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CRYSTAL CHEMICAL STUDIES OF CERTAIN URANYL SULFATE COMPOUNDS

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This report is preliminary and has not been edited or reviewed for conformity with Geological Survey standards and nomenclature.

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CRYSTAL CHEMICAL STUDIES OF CERTAIN URANYL SULFATE COMPOUNDS

By Malcolm Ross

ABSTRACT

Various uranyl sulfate compounds have been prepared by slow evaporation of aqueous solutions. Five compounds were synthesized: $K_2UO_2(SO_4)_2 \cdot 2H_2O$, $Rb_2UO_2(SO_4)_2 \cdot 2H_2O$, $(NH_4)_2UO_2(SO_4)_2 \cdot 3H_2O$, $Cs_2(UO_2)_2(SO_4)_3$, and an orthorhombic cesium uranyl sulfate (exact composition unknown). Unit cell, space group, chemical, and optical data are given for these compounds.

The crystal structure of $Cs_2(UO_2)_2(SO_4)_3$ has been determined by direct X-ray diffraction methods. The compound is tetragonal $P\bar{4}2_1m$-D_{2d}^3, $\underline{a} = 9.62 \pm 0.03$, $\underline{c} = 8.13 \pm 0.01$ A, Z = 2; sp. gr. (calc.) = 4.80, sp. gr. (obs.) = 4.74 ± 0.05. The compound forms plates parallel to (001) bounded by the form {110}. Intensity data were obtained from precession photographs of the hk0 and 0kℓ reciprocal lattice nets. No corrections for absorption were made. The coordinates of the U and Cs atoms were obtained by interpretation of the Patterson projections along [001] and [100]. Electron density projections along [001] and [100] yielded enough information to give a plausible structure. Subtraction of the heavy atoms yielded electron density projections along [001] and [100] in which most of the light atoms were resolved.

The compound has a layer structure consisting of $(UO_2)_{2n}(SO_4)_{3n}^{-2n}$ sheets parallel to (001), tied together by cesium atoms. The UO_2^{+2} ion is coordinated by five sulfate oxygens which form a nearly plane pentagon approximately normal to the axis of the uranyl ion. The Cs_1 atom is coordinated by 10 oxygens and the Cs_2 atom by 8 oxygens.

The reliability factor R is 13.7 percent for the hk0 reflections and 14.3 percent for the 0kℓ reflections. The coordinates of the atoms are: 4 U in (e), x = 0.306, y = 0.194, z = 0.864; 2 Cs_1 in (c), z = 0.631; 2 Cs_2 in (b); 4 S_1 in (e), x = 0.170, y = 0.330, z = 0.250; 2 S_2 in (a); 4 O_1 in (e), x = 0.218, y = 0.282, z = 0.702; 4 O_2 in (e), x = 0.394, y = 0.106, z = 0.026; 8 O_3 in (f), x = 0.032, y = 0.294, z = 0.310; 4 O_4 in (e), x = 0.170, y = 0.330, z = 0.071; 4 O_5 in (e), x = 0.271, y = 0.229, z = 0.310; 8 O_6 in (f), x = 0.078, y = 0.092, z = 0.876.

I. INTRODUCTION

The complex ions formed by hexavalent uranium in aqueous solution are now considered to play an important role in the transport and deposition of uranium in nature, as well as in the weathering of uraniferous ore bodies (13). Not the least important of these naturally occurring complexes are the uranyl sulfate compounds. The present investigation was undertaken in an effort to determine the crystal structure of one of the synthetic uranyl sulfate compounds. It was hoped that information concerning the coordination of the uranyl ion might cast some light upon the nature of the complex uranyl sulfate ion and its role in the transport of uranium (VI) in ground water. A secondary objective of this investigation was to synthesize various uranyl sulfate double salts for future crystallographic investigations.

Acknowledgments

I particularly wish to thank Howard T. Evans, Jr., U. S. Geological Survey, and George M. Brown, University of Maryland for their advice and interest in the problem. I also wish to thank the following U. S. Geological Survey colleagues: Daniel E. Appleman, who made the extensive computations needed for the solution of the crystal structure; Daphne R. Ross, who did the X-ray powder identifications; Clarence S. Ross, who determined the optical properties of the uranyl sulfate compounds; Blanche L. Ingram, who made the chemical analyses; and Katherine V. Hazel, who made the spectroscopic analysis.

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II. THE CHEMICAL AND GEOLOGIC BEHAVIOR OF HEXAVALENT URANIUM

A. General

Aqueous solutions containing hexavalent uranium are characterized by the presence of the uranyl ion, UO_2^{+2}, and by the tendency of the uranyl ion to form soluble complexes with a number of common anions.

Ahrland (1) has shown that the ionic species U^{+6} does not exist in aqueous solution. Hexavalent uranium, if present, is in the form of the uranyl ion (UO_2^{+2}) over a pH range from the most acid solutions up to pH 2.5. As the pH is increased, hydrolysis occurs, with the formation of complexes that were at first thought to be of the type $(UO_2)_2O$ or $(UO_2)_2(OH)_2$. The uranyl ion is regarded as a complex-forming central group, analogous to other metal ions in this respect. In a more recent paper (5) it is shown that in terms of newly-developed polynuclear complex theory, the most probable complexes have the formula $UO_2\text{-}(OH)_2UO_2\text{-}_n^{+2}$ or $UO_2(OUO_2)_n^{+2}$. The first form agrees better with structural data, which indicate that in crystals the complexes are probably sheet-like, with double (OH) bridges. When the pH is raised to the range of 4.5 to 5, insoluble uranate compounds are precipitated.

The theoretical model of the uranyl ion proposed by Connick and Hugus (10) consists of a dumbbell-shaped linear O-U-O group. In a zone perpendicular to the length of the uranyl group and bisecting the uranium atom, the uranyl ion appears as a highly charged cation. When viewed from the end of the dumbbell, the uranyl group appears as a weakly charged cation. This model is stated to give a much better agreement with observed entropy values than does a model consisting of a simple large bivalent cation.

Crystal-chemical studies of compounds of hexavalent uranium, summarized by Zachariasen (21), have shown that the uranyl ion is invariably present; and in all structures in which the shape of the uranyl ion has been directly determined, it is symmetrical and collinear. Zachariasen also establishes the fact that the length of the U-O bond varies with the coordination of the ion, and is observed to range from 2.08 Å to 1.76 Å.

B. Uranyl Sulfate Complexes

Ahrland (3) has found that in aqueous uranyl sulfate solutions at 20°C., three complexes formed. All appear to be mononuclear with one, two, and three sulfate groups, $[UO_2SO_4]$, $UO_2(SO_4)_2^{-2}$ and $UO_2(SO_4)_3^{-4}$. Stability constants show that these uranyl sulfate complexes, although considerably more stable than most uranyl complexes, are much less stable than the uranyl carbonate complexes. Appleman (6), from a crystal structure determination of johannite $[Cu(UO_2)_2(SO_4)_2(OH)_2 \cdot 6H_2O]$, shows that discrete uranyl sulfate ions are not present. The structure instead contains sheets of the type $[(UO_2)_2(SO_4)_2(OH)_2]_n^{-2n}$.

C. Other Uranyl Complexes

Dullwinkel (9) has found that in solutions containing excess HCO_3^- or CO_3^{-2}, a very stable anion complex is present with a carbonate-to-uranyl ratio of 3:1. This complex, $UO_2(CO_3)_3^{-4}$, is also found in aqueous solutions of compounds such as sodium uranyl tricarbonate. It does not dissociate into lower complexes and carbonate ion. A second uranyl carbonate complex, $UO_2(CO_3)_2(H_2O)_2^{-2}$, is stable in carbonate-deficient solutions. Equilibrium constants for the formation of various uranyl-containing complex ions show that the carbonate complexes are by far the most stable of the known mononuclear uranyl complexes.

The complexes of the uranyl ion with acetate and nitrate have been studied both in solution (2, 4) and in crystals (12, 14). The acetate complexes appear to be comparatively stable whereas the nitrate complexes are among the weakest known. Structurally, both complexes contain uranyl ions coordinated in a zone bisecting the O-U-O axis by six oxygen atoms from the acetate or nitrate groups. In sodium uranyl acetate, six acetate oxygens form a puckered ring around the uranyl ion. Rubidium uranyl nitrate contains uranyl ions coordinated by three coplanar nitrate groups, in a configuration very similar to the uranyl tricarbonate ion.

D. Geologic Implications

Garrels and Christ (13) have described the oxidation processes of the uranium minerals of the Colorado Plateau in some detail. The following discussion is based on their work.

The predominant U(IV) minerals occurring on the Colorado Plateau are uraninite (ideally UO_2) and coffinite [probably $U_2(SiO_4)_{2-x}(OH)_{4x}$]. It is believed that uraninite and coffinite slowly oxidize (by a solid state reaction) to U(VI), perhaps as amorphous UO_3. UO_3 is relatively unstable in pure water and will hydrolize to give various uranyl hydroxide hydrates [i.e. $UO_2(OH)_2 \cdot H_2O$, and $UO_2(OH)_2$]. If the ground water is high in HCO_3^- the U(VI) may complex as $[UO_2(CO_3)_3]^{-4}$ or $[UO_2(CO_3)_2(H_2O)_2]^{-2}$. These complexes are most stable at pH 6-8, and thus the nearly neutral ground water could be expected to be important for the transport of uranium.

Sulfate groups also form complexes with uranyl ions. Thus ground water containing sulfate ions may also be important in uranium transport.

If the uranyl ion is formed in the presence of the vanadate, phosphate, or arsenate ion very insoluble minerals such as carnotite $[K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O]$, tyuyamunite $[Ca(UO_2)_2(VO_4)_2 \cdot 7\text{-}10H_2O]$, autunite $[Ca(UO_2)_2(PO_4)_2 \cdot 10\text{-}12H_2O]$, and abernathyite $[KUO_2AsO_4 \cdot 4H_2O]$, may precipitate. All of these minerals have the same basic structure, consisting of sheets made up of a combination of uranyl ions and vanadate, phosphate, or arsenate ions, various metal ions, and water rather loosely bound between the sheets. The vanadate, arsenate, and phosphate ions are coordinated around the uranyl ion. Since the bonds within the layer are very strong, the sheets may develop indefinitely. This possibility of "infinite" sheets explains why the vanadates, phosphates, and arsenates are so slightly soluble, whereas the carbonates and sulfates, which contain finite groups, are so soluble.

