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Structure of Tris(urea)dioxouranium(VI) Sulfate, $UO_2(OC(NH_2)_2)_3SO_4$

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As part of a study of structures of uranium complexes we have determined the crystal structure of tris(urea)uranyl sulfate by single-crystal X-ray diffraction methods. The uranyl ion is coordinated to oxygen atoms from the three urea molecules and from the sulfate ions in a pentagonal-bipyramid arrangement in which the pentagonal bipyramids are bridged by the sulfate ions to form an infinite chain. This result is in contrast to the structure of pentakis(urea)dioxouranium(VI) dinitrate[2] in which the oxygen atoms of the five urea molecules are coordinated to the uranyl ion to form discrete complexes with the same pentagonal-bipyramidal geometry; the nitrate ions are not coordinated to the uranyl ion.

Experimental Section

Slow evaporation of an aqueous solution of uranyl sulfate and urea in a 1:5 molar ratio yielded fluorescent lime green crystals similar in color to crystals of $UO_2(OC(NH_2)_2)_5(NO_3)_2$.[2] The crystals were stable in air during the month of X-ray investigation. Weissenberg photography showed the crystal to be monoclinic.

A crystal of approximate dimensions 0.09 × 0.10 × 0.14 mm was glued to a glass fiber and examined with a Picker FACS-I automatic diffractometer equipped with a graphite monochromator and a Mo X-ray tube. ω scans of the 200, 040, and $00\bar{2}$ reflections showed peaks with widths at half-height of 0.15, 0.21, and 0.13°, respectively. A least-squares refinement of the setting angles of 12 manually centered reflections ($45° < 2\theta < 50°$) using Mo $K\alpha_1$ ($\lambda = 0.70930$ Å) radiation at 22 ± 1 °C gave $a = 7.619$ (2) Å, $b = 24.706$ (8) Å, $c = 6.928$ (2) Å, $\beta = 91.06$ (2)°, and $V = 1303.9$ Å^3. The observed extinctions are unique to space group $P2_1/n$. For $Z = 4$ and mol wt 546.26, the calculated density is 2.78 g cm^{-3}; the density measured by flotation in a mixture of tetrachloromethane and tribromomethane was 2.79 g cm^{-3}.

Intensity data were collected to 56° in 2θ by using θ–2θ scans with a scan speed of 2°/min on 2θ, with a scan range from 0.85° below the $K\alpha_1$ peak to 0.85° above the $K\alpha_2$ peak, and with backgrounds counted for 10 s at each end of the scan range. Three standard reflections, measured after every 200th reflection, showed only random fluctuations in intensity and no indication of crystal decay. Intensities of 5958 reflections were measured.

An absorption correction was applied[3] ($\mu = 120$ cm^{-1} for Mo $K\alpha$ radiation) with the crystal described by nine faces. The crystal dimensions were adjusted to fit the intensity variations of 12 azimuthal scans. Maximum and minimum corrections were 3.15 and 1.82, respectively. Intensities were also corrected for Lorentz and polarization factors, and equivalent reflections were averaged to give 3153 unique reflections.

Table I. Positional Parameters[a]

