National Magnet Laboratory. We thank J. M. Berg for structural calculations and Dr. P. K. Mascharak for experimental assistance.

Registry No. 1, 85269-29-0; $(Et_4N)_2[Fe_4S_4(S\text{-}p\text{-}C_6H_4Br)_4]$, 85269-27-8.

Supplementary Material Available: Tables S-I–S-IV, showing anisotropic temperature factors, hydrogen atom coordinates and isotropic temperature factors, best-weighted least-squares planes, and observed and calculated structure factors, and a stereoview of $(Et_4N)_3[Fe_4S_4(S\text{-}p\text{-}C_6H_4Br)_4]$ (15 pages). Ordering information is given on any current masthead page.

Notes

Contribution from the Department of Chemistry,
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Uranyl(VI) Compounds. 3.[1] Crystal Structures of Two Forms of Bis(urea)dioxouranium(VI) Sulfate[2]

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Received September 27, 1982

Uranyl sulfate forms several crystalline hydrates of the general formula $UO_2SO_4\cdot nH_2O$. Detailed X-ray crystallographic studies of $UO_2SO_4\cdot 2^1/_2H_2O$[3] and $UO_2SO_4\cdot 3^1/_2H_2O$[4,5] have been carried out earlier. The structures consist of infinite double chains formed by alternating UO_7 and SO_4 polyhedra. In aqueous solution urea molecules are capable of replacing water molecules in the coordination sphere of the uranyl ion and complexes of the type $UO_2SO_4\cdot nCO(NH_2)_2$ may be precipitated by evaporation. The replacement of water by urea leads to different networks as seen in the structures of the tris(urea)[6] and tetrakis(urea)[7] complexes. The former structure consists of single chains, whereas the latter is monomeric.

The X-ray crystallographic investigation carried out in this work has revealed that the bis(urea) complex forms two structurally related polymorphs. The crystal structures of the two polymorphs are described below.

Experimental Section

Crystals of both polymorphs of $UO_2SO_4\cdot 2CO(NH_2)_2$ were obtained upon evaporation of an aqueous solution containing uranyl sulfate and urea in the molar ratio of 1:2 at room temperature. Chemical analysis showed that the crystals have the same composition. However, the polymorphs differed in color. The greenish and yellowish crystals were distinguished by the prefixes α and β, respectively. Fast evaporation yielded predominantly the β form. Preliminary DSC investigation revealed no polymorphic transitions for α and β forms.

Table I. Data for the X-ray Diffraction Study of $UO_2SO_4\cdot 2CO(NH_2)_2$

	α-$UO_2SO_4\cdot 2CO(NH_2)_2$	β-$UO_2SO_4\cdot 2CO(NH_2)_2$
(A) Crystal Data		
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a, Å	6.856 (1)	6.747 (1)
b, Å	12.760 (2)	14.110 (3)
c, Å	11.571 (1)	11.348 (1)
β, deg	91.73 (1)	106.53 (1)
V, Å^3	1011.80	1035.62
Z	4	4
cryst size, mm	0.15 × 0.15 × 0.3	0.15 × 0.15 × 0.25
fw	486.23	486.23
ρ(calcd), g cm^{-3}	3.191	3.118
ρ(obsd),[a] g cm^{-3}	3.14	3.08
μ(Mo Kα), cm^{-1}	157.9	154.3
cell const determn	25 reflctns, $35 < 2\theta < 40°$[b]	25 reflctns, $35 < 2\theta < 40°$[b]
(B) Measurement of Intensity Data		
radiation	Mo Kα, graphite monochromator	
reflections measd	$+h, +k, \mp l$	
2θ range, deg	5–60	
scan type	θ/2θ	
scan speed, deg min^{-1}	2.0	
scan range, deg	(2θ(Mo Kα) − 1)–(2θ(Mo Kα) + 1)	
bkgd measmt	at beginning and end of the 2θ range, each for half of the total scan time	
no. of reflctns measd	3311	3376
std reflctns	$11\bar{1}$, 202	$\bar{1}41$, $\bar{2}02$
range of transmission factors	0.36–0.66	0.35–0.60
no. of unique data with $I > 3\sigma(I)$	2554	2587
extinction coeff *g*	0.00131 (4)	0.00129 (3)
$R = \Sigma \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$	0.060	0.069

[a] Measured by flotation. [b] λ(Mo Kα) = 0.7107.