III. PREVIOUS WORK ON URANYL SULFATE COMPOUNDS

A. Uranyl sulfates occurring naturally

A number of naturally occurring uranyl sulfates have been reported but only three at present appear to be well established. These are: johannite $[Cu(UO_2)_2(SO_4)_2(OH)_2 \cdot 6H_2O]$, uranopilite $[(UO_2)_6SO_4(OH)_{10} \cdot 12H_2O]$ and zippeite $[(UO_2)_2SO_4(OH)_2 \cdot 3H_2O?]$. The physical and crystallographic properties of these minerals are summarized in Table I.

Appleman (6) has worked out the structure of johannite by X-ray techniques. He finds that the uranyl ion is approximately parallel to (001) and perpendicular to (100) and is coordinated by three oxygen atoms from three different sulfate groups. One group is above, one below, and one at about the same level as the uranium atom. Each sulfate group shares oxygen atoms with three different uranyl ions. The endless double chains thus formed parallel to [001] are probably linked by $(OH)^-$ ions that are shared between two adjacent uranyl ions. The resulting structure consists of sheets with the composition $[(UO)_2(SO_4)_2(OH)_{2-n}]^{-2}$ parallel to (001), cross-linked by copper atoms which are bonded to the fourth sulfate oxygen. The coordination of the uranyl ion is probably five in this structure.

B. Synthetic Uranyl Sulfates

Traill (18) prepared a number of synthetic uranyl sulfates, the physical and crystallographic properties of which are summarized in Table II.

Dieke and Duncan (11) synthesized a large number of uranium compounds for spectroscopic analysis, including the following uranyl sulfates: $(NH_4)_2UO_2(SO_4)_2 \cdot 2H_2O$, $K_2UO_2(SO_4)_2 \cdot 2H_2O$, $(CH_2)_6N_4 \cdot H_2SO_4 \cdot 2H_2O$,

$Cs_2UO_2(SO_4)_2 \cdot 3H_2O$, $Rb_2UO_2(SO_4)_2 \cdot 2H_2O$, $K_2UO_2(SO_4)_2$ and $Tl_2UO_2(SO_4)_2$. Unfortunately no physical properties are given for the above compounds (except for fluorescence spectra).

Nichols and Howes (16) published a detailed description of fluorescence in uranyl salts which was the standard work on this subject until the work of Dieke and Duncan (11). Nichols and Howes sythesized a number of uranyl sulfates for their work. These include: $UO_2SO_4 \cdot 3H_2O$, $(NH_4)_2UO_2(SO_4)_2 \cdot 2H_2O$, $Na_2UO_2(SO_4)_2 \cdot 2H_2O$, $K_2UO_2(SO_4)_2 \cdot 2H_2O$, $Rb_2UO_2(SO_4)_2 \cdot 2H_2O$, $Cs_2UO_2(SO_4)_2 \cdot 2H_2O$ and $Tl_2UO_2(SO_4)_2 \cdot 3H_2O$. Some crystallographic data are given for a few of these compounds.

Table I. Physical Properties, Chemical Formulas and Crystallographic Data of the Uranyl Sulfate Minerals.

Mineral	Johannite	Uranopilite	Zippeite
Chemical formula	$Cu(UO_2)_2(SO_4)_2(OH)_2 \cdot 6H_2O$	$(UO_2)_6SO_4(OH)_{10} \cdot 12H_2O$	$(UO_2)_2SO_4(OH)_2 \cdot 3H_2O$?
Crystallography	Triclinic, $P\bar{1}$ $a_o = 8.91$ Å, $b_o = 9.51$ Å, $c_o = 6.81$ Å; $\alpha = 109°49'$ $\beta = 112°07'$, $\gamma = 100°26'$ $Z = 1$	Monoclinic ?	Orthorhombic ?
Specific gravity	3.31 calc., 3.32 obs.	3.96 obs.	
Cleavage	{100} good	{010} perfect or good	Probably a perfect cleavage on {010}
Hardness	2-2.5	low	
Habit	Prismatic [001] and thick tabular {100}	Elongated laths; needles [001], flattened {010}. Fine fibrous clusters; felted aggregates, crusts.	Crystals flattened {010} and usually are spindle or lens-shaped, sometimes rhombohedral or lath-like.

Table II. Physical and Crystallographic Properties of Synthetic Uranyl Sulfates (Traill)

Compound	V	W	Y	Z
Cell Contents	$4[(NH_4)_2UO_2(SO_4)_2 \cdot 2H_2O]$	$8[UO_2SO_4 \cdot 3H_2O]$	$4[H_2(UO_2)_2(SO_4)_3 \cdot 5H_2O]$	$4[K_2UO_2(SO_4)_2 \cdot 2H_2O]$
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic
Space Group	$P2_1/n$	Pbnm	Pnnm	Pcnb
Unit cell dimensions a_o	20.53 Å	12.58 Å	12.86 Å	11.55 Å
b_o	7.30	17.00	12.99	13.78
c_o	7.74	16.73	11.57	7.28
β	99°25'	-	-	-
Specific gravity (meas.)	3.07	3.84	-	3.33
Specific gravity(calc.)	3.10	3.88	3.16	3.31
Indices of refraction α	n.d.	1.574	1.555	n.d.
β	1.555	1.589	1.586	1.529
γ	1.600	1.593	1.586	1.575
Pleochroism x	Colorless	Colorless	Colorless	Not Pleochroic
Y	Colorless	Pale green	Pale yellow	
Z	Pale green	Greyish green	Pale yellow	
Optical orientation		Z = c	Z = c	

IV. SYNTHESIS OF URANYL SULFATES

In this investigation an attempt was made to crystallise from solution, by evaporation, uranyl sulfate double salts containing the following cations: K^{+}, Li^{+}, Zn^{++}, Na^{+}, Ni^{++}, Cu^{++}, Fe^{++}, Mg^{++}, Al^{+3}, NH_4^{+}, Cd^{++}, Zr^{+4}, VO^{++}, Ce^{+4}, Mn^{++}, Cs^{+}, and Rb^{+}. In all cases uranyl sulfate was dissolved in hot distilled water to which the soluble sulfate of the cation was added. Table III gives a summary of the various solutions prepared and the results obtained. In those cases where good crystals were obtained the experiment was repeated to be sure the results could be duplicated.

The solutions were allowed to cool in 50 ml. beakers. Watch glasses were used to protect the solutions from dust particles which might act as nuclei. The solutions were allowed to stand for a period of several weeks or until crystallisation occurred. In many cases the solutions became gels after several weeks of slow evaporation. Although crystals were obtained in many of the experiments, only a few were suitable for X-ray analysis. Such crystals should have dimensions of 0.01 to 0.3 mm. and be free of intergrowths, satellites, and so forth.

The experiments listed in Table III yielded crystals of five different compounds which were suitable for X-ray analysis. These are: $K_2UO_2(SO_4)_2 \cdot 2H_2O$, $(NH_4)_2UO_2(SO_4)_2 \cdot 3H_2O$, $Rb_2UO_2(SO_4)_2 \cdot 2H_2O$, tetragonal $Cs_2(UO_2)_2(SO_4)_3$, and an orthorhombic cesium uranyl phosphate of possible composition $Cs_2(UO_2)_2(SO_4)_3$. The chemical compositions of all but the last-mentioned compound were verified by chemical analysis (Table IV, Blanche L. Ingram, Analyst). The potassium and ammonium uranyl sulfates have been previously described by Traill (18). The

identification of the potassium and ammonium compounds was made on the basis of X-ray powder patterns and chemical analyses. Table V gives a summary of the data obtained on the five compounds.

Only a very small amount of the orthorhombic cesium uranyl sulfate was made (20 mg.). Repeated experiments yielded only the tetragonal cesium uranyl sulfate $Cs_2(UO_2)_2(SO_4)_3$. Spectroscopic analysis of the orthorhombic form showed that cesium and uranium are major constituents in the compound (Katherine V. Hasel, Analyst). No specific gravity could be obtained on the very small crystals obtained. X-ray data indicate that the unit cell volume of the orthorhombic cesium uranyl sulfate is almost exactly twice that of the tetragonal cesium uranyl sulfate. This might indicate that the orthorhombic form has twice the matter per unit cell as does the tetragonal form. The formula $Cs_2(UO_2)_2(SO_4)_3$ with $Z=4$ is therefore tentatively proposed for the orthorhombic form.

Chemical analysis (Table IV) shows that the tetragonal cesium uranyl sulfate has the composition $Cs_2(UO_2)_2(SO_4)_3$ which is apparently a new compound not previously described. A complete X-ray structure analysis has verified this formula.

Table III. Summary of Syntheses of Various Uranyl Sulfate Double Salts

Ref. No.	Materials Used		Results Obtained
R-1A	$UO_2SO_4 \cdot 3H_2O$	2.2 g.	Exceptionally large crystals of an unknown phase formed.
	K_2SO_4	1.0 g.	
	H_2O	20 ml.	
R-1B	Same as R-1A		Small cyrstals identical to Traill's compound Z $[K_2UO_2(SO_4)_2 \cdot 2H_2O]$
R-2	$UO_2SO_4 \cdot 3H_2O$	4.0 g.	No crystallization
	$Li_2SO_4 \cdot H_2O$	1.2 g.	
	H_2O	15 ml.	
R-3	$UO_2SO_4 \cdot 3H_2O$	2.0 g.	No crystallization
	$ZnSO_4 \cdot 7H_2O$	1.4 g.	
	H_2O	12 ml.	
R-4	$UO_2SO_4 \cdot 3H_2O$	2.0 g.	Material crystallized as minute needles.
	Na_2SO_4	0.7 g.	
	H_2O	12 ml.	
R-5	$UO_2SO_4 \cdot 3H_2O$	2.0 g.	No crystallization
	$NiSO_4 \cdot 6H_2O$	1.2 g.	
	H_2O	12 ml.	
R-6	$UO_2SO_4 \cdot 3H_2O$	2.0 g.	Large blue crystals formed having a rhombohedral habit.
	$CuSO_4 \cdot 5H_2O$	1.2 g.	
	H_2O	12 ml.	
R-7	$UO_2SO_4 \cdot 3H_2O$	2.0 g.	No crystallization
	$FeSO_4 \cdot 7H_2O$	1.3 g.	
	H_2O	12 ml.	
R-8	$UO_2SO_4 \cdot 3H_2O$	2.0 g.	No crystallization
	$MgSO_4 \cdot nH_2O$	1.0 g.	
	H_2O	12 ml.	
R-9	$UO_2SO_4 \cdot 3H_2O$	2.0 g.	No crystallization
	$Al_2(SO_4)_3 \cdot 18\ H_2O$	3.1 g.	
	H_2O	12 ml.	