atom	x	y	z
U	0.26435 (2)	0.62058 (1)	0.20427 (2)
S	0.1033 (1)	0.63504 (4)	0.7003 (1)
O(1)	0.4112 (4)	0.6762 (1)	0.2023 (4)
O(2)	0.1169 (3)	0.5655 (1)	0.2081 (4)
O(3)	0.2148 (4)	0.6473 (1)	−0.1265 (4)
O(4)	0.4541 (3)	0.5707 (1)	0.0078 (4)
O(5)	0.4685 (3)	0.5696 (1)	0.4021 (4)
O(6)	0.2192 (3)	0.6451 (1)	0.5319 (4)
O(7)	0.0180 (4)	0.6751 (1)	0.2015 (4)
O(8)	−0.0416 (4)	0.6738 (1)	0.6940 (4)
O(9)	0.0417 (4)	0.5798 (1)	0.7011 (5)
N(1)	−0.0876 (7)	0.7458 (2)	0.0344 (6)
N(2)	−0.1098 (6)	0.7425 (2)	0.3616 (6)
N(3)	0.6255 (6)	0.6288 (2)	−0.1564 (8)
N(4)	0.7101 (6)	0.5426 (2)	−0.1081 (9)
N(5)	0.7308 (5)	0.6092 (2)	0.3446 (7)
N(6)	0.7153 (6)	0.5180 (2)	0.3944 (8)
C(1)	−0.0581 (5)	0.7206 (2)	0.1987 (6)
C(2)	0.5938 (5)	0.5807 (2)	−0.0841 (6)
C(3)	0.6350 (6)	0.5655 (2)	0.3817 (6)
H(1)	−0.065 (7)	0.730 (2)	−0.084 (8)
H(2)	−0.139 (8)	0.773 (2)	0.041 (8)
H(3)	−0.102 (7)	0.724 (2)	0.468 (8)
H(4)	−0.174 (7)	0.768 (2)	0.369 (8)
H(5)	0.556 (8)	0.647 (2)	−0.149 (9)
H(6)	0.728 (6)	0.639 (2)	−0.215 (8)
H(7)	0.698 (8)	0.520 (3)	−0.052 (9)
H(8)	0.802 (7)	0.547 (2)	−0.167 (8)
H(9)	0.664 (7)	0.647 (2)	0.292 (7)
H(10)	0.861 (7)	0.609 (2)	0.261 (7)
H(11)	0.661 (7)	0.488 (2)	0.436 (8)
H(12)	0.829 (7)	0.515 (2)	0.379 (8)

[a] In this and the following tables the numbers in parentheses are the estimated standard deviations in the least significant digits.

Table II. Selected Interatomic Distances (Å)

U–O(1)	1.772 (3)	C(1)–O(7)	1.266 (5)	N(1)–H(1)	0.92 (5)
–O(2)	1.765 (3)	–N(1)	1.314 (5)	–H(2)	0.77 (6)
–O(3)	2.407 (3)	–N(2)	1.318 (5)	N(2)–H(3)	0.87 (5)
–O(4)	2.353 (3)	C(2)–O(4)	1.275 (5)	–H(4)	0.80 (6)
–O(5)	2.409 (3)	–N(3)	1.315 (6)	N(3)–H(5)	0.70 (6)
–O(6)	2.380 (3)	–N(4)	1.305 (6)	–H(6)	0.92 (5)
–O(7)	2.310 (3)	C(3)–O(5)	1.283 (5)	N(4)–H(7)	0.69 (6)
S–O(3)	1.489 (3)	–N(5)	1.331 (6)	–H(8)	0.82 (5)
–O(6)	1.497 (3)	–N(6)	1.326 (6)	N(5)–H(9)	1.12 (6)
–O(8)-	1.461 (3)			–H(10)	1.16 (5)
–O(9)	1.443 (3)			N(6)–H(11)	0.91 (5)
				–H(12)	0.88 (5)

Trial coordinates for the uranium atom were obtained from a three-dimensional Patterson function. After two series of least-squares refinement followed by Fourier calculations, all of the nonhydrogen atoms were found. After least-squares refinement for all nonhydrogen atoms, with only the uranium atom treated with anisotropic temperature factors, an empirical extinction correction was applied where $F_{cor} = F_o(1 + 1.5 \times 10^{-7}I)$; F_{cor} and F_o are the corrected and observed structure factors, and I is the observed intensity. The anisotropic thermal parameters and the positional parameters for all the nonhydrogen atoms were refined for several cycles. A difference Fourier calculation showed peaks near expected hydrogen-atom positions. For the final cycles of least-squares refinement, positional parameters for all 12 hydrogen atoms and a single isotropic hydrogen-atom temperature factor were also refined; the refinement converged to the positions given in Table I. Thermal parameters and structure factor amplitudes are available in the supplementary material. The full-matrix least-squares program minimized the function $\sum w|\Delta F|^2/\sum wF_o^2$ where the assigned weights $w = [\sigma(F)]^{-2}$ are derived from $\sigma(F^2) = [S^2 + (pF^2)^2]^{1/2}$; S^2 is the variance due to counting statistics and $p = 0.01$. Neutral-atom scattering factors for the nonhydrogen atoms from Doyle and Turner[4] and for hydrogen from Stewart, Davidson, and Simpson[5] were used, and anomalous dispersion corrections[6] were applied. The discrepancy indices with 218 parameters varied and 2491 data with $F^2 > 3\sigma(F^2)$ are

$$R = \sum||F_o| - |F_c||/\sum|F_o| = 0.019$$

$$R_w = \sum[w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.017$$

R for all 3153 data is 0.035. The error in an observation of unit weight is 1.22. In the last cycle of refinement all parameter changes were