The crystal data given in Table I are in agreement with the unit cell values for the β form given by Durski et al.[8] and with those reported recently by Serezhkin et al.;[9] the latter authors have also prepared the α form. The details of the intensity data collection with a Syntex $P2_1$ single-crystal diffractometer are included in Table I. Empirical absorption corrections were made from ψ-scan data, after which Lorentz and polarization corrections were applied to both sets of data.

The structures were solved by the heavy-atom method and refined by least-squares techniques using anisotropic temperature factors for all non-hydrogen atoms. In the final stages of the least-squares refinement the calculated positional parameters for all hydrogen atoms were introduced but not refined (fixed isotropic temperature factor $U = 0.10$ Å^2). The extinction correction was applied for both structures. Scattering factors for the non-hydrogen atoms were according to Cromer and Mann,[10] and those for hydrogen were according to Stewart et al.[11] Anomalous dispersion correction was applied for uranium.[12] Calculations were carried out with the X-RAY 76 program system.[13] The final positional parameters are given in Table II. Thermal parameters, hydrogen atom coordinates, and observed and calculated structure factors are available as supplementary material.

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Table II. Atomic Coordinates with Estimated Standard Deviations in Parentheses

	α-$UO_2SO_4 \cdot 2CO(NH_2)_2$			β-$UO_2SO_4 \cdot 2CO(NH_2)_2$		
atom	x	y	z	x	y	z
U	0.74242 (5)	0.47139 (3)	0.29390 (3)	0.78638 (5)	0.32440 (2)	0.55465 (3)
S	0.2494 (4)	0.4405 (2)	0.3959 (2)	0.2899 (4)	0.4357 (2)	0.5598 (2)
O(1)	0.7389 (14)	0.6035 (6)	0.2373 (7)	0.8500 (12)	0.3383 (5)	0.7164 (8)
O(2)	0.7503 (15)	0.3381 (7)	0.3479 (9)	0.7250 (12)	0.3096 (5)	0.3934 (7)
O(3)	0.4290 (11)	0.5009 (7)	0.3694 (7)	0.4479 (11)	0.3842 (6)	0.5214 (9)
O(4)	0.7815 (13)	0.5545 (8)	0.4782 (8)	0.8097 (10)	0.4939 (4)	0.5371 (5)
O(5)	1.0816 (12)	0.4922 (7)	0.3349 (8)	1.1332 (12)	0.3678 (6)	0.5659 (11)
O(6)	0.2664 (14)	0.3317 (7)	0.3624 (8)	0.3798 (19)	0.4834 (7)	0.6756 (8)
O(7)	0.9104 (12)	0.4198 (7)	0.1280 (7)	0.9977 (11)	0.1854 (5)	0.5787 (7)
O(8)	0.5119 (12)	0.4347 (6)	0.1434 (7)	0.5605 (10)	0.1919 (5)	0.5565 (6)
N(1)	1.0411 (18)	0.3480 (9)	−0.0281 (10)	1.2822 (16)	0.1315 (9)	0.7166 (9)
N(2)	0.9406 (20)	0.2440 (9)	0.1183 (11)	0.9618 (17)	0.0868 (8)	0.7274 (9)
N(3)	0.5299 (17)	0.3518 (8)	−0.0280 (9)	0.2800 (15)	0.1461 (9)	0.4105 (9)
N(4)	0.4386 (22)	0.2634 (9)	0.1310 (10)	0.5988 (17)	0.0902 (8)	0.4108 (10)
C(1)	0.9610 (18)	0.3389 (10)	0.0732 (11)	1.0778 (15)	0.1369 (7)	0.6753 (9)
C(2)	0.4928 (17)	0.3523 (9)	0.0832 (10)	0.4799 (16)	0.1443 (7)	0.4591 (9)

