Achieving and Stabilizing Uranyl Bending via Physical Pressure

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Supporting Information Placeholder

ABSTRACT: Applying physical pressure in the uranyl-sulfate system has resulted in the formation of the first purely inorganic uranyl oxo-salt phase with a considerable uranyl bend: $Na_4[(UO_2)(SO_4)_3]$. In addition to a strong bend of the typically almost linear O=U=O, the typically equatorial plane is broken up by two out-of-plane oxygen positions. Computational investigations show the origin for the bending to lie in the applied physical pressure and not in electronic influence or steric hindrance. The increase of pressure onto the system has shown to increase uranyl bending. Furthermore, the phase formation is compared to a reference phase of a similar structure without uranyl bending and a transition pressure of 2.5 GPa is predicted - well in agreement with the experimental results.

Uranium is the actinide element studied most extensively in past decades. This can be accorded by its comparably high abundance within nature as well as its importance for the nuclear industry[1-3]. Uranium is known to stabilize in oxidation states ranging from +II to +VI, however +IV and +VI being the most prevalent. In the lower oxidation states (+II to +IV), U adopts an isotropic bond coordination, whereas at higher oxidation states (+V, +VI), U is known to form linear *trans*-dioxo-cations. These cations, termed *uranyl*, possess two short bonds and further coordination is typically achieved in the perpendicular equatorial plane. The uranyl bond shows a remarkable chemical robustness with strong covalent bonds[4]. Due to this, the reactivity of the uranyl is distinctly lowered and ligand coordination is forced to occur in the equatorial plane.

Controlling the coordination chemistry of uranyl groups has been in the focus of actinide chemists in the last few decades. Two promising strategies to alter the coordination environment of the uranyl have been (a) distorting the planarity of the equatorial plane[5-7] as well as (b) breaking the linearity of the uranyl group[5, 8-9]. However, these strategies always involve organic and metal-organic approaches with bulky ligands or complex multi-step procedures to obtain atypical coordination environments. Recently, a very simple approach of dropping 1,10-phenanthroline (phen) into a uranyl chloride solution in acetone has resulted in $[UO_2Cl_2(phen)_2]$[5]. The uranyl group is strongly bent (161.8(1)°) and the equatorial plane is broken up, representing a rare case for a uranyl bearing phase showing both uranyl bending as well as planarity distortion[5].

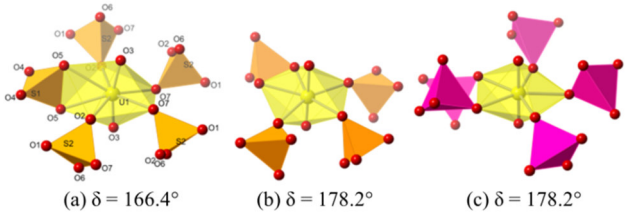

Figure 1: Uranium coordination in different uranyl oxo-salts: (a) $Na_4[(UO_2)(SO_4)_3]$ this work; (b) $Na_{10}[(UO_2)(SO_4)_4](SO_4)_2 \cdot 3H_2O$[14]; and (c) $Na_4[(UO_2)(CrO_4)_3]$[15]. Additionally the uranyl bending angle δ is given.

To further understand the origin of the O-U-O bending, Hayton[10] has published a review of uranyl phases showing uranyl angles of lower than 172°. Herein, Hayton has singled out two distinctive causes for uranyl bending: firstly, bending as a result of steric hindrance of the equatorial ligands and the uranyl oxo-group and secondly, bending due to an electronic origin. He lists multiple phases for both cases, as for example $UO_2Cl_2(HN_4)$ (HN_4 = 2,11-diaza[3,3](2,6) pyridinophane)[11] or the above mentioned $[UO_2Cl_2(phen)_2]$[5] for steric hindrance and for example $[(UO_2)_2(\mu_3\text{-}O)(C_8H_{12}O_4)(C_{10}H_8N_2)(H_2O)]_2$[12] and $UO_2(BIPM\ TMS)(dmap)_2$[13] (BIPMTMS = $C(PPh_2NSiMe_3)_2$; dmap = 4-(dimethylamino)pyridine) for bending due to an electronic origin. The former were found to be more common in comparison to the rarer latter case. The effect via steric hindrance was found to be stronger in comparison to the effect via electronic perturbation indicated by the larger achievable bonding angles for the first case of up to 161.7(5)°[11] compared to the latter case with an angle of up to 167.16(9)°[10].

