certain anions with electrophilic molecules augurs well for the facilitation of some S_N2 reactions.

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Unusual Uranyl Tellurites Containing $[Te_2O_6]^{4-}$ Ions and Three-Dimensional Networks[**]

Philip M. Almond, Michael L. McKee, and Thomas E. Albrecht-Schmitt[*]

Solid-state chemistry of the actinides is the subject of significant investigation because of its relevance to nuclear waste disposal and power generation,[1] mineralogy,[2] and catalysis.[3] One system that is poorly understood is that of the uranyl tellurites, which are currently known only from three minerals, $UO_2(Te_3O_7)$,[4] $PbUO_2(TeO_3)_2$,[5] and $UO_2(TeO_3)$,[6] and the synthetic phase $Pb_2UO_2(TeO_3)_3$.[7] In spite of their low representation, these compounds differ substantially in their dimensionality,[2] the coordination environments of the U^{VI} center, and in the Te^{IV} oxoanions present.

The ubiquitous presence of a stereochemically active lone pair of electrons on the Te^{IV} centers certainly plays a substantial role in the crystalline architecture of this family of compounds. However, the general tendency is for oxoanions containing nonbonding electrons to either not affect the overall dimensionality of U^{VI} compounds, or to reduce it from two-dimensional to one-dimensional, as demonstrated by uranyl iodates[8,9] and selenites.[10] In uranyl tellurites this trend is not observed. The ability of Te^{IV} to bind four or five O atoms in its inner sphere, as found in the ternary phases, $BaTe_3O_7$,[11] $BaTe_4O_9$,[11] $TeSeO_4$,[12] $UO_2(TeO_3)$,[6] and $UO_2(Te_3O_7)$[4] does not offer a satisfying explanation for the atypical behavior of uranyl tellurites because $Pb_2UO_2(TeO_3)_3$ contains only TeO_3^{2-} ions, and yet it still adopts a three-dimensional architecture.[7]

To address the unusual bonding in the uranyl tellurite system we are systematically preparing a series of compounds by hydrothermal methods that differ primarily in their countercations. For example, the reaction of TlCl with $UO_2(C_2H_3O_2)_2{\cdot}2H_2O$ and Na_2TeO_3 at 180°C in aqueous media for three days produces $Tl_2[UO_2(TeO_3)_2]$ (**1**), whereas, in the absence of TlCl, $Na_8[(UO_2)_6(TeO_3)_{10}]$ (**2**) is isolated instead.

The simplicity of the formula of **1** is quite misleading because its structure is far from predictable. The uranyl tellurite architecture in this compound is constructed from uranyl moieties that are bound by five O atoms to create UO_7 pentagonal bipyramids. These polyhedra edge-share to form dimers. The dimers are joined by bridging TeO_3^{2-} ions to yield one-dimensional chains. The chains are in turn linked by $[Te_2O_6]^{4-}$ ions that are bischelating/bridging, producing two-dimensional ${}^{2}_{\infty}[UO_2(TeO_3)_2]^{2-}$ sheets that are separated by Tl^+ ions. Part of a ${}^{2}_{\infty}[UO_2(TeO_3)_2]^{2-}$ sheet is illustrated in Figure 1. Bond valence sum calculations are consistent with U^{VI} and

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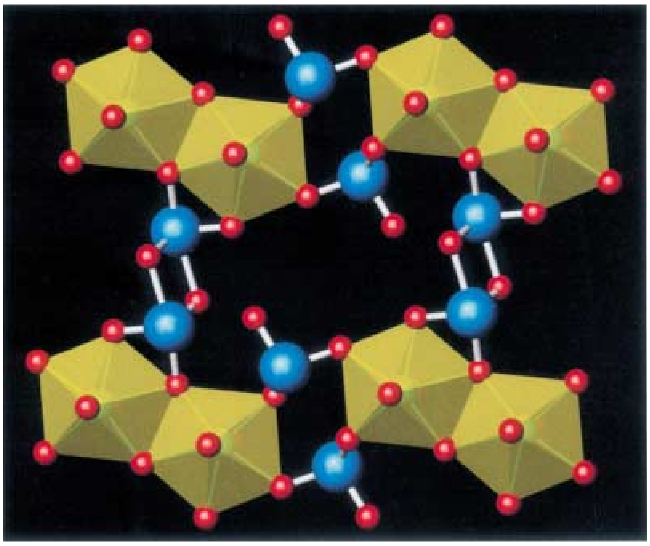