Table III. Continued

Ref. No.	Materials Used		Results Obtained
R-10	$UO_2SO_4 \cdot 3H_2O$ $(NH_4)_2SO_4$ H_2O	2.0 g. 0.6 g. 12 ml.	Excellent crystals identical to Traill's compound V $[(NH_4)_2UO_2(SO_4)_2 \cdot 3H_2O]$
R-11	$UO_2SO_4 \cdot 3H_2O$ $3CdSO_4 \cdot 8H_2O$ H_2O	2.0 g. 1.2 g. 12 ml.	Large aggregates of crystals formed, yellow-green in color
R-12	$UO_2SO_4 \cdot 3H_2O$ $Zr(SO_4)_2 \cdot 4H_2O$ H_2O	1.0 g. 0.8 g. 12 ml.	No crystallisation
R-14	$UO_2SO_4 \cdot 3H_2O$ K_2SO_4 H_2O H_2SO_4	2.0 g. 2.0 g. 12 ml. 1 drop	Excellent crystals formed - identical to Traill's compound Z $[K_2UO_2(SO_4)_2 \cdot 2H_2O]$
R-15	$UO_2SO_4 \cdot 3H_2O$ K_2SO_4 H_2O	2.0 g. 1.0 g. 10 ml.	Two phases crystallised, one identical to Traill's compound Z, the other identical to crystals obtained in experiment R-14.
R-18	$UO_2SO_4 \cdot 3H_2O$ K_2SO_4 H_2O	2.0 g. 1.0 g. 10 ml.	Crystals formed identical to Traill's compound Z $[K_2UO_2(SO_4)_2 \cdot 2H_2O]$
R-19	$UO_2SO_4 \cdot 3H_2O$ Na_2SO_4 H_2O	2.0 g. 1.0 g. 10 ml.	Material crystallised as minute needles (same as R-4?)
R-20	Same as R-18		Same as R-18
R-21	Same as R-18		Same as R-18
R-22	$UO_2SO_4 \cdot 3H_2O$ $Li_2SO_4 \cdot H_2O$ H_2O	2.0 g. 0.6 g. 10 ml.	No crystallisation

Table III. Continued

Ref. No.	Materials Used		Results Obtained
R-23	$UO_2SO_4 \cdot 3H_2O$	2.0 g.	No crystallization
	$3CdSO_4 \cdot 8H_2O$	1.2 g.	
	H_2O	10 ml.	
R-24	$UO_2SO_4 \cdot 3H_2O$	2.0 g.	No crystallization
	$VOSO_4 \cdot 2H_2O$	1.0 g.	
	H_2O	10 ml.	
R-25	$UO_2SO_4 \cdot 3H_2O$	2.0 g.	No crystallization
	$CuSO_4 \cdot 5H_2O$	1.2 g.	
	H_2O	10 ml.	
R-26	$UO_2SO_4 \cdot 3H_2O$	2.0 g.	No crystallization
	$HgSO_4 \cdot nH_2O$	1.0 g.	
	H_2O	10 ml.	
R-27	$UO_2SO_4 \cdot 3H_2O$	2.0 g.	No crystallization
	$ZnSO_4 \cdot 7H_2O$	1.4 g.	
	H_2O	10 ml.	
R-28	$UO_2SO_4 \cdot 3H_2O$	2.0 g.	No crystallization
	$Al_2(SO_4)_3 \cdot 18H_2O$	2.0 g.	
	H_2O	10 ml.	
R-29	$UO_2SO_4 \cdot 3H_2O$	2.0 g.	No crystallization
	$Ce(SO_4)_2$	1.0 g.	
	H_2O	10 ml.	
R-30	Same as R-10		Same as R-10
R-31	Same as R-10		Same as R-10
R-32	$UO_2SO_4 \cdot 3H_2O$	2.0 g.	No crystallization
	$MnSO_4 \cdot H_2O$	1.0 g.	
	H_2O	10 ml.	

Table III. Continued

Ref. No.	Materials Used		Results Obtained
R-33	$UO_2SO_4 \cdot 3H_2O$ Na_2SO_4 H_2O	2.0 g. 6.2 g. 10 ml.	No crystallisation
R-34	$UO_2SO_4 \cdot 3H_2O$ K_2SO_4 H_2O	2.0 g. 6.0 g. 10 ml.	Two or more phases crystallised
R-35	Same as R-10		Same as R-10
R-36	Same as R-10		Same as R-10
R-37,38, 39,44	$UO_2SO_4 \cdot 3H_2O$ Rb_2SO_4 H_2O	2.0 g. 1.2 g. 10 ml.	Excellent crystals obtained; yellow-green in color $[Rb_2UO_2(SO_4)_2 \cdot 2H_2O]$
R-40	$UO_2SO_4 \cdot 3H_2O$ Cs_2SO_4 H_2O	1.0 g. 0.8 g. 20 ml.	Two phases appeared; one (I) as minute yellow-green prisms; the other (II) as minute yellow-green plates.
R-41,42, 43,45, 46	Same as R-40		Phase (II) of R-40 appeared $[Cs_2(UO_2)_2(SO_4)_3]$
R-47,49	$UO_2SO_4 \cdot 3H_2O$ Cs_2SO_4 H_2O	0.5 g. 1.0 g. 20 ml.	Phase (II) of R-40 appeared
R-48	$UO_2SO_4 \cdot 3H_2O$ Cs_2SO_4 H_2O	1.0 g. 0.4 g. 20 ml.	Phase (II) of R-40 appeared

Table IV. Chemical Analyses of Synthetic Uranyl Sulfates.

(Blanche L. Ingram, Analyst, U. S. Geological Survey)

Sample No.	R-20, 21		R-37,38, 39		R-30,35,36		R-45	
Constituent	%	Ratio	%	Ratio	%	Ratio	%	Ratio
K_2O	16.4	1.0	---	---	---	---	---	---
Rb_2O	---	---	28.3	1.0	---	---	---	---
NH_3	---	---	---	---	6.4	2.1	---	---
UO_3	49.7	1.0	42.9	1.0	53.8	1.0	51.9	2.0
SO_3	28.3	2.0	24.5	2.0	30.1	2.0	21.9	3.0
H_2O	6.3	2.0	5.3	1.9	9.7	2.9	<.05	---
Cs_2O	---	---	---	---	---	---	25.9	1.0
Total	100.7		100.9		100.0		99.7	

NOTES

a. For the potassium, rubidium and ammonium compounds 25 mg. samples were dissolved and the uranium was precipitated with NH_4OH. The rubidium and potassium in the filtrates were determined gravimetrically after conversion to sulfates.

b. Ammonia was determined by the micro-Kjeldahl procedure on a 25 mg. sample.

c. Except for sample R-45, uranium was determined spectrophotometrically using thiocyanate in an acetone-water medium. 100 mg. samples were dissolved and diluted to a definite volume. Aliquots of these solutions were used for the uranium and sulfur trioxide determinations.

d. The sulfur trioxide was determined gravimetrically be precipitating sulfate as $BaSO_4$.

Table IV. Notes, Continued

e. Water in the potassium, rubidium and cesium samples was determined by use of a modified microcombustion train of the type used for the determination of carbon and hydrogen in organic compounds. The samples were decomposed by ignition at 900°C in a stream of oxygen. Sample size was approximately 80 mg. The water in the ammonium sample was determined by obtaining an ignition loss. The loss due to NH_3, SO_3, and conversion of UO_3 to U_3O_8 as a result of the ignition, was calculated from the values for those determinations. The difference of the two values represents the loss due to H_2O. Sample size was approximately 50 mg.

f. Approximately 50 mg. of the cesium sample was dissolved in HCl. The uranium was precipitated with NH_4OH and ignited and weighed as U_3O_8. Cesium was determined in the filtrate by conversion to Cs_2SO_4. A twenty-five mg. sample was dissolved in HCl. The solution was passed through a cation exchange resin to remove U and Cs. The sulfate was precipitated and weighed as $BaSO_4$.

Table V. Summary of the Uranyl Sulfate Compounds*

Compound	$K_2UO_2(SO_4)_2 \cdot 2H_2O$	$(NH_4)_2UO_2(SO_4)_2 \cdot 3H_2O$	$Rb_2UO_2(SO_4)_2 \cdot 2H_2O$	$Cs_2(UO_2)_2(SO_4)_3$	$Ca_2(UO_2)_2(SO_4)_3$?
Z No.	4	4	4	2	4 ?
Specific gravity (Calc.)	3.31	n.d.	3.87	4.80	4.80 ?
(Measured)**	3.26	3.08	3.82	4.74	n.d.
Crystal system	Orthorhombic	n.d.	Orthorhombic	Tetragonal	Orthorhombic
Space group	$Pmnb-D_{2h}^{16}$ or $P2_1nb-C_{2v}^{9}$	n.d.	$Pbnm-D_{2h}^{16}$ or $Pbn2_1-C_{2v}^{9}$	$P\bar{4}2_1m-D_{2d}^{3}$	$Pcnm-D_{2h}^{16}$ or $Pc2_1n-C_{2v}^{9}$
Unit cell dimensions a_o	11.55 Å	n.d.	11.50 Å	9.62 Å	12.62 Å
b_o	13.76		13.48	-	13.29
c_o	7.27		7.42	8.13	9.24
Indices of refraction α	1.528	n.d.	1.568	1.643	1.582
β	1.540		1.572	-	1.617
γ	1.571		1.605	1.615	1.627
B	0.043		0.037	-	0.045
Pleochroism X	light golden	n.d.	golden yellow	light yellow	golden yellow
Y	almost colorless		almost colorless	-	paler yellow
Z	light yellow		-	n.d.	
2V(axial angle)	60°	n.d.	60°	-	40°
Extinction	parallel	n.d.	parallel	parallel	parallel
Dispersion	r > v, strong	n.d.	r < v, strong	-	not observed
Habit	Prismatic	Thin tablets	Thin tablets flattened on {010} with {110}	Tablets flattened on {001} with {110}	Prismatic

* Optical properties were determined by C. S. Ross, U. S. Geological Survey.
** Specific gravity was determined with a Berman balance on about 20 mg. of material.