In our study, we inadvertently obtained a most unique phase. Our focus of the study was investigating the phase formation behavior of actinide oxo-chalcogenates under high temperature/ high pressure conditions. As examples of findings in this field are the report of rich non-centrosymmetry in the Na-U-Te oxo-system[16] or increased atypical structure types with more complex structures and dimensionalities in the K-U-Te or K-U-Mo oxo-systems[17,18]. The title phase, $Na_4[(UO_2)(SO_4)_3]$, was obtained upon extreme conditions study of A^I-U-S system (A^I – alkali metals). This phase shows both, considerable uranyl bending as well as planarity distortion (Figure 1a) and is found to be the first inorganic uranyl oxo-phase to show such behavior.

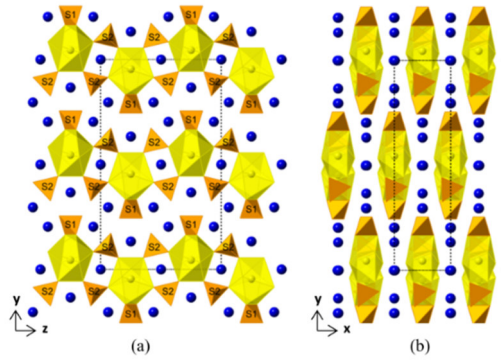

Figure 2. Structural overview of $Na_4[(UO_2)(SO_4)_3]$ parallel to [100] in (a) and parallel to [001] in (b). UO_8, SO_4 and Na-atoms are yellow, orange and blue, respectively.

Initial UO_2, SeO_2, and NaS_2O_3 were mixed and filled into a sealed platinum crucible. A pressure of 3.5 GPa was applied with a maximum temperature of 1000°C in a piston-cylinder press. The exact experimental details are given in the Supporting Information. The structure was determined by single crystal X-ray diffraction.

$Na_4[(UO_2)(SO_4)_3]$ crystallizes in the orthorhombic space group $\boldsymbol{C}222_1$ and shows a one-dimensional chain structure (Figure 2). A single U position, two sulfur positions, three sodium positions and seven oxygen positions are present. The latter are all part of sulfate tetrahedra or uranyl groups. H_2O molecules are not present within the structure.

Uranium is coordinated by eight oxygen atoms. Typically, this would result in a hexagonal bipyramid. In this case, however, the coordination is distinctly different and is more comparable to a UO_7 coordination. Four equatorial oxygen positions are identical to a pentagonal bipyramid and the fifth is split into two separate oxygen positions perpendicular to the equatorial plane, or in other words parallel to the uranyl group (Figure 1a). As a result of this coordination, the bond angle of the uranyl ion is strongly bent away from this bidentate sulfate, yielding a much more compact 165.6(12)°. The U-O bond distances for the uranyl groups are 1.765(15) Å. Figure 1 also shows two alternate more typical coordination environments, which typically can be found within uranyl oxo-phases.

Two UO_8 polyhedra are interconnected by two sulfate polyhedra with U-O bond lengths of 2.397(14) to 2.438(17) Å. These two crystallographically identical sulfur positions (S2) are coordinated by four oxygen atoms with S-O bond distances of 1.457(18) Å, 1.464(17) Å, 1.502(14) Å and 1.516(17) Å, for O1, O6, O2 and O7, respectively. The latter two are part of the monodentate bridging, the former two are terminal positions. The two oxygen atoms involved in the bidentate bridging between U and S1, are distinctively further apart with a bond distance of 2.625(19) Å to the uranium position. The S1-O bond distances are 1.461(16) to 1.507(17) Å. The longer bonds are part of the bidentate bridging and the shorter bonds belong to terminal oxygen positions.The interspace between $[(UO_2)(SO_4)_3]^{4-}{}_\infty$ chains is filled by sodium cations achieving charge neutrality.

The resulting one-dimensional chains resemble the chains of $Na_4[(UO_2)(CrO_4)_3]$[15] and $Mn[(UO_2)(SO_4)_2(H_2O)](H_2O)_4$ [19] in their basic backbone, which can be made visible by applying a topological representation introduced into actinide oxo-salts by Krivovichev and Burns[20-21] (Figures S1 and S2). The difference between the reported structure with the two afore mentioned structures is a geometry of the local coordination of uranyl groups. Twofold connection to S1 for the title compound and only one-fold for similar oxo-groups in $Na_4[(UO_2)(CrO_4)_3]$. This is indicated by the double line in the topology graph of the title compound (Figure S1) and the single line in the corresponding topology graph for the other two structures (Figure S2).