Figure 1. Section of the two-dimensional $^{2}_{\infty}[UO_2(TeO_3)_2]^{2-}$ sheets in **1**.

provide a value of 5.90,[13] and the UV/Vis diffuse reflectance spectrum shows characteristic uranyl absorptions near 420 nm.

At first glance the $[Te_2O_6]^{4-}$ ion (Figure 2) appears merely to be two TeO_3^{2-} ions forming short interactions with one another, as is common in solids containing the isoelectronic iodate, IO_3^- ion.[8,9] However, it is important to note that the interactions between iodate anions do not result in a perturbation of the geometry around the I^V centers. In contrast, the bonding around the Te^{IV} centers in the $[Te_2O_6]^{4-}$ ions consists of two short Te–O bonds of 1.878(6) and 1.887(7) Å, one intermediate bond of 1.977(6) Å, and one long bond of 2.285(7) Å. Therefore, the interactions between the two tellurite anions has resulted in a significant change in the bonding around the Te^{IV} centers. The geometry around each tellurium atom is intermediate between that expected for square-pyramidal TeO_4^{4-} and trigonal-pyramidal TeO_3^{2-} ions. This type of $TeO_3^{2-}\cdots TeO_3^{2-}$ interaction has been described as a TeO_{3+1} polyhedron where the additional long Te–O bond represents the fourth vertices.[11,14] If the long Te–O bonds between tellurite anions are removed, the resultant $^{1}_{\infty}[UO_2(TeO_3)_2]^{2-}$ chains are very similar to those found in $Sr[UO_2(SeO_3)_2]\cdot 2H_2O$ where there are no close Se⋯O interactions between selenite anions.[15]

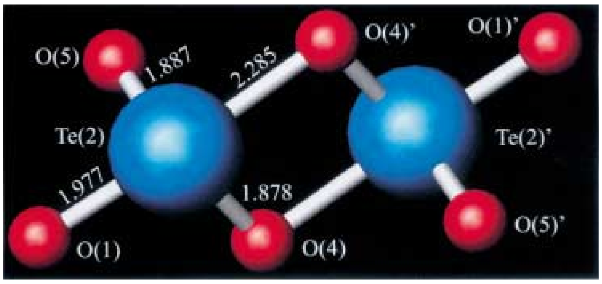

Figure 2. The $[Te_2O_6]^{4-}$ ion found in **1**.

In order for the $[Te_2O_6]^{4-}$ ion to form from two TeO_3^{2-} ions, significant repulsive coulombic forces must be overcome. The ligation of the $[Te_2O_6]^{4-}$ ion to two highly electron-withdrawing U^{VI} centers is the likely source of stabilization in this system. To test this theory, we modeled the $[Te_2O_6]^{4-}$ ion as the neutral $[AlTe_2O_6Al]$ unit using B3LYP density functional methods[16] with the 6-31G(d) basis set for Al and O and an effective core potential for Te.[17] All calculations were made with the Gaussian program.[18]

In the absence of metal centers for binding the tellurite anions, the $[Te_2O_6]^{4-}$ anionic dimer is not stable and simply separates into two TeO_3^{2-} ions as the structure is minimized. However, when Al^{2+} ions are placed at opposite edges, the $[Te_2O_6]^{4-}$ ion becomes a stable minimum, and the Te–O bond lengths and O-Te-O bond angles determined from this calculation, are in reasonable agreement with those measured from the crystal structure. The calculated distances and angles are given in Table 1. Based upon these calculations it does indeed appear that the metal centers stabilize the formation of the $[Te_2O_6]^{4-}$ ion. In contrast, if the same calculation is carried out with SeO_3^{2-}, a stable dimer does not form.