V. X-RAY CRYSTALLOGRAPHY

A. General

The unit cell and space group were determined for the potassium, rubidium and both cesium uranyl sulfates. The Buerger precession camera and molybdenum radiation was used for all work.

The various uranyl sulfates were mounted with shellac on the tips of glass fibers. The fiber was then mounted on a goniometer head. A principal zone axis of the crystal was brought into alignment with the goniometer axis by means of a two circle optical goniometer. The goniometer head was then transferred to the precession camera for the final orientation and photography. In all cases the crystals were chosen so that their largest dimension was not greater than 0.5 mm.

B. Potassium Uranyl Sulfate $K_2UO_2(SO_4)_2 \cdot 2H_2O$

From the precession photographs, the following unit cell was obtained:

$a_o = 11.55 \pm 0.01$ Å
$b_o = 13.76 \pm 0.02$
$c_o = 7.27 \pm 0.01$
Crystal system - orthorhombic

The $hk0$, $h0\ell$, $h1\ell$, $0k\ell$, and $1k\ell$ reciprocal lattice nets were photographed. The following conditions for presence of reflections were observed:

$hk0$: $k = 2n$
$h0\ell$: $h+\ell = 2n$

These conditions fix the space group as either $Pnnb\text{-}C_{2h}^{16}$ or $P2_1nb\text{-}C_{2v}^{9}$. The above data agree with those of Traill (18).

C. Rubidium Uranyl Sulfate $Rb_2UO_2(SO_4)_2 \cdot 2H_2O$

The following unit cell data were found for this compound:

$a_o = 11.50 \pm 0.02$ Å
$b_o = 13.48 \pm 0.01$
$c_o = 7.42 \pm 0.01$
Crystal system - orthorhombic

The hk0, h0ℓ, h1ℓ, 0kℓ, 1kℓ and 2kℓ reciprocal lattice nets were photographed. The following conditions for reflections were observed:

$$h0\ell: \; h+\ell = 2n$$
$$0k\ell: \; k = 2n$$

These conditions fix the space group as either $Pbam\text{-}D_{2h}^{16}$ or $Pbn2_1\text{-}C_{2v}^{9}$. Photographs of the hk0, 1kℓ and 2kℓ reciprocal lattice nets show spots which are streaked parallel to b^* indicating a disordered structure in the b direction. The rubidium crystals develop as very thin tablets on {010}. This would suggest a sheet structure in which the sheets extend infinitely in the a and c directions. The streaked photographs probably indicate that there is a disorder in stacking of the sheets. Because of this disorder the compound was not considered suitable for crystal structure analysis.

D. Tetragonal Cesium Uranyl Sulfate $[Cs_2(UO_2)_2(SO_4)_3]$

The following unit cell data were obtained:

$$a_o = 9.62 \pm 0.03 \text{ Å}$$
$$c_o = 8.13 \pm 0.01$$
Crystal system - tetragonal

The hk0, hkℓ, 0kℓ, 1kℓ and hhℓ reciprocal lattice nets were photographed. The only condition for presence of reflections is:

$$h00: \; h = 2n$$

This condition fixes the space group as either $P\bar{4}2_1m\text{-}D_{2d}^{3}$ or $P4_12_12\text{-}D_4^2$.

E. Orthorhombic Cesium Uranyl Sulfate $[Cs_2(UO_2)_2(SO_4)_3]$

Although a chemical analysis could not be obtained on this material, it was thought that crystallographic information would be useful and possibly a structure analysis might be accomplished without quantitative chemical data. Spectroscopic analysis shows major U and Cs in this compound.

The following unit cell data were found for this compound:

$a_o = 12.62 \pm 0.02$ Å
$b_o = 13.29 \pm 0.02$
$c_o = 9.24 \pm 0.02$
Crystal system - orthorhombic

The hk0, hk1, h0ℓ, h1ℓ, 0kℓ and 1kℓ reciprocal lattice nets were photographed. The following conditions for reflections were observed:

hk0: $h + k = 2n$
0kℓ: $\ell = 2n$

These conditions fix the space group as either Pcnn-D_{2h}^{16} or $Pc2_1n$-C_{2v}^{2}. Table V gives a summary of the X-ray data collected for these compounds.

VI. THE CRYSTAL STRUCTURE OF TETRAGONAL CESIUM URANYL SULFATE $[Cs_2(UO_2)_2(SO_4)_3]$

A. Experimental Work

It was hoped that material could be found which could be ground into spheres so that absorption errors could be minimized. None of the uranyl sulfate crystals, however, could be ground without being cleaved into thin plates. The linear absorption coefficient (μ) of this material is 376 cm.$^{-1}$ for $\lambda = 0.7107$ Å.

Crystal structure studies were started on $K_2UO_2(SO_4)_2 \cdot 2H_2O$, orthorhombic cesium uranyl sulfate, and tetragonal $Cs_2(UO_2)_2(SO_4)_3$. Only the structure of the latter compound will be treated in this thesis.

The tetragonal $Cs_2(UO_2)_2(SO_4)_3$ crystals grew as thin plates on {001}. The only other form appearing is {110}. The size of the crystal chosen for X-ray study was approximately 0.01 mm. thick and 0.1 mm. on edge. Intensity data were gathered for $hk0$ and $0k\ell$ reciprocal lattice nets with a Buerger precession camera. A μ setting of 30° was used for all photographs. The $hk0$ nets were photographed with zirconium-filtered molybdenum radiation with exposures of 103, 23, 5, 2, and 1 hour. For the $0k\ell$ reflections, films were exposed for 62, 41, 31, 16 and 8 hours. The 41 hour exposure was obtained with unfiltered molybdenum radiation; the rest were obtained using zirconium-filtered molybdenum radiation. The intensities were estimated visually with a calibrated intensity strip prepared with a precession camera. The controlled exposures on the intensity strip were made so that the intensity of the nth spot is given by $I_n = I_0(2)^{n/2}$, where I_0 corresponds to a barely perceptible blackening of the film.

The films of each zone were scaled together by finding the average spot number difference between two films. The average spot difference was added to each spot number of the film of shorter exposure. In this way all film spot numbers were brought up to those of the film having the largest exposure. The spot numbers of all films of a zone were then averaged. The average spot numbers were then converted to intensities (relative exposure times).

Lorentz and polarization corrections were made as a 1/LP correction, using a transparent overlay based on the Waser charts (19). This overlay is contoured in terms of 1/LP corrections and fits over the precession photograph. The 1/LP corrections are read directly by observing on which contour each spot falls.

The intensities of each zone were converted to F^2 by multiplying by 1/LP. No absorption corrections were made. 71 non-equivalent hk0 reflections and 119 non-equivalent 0kl reflections were measured.

B. Solution of the Structure

The space group of tetragonal $Cs_2(UO_2)_2(SO_4)_3$, as already discussed, was found to be either $P\bar{4}2_12\text{-}D_4^2$ or $P\bar{4}2_1m\text{-}D_{2d}^3$. The equivalent positions and conditions limiting possible reflections of these space groups are tabulated in Table VI. Careful examination of the hk0 and 0kl reflections showed no evidence that the heavy uranium atoms are in positions that impose special conditions on the reflections. For example, if the four uranium atoms are in any of the special 4-fold or 2-fold positions of the space group $P4_12_12\text{-}D_4^2$ (No. 90, Table VI) those reflections in which h + k is odd or k is odd might be expected to be weak in comparison to the other reflections. The space group $P\bar{4}2_1m\text{-}D_{2d}^3$ (No. 113, Table VI) on the other

Table VI. Equivalent Positions and Conditions Limiting Possible Reflections of Space Groups $Ph2_12$-D_2^1 and $P\bar{4}2_1m$-D_{2d}^3*

$Ph2_12$ (No. 90)		$P\bar{4}2_1m$ (No. 113)	
No. of Pos.	Conditions	No. of Pos.	Conditions
8 g (general)	hOO: h = 2n (general)	8 f (general)	hOO: h = 2n (general
4 f	Okℓ: k = 2n	4 e	no extra conditions
4 e	Okℓ: k = 2n	4 d	hkℓ: h + k = 2n
4 d	hkℓ: h + k = 2n	2 c	hkO: h + k = 2n
2 c	hkO: h + k = 2n	2 b	hkℓ: h + k = 2n
2 b	hkℓ: h + k = 2n	2 a	hkℓ: h + k = 2n
2 a	hkℓ: h + k = 2n		

* From pages 180 and 203 of International Tables for X-ray Crystallography (15).

hand has a 4-fold position (4e) that imposes no extra conditions on the reflections. For these reasons space group No. 113 was thought to be the most probable one for $Cs_2(UO_2)_2(SO_4)_3$. The solution of the structure has verified this assumption.

To locate the four uranium atoms and possibly the four cesium atoms, Patterson projections were made on (001) and (100). These two projections are shown in Figures I and II respectively. For the Patterson map on (001), it was assumed, to start, that the four uranium atoms were in positions 4e (Table VI). Uranium-uranium interactions for such positions correspond to peaks No. 1 in Figure I. The cesium-cesium and cesium-uranium interactions were identified by assuming that the four cesium atoms were in 2-fold positions (positions 2c and 2b, Table VI). By placing the heavy atoms in these special positions the peaks in Figure I may be identified as follows:

peaks No. 1 - Uranium-uranium interactions
peaks No. 2 - Cesium(1)-uranium interactions
peaks No. 3 - Cesium(2)-uranium interactions
peaks No. 4 - Cesium-cesium interactions

These peak assignments are based on the following coordinates for the heavy atoms:

4U in 4e at $x = 0.31$, $y = 0.19$
$2Cs_1$ in 2c at $x = 1/2$, $y = 0$
$2Cs_2$ in 2b at $x = 0$, $y = 0$

The relative expected and experimental peak heights in this projection are in agreement.

