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Optical and X-ray Data on a Group of Isostructural Uranium and Plutonium Compounds*

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A group of isostructural compounds of hexavalent and tetravalent uranium and plutonium with tetraethyl and tetramethyl ammonium chloride (types = $(R_4N)_2MCl_6$ and $(R_4N)_2MO_2Cl_4$) have been characterized by their optical properties and by X-ray diffraction analysis. Some errors in earlier data have been corrected and explained. The isostructuralism is maintained throughout the group, as evidenced by both crystal morphology and X-ray crystallography, although the space groups range from cubic to monoclinic. The monoclinic crystal has a β angle of 90·0°.

1. Introduction

This investigation was undertaken to resolve certain discrepancies between reports in the literature and some of our preliminary observations on a group of compounds of the type R_2MCl_6, where R ranges from univalent elements to substituted ammonium groups.

A number of compounds of this type have been described in the literature. Early studies of crystal morphology have been summarized by Groth (1906–19, vol. 1, pp. 478–479, 527). The structure type *H*-61, whose first representative $(NH_4)_2PtCl_6$ was described by Wyckoff & Posnjak (1921), is closely resembled by type *OH*-61 first given by Huggins (1926) for $\{(CH_3)_4N\}_2PtCl_6$. Similar compounds have been described by Wyckoff & Corey (1929*a*, *b*) with tin in place of platinum and with more complex substituted ammonium groups. Rimbach (1904) described the compounds $\{(CH_3)_4N\}_2UO_2Cl_4$ and its tetraethyl analogue, the structural analogy of which to type *OH*-61 will appear in this work. Preparation of $\{(CH_3)_4N\}_2PuCl_6$ has been described by Anderson (1949).

That these compounds, whose optical properties indicated symmetries ranging from cubic to monoclinic, might be closely related to the same structure type was suggested by morphological resemblances, all the salts observed showing isometric or pseudo-isometric habit. A further indication of basic resemblance was given by the transformation of the lower symmetry salts to isometric or tetragonal forms upon heating.

The compounds examined in this investigation are:

1. Di-(tetramethyl ammonium) uranium hexachloride, $\{(CH_3)_4N\}_2UCl_6$
2. Di(tetramethyl ammonium) plutonium hexachloride, $\{(CH_3)_4N\}_2PuCl_6$
3. Di-(tetraethyl ammonium) uranium hexachloride, $\{(C_2H_5)_4N\}_2UCl_6$
4. Di(tetraethyl ammonium) plutonium hexachloride, $\{(C_2H_5)_4N\}_2PuCl_6$
5. Di-(tetramethyl ammonium) uranyl tetrachloride, $\{(CH_3)_4N\}_2UO_2Cl_4$
6. Di-(tetramethyl ammonium) plutonyl tetrachloride, $\{(CH_3)_4N\}_2PuO_2Cl_4$
7. Di-(tetraethyl ammonium) uranyl tetrachloride, $\{(C_2H_5)_4N\}_2UO_2Cl_4$
8. Di-(tetraethyl ammonium) plutonyl tetrachloride, $\{(C_2H_5)_4N\}_2PuO_2Cl_4$

2. Preparation of compounds

The compounds were prepared by adding ditetramethyl or ditetraethyl ammonium chloride, in 30% excess over stoichiometric requirement, to a concentrated solution of UCl_4, UO_2Cl_2 or the plutonium analogues in 4*M* HCl, diluting with water until any precipitate which might have formed dissolved, and allowing the solution to crystallize by evaporation at room temperature. In case of the salts of tetravalent uranium the evaporation was allowed to take place under vacuum to guard against oxidation. While, for the sake of uniformity, this procedure was adhered to in preparing crystals for X-ray analysis, the conditions for preparing these salts are not critical. Crystals formed by evaporation of moderately acid solutions or salted out from solution with alcohol had similar morphological and optical properties.

3. Procedures

X-ray diffraction powder diagrams were obtained with compounds 1, 2 and 5. The others were analyzed by single-crystal X-ray methods. Single crystals used were roughly equiaxed and ranged in diameter from 0·03 to 0·20 mm. No attempt was made to obtain accurate intensities because of the high absorption. Cu $K\alpha$ was the radiation used throughout.