The structure of **2** is substantially different from that of **1** even though they share some of the same structural features. Here the UO_7 pentagonal bipyramids are observed again. However, the Te^{IV} oxoanions consist solely of C_{3v}, TeO_3^{2-} ions. The Te–O bond lengths show little variation with distances ranging from 1.848(5) to 1.891(5) Å. These anions bridge UO_7 units to create a three-dimensional network structure that is chiral. Part of the network is shown in Figure 3 with the Na^+ ions omitted. The Na^+ ions reside in small twisting interconnected cavities and channels. Three-dimensional network structures are not common with U^{VI} and typically require cross-linking of uranium oxide layers by additional building units,[19] or the orthogonal orientation of uranyl polyhedra with respect to one another.[20,21]

The chiral nature of **2** is likely a consequence of the presence of stereochemically active lone pairs of electrons on the Te^{IV} centers. While anions of this type often promote the formation of noncentrosymmetric structures due to the alignment of the lone pairs of electrons,[22] this property is not typically observed in uranyl structures, because the

Table 1. Selected bond lengths [Å] and angles [°] for the $[Te_2O_6]^{4-}$ ion in **1**. Calculated bond lengths and angles from DFT calculations are given in parentheses.

	Bond lengths [Å]		
Te(2)-O(1)	1.977(6) (2.036)	Te(2)-O(4)′	2.285(7) (2.138)
Te(2)-O(4)	1.878(6) (1.903)	Te(2)-O(5)	1.887(7) (1.959)
	Bond angles [°]		
O(1)-Te2-O(4)	92.6(3) (89.8)	O(4)-Te2-O(4)′	78.1(3) (76.6)
O(1)-Te2-O(4)′	160.6(3) (160.3)	O(4)-Te2-O(5)	97.4(3) (100.6)
O(1)-Te2-O(5)	82.9(3) (79.3)	O(4)′-Te2-O(5)	81.5(3) (89.4)

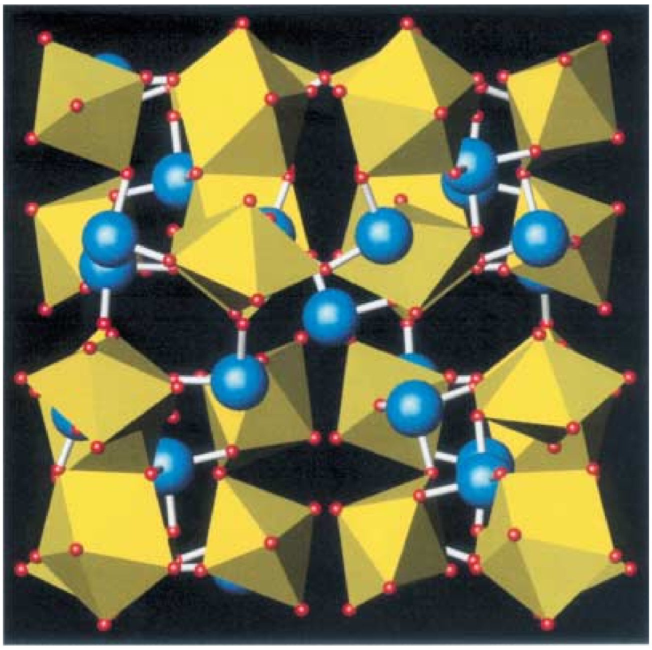

Figure 3. Part of the three-dimensional network structure of **2**. Na^+ ions have been omitted for clarity.

uranium atoms in UO_6 tetragonal bipyramids or UO_8 hexagonal bipyramids often reside on centers of inversion or higher symmetry. While UO_7 pentagonal bipyramids cannot be placed on inversion centers without disorder, they are often related to one another through such centers. A consequence of the chirality of **2** is that it should display second-harmonic generation (SHG) properties. This attribute was confirmed by irradiating a sample with a 1064 nm laser; the compound revealed a distinct green emission (532 nm) consistent with second-harmonic generation with a response of approximately 5 × that of α-SiO_2.