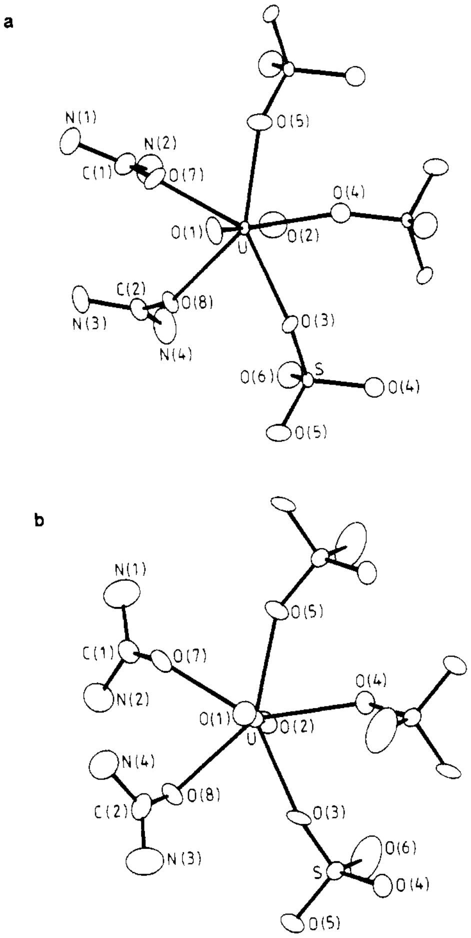

Figure 1. Labeling of the atoms in (a) α-$UO_2SO_4 \cdot 2CO(NH_2)_2$ and (b) β-$UO_2SO_4 \cdot 2CO(NH_2)_2$. Hydrogen atoms are not included.

Results and Discussion

The structures of the α and β forms of $UO_2SO_4 \cdot 2CO(NH_2)_2$ are very similar. The uranium atom lies at the center of a pentagonal bipyramid formed by the oxygen atoms. Of the five equatorial oxygens, three belong to sulfate groups and two to urea molecules (see Figure 1). The bridging tridentate sulfate groups join the bipyramids into infinite double chains in the same fashion as in uranyl sulfate hydrates.[3-5]

Selected interatomic distances and angles are listed in Table III. The distances and angles in UO_7 polyhedra are in close agreement with the values reported for other related uranyl sulfates.[3-7] The U–O(uranyl) bond distances in the α form are exceptionally long, exceeding 1.80 Å, as observed also in $(NH_4)_2UO_2(SO_4)_2 \cdot 2H_2O$.[14]

Table III. Selected Interatomic Distances (Å) and Angles (deg)

	α-$UO_2SO_4 \cdot 2CO(NH_2)_2$	β-$UO_2SO_4 \cdot 2CO(NH_2)_2$
U-O(1)	1.808 (8)	1.773 (8)
-O(2)	1.813 (9)	1.770 (8)
-O(3)	2.374 (8)	2.362 (7)
-O(4)	2.389 (9)	2.409 (6)
-O(5)	2.374 (8)	2.387 (9)
-O(7)	2.362 (9)	2.395 (7)
-O(8)	2.363 (8)	2.417 (7)
S-O(3)	1.493 (8)	1.456 (9)
-O(4)	1.480 (9)	1.493 (6)
-O(5)	1.486 (9)	1.443 (9)
-O(6)	1.447 (9)	1.447 (9)
C(1)-O(7)	1.265 (15)	1.275 (11)
-N(1)	1.315 (17)	1.326 (14)
-N(2)	1.328 (17)	1.314 (16)
C(2)-O(8)	1.265 (14)	1.275 (11)
-N(3)	1.318 (15)	1.304 (14)
-N(4)	1.321 (17)	1.333 (17)
O(1)-U-O(2)	178.5 (4)	179.4 (4)
-O(3)	89.0 (4)	93.7 (4)
-O(4)	84.8 (3)	88.5 (3)
-O(5)	88.3 (4)	88.4 (4)
-O(7)	88.0 (3)	90.7 (3)
-O(8)	85.2 (3)	92.5 (3)
O(2)-U-O(3)	92.3 (4)	86.9 (3)
-O(4)	96.2 (4)	91.9 (3)
-O(5)	91.0 (4)	91.3 (4)
-O(7)	90.5 (4)	88.7 (3)
-O(8)	94.6 (4)	87.4 (3)
O(3)-U-O(4)	71.3 (3)	73.4 (2)
O(4)-U-O(5)	71.9 (3)	70.4 (3)
O(5)-U-O(7)	72.2 (3)	70.2 (3)
O(7)-U-O(8)	71.2 (3)	73.8 (2)
O(8)-U-O(3)	73.1 (3)	72.2 (3)
U-O(7)-C(1)	141.4 (8)	129.1 (7)
U-O(8)-C(2)	128.8 (7)	120.9 (7)