The strong bend of uranyl that we observed has not been previously reported within inorganic uranyl oxo-phases. The first report of a similar bent was reported in 2007 by Charushnikova and Den Auwer in $[(UO_2)_2(Trpy)_2(OH)_2]_2[UO_2(NO_3)_3(H_2O)](NO_3)_3{\cdot}3H_2O$ coordination phase[22]. Hereby, even a nine-fold coordination was obtained with five equatorial oxygen positions, two uranyl and two split perpendicular oxygen positions. The bend is 167° in that case and it was achieved by using 2,2'-6,2"-terpyridine (Trpy).

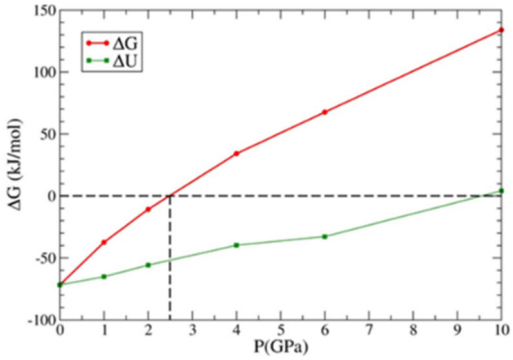

Figure 3. Difference in free energy (ΔG) and total internal energy (ΔU) for $Na_4[(UO_2)(SO_4)_3]$ and *pseudo*-$Na_4[(UO_2)(SO_4)_3]$ in dependence of pressure.

To further understand the phase formation, we performed a series of ab initio calculations. First, we considered the title phase and the chemically similar chromate structure $Na_4[(UO_2)(CrO_4)_3]$. Both structures were relaxed at a series of different pressures in order to detect any pressure-induced structural changes. Chromates and sulfates are known to behave very similar in regard to their crystal chemistry. Therefore, the Cr of the latter phase was replaced by S to obtain a *pseudo*-$Na_4[(UO_2)(SO_4)_3]$ structure as an ambient state reference phase. Indeed, for P=0 GPa it is by ~72kJ/mol lower free energy than the measured sulfate structure (Figure 3). The evolution of difference in free energy (ΔG, which is approximated by ΔH assuming negligible ΔS for such similar phases) and the total internal energy (ΔU) is shown in Figure 3. The internal energy of the *pseudo*-$Na_4[(UO_2)(SO_4)_3]$ structure is lower for P up to ~9.5 GPa and for higher pressures the internal energy of the new phase becomes lower. However, because the title phase is more compact, the Gibbs free energy of the new phase becomes lower already at P=2.5 GPa, allowing for its synthesis at P=3.5 GPa.

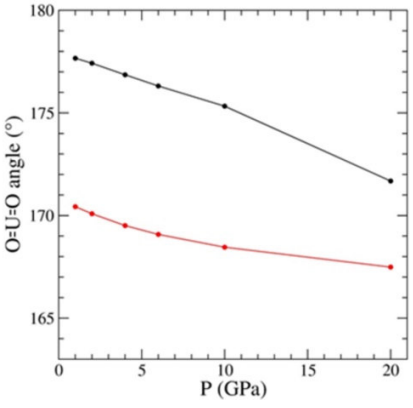

Figure 4. O=U=O bending angle δ in dependence of pressure. The bending angle strongly decreases with increased pressure. The black points coincide with *pseudo*-$Na_4[(UO_2)(SO_4)_3]$ and the red with $Na_4[(UO_2)(SO_4)_3]$.

Investigation of the two computed structures has shown that bending is present in both phases and more prevalent with increased pressure (Figure 4). The computed bending angle at ambient conditions is 171° and 178°, respectively. It decreases with

pressure, reaching 169.7° at P=3.5 GPa for the title phase. We notice that this is slightly larger than the measured angle of 166.4°. We attribute the origin of this small discrepancy to the fact that calculations were performed assuming a temperature of zero K, so, no thermal expansion and thermal motion effects are considered.

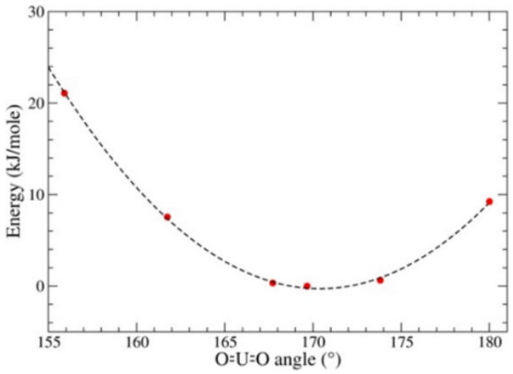

Figure 5. The energy of the modified $Na_4[(UO_2)(SO_4)_3]$ structure with different uranyl bending angle. The equilibrium phase with angle of 169.7° is takes as a reference.