In conclusion, we have demonstrated that the A-UO_2^{2+}-Te-O system is quite unlike that found with other uranyl compounds that contain oxoanions with nonbonding electrons. The stabilization of acceptor orbitals on the Te^{IV} centers by uranyl cations offers a partial explanation of the unusual bonding observed thus far. Further studies are needed to explain why uranyl tellurites containing only TeO_3^{2-} ions are often three-dimensional.

Experimental Section

1: Na_2TeO_3 (320 mg, 1.45 mmol), $UO_2(C_2H_3O_2)_2{\cdot}2\,H_2O$ (180 mg, 0.424 mmol), TlCl (130 mg, 0.542 mmol), and distilled and Millipore filtered water (1.5 mL) were loaded in a 23-mL PTFE-lined autoclave. The autoclave was heated at 180 °C for three days, and slow cooled at $9\,K\,h^{-1}$ to 22 °C. The product consisted of orange tablets of **1**. Yield for **1**: 75 mg (17 % based on U). EDX analysis provided a Tl:U:Te ratio of 2:1:2.

2: Na_2TeO_3 (500 mg, 2.26 mmol), $UO_2(C_2H_3O_2)_2{\cdot}2\,H_2O$ (180 mg, 0.424 mmol), CsCl (150 mg, 0.891 mmol), and distilled and Millipore filtered water (1.5 mL) were loaded in a 23-mL PTFE-lined autoclave. All other conditions were the same as for **1**. The product consisted of bright yellow dodecahedral crystals of **2**. Yield for **2**: 190 mg (76 % based on U). EDX analysis provided a Na:U:Te ratio of 8:6:10.

X-ray structural analyses: $Tl_2[UO_2(TeO_3)_2]$ (**1**): orange tablet, crystal dimensions $0.102 \times 0.125 \times 0.150$ mm, triclinic, $P\bar{1}$, $Z = 2$, $a = 7.4054(9)$, $b = 7.9268(9)$, $c = 8.994(1)$ Å, $\alpha = 94.122(2)$, $\beta = 107.438(2)$, $\gamma = 107.180(2)°$, $V = 471.08(9)$ Å^3 ($T = 193$ K), $\mu = 573.50\ cm^{-1}$, $R_1 = 0.0319$, $wR2 = 0.0811$.[23] $Na_8[(UO_2)_6(TeO_3)_{10}]$ (**2**): yellow dodecahedron, crystal dimensions $0.116 \times 0.124 \times 0.140$ mm, cubic, $I2_13$, $Z = 4$, $a = 16.8969(5)$, $V = 4824.2(2)$ Å^3 ($T = 193$ K), $\mu = 261.76\ cm^{-1}$, $R_1 = 0.0178$, $wR2 = 0.0505$.[23] Bruker APEX CCD diffractometer: $\theta_{max} = 56.60°$ (**1**) and 56.48° (**2**), $Mo_{K\alpha}$, $\lambda = 0.71073$ Å, 0.3° ω scans, 4745 (**1**) and 24374 (**2**) reflections measured, 2301 (**1**) and 2013 (**2**) independent reflections all of which were included in the refinement. The data was corrected for Lorentz polarization effects and for absorption (analytical and SADABS), solutions were solved by direct methods, anisotropic refinement of F^2 by full-matrix least-squares, 119 (**1**) and 108 (**2**) parameters. Further details on the crystal structure investigation(s) may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-412560 and CSD-412561.

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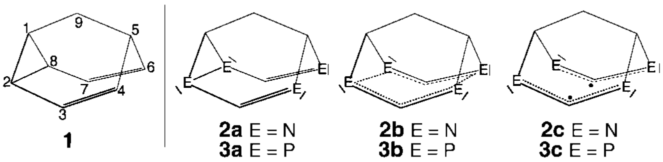

Figure 1. Barbaralane **1** and some possible heterobarbaralanes **2**.