The U–O(urea) distances in the β form are slightly longer than in the α form. It may be added that except for the angle U–O(7)–C(1), the U–O–C angles are somewhat smaller than the mean value (135°) calculated for a number of M^{2+} cations in a comprehensive survey[15] and smaller than values recently found for uranyl–urea complexes.[6,7,16]

The orientation of the planar urea molecules is different in the α and β forms. In the α form the two urea molecules are approximately perpendicular to the uranyl equatorial plane

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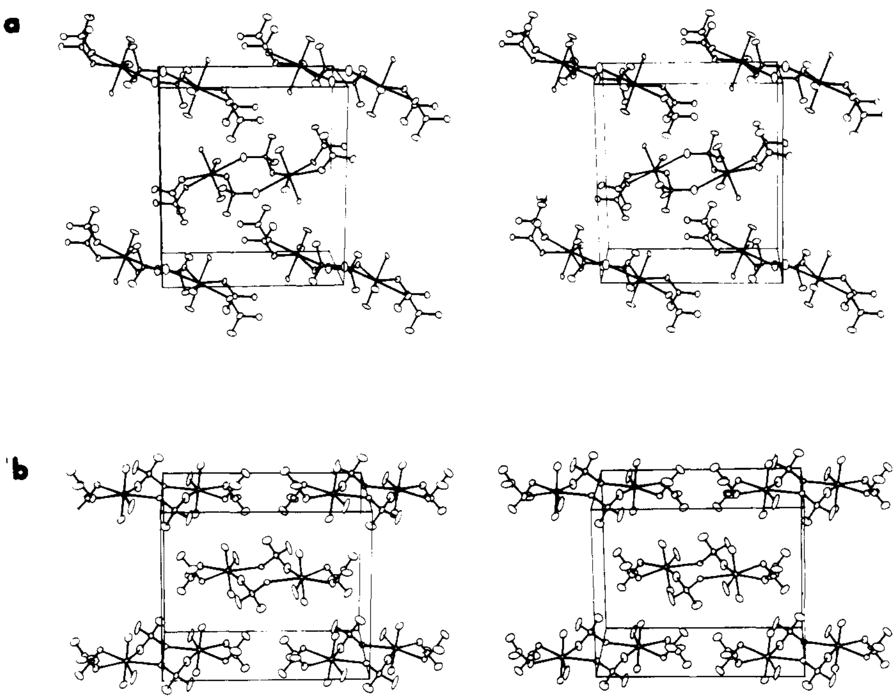

Figure 2. Stereoscopic drawings of the unit cell of (a) α-$UO_2SO_4 \cdot 2CO(NH_2)_2$ and (b) β-$UO_2SO_4 \cdot 2CO(NH_2)_2$ as viewed along the *a* axis. In the α form the *c* axis is running horizontally and the *b* axis vertically and in the β form the *b* axis is running horizontally and the *c* axis vertically. Hydrogen atoms are not included.

Table V. Possible Hydrogen Bond Distances (Å) and Angles (deg)

(A) α-$UO_2SO_4 \cdot 2CO(NH_2)_2$

atoms^{a}	N···O	H-O	N-H-O
N(1)-H(1)···O(6)$^{\mathrm{i}}$	3.061 (15)	2.10	157
-H(2)···O(7)$^{\mathrm{ii}}$	3.201 (14)	2.21	173
N(2)-H(3)···O(4)$^{\mathrm{iii}}$	3.294 (16)	2.39	152
-H(4)···O(2)	3.226 (17)	2.38	141
N(3)-H(5)···O(6)$^{\mathrm{iv}}$	3.197 (14)	2.37	139
-H(5)···O(2)$^{\mathrm{iv}}$	3.217 (14)	2.44	133
-H(6)···O(8)$^{\mathrm{v}}$	3.043 (13)	2.17	145
N(4)-H(7)···O(4)$^{\mathrm{vi}}$	3.295 (16)	2.39	148
-H(8)···O(6)	3.084 (16)	2.19	150