In order to check the potential influence of thermal motion of uranyl bending, we computed a series of structures with different uranyl angles ranging from 180° to 150°. The resulted internal energies are reported in Figure 5. Indeed, the thermal motions of the energy of ~2.5kJ/mol should permit realization of structures with bending between 164° and 176°.

The origin of the significant bend of 165.6(12)° cannot be explained by steric hindrance of the ligand molecules, as only simple sulfate groups are present here. The theoretical calculations described above however show the influence of pressure on the system to be the origin of the uranyl bending. Strong equatorial donors are known to weaken the U-O bonds of the uranyl[23]. Sulfate is such a donor and the addition of physical pressure can apparently lead to the strongly distorted coordination of the title compound. The question however remained whether the parallel orientation of the bidentate coordination of the $S1O_4$ group leads to the bending of the uranyl group or whether the uranyl bending implied by the physical pressure allows the sulfate to coordinate in this unique fashion (Figure 6). For this, the structure of the $Na_4[(UO_2)(SO_4)_3]$ was modified in two different ways and subsequently relaxed. For the first case, the bending angle δ of the O=U=O was fixed to 166.4° by fixing the two involving oxygen positions and the U position. The bidentate coordinated sulfate tetrahedron was rotated to be in-plane with the equatorial plane. The theoretical calculations resulted in back rotation of 90° of the sulfate tetrahedron and reformation of the measured structure. The internal energy difference between the structure with the rotated sulfate tetrahedron and the measured one is 58 kJ/mol and no significant volume change is observed. On the other hand, the measured structure but with uranyl angle fixed at 180° is higher in energy from the measured structure by only 10 kJ/mol (Fig. 5).

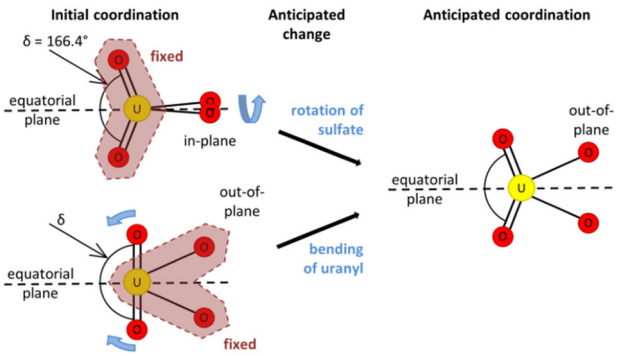

Figure 6. Modeling of different initial configurations to determine the origin of the uranyl bending in $Na_4[(UO_2)(SO_4)_3]$. The local coordination of uranium was manually changed and the structure was relaxed under a pressure coinciding with the experimental pressure of 3.5 GPa. The left shows the initial coordinations, the center the anticipated change and the right the anticipated coordination found in $Na_4[(UO_2)(SO_4)_3]$. The fixed positions are shaded in red.

To conclude, this study reports the first inorganic uranyl phase with considerable uranyl bending. In contrast to several techniques involving large organic ligands showing considerable steric hindrance which can be considered as chemical pressure, the method shown here was the application of physical pressure. The title compound $Na_4[(UO_2)(SO_4)_3]$ may well be the first example for a unique coordination of uranium with a bent uranyl group as well as a distorted planarity of the equatorial plane. The applied method shows promising potential in achieving a *cis*-coordination for the uranyl group – following the physical pressure path in contrast to the chemical pressure path. The goal here is to better unravel the interactions taking place under high pressure.

ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data in CIF format, experimental procedure, table with crystallographic information, topology, and BVS. The Supporting Information is available free of charge on the ACS Publications website.

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Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

The work has been supported by the Deutsche Forschungsgemeinschaft (DFG) grant AL1527/3-1. S. Wang acknowledge funding support from National Natural Science Foundation of China (21761132019).

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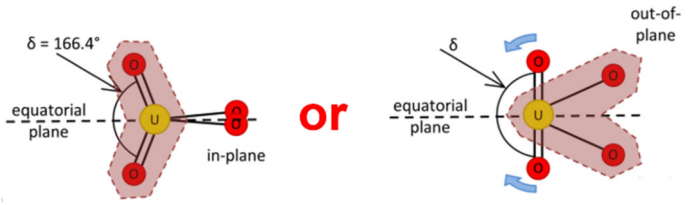
Synopsis



A strong bending of axial uranyl group in purely inorganic phase has been archived via application of physical pressure. At the same time coordination geometry of the uranyl group within equatorial plane changes dramatically. With application of DFT+U computational methods the pressure-energy-geometry dependence has been studied.