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Table III. Selected Angles (Deg)

O(1)–U–O(2)	179.4 (1)	O(8)–S–O(9)	112.0 (2)
O(1)–U–O(3)	82.4 (1)	O(7)–C(1)–N(1)	120.4 (4)
O(1)–U–O(4)	90.4 (1)	O(7)–C(1)–N(2)	119.8 (4)
O(1)–U–O(5)	90.5 (1)	N(1)–C(1)–N(2)	119.9 (4)
O(1)–U–O(6)	85.0 (1)	O(4)–C(2)–N(3)	121.8 (4)
O(1)–U–O(7)	93.5 (1)	O(4)–C(2)–N(4)	119.9 (4)
O(3)–U–O(4)	71.3 (1)	N(3)–C(2)–N(4)	118.3 (4)
O(4)–U–O(5)	70.0 (1)	O(5)–C(3)–N(5)	120.3 (5)
O(5)–U–O(6)	72.2 (1)	O(5)–C(3)–N(6)	121.2 (5)
O(6)–U–O(7)	74.2 (1)	N(5)–C(3)–N(6)	118.5 (5)
O(7)–U–O(3)	73.7 (1)	H(1)–N(1)–H(2)	121 (5)
O(3)–S–O(6)	105.0 (2)	H(3)–N(2)–H(4)	113 (5)
O(3)–S–O(8)	108.1 (2)	H(5)–N(3)–H(6)	119 (6)
O(3)–S–O(9)	111.7 (2)	H(7)–N(4)–H(8)	119 (6)
O(6)–S–O(8)	108.9 (2)	H(9)–N(5)–H(10)	104 (4)
O(6)–S–O(9)	110.9 (2)	H(11)–N(6)–H(12)	115 (5)

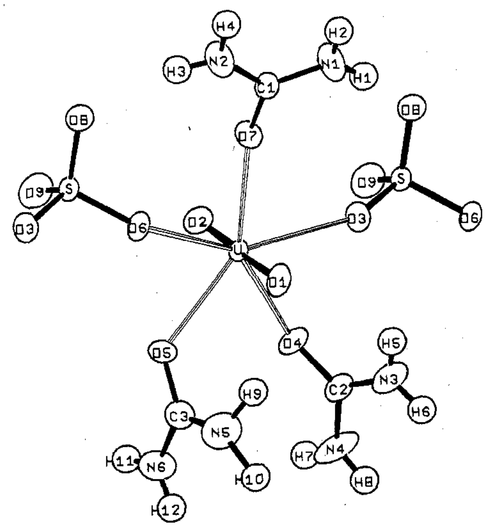

Figure 1. ORTEP drawing of the tris(urea)dioxouranium(VI) sulfate structure. An additional sulfate group is included to show the bridging. The sulfate on the right is related to the one on the left by a translation along *c* of one unit cell length.

less than 0.09σ. A difference Fourier calculation after the last cycle of refinement had a maximum electron density of 1.2 e Å^{-3}, at a location near that of uranium.