The Patterson projection on (100) is readily interpreted by assuming peaks No. 1 (Figure II) are uranium-uranium interactions. Peaks No. 2 are then cesium(1)-uranium interactions; peaks No. 3 are cesium(2)-uranium interactions. The cesium-cesium interactions in Figure II are not well-resolved except for the peak at $y = 0$, $z = 0.14$. These peak assignments

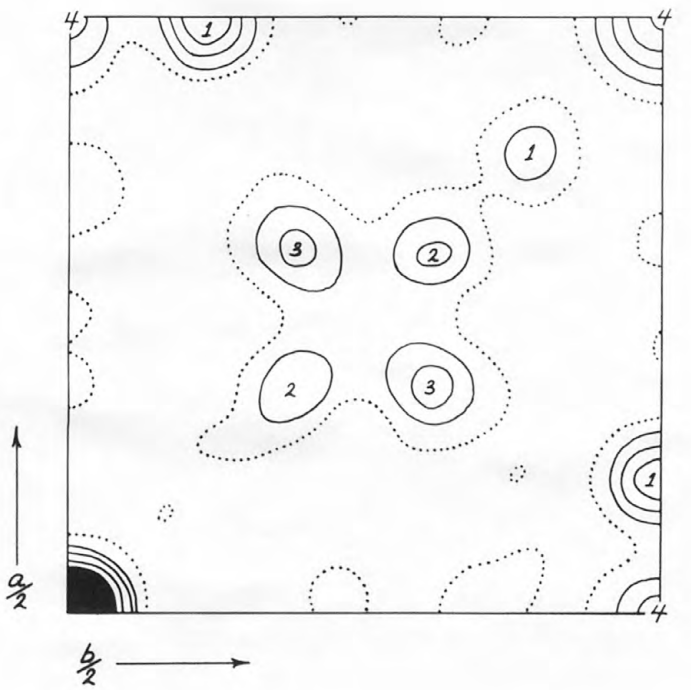

Figure I: Patterson projection of $Cs_2(UO_2)_2(SO_4)_3$ on (001).

Peaks No. 1, uranium-uranium interactions.
Peaks No. 2, uranium-cesium(1) interactions.
Peaks No. 3, uranium-cesium(2) interactions.
Peaks No. 4, cesium-cesium interactions.

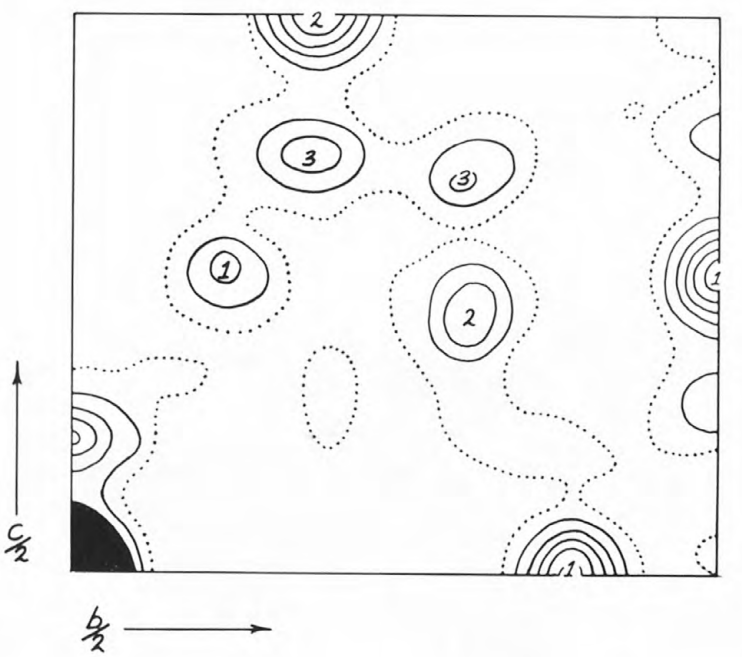

Figure II. Patterson projection of $Cs_2(UO_2)_2(SO_4)_3$ on (100).

Peaks No. 1, uranium-uranium interactions.
Peaks No. 2, uranium-cesium(1) interactions.
Peaks No. 3, uranium-cesium(2) interactions.

are based on the following coordinates for the heavy atoms:

$4U$ in 4e at $y = 0.19$ $z = 0.86$
$2Cs_1$ in 2a at $y = 0$ $z = 0.37$
$2Cs_2$ in 2b at $y = 0$ $z = 1/2$

Except for the cesium-cesium interactions the expected and experimental peak heights are in agreement.

Structures belonging to space group No. 113 are non-centrosymmetric; thus the phases of the $hk\ell$ structure factors are complex. The phases of the $hk0$ and $0k\ell$ structure factors for this space group are real or complex depending on the origin chosen for the unit-cell. If the origin given in the International Tables for X-ray Crystallography (15, p. 203) is used, the $hk0$ structure factors are real and the $0k\ell$ structure factors are complex (Appendix). If, however, the origin given in the International Tables is moved $1/4$ along the y axis the phases of the $0k\ell$ structure factors become real (Appendix). With the proper choice of origins the computation of signs of the $hk0$ and $0k\ell$ structure factors is straightforward.

Signs were calculated for 61 $hk0$ reflections and 88 $0k\ell$ reflections on the basis of the heavy atom positions given above. Fourier projections on (001) and (100) confirm the positions of the heavy atoms given by the Patterson maps and also resolve the sulfur atoms and a number of oxygen atoms. A model was then made of the structure and tentative positions assigned to all atoms.

On the basis of the positions of all the atoms (as obtained from the preliminary Fourier maps and from the model) structure factors were calculated (F_c). The temperature and scaling factors (B and k respectively) were found by the method of least squares. The two factors were refined together to obtain the best fit. For $hk0$ zone $B = 1.03$ Å^2; for the $0k\ell$ zone $B = 0.85$ Å^2.

The contribution of the uranium and cesium atoms (F_h) to the structure factors was calculated and then subtracted from kF_o. Subtraction syntheses of the form

$$P(x,y) = \frac{c}{V} \sum_h \sum_k (kF_o - F_h) \exp \left\{-2\pi i (hx + ky)\right\}$$

were made on (001) and (100). These subtraction maps are shown in Figures III and IV respectively. These maps yield the positions of most of the light atoms. A few of the light atoms were obscured by overlapping of peaks. The positions of the obscured atoms were evaluated by geometrical considerations. The subtraction maps contained residual peaks at the uranium positions and also showed considerable evidence for a large temperature motion at the cesium(?) positions. Since these residual peaks did not interfere with the interpretation of the structure, no attempt was made to adjust the scattering curve of uranium or to introduce special temperature factors for the cesium atoms.

A new model for the structure was obtained on the basis of these subtraction syntheses and signs were calculated for all observed $hk0$ and $0k\ell$ reflections. The contributions of all the atoms in the unit-cell were used to calculate the signs. Using these signs, Fourier projections on (001) and (100) were again calculated. (Figures V and VI respectively). Most of the atoms are resolved in these final Fourier projections, although the light atoms are generally more distorted than in the subtraction maps.

The atomic coordinates of all the atoms are given in Table VII. Most of the light atom positions were obtained from the subtraction maps. The heavy atom positions were obtained from the final Fourier projections (Figures V and VI).

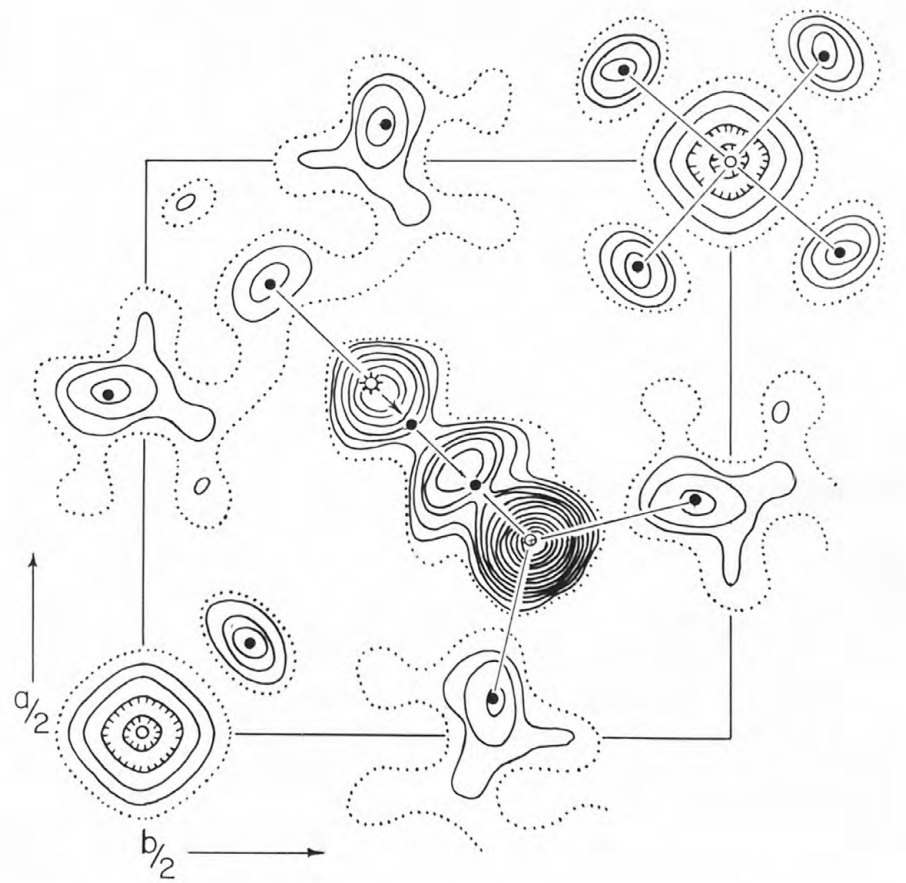

Figure III. Subtraction Fourier projection of $Cs_2(UO_2)_2(SO_4)_3$ on (001).

Open circles - sulfur atoms.
Solid circles - oxygen atoms.
"Spoked wheels" - uranium atoms (subtracted).