A C_{2v}-Symmetric Barbaralane**

Markus Reiher* and Barbara Kirchner*

Barbaralane **1** (see Figure 1) is one of the fluxional molecules that undergo a degenerate Cope rearrangement. It was proposed by W. von E. Doering that the activation barrier of the Cope rearrangement is lower in **1** than in 3,4-homotropilidene[1] as barbaralane is already fixed in the appropriate boat conformation by a bridge between the two corner atoms C1 and C5. If this activation barrier were lowered even further, one might arrive at a symmetrical and therefore homoaromatic, biradical, or biradicaloid ground state. The objective is to transform the double-minimum system **1** into one with a single minimum by increasing the symmetry, that is, by changing from a C_s- to a more symmetric (C_{2v}) ground-state structure. Much effort was made to find a symmetrical ground-state structure by studying various derivatives experimentally and theoretically (e.g., semiempirical MO calculations[2,3]). The most valuable overview was given by Quast et al.[4] Additional reviews can be found in refs. [1,5,6] and references cited therein. These investigations yielded the following results: At the C2 and the C6 positions only electron-withdrawing groups that are π acceptors lower the barrier. Aryl groups at these positions are most effective. The same π-acceptor substituent causes only slight changes at the C3 and C7 positions.

From the possible derivatives of **1** we chose to replace the 2,4,6,8-positions of barbaralane by heteroatoms (Figure 1). The use of nitrogen or oxygen has been suggested.[4] A derivative of 2,4,6,8-tetraazabarbaralane (**2a**) was studied before; it does not give a symmetrical ground state (**2b** or **2c**), but the activation barrier of the Cope rearrangement is lowered relative to that of the carbon analogue.[7] This is in accordance with the observation of Schnieders et al., who found lowering of the Cope barrier in a 2,6-diazasemibullvalene derivative[8] relative to the carbon analogue. A logical consequence from these studies is replacement of carbon by phosphorus atoms, which can be achieved by replacing a CH moiety with a P atom as they are valence isoelectronic. Phosphorus produces smaller bond angles than carbon, and this can affect the stability of cyclic compounds.[9] Hence, we proposed to study the novel compound 2,4,6,8-tetraphosphabarbaralane (**3**), and we also re-examined parent barbaralane (**1**) and 2,4,6,8-tetraazabarbaralane (**2a**).

Figure 2 shows the three molecules with selected bond lengths, as obtained from DFT geometry optimizations (see Methods of Calculation). The most striking feature is that **3** clearly has C_{2v} symmetry. Frequency analysis of this geometrical arrangement indeed confirmed a minimum structure.

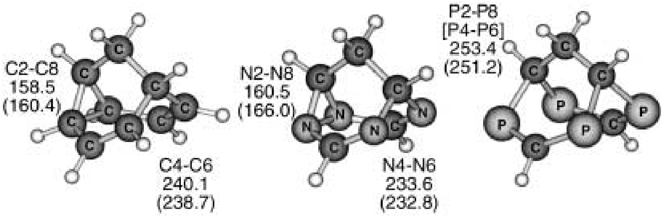

Figure 2. B3LYP/TZVPP optimized structures of barbaralane (left), tetraazabarbaralane (middle), and tetraphosphabarbaralane (right). Distances are given in picometers (BP86/TZVPP values in parentheses).

The overall agreement between the B3LYP and BP86 (in parentheses) bond lengths is very good: deviations are less than 2 pm (with the exception of the N2–N8 bond length, for which the BP86 value deviates by 5.5 pm from the B3LYP value). Therefore, in the following discussion we concentrate on B3LYP/TZVPP data. Closer inspection reveals that the C1-C9-C5 substructure (1,5-bridge) is almost identical in all the barbaralanes (e.g., the C9–C5 distances vary between 154.7 and 152.1 pm). Deviations are within 2.6 pm and are due to bond shortening in the heterobarbaralanes compared to the parent barbaralane. The two bonds building this bridge are of almost identical length in **1** and **2a**, and completely identical in **3**. Whereas all nitrogen–carbon distances are contracted by about 5 pm compared to the equivalent C–C distances in parent barbaralane, the N2–N8 distance is longer and the N4–N6 distance is shorter than the equivalent C–C distance, and this results in a molecule more symmetrical than the parent barbaralane.

In **3** we found for every interatomic distance involving phosphorus a bond elongation by more than 25 pm compared to the parent barbaralane **1**. Since the P2[4]–P8[6] distances (253.4 pm) are larger than the typical σ bond lengths in P_6[10]

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