordination environment of uranium is square-bipyramidal, with the uranyl O atoms 180° apart and four equatorial S atoms (Figure 2). The U−O interatomic distance of 1.891(2) Å (Table 2) may be compared to those of 1.849(8) and 1.869(8) Å in $Na_4(UO_2)Cu_2S_4$.[6] The U−S distances of 2.652(1) and 2.655(1) Å may be compared to that of 2.612(1) Å in $Rb_6Cu_{12}U_2S_{15}$ in which there are $U^{6+\text{ or }5+}S_6$ octahedra.[10]

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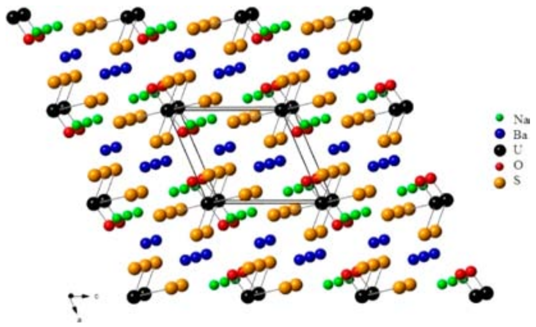

Figure 1. Structure of $Na_2Ba_2(UO_2)S_4$ viewed along the *b* axis.

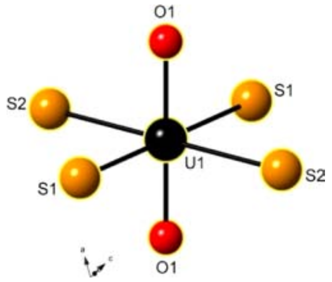

Figure 2. Coordination environment of the centrosymmetric U^{6+} center in $Na_2Ba_2(UO_2)S_4$.

Table 2. Selected Interatomic Distances for $Na_2Ba_2(UO_2)S_4$

	distance (Å)		distance (Å)
U1−O1 ×2	1.891(2)	Ba1−S1	3.192(1)
U1−S1 ×2	2.652(1)	Ba1−S2	3.198(1)
U1−S2 ×2	2.655(1)	S1−Na1	2.791(1)
Ba1−O1	2.772(1)	S1−Na1	2.853(1)
Ba1−O1	2.783(1)	S2−Na1	2.944(1)
Ba1−S1	3.172(1)	S2−Na1	3.181(1)
Ba1−S1	3.179(1)	S2−Na1	3.219(1)
Ba1−S2	3.182(1)	Na1−O1	2.382(2)

Uranyl O atoms rarely bond to other cations.[11] However, the $[(UO_2)S_4]^{6-}$ anion is stabilized by Na^+ and Ba^{2+} cations. The Na^+ cations in $Na_2Ba_2(UO_2)S_4$ are coordinated to one O atom and five S atoms in a distorted octahedral arrangement (Figure 3). The Na−O distance of 2.382(2) Å is unusually short for typical U^{6+} structures that do not have interactions with uranyl O atoms but is consistent with distances seen in the condensed phase Na_2UO_4.[12] Ba^{2+} cations in $Na_2Ba_2(UO_2)S_4$ are seven-coordinate with interactions to two O atoms and five S atoms (Figure 3). The Ba−O distances of 2.772(1) and 2.783(1) Å are consistent with the distances seen in $BaUO_4$ for Ba−O interactions.[13] The Ba−S distances of 3.172(1)−3.198(1) Å are typical of those found in condensed phases.[14,15]

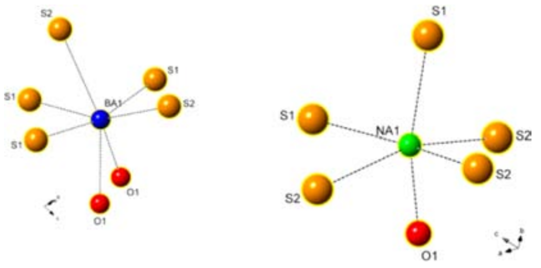

Figure 3. Coordination environments of barium and sodium in $Na_2Ba_2(UO_2)S_4$.

In the spectrum of $Na_2Ba_2(UO_2)S_4$ (Figure 4), the symmetric U−S stretching mode is evident at 305 cm^{-1}. Although 800−950 cm^{-1} is the usual region[16,17] for the U═O symmetric stretch in uranyl(VI) complexes, we assign it here to the intense band at 650 cm^{-1}. A quantum-chemical probe[18] of uranyl(VI) complexes at the B3LYP level affords a surprising linear relationship between the calculated U═O distance and the Raman frequency.[18] In Figure 5, those results are plotted and extrapolated to the current U═O bond distance of 1.891 Å to yield a predicted frequency of 649 cm^{-1}.

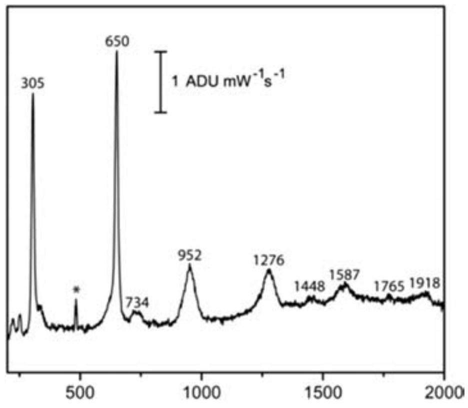

Figure 4. Raman spectrum from the single crystal of $Na_2Ba_2(UO_2)S_4$ used in the X-ray study (λ_{ex}= 532 nm, P_{ex} = 3.5 mW, and t_{acq} = 10 accumulations of 60 s). * = admitted light. The band at 734 cm^{-1} arises from residual polyisobutlyene oil.[21]

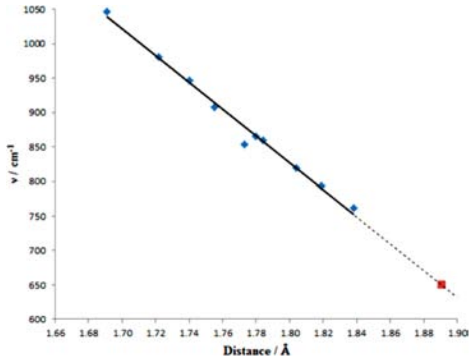

Figure 5. U═O distance versus Raman frequency for uranyl(VI) complexes.[18] Extrapolatian to the present results is shown.

Clearly, cation interactions[19,20] and the substitution of sulfur for oxygen in the equatorial positions have weakened the U═O bond.

Although in reaction systems as complex as the present one, involving initially uranium, Na^+, Ba^{2+}, O^{2-}, and S^{2-}, it is impossible to predict what thermodynamic product or products will result, we gave thought to what was needed to obtain a uranyl sulfide compound. We chose a reaction temperature (873 K) high enough to favor thermodynamic products and minimize the formation of polysulfides as well as binaries, we chose Ba^{2+} over, for example, Cs^+,[3] because its increased charge should enhance cation-stabilizing effects, and we chose the oxygen-transfer agent Na_2O_2 over, for example, SeO_2,[3,6] because we gained a cation and avoided selenium in the reaction mixture. We did explore other reaction conditions, but the one described here gave reproducible results and the highest yield. Other reaction conditions that were attempted included the use of various A_2Q_x (Q = S, Se) fluxes instead of BaS as well as the use of BaO_2 in place of Na_2O_2. These produced only U/Q binaries and UOS. It is clear that under the right reaction conditions the UO_2^{2+} species can be produced in situ and result in totally new chalcogen derivatives.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic CIF file for $Na_2Ba_2(UO_2)S_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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