Most of the optical observations were made on the stage of a petrographic microscope. Measurements of optic orientation on compound 7 were made with a

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Table 1. *X-ray and partial optical data*

Compound	Symmetry, space group, and lattice constants	Density meas. (d); X-ray (ϱ) (g.cm.$^{-3}$)	No. of molecules per unit cell	Crystal habit, twinning	Optic character, axial angle, dispersion	Optic orientation	Refractive indices (5893)	Color and absorption
1. $\{(CH_3)_4N\}_2UCl_6$	Isometric Face-centered cubic $a_0 = 13{\cdot}03$ kX.	$d = 1{\cdot}791$ $\varrho = 1{\cdot}788$	4	{100}, {111}	Isotropic		1·511	Green
2. $\{(CH_3)_4N\}_2PuCl_6$	Isometric Face centered cubic $a_0 = 12{\cdot}94$ kX.	$\varrho = 1{\cdot}830$	4	{100}, {111}	Isotropic		1·526	Orange yellow
3. $\{(C_2H_5)_4N\}_2UCl_6$	Orthorhombic $Fmmm{-}D_{2h}^{23}$ $a_0 = 14{\cdot}2$, $b_0 = 14{\cdot}7$, $c_0 = 13{\cdot}3$ kX.	$d = 1{\cdot}693$ $\varrho = 1{\cdot}69$	4	{111}, {100} {010}, {001}	Negative $2V = 35°$ $r > v$ mod.	$X = c$ $Y = a$ $Z = b$	1·548 1·555 1·556	Light green $Z = Y > X$
4. $\{(C_2H_5)_4N\}_2PuCl_6$	Orthorhombic $Fmmm$ $a_0 = 14{\cdot}2$, $b_0 = 14{\cdot}5$, $c_0 = 13{\cdot}5_6$ kX.		4	{111}, {100} {010}, {001}	Negative $2V = 24°$ $r > v$ extreme	$X = c$ $Y = a$ $Z = b$	1·560 1·568 1·569	Yellow $Z = Y > X$
5. $\{(CH_3)_4N\}_2UO_2Cl_4$	Tetragonal $I4/m$ $a_0 = 9{\cdot}12$, $c_0 = 11{\cdot}77$ kX.	$d = 1{\cdot}889$ $\varrho = 1{\cdot}889$	2	{001}, {110} {101},	Positive Uniaxial	O E	1·516 1·526	Yellow $E > O$
6. $\{(CH_3)_4N\}_2PuO_2Cl_4$	Tetragonal $I/4m{-}C_{4h}^5$ $a_0 = 9{\cdot}2$, $c_0 = 11{\cdot}9$ kX.		2	{001}, {110} {101}	Positive Uniaxial	O E	1·526 1·541	Yellow $E > O$
7. $\{(C_2H_5)_4N\}_2UO_2Cl_4$	Monoclinic $a_0 = 16{\cdot}3$, $b_0 = 10{\cdot}0$, $c_0 = 12{\cdot}9_0$ kX., $\beta = 142°$ [Geometrically equivalent to an orthorhombic $Immm$ with $a = 9{\cdot}96$, $b = 10{\cdot}07$, $c = 12{\cdot}9$ kX.]	$d = 1{\cdot}723$ $\varrho = 1{\cdot}71_5$	2	{001}, {110} {010}, {101} {$\bar{1}$01}	Negative $2V = 33°$ $r > v$ mod.	$X \wedge c = 10°$ $Y = b$ Z	1·531 1·558 1·559	Yellow $Z = Y > X$
8. $\{(C_2H_5)_4N\}_2PuO_2Cl_4$	Tetragonal $a_0 = 10{\cdot}0$, $c_0 = 12{\cdot}9$ kX. $I/4m{-}C_{4h}^5$		2	{001}, {110} {101}	Negative Uniaxial	E O	1·539 1·566	Yellow $O > E$

single-circle goniometer equipped with a polarizer and analyzer. Thermal transformations occuring above 90° C. were studied on a Kofler hot stage. Below this temperature, and to facilitate measurement of optic axial angles, an Emmons temperature cell was used.