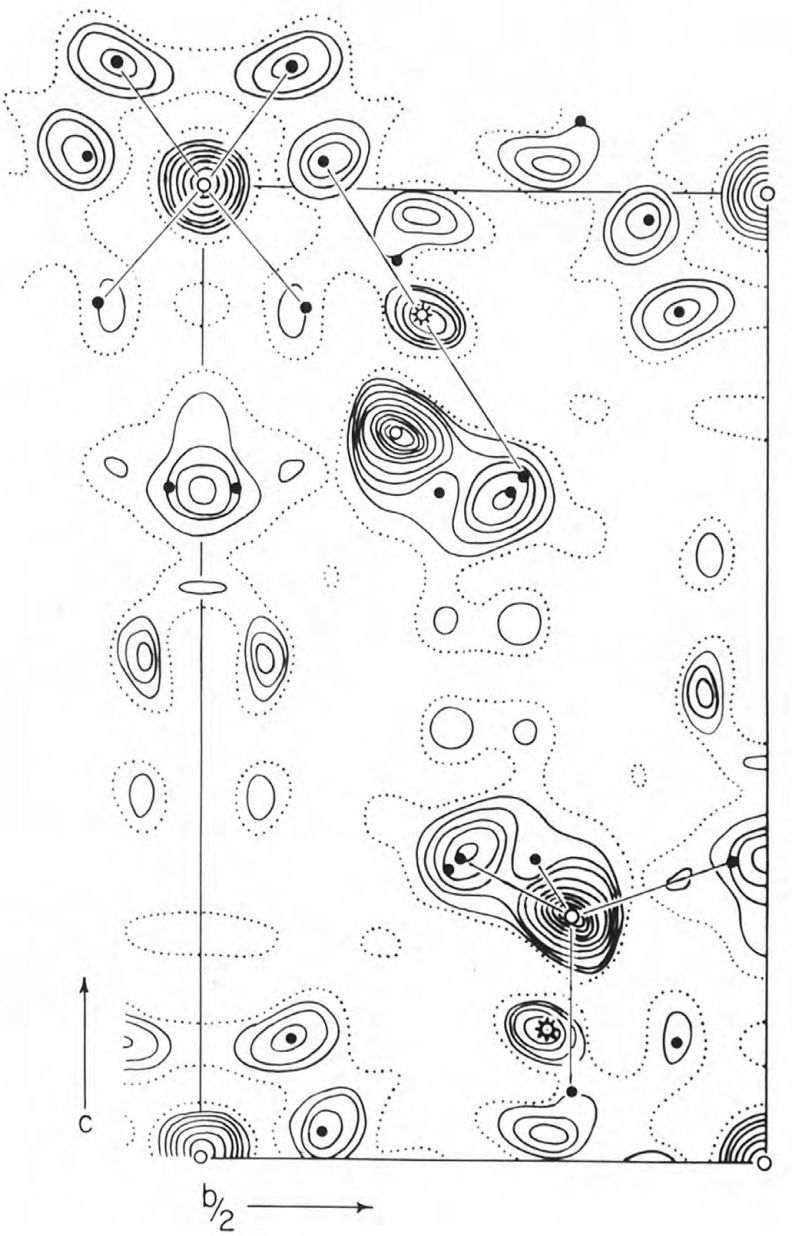

Figure IV. Subtraction Fourier projection of $Cs_2(UO_2)_2(SO_4)_3$ on (100).

Open circles - sulfur atoms.
Solid circles - oxygen atoms.
"Spoked wheels" - uranium atoms (subtracted).

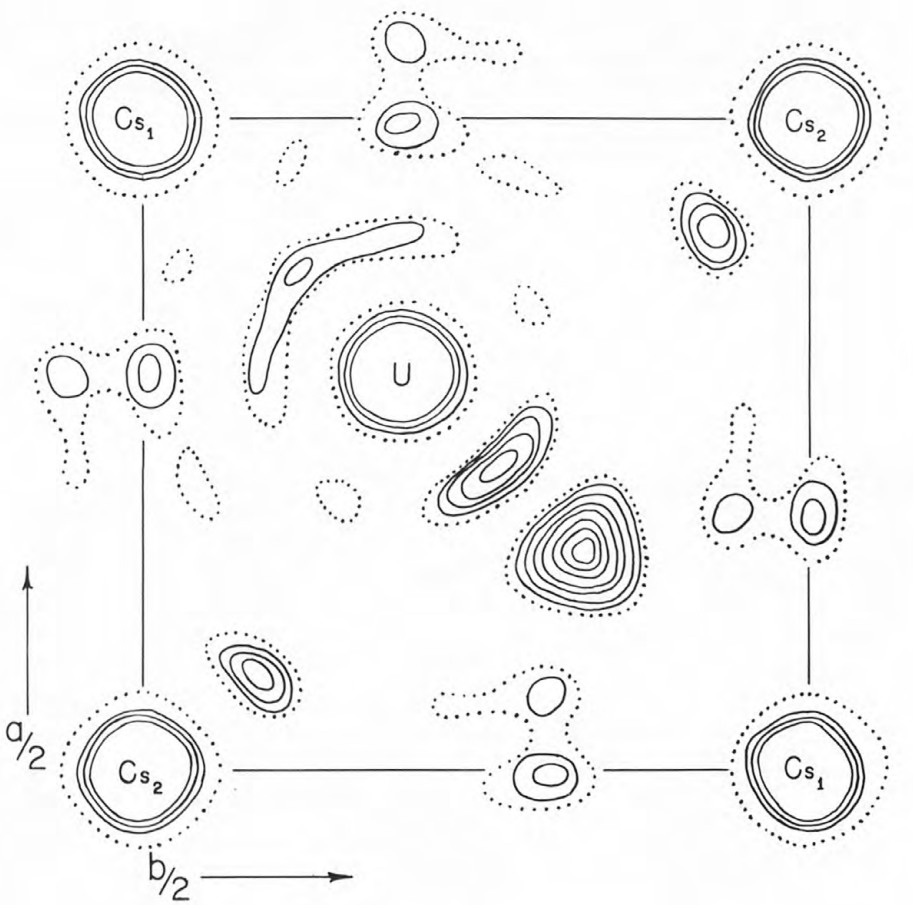

Figure V: Final Fourier projection of $Cs_2(UO_2)_2(SO_4)_3$ on (001).

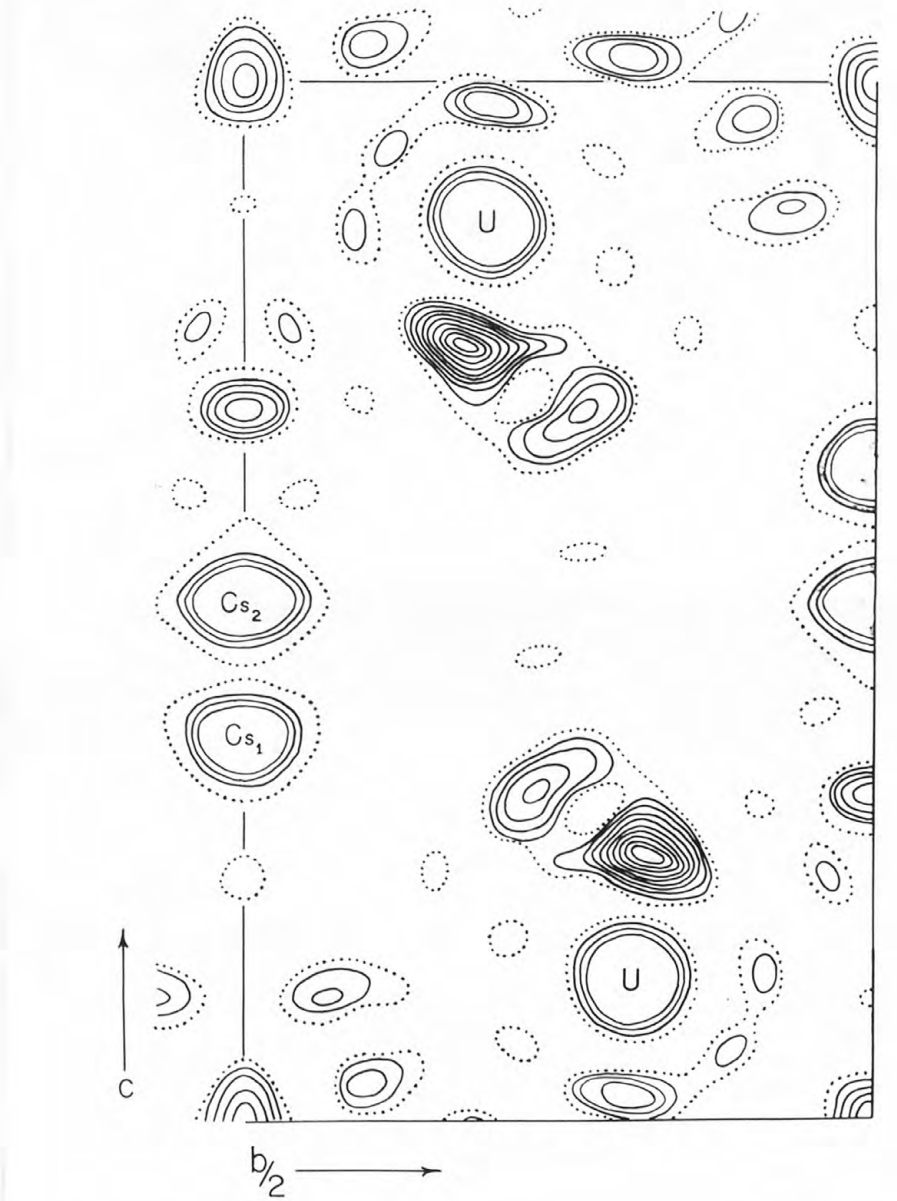

Figure VI: Final Fourier projection of $Cs_2(UO_2)_2(SO_4)_3$ on (100).