Results and Discussion

Atomic positions, distances, and angles are listed in Tables I–III. The structure (Figure 1) consists of chains of alternate tris(urea)dioxouranium(VI) ions and sulfate ions, with sulfate ions contributing two oxygen atoms to the pentagonal bipyramid of oxygen atoms coordinated to the uranium(VI) ion. The U–O(4) and U–O(5) bonds are perpendicular to the uranyl ion axis; the third urea oxygen atom (O(7)) is 0.16 Å from the equatorial plane defined by U, O(4), and O(5) while the two sulfate oxygen atoms are 0.30 Å (O(3)) and 0.20 Å (O(6)) from the equatorial plane on the side opposite to O(7). The urea molecules are planar. The H(9) and H(10) atoms appear to be out of the plane of their urea molecule, but we attribute this as an inaccuracy in the determination of these hydrogen-atom positions. One urea molecule is held approximately coplanar with the uranyl equatorial plane by hydrogen bonds to two of the sulfate oxygen atoms (N(1)–H(1)---O(8) and N(2)–H(3)---O(8) in Figure 1), while the other two urea molecules are approximately perpendicular to the uranyl equatorial plane. Bond distances and angles for urea and for the uranium(VI) coordination polyhedron are in close agreement with those in $[\mathrm{UO_2(OC(NH_2)_2)_5}](\mathrm{NO_3})_2$[2] and $[\mathrm{UO_2(H_2O)(OC(NH_2)_2)_4}](\mathrm{NO_3})_2$.[7] The present compound, with two sulfate oxygen atoms coordinated to the uranyl ion, is structurally similar to the nitrate salts mentioned above, in which the nitrate ions are not coordinated to the uranyl ion so that anion bridging between cation complexes cannot occur, and the two forms of $\mathrm{2UO_2SO_4{\cdot}7H_2O}$,[8,9] in which three sulfate oxygen atoms are coordinated to the uranyl ion, resulting in complex anion bridging between cation complexes. Possible hydrogen bonds for which the N---O distance is less than 3.2 Å, the O---H distance is less than 2.4 Å, and the N–H---O angle is greater than 120° are listed in Table IV. The values in Table IV are comparable to the hydrogen-bond lengths (2.99, 3.03 Å) and angles (151, 167°) found in urea.[10]

Table IV. Possible Hydrogen Bond Distances (Å) and Angles (Deg)

atoms^{a}	N–H dist	H—O dist	N···O dist	N–H–O angle
N(1)–H(1)--O(8)$^{\mathrm{i}}$	0.92 (5)	2.09 (5)	2.980 (5)	162 (5)
N(1)–H(2)--O(6)$^{\mathrm{ii}}$	0.77 (6)	2.30 (6)	3.070 (5)	174 (6)
N(2)–H(3)--O(8)	0.87 (5)	2.05 (6)	2.901 (5)	168 (5)
N(2)–H(4)--O(3)$^{\mathrm{ii}}$	0.80 (6)	2.25 (6)	3.034 (5)	164 (6)
N(3)–H(6)--O(8)$^{\mathrm{iii}}$	0.92 (5)	2.06 (5)	2.973 (5)	169 (5)
N(4)–H(8)--O(9)$^{\mathrm{iii}}$	0.82 (5)	2.21 (5)	3.016 (5)	165 (6)
N(5)–H(9)--O(1)	1.11 (6)	2.14 (5)	3.090 (6)	141 (4)
N(5)–H(10)—O(7)$^{\mathrm{iv}}$	1.16 (5)	2.08 (5)	3.090 (6)	126 (4)
N(6)–H(11)—O(5)$^{\mathrm{v}}$	0.91 (5)	2.07 (5)	2.952 (6)	164 (5)

^{a} Symmetry transformations: (i) $x, y, z-1$; (ii) $x-{}^1/_2, 1+{}^1/_2-y, {}^1/_2+z$; (iii) $1+x, y, z-1$; (iv) $1+x, y, z$; (v) $1-x, 1-y, 1-z$.

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Registry No. $\mathrm{UO_2(OC(NH_2)_2)_3SO_4}$, 72318-07-1.

Supplementary Material Available: Listings of structure factor amplitudes and atomic thermal parameters (13 pages). Ordering information is given on any current masthead page.

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Some Bis(*tert*-butylimido) Complexes of the Group 6 Transition Metals and a Related Alkylamido Derivative

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Recently we reported[1] the preparation of four-coordinate d^0 organoimido complexes of the group 4 and 5 transition metals and of rhenium. We now report the extension of our synthetic studies to the group 6 metals. A number of group 6 organoimido derivatives are known[2] although only one example of a four-coordinate d^0 complex has been reported.[3]

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