Densities of the four uranium compounds were determined by the flotation method on selected crystals free from cracks or occluded mother liquor. Mixtures of *s*-tetrabromoethane and α-bromonaphthalene were the suspension liquids used.

In order to achieve a better correlation of the optical and X-ray diffraction observations two techniques were used which may be worth a brief mention:

(*a*) *A microscope adapter for the X-ray goniometer head*

This adapter, based on a similar instrument in the laboratory of Prof. I. Fankuchen at the Polytechnic Institute of Brooklyn, holds a Unicam X-ray goniometer head on the stage of a polarizing microscope. The combination of movements provided permits rapid and accurate preliminary alignment and helps relate the optical and X-ray data.

(*b*) *Reorienting crystals on a new axis*

The scarcity of untwinned crystals in the preparations and the need for knowing the relations among the optical and crystallographic directions made it necessary to remount the same crystal several times in a precisely controlled manner. This was accomplished by use of the technique described by one of us previously (Singer & Ellinger, 1950) with very small quantities of Saureisen cement serving to bind the two fibers together firmly and quickly. The desired reorientation was generally obtained within 3° on each arc, and there was no doubt as to the new direction in each case, despite the octahedral habit of the crystals.

4. Experimental data

X-ray and partial optical data have been summarized in Table 1. Some additional observations are given below.

(*a*) *Precision of measurements*

In the case of compounds 1, 2 and 5, for which lattice constants were obtained by the powder method, these are correct to $\pm 0{\cdot}01$ kX. and the derived densities to $\pm 0{\cdot}004$ g.cm.$^{-3}$. The lattice constants of other compounds were measured from relatively low-order reflections and are estimated to be accurate to $\pm 0{\cdot}05$ kX. Densities measured by the flotation method are believed to be correct to $\pm 0{\cdot}001$ g.cm.$^{-3}$ and the indices of refraction to $\pm 0{\cdot}001$.

(*b*) *Morphological data*

All compounds under consideration are characterized by good cleavage. In the case of salts of tetravalent metals the cleavage direction is $\{111\}$. For the tetragonal uranyl and plutonyl compounds the cleavage direction is $\{101\}$, for the monoclinic $\{(C_2H_5)_4N\}_2UO_2Cl_4$ $\{011\}$, $\{101\}$ and $\{\bar{1}01\}$, equally well developed. Compounds 5, 6 and 7 commonly form twins, either simple or repeated with $\{110\}$ as the twinning plane in all cases.

(*c*) *Optical data*

Measurements of optic axial angles (Table 1) were made with sodium light. For compound 4, which exhibited extreme dispersion of optic axes, additional measurements were made with monochromatic light (Table 2).

Table 2. *Optic axial angles of Compound* 4

Wavelength (millimicrons)	$2V$
470	19°
589	24°
664	27°

The optic axial angle of $\{(C_2H_5)_4N\}_2UO_2Cl_4$, measured at room temperature, was found to vary between 28 and 36° in different crystals. There appeared to be no correlation of such variations with the temperature at which crystals were formed, within the limits of 3 to 57° C. A general trend was noted for crystals grown from more acid solutions to be characterized by greater values of $2V$. Some other factors, however, must also be influencing this property, because a single crop crystallized at room temperature from an aqueous solution contained crystals with $2V$ ranging from 28 to 32°.

In the case of the five compounds for which reliable density values were available, molar refractivities have been calculated by means of the Lorentz–Lorenz relation: $R = M(n^2-1)/d(n^2+2)$, where M is the molecular weight, d the density and n the index of refraction. For birefringent crystals the geometric mean of the three principal refractive indices was used according to Wulff & Heigl (1931). This information, together with similar data determined for some related compounds, is brought together in Table 3.