Table VII. Final Positional Parameters for 2 $[Cs_2(UO_2)_2(SO_4)_3]$ *

Atom	x	y	z	Group or ion
4 U in e	0.306	0.194	0.864	UO_2^{++}
2 Cs_1 in c	1/2	0	0.369	Cs_1^{+}
2 Cs_2 in b	0	0	1/2	Cs_2^{+}
4 S_1 in e	0.170	0.330	0.250	$(SO_4)_I^{-2}$
2 S_2 in a	0	0	0	$(SO_4)_{II}^{-2}$
4 O_1 in e	0.218 **	0.282 **	0.702 **	UO_2^{++}
4 O_2 in e	0.394	0.106	0.026	UO_2^{++}
8 O_3 in f	0.032	0.294	0.310 **	$(SO_4)_I^{-2}$
4 O_4 in e	0.170 **	0.330 **	0.071 **	$(SO_4)_I^{-2}$
4 O_5 in e	0.271 **	0.229 **	0.310 **	$(SO_4)_I^{-2}$
8 O_6 in f	0.078	0.092	0.876	$(SO_4)_{II}^{-2}$

* Most of the parameters were evaluated from difference maps and Fourier projections by the method of Booth (8).

** Due to distortion and overlapping, these parameters were evaluated by geometrical considerations; assuming an undistorted $(SO_4)_I^{-2}$ tetrahedron with S_2-O_3, S_1-O_4, S_1-O_5 distances of 1.45 Å, and a linear UO_2^{++} ion with a U-O_1 distance of 1.78 Å.

Tables VIII and IX give the observed and calculated structure factors for the hk0 and 0kl zones respectively. The signs of the 0kl structure factors are for a centro-symmetric projection with an origin $\frac{1}{4}, \frac{1}{4}, 0$ from the origin of the hk0 projection (Appendix).

The reliability, R, where

$$R = \Sigma |kF_o - F_c| / \Sigma kF_o$$

for the final structure is 0.137 for the hk0 zone and 0.143 for the 0kl zone.

The reliability was also calculated for a structure consisting only of the uranium and cesium atoms. New temperature and scaling factors were again obtained by the method of least squares. The reliability for the structure containing the heavy atoms only is 0.206 for hk0 zone and 0.258 for the 0kl zone.

The Burroughs 205 digital computer was used for all computations involved in this work.

C. Discussion of the Structure

$Cs_2(UO_2)_2(SO_4)_3$ crystallizes as tablets flattened on {001}. The crystals have perfect basal cleavage.

This compound has a layer structure, the layer being composed of sulfate and uranyl groups. The layers, consisting of $(UO_2)_{2n}(SO_4)_{3n}^{-2n}$ sheets parallel to (001), are tied together by the cesium atoms. Such a structure would be expected to show perfect cleavage parallel to the layer.

The sheets can be considered to be composed of $UO_2(SO_4)_5^{-8}$ groups. In addition to the uranyl oxygens, the uranium atom is coordinated by five oxygen atoms, one from each of five different sulfate groups. All O_3 and O_4 oxygens of the $(SO_4)_I^{-2}$ group and all oxygens (O_6) of the $(SO_4)_{II}^{-2}$

Table VIII. Observed and Calculated Structure Factors for the (hk0) Zone. Space Group - $P\bar{4}2_1m$ - Origin at $\bar{4}$.

hk0	F_o	F_c	hk0	F_o	F_c
200	89	- 74	930	20	- 16
400	224	223	10,30	44	29
600	274	267	11,30	108	88
800	99	- 70	12,30	44	- 33
10,00	227	238	440	218	222
12,00	18	41	540	29	- 18
110	31	- 22	640	126	146
210	153	130	740	114	97
310	178	165	840	72	96
410	200	-204	940	178	-143
510	131	-116	10,40	79	108
610	155	144	11,40	105	98
710	36	48	12,40	21	45
810	76	- 89	550	222	-209
910	< 16	16	650	31	- 36
10,10	38	- 27	750	120	132
11,10	33	- 18	850	39	28
12,10	103	87	950	16	24
13,10	37	47	10,50	< 16	- 12
220	352	424	11,50	97	- 67
320	65	62	660	201	221
420	104	114	760	118	- 94
520	< 16	0	860	30	12
620	24	37	960	110	103
720	73	- 52	10,60	104	122
820	240	246	11,60	67	- 55
920	114	97	770	52	- 50
10,20	28	17	870	45	- 42
11,20	78	- 68	970	< 16	21
12,20	84	110	10,70	24	- 23
330	221	-229	11,70	28	28
430	136	136	880	169	206
530	244	235	980	47	- 46
630	98	- 99	10,80	49	- 15
730	81	- 73	990	23	- 24
830	25	28			

Table IX. Observed and Calculated Structure Factors for the (Okl) Zone. Space Group - $P\bar{4}2_1m$ - Origin at $\bar{4}$, 4, 0/7 from $\bar{4}$.

Okl	F_o	F_c	Okl	F_o	F_c	Okl	F_o	F_c
020	92	75	083	172	138	0,11,6	90	100
040	249	224	093	< 13	- 10	007	114	106
060	299	-270	0,10,3	100	101	017	13	1
080	106	- 72	0,11,3	22	- 9	027	225	211
0,10,0	223	-246	0,12,3	46	27	037	107	-103
001	95	126	004	181	-206	047	42	- 50
011	74	62	014	18	- 19	057	46	- 22
021	257	267	024	151	-161	067	25	24
031	308	291	034	42	- 49	077	39	- 40
041	175	-153	044	27	- 20	087	171	-173
051	203	151	054	49	- 49	097	< 13	22
061	< 13	39	064	46	41	0,10,7	87	- 48
071	115	114	074	32	- 34	008	275	241
081	195	-198	084	155	150	018	53	34
091	70	- 76	094	< 13	- 26	028	25	- 18
0,10,1	71	- 30	0,10,4	123	112	038	55	44
0,11,1	73	- 57	0,11,4	15	19	048	86	84
0,12,1	41	- 73	0,12,4	48	58	058	112	83
0,13,1	82	-110	005	188	188	068	149	-147
002	< 13	- 16	015	< 13	- 5	078	27	25
012	152	185	025	70	- 78	088	70	- 23
022	174	-195	035	176	-185	009	< 13	- 21
032	198	186	045	37	- 52	019	< 13	4
042	48	43	055	90	- 91	029	56	59
052	340	309	065	35	40	039	195	166
062	< 13	- 38	075	128	-141	049	28	- 46
072	80	59	085	69	60	059	130	93
082	92	105	095	< 13	7	069	< 13	44
092	27	50	0,10,5	49	59	079	125	95
0,10,2	30	- 41	0,11,5	45	27	00,10	72	- 43
0,11,2	121	-123	006	140	163	01,10	56	62
0,12,2	< 13	45	016	154	-135	02,10	115	- 89
0,13,2	63	- 60	026	24	- 41	03,10	53	36
003	129	-161	036	97	- 84	04,10	< 13	37
013	40	- 28	046	105	117	05,10	151	114
023	117	-129	056	196	-189	00,11	123	-117
033	155	164	066	59	- 70	01,11	18	- 22
043	< 13	4	076	42	- 30			
053	76	72	086	14	28			
063	85	81	096	< 13	- 39			
073	120	109	0,10,6	76	-104			

group coordinate the uranium atoms. The $(SO_4)^{-2}_I$ group is linked to three uranyl groups by O_3 and O_4 oxygens. The $(SO_4)^{-2}_{II}$ group is linked to four uranyl groups by the O_6 oxygens.

The UO_2^{+2} group appears to be linear, although O_1 oxygen is partly obscured. The uranyl group lies within the mirror plane and is tilted 42° from the c-axis. The $U-O_2$ bond distance is 1.78 ± 0.05 Å. The uranyl group with the five coordinating sulfate oxygens has the shape of a pentagonal bipyramid, the uraryl oxygens being at the apices of the bipyramid. The five coordinating oxygens from the sulfate groups form a nearly plane pentagon which is approximately normal to the axis of the uranyl ion. The bond distances between the uranium atom and these oxygen atoms are:

$U-O_3(2)$..... 2.6 ± 0.1 Å
$U-O_4$..... 2.5
$U-O_6(2)$..... 2.4

The projections of the uranyl and sulfate groups on (001) and ($\bar{1}$00) are shown in Figures III and IV respectively.

The $(SO_4)^{-2}_{II}$ group lies on the $\bar{1}$ axis and appears to be a slightly distorted tetrahedron with an S_2-O_6 bond distance of 1.54 ± 0.05 Å. The $(SO_4)^{-2}_I$ group appears to be a regular tetrahedron with the S_1-O_4 bond approximately parallel to the c-axis. The S_1-O_3 bond distance is 1.45 ± 0.05 Å. Some of the oxygen peaks of the $(SO_4)^{-2}_I$ group are somewhat distorted or are obscured by overlapping with other atoms. The $(SO_4)^{-2}_I$ group may be slightly distorted and slightly tilted with respect to the c-axis.

The Cs_2 atom has 8-fold coordination. All O_6 and O_3 oxygens enter into this coordination. The Cs_2-O_3 bond distance is 3.2 ± 0.1 Å; the Cs_2-O_6 bond distance is 3.3 ± 0.1 Å.

The Cs_1 atom has 10-fold coordination; all O_1, O_2, O_3 and O_5 oxygens enter into this coordination. The following bond distances were found:

Cs_1-O_1 ..... 3.0 ± 0.1 Å
Cs_1-O_2 ..... 3.1
Cs_1-O_3 ..... 3.3
Cs_1-O_5 ..... 3.2

Figure VII shows a projection of the $Cs_2(UO_2)_2(SO_4)_3$ structure on (001) and (100). The SO_4^{-2} groups are shown as tetrahedra, the cesium atoms as large open circles, the oxygen atoms of the uranyl ions as smaller open circles, and the uranium atoms as small shaded circles.

The structure of $Cs_2(UO_2)_2(SO_4)_3$ resembles that of $K_3UO_2F_5$ in certain respects (20). Zachariasen found the structure to be composed of $(UO_2F_5)^{-3}$ complexes of the same shape as the pentagonal bipyramid described above. The U-O distance of the uranyl ion was found by Zachariasen to be 1.76 Å [vs. 1.78 Å for $Cs_2(UO_2)_2(SO_4)_3$].

The $Cs_2(UO_2)_2(SO_4)_3$ structure represents the fifth occurrence of five-fold coordination in uranyl compounds. Other structures showing this five-fold coordination are $K_3UO_2F_5$ (mentioned above), uranophane [$Ca(H_3O)_2(UO_2)_2(SiO_4)_2 \cdot 3H_2O$] (17), johannite [$Cu(UO_2)_2(SO_4)_2(OH)_2 \cdot 6H_2O$] (6), and carnotite [$K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$] (7).