(B) β-$UO_2SO_4 \cdot 2CO(NH_2)_2$

atoms^{b}	N···O	H-O	N-H-O
N(1)-H(1)···O(6)$^{\mathrm{i}}$	3.079 (16)	2.35	128
-H(2)···O(8)$^{\mathrm{ii}}$	3.081 (14)	2.12	162
N(2)-H(3)···O(4)$^{\mathrm{i}}$	2.982 (11)	1.99	169
-H(4)···O(8)	3.209 (12)	2.42	135
N(3)-H(6)···O(7)$^{\mathrm{iii}}$	3.105 (14)	2.23	147
N(4)-H(7)···O(6)$^{\mathrm{iv}}$	2.853 (13)	1.86	165
-H(8)···O(7)	3.124 (12)	2.36	134

[a] Symmetry transformations: (i) $1 + x, {}^1/_2 - y, z - {}^1/_2$; (ii) $2 - x, 1 - y, -z$; (iii) $2 - x, y - {}^1/_2, {}^1/_2 - z$; (iv) $x, {}^1/_2 - y, z - {}^1/_2$; (v) $1 - x, 1 - y, -z$; (vi) $1 - x, y - {}^1/_2, {}^1/_2 - z$. [b] Symmetry transformations: (i) $2 - x, y - {}^1/_2, 1{}^1/_2 - z$; (ii) $1 + x, y, z$; (iii) $x - 1, y, z$; (iv) $x, {}^1/_2 - y, z - {}^1/_2$.

and are situated on the same side of it, whereas in the β form they are on opposite sides of the uranyl equatorial plane, forming angles of 48 and 59° with it. Table IV[17] gives the deviations of the atoms from the least-squares plane.

The urea molecules are involved in the hydrogen bonding within and between the chains. Table V lists the distances and angles for probable hydrogen bonds, which appear to be weak ones. In the α form there are hydrogen bonds N(2)-H(4)···O(2) and N(4)-H(8)···O(6) within the chain, while in the β form NH_2 groups and oxygen atoms O(7) and O(8) form a hydrogen-bonding network along the edges of the chains.

The main structural difference between the two forms lies in the packing of the chains. In spite of the roughly equal geometry of the unit cells the orientation of the chains is different, as seen in Figures 2 and 3.[17] In the α form the chains are propagated along the *a* axis in the *ac* plane, whereas in the β form they are in the *ab* plane. The shortest U-U distances within the chains are 5.89 and 6.04 Å and between the chains 7.52 and 6.05 Å, for the α and β forms, respectively. The packing efficiency is slightly greater in the α form as the unit cell volume is 2.3% smaller.

Acknowledgments. We are grateful to Magnus Fagerström, M.Sc. (Eng.), for preparing the crystals used in this study. We also thank Dr. Risto Laitinen for useful discussions.

Note Added in Proof. It has recently come to our attention that Soldatkina et al. have reported their work concerning the structure of $UO_2SO_4 \cdot 2CO(NH_2)_2$ (the α form in this work). For the original reference, see: Soldatkina, M. A.; Serezhkin, V. N.; Trunov, V. K. *Zh. Strukt. Khim.* **1981**, *22*, 146.

Registry No. $UO_2SO_4 \cdot 2CO(NH_2)_2$, 80315-67-9.

Supplementary Material Available: Listings of thermal parameters, hydrogen atom coordinates, least-squares planes (Table IV), and observed and calculated structure factors and an illustration of the projections of the structures (Figure 3) (42 pages). Ordering information is given on any current masthead page.

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Metal-Metal Multiple Bonds. 12. Synthesis and Fluxional Behavior of $Cp_2MoW(CO)_4$[1]

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Received September 27, 1982

In contrast to the large number of heteronuclear dimers and clusters that contain metal-metal single bonds, there is a

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(17) Supplementary material.