Table 3. *Molar refractivities*

Compound	n	d (g.cm.$^{-3}$)	R
$\{(CH_3)_4N\}_2SnCl_6$	1·511	1·498	95·9
$\{(CH_3)_4N\}_2UCl_6$	1·511	1·791	100·2
$\{(CH_3)_4N\}_2PuCl_6$	1·526	1·830	100·6
$\{(CH_3)_4N\}_2PtCl_6$	1·577	1·802	102·3
$\{(CH_3)_4N\}_2TeCl_6$	1·605	1·508	111·6
$\{(C_2H_5)_4N\}_2SnCl_6$	1·554, 1·563, 1·565	1·468	130·5
$\{(C_2H_5)_4N\}_2UCl_6$	1·548, 1·555, 1·556	1·693	134·5
$\{(C_2H_5)_4N\}_2PtCl_6$	1·613, 1·620, 1·620	1·706	137·2
$\{(CH_3)_4N\}_2UO_2Cl_4$	1·516, 1·516, 1·526	1·889	90·0
$\{(C_2H_5)_4N\}_2UO_2Cl_4$	1·531, 1·558, 1·559	1·723	124·0

(*d*) *Thermal transformations*

The orthorhombic $\{(C_2H_5)_4N\}_2UCl_6$ was found to undergo a transformation to an isotropic form on heating. The transformation point at 94° C. is sharp.

Before it is reached, however, at 89° C. a marked reduction of birefringence occurs, probably indicating the existence of a third, intermediate, polymorphic form. Both transformations are reversible.

Similar reversible transformations were observed with $\{(C_2H_5)_4N\}_2PuCl_6$. Decrease of birefringence occurred at 87° C. and the crystals became isotropic at 97° C. A powder X-ray pattern prepared at 112° C. corresponded to a face-centered cubic cell with $a_0 = 14{\cdot}16 \pm 0{\cdot}01$ kX.

Corresponding transformations of other ditetraethyl ammonium compounds to the isometric form were observed at 105° C. for $\{(C_2H_5)_4N\}_2SnCl_6$ and at 97·5° C. for $\{(C_2H_5)_4N\}_2PtCl_6$.

The monoclinic $\{(C_2H_5)_4N\}_2UO_2Cl_4$ was found to undergo a reversible transformation to a uniaxial (tetragonal) form. The transition is gradual, the optic axial angle and inclination of the acute bisectrix to the crystallographic *c* axis decreasing continuously on heating. Both processes are greatly accelerated at higher temperatures and the two angles become zero at 81° C. The following values of the two angles were determined at different temperatures:

Temperature	$2V$	$X \wedge c$
24° C.	36°	10°
50	34	9
60	31	8
70	26	7
75	20	4
77	17	3
78	10	1
81	0	0

5. Discussion

Although no fewer than four systems of symmetry are represented by this group of compounds, it is apparent that all structures are closely related and derivable from the most symmetrical one, the face-centered cubic cell with a 13 Å edge, which contains four molecules of the double chlorides of ditetramethyl ammonium with tetravalent uranium or plutonium. Substitution of ethyl for methyl groups lowers the symmetry to that of the orthorhombic space group *Fmmm*.

The two di-(tetramethyl ammonium) compounds of hexavalent uranium and plutonium are body centered tetragonal with space group *I4/m* and two molecules per unit cell. In order to bring out the relation to the compounds with the tetravalent metal ions we may regard the former as belonging to the face-centered tetragonal space group, *F4/m*, with a cell of double volume which, in the case of the uranyl methyl compound, would have the lattice constants $a_0 = 12{\cdot}90$, $c_0 = 11{\cdot}77$ kX. This interpretation finds further support in observations on the crystal morphology. Compounds of the tetravalent elements crystallize with cubo-octahedral habit illustrated by Fig. 1, while Fig. 2 represents the typical habit of the four compounds with a XO_2 group. While, in the case of the monoclinic salt illustrated, the directions of crystallographic axes are fixed uniquely by optical symmetry, we are free, for the tetragonal members of the group, to choose the orientation adopted by Sachs and to re-index the forms {101}, {110} to {111}, {100}.