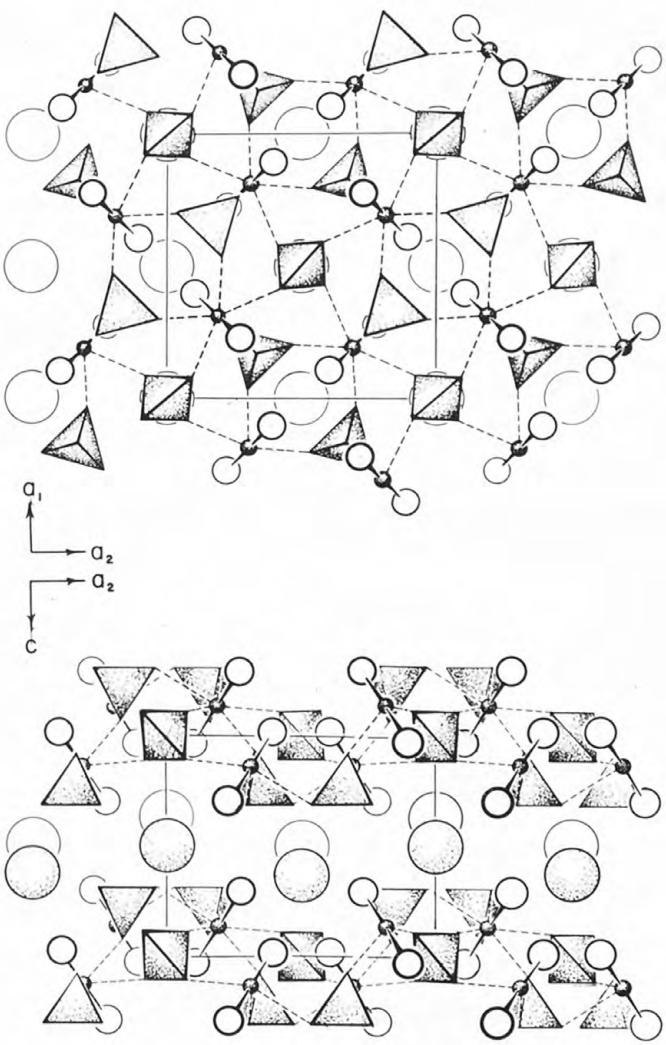

Figure VII: Projection of the $Cs_2(UO_2)_2(SO_4)_3$ Structure on (001) and (100). (Figure prepared by H. T. Evans, Jr.)

VII. SUMMARY

Five uranyl sulfate compounds, suitable for X-ray diffraction analysis were made by slow evaporation of aqueous solutions. These compounds include: $K_2UO_2(SO_4)_2 \cdot 2H_2O$, $Rb_2UO_2(SO_4)_2 \cdot 2H_2O$, $(NH_4)_2UO_2(SO_4)_2 \cdot 3H_2O$, $Cs_2(UO_2)_2(SO_4)_3$, and an orthorhombic cesium uranyl sulfate. Optical, X-ray and chemical data were obtained from most of these compounds.

The crystal structure of $Cs_2(UO_2)_2(SO_4)_3$ was solved by direct X-ray methods. Electron density projections on (001) and (100) yielded enough information to give a plausible structure. Subtraction of the heavy atoms gave electron density maps in which most of the light atoms were resolved. The compound has a layer structure consisting of $(UO_2)_{2n}(SO_4)_{3n}^{-2n}$ sheets parallel to (001), tied together by cesium atoms. The UO_2^{+2} ion is coordinated by five sulfate oxygens which form a nearly plane pentagon approximately normal to the axis of the uranyl ion. The Cs_1 atom is coordinated by 10 oxygens and the Cs_2 atom by 8 oxygens.

APPENDIX

The Structure Factor

The general expression for the structure factor is:

$$F(hk\ell) = \sum_{n}^{N} f_n \exp\left\{2\pi i \phi_n (hk\ell)\right\}$$

where

$$\phi(hk\ell) \equiv (hx + ky + \ell z)$$

and f_n is the scattering factor of the nth atom. Also,

$$F(hk\ell) = A' + iB'$$

where

$$A' = \sum_{n} f_n \cos 2\pi (hx_n + ky_n + \ell z_n)$$

$$B' = \sum_{n} f_n \sin 2\pi (hx_n + ky_n + \ell z_n).$$

Let the trigometric contribution to the structure factor be given by:

$$A = \cos 2\pi (hx + ky + \ell z)$$

and

$$B = \sin 2\pi (hx + ky + \ell z).$$

By evaluating A and B we may determine the phase of the structure factor $F(hk\ell)$. If B is zero $F(hk\ell)$ is real, if $B \neq 0$ $F(hk\ell)$ is complex.

Also,

$$F(\overline{hk\ell}) = A - iB$$

provided

$$|F(hk\ell)| = |F(\overline{hk\ell})| .$$

The phase angle $\delta(hk\ell)$ of the structure factor is given by:

$$\tan \delta(hk\ell) = B'/A'$$

$$\cos \delta(hk\ell) = A'/|F(hk\ell)|$$

$$\sin \delta(hk\ell) = B'/|F(hk\ell)|.$$

We can determine the phases of structure factors for any particular space group by determining the scattering factors (f) for the atoms in the unit cell and also the values of A and B which are characteristic of the space group. If B = 0 (for centro-symmetric space groups) the determination of phases is greatly simplified; their value being either 0 or π.

Evaluation of A and B for Space Group No. 113

For the space group $P\bar{4}2_1m$ (No. 113) atoms found in the general 8-fold positions have the following coordinates:

x,y,z	$1/2-x,\ 1/2+y,\ \bar{z}$
$\bar{x},\bar{y},z$	$1/2+x,\ 1/2-y,\ \bar{z}$
$\bar{y},x,\bar{z}$	$1/2+y,\ 1/2+x,\ z$
$y,\bar{x},\bar{z}$	$1/2-y,\ 1/2-x,\ z$

A and B are characteristic of the space group being dependent entirely on the co-ordinates of the equivalent positions. The simplest form of A for the general equivalent positions of space group No. 113 is obtained as follows:

$$A = \cos 2\pi(hx+ky+\ell z) + \cos 2\pi(-hx-ky+\ell z) + \cos 2\pi(-hy+kx-\ell z)$$
$$+ \cos 2\pi(hy-kx-\ell z) + \cos 2\pi\left[-hx+ky-\ell z+\left(\frac{h+k}{2}\right)\right]$$
$$+ \cos 2\pi\left[hx-ky-\ell z+\left(\frac{h+k}{2}\right)\right] + \cos 2\pi\left[hy+kx+\ell z+\left(\frac{h+k}{2}\right)\right]$$
$$+ \cos 2\pi\left[hy-kx+\ell z+\left(\frac{h+k}{2}\right)\right]$$

$$A = 2\cos 2\pi\ell z\ \cos 2\pi(hx+ky) + 2\cos 2\pi\ell z\ \cos 2\pi(hy-kx)$$
$$+ 2\cos 2\pi\left[-\ell z+\left(\frac{h+k}{2}\right)\right]\cos 2\pi(hx-ky)$$
$$+ 2\cos 2\pi\left[\ell z+\left(\frac{h+k}{2}\right)\right]\cos 2\pi(hy+kx)$$

$$A = 2\cos 2\pi l z \left\{\cos 2\pi (hx + ky) + \cos 2\pi (ky - hx) + \cos 2\pi \left[hx - ky + \left(\frac{h+k}{2}\right)\right] + \cos 2\pi \left[ky + hx + \left(\frac{h+k}{2}\right)\right]\right\}$$

$$A = 4\cos 2\pi l z \left\{\cos 2\pi \left[hx + \left(\frac{h+k}{4}\right)\right] \cos 2\pi \left[ky - \left(\frac{h+k}{4}\right)\right] + \cos 2\pi \left[ky + \left(\frac{h+k}{4}\right)\right] \cos 2\pi \left[hx + \left(\frac{h+k}{4}\right)\right]\right\}.$$

By similar procedures we can evaluate B, which in its simplest form is:

$$B = -4\sin 2\pi l z \left\{\sin 2\pi \left[hx + \left(\frac{h+k}{4}\right)\right] \sin 2\pi \left[ky - \left(\frac{h+k}{4}\right)\right] + \sin 2\pi \left[kx + \left(\frac{h+k}{4}\right)\right] \sin 2\pi \left[hy + \left(\frac{h+k}{4}\right)\right]\right\}.$$

Further simplification of A and B may be made if we consider only the hk0 and 0kl structure factors. We find that for the hk0 terms, where $h + k = 2n$,

$$A = \cos 2\pi\, hx \cos 2\pi\, ky + \cos 2\pi\, kx \cos 2\pi\, hy$$

$$B = 0$$

and where $h + k = 2n + 1$,

$$A = -\sin 2\pi\, hx \sin 2\pi\, ky + \sin 2\pi\, kx \sin 2\pi\, hy$$

$$B = 0.$$

For the 0kl structure factors, where $k = 2n$, we find that

$$A = 4\cos 2\pi l z \left[\cos 2\pi\, ky + \cos 2\pi\, kx\right]$$

$$B = 0$$

and where $k = 2n + 1$,

$$A = 0$$

$$B = -4\sin 2\pi l z \left[-\cos 2\pi\, ky + \cos 2\pi\, kx\right].$$

Shift of Origin to $[-1/4, 1/4, 0]$

We may simplify the calculation of phases of the 0kℓ structure factors if we shift the origin of space group No. 113 (as given in International Tables for X-ray crystallography, 1952, p.203) by $[-1/4, 1/4, 0]$. Such a shift now makes the phases of the 0kℓ structure factors either 0 or π.

The effect of this shift on the form of A (B = 0) is given in the following equations.

If $k = 2n$,

$$A = h\cos 2\pi \ell z \cos 2\pi \left(\frac{k}{4}\right)[\cos 2\pi ky + \cos 2\pi kx].$$

If $k = 2n + 1$,

$$A = -h\sin \pi \ell z \sin 2\pi \left(\frac{k}{4}\right)[-\cos 2\pi ky + \cos 2\pi kx].$$

These equations may be derived from first principles as shown previously in the Appendix. When Fourier projections are made on (100) using signs derived by the above formulas it must be remembered that the true origin is not the origin of the projection but 1/4 b from it.

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