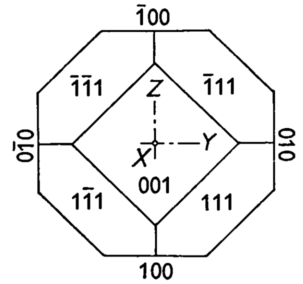
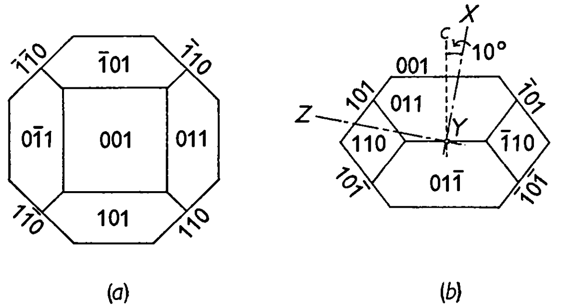


Fig. 1. Crystal habit and optic orientation of $\{(C_2H_5)_4N\}_2UCl_6$, projected parallel to [001].



(*a*) (*b*)

Fig. 2. Crystal habit and optic orientation of $\{(C_2H_5)_4N\}_2UO_2Cl_4$. (*a*) Projected parallel to [001]. (*b*) Projected parallel to [010].

This brings out the close morphological relation to the group of compound represented by Fig. 1.

Di-(tetraethyl ammonium) uranyl tetrachloride has been reported by Rimbach (1904) as tetragonal and isomorphous with the corresponding methyl salt on the basis of morphological measurements by Sachs, while optical measurements indicate monoclinic symmetry. Weissenberg X-ray diagrams resolved a 1% difference between the *a* and *b* cell edges, indicating orthorhombic symmetry. Sixth-layer Weissenberg patterns about the 12·9 Å axis failed to indicate deviations from orthorhombic symmetry. On the basis of the X-ray data alone this compound would be assigned the space group *Immm*, with lattice constants $a = 9{\cdot}96$, $b = 10{\cdot}07$, $c = 12{\cdot}90$ Å, which brings out the relation to the tetragonal cells of the compounds, discussed previously. In view of the optical evidence we must regard this compound as having a monoclinic space group. For instance *C2/m* retains two of the cell edges of the above orthorhombic cell.

The agreement between calculated and measured densities of the uranyl salts, as well as their isostructural relation to corresponding salts of tetravalent elements, leaves no doubt that both compounds are anhydrous, as required by formulae proposed by Rimbach (1904), and not monohydrated, as claimed by Dieke & Duncan (1949).

It appears that the compounds investigated belong to a group of isostructural crystals, approximating to cubic morphology, whose composition can be represented by

$$\{(R')_n(R'')_{4-n}\mathrm{N}\}_2M^{\mathrm{IV}}X_6$$
$$\{(R')_n(R'')_{4-n}\mathrm{N}\}_2M^{\mathrm{VI}}\mathrm{O}_2X_4\,,$$

where R' and R'' can represent CH_3, C_2H_5, C_3H_7 or C_4H_9. The alkyl radicals may be replaced by hydrogen. The ammonia nitrogen may be substituted by phosphorus or antimony. The tetravalent elements Si, Ti, Ru, Pd, Ir, Os, Pt, Sn, Pb, Se, Te, Po, U and Pu, as well as the uranyl and plutonyl groups, have been encountered in place of M. The halogens F, Cl, Br or I have appeared for X.

The writers wish to express appreciation to F. H. Ellinger, who prepared the X-ray diffraction powder diagrams, and to A. L. Truitt, who determined some of the optical properties.

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Tables of Absorption Factors for Spherical Crystals

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Correction of single-crystal X-ray diffraction intensity measurements for absorption in the crystal is greatly simplified if the crystal is ground into a sphere. The factor by which the intensity of a diffraction beam is reduced by absorption is a function then only of the dimensionless product of the linear absorption coefficient and the radius of the sphere, and the Bragg angle 2θ. Tables are given in this paper which give the absorption factor in terms of the two variables. The tables are analogous to the standard tables for cylinders.

In the accurate measurement of intensities of diffraction beams produced by small single crystals as used for structure analysis, one of the most troublesome problems encountered is that of properly accounting for the effect of absorption. Such crystals generally have a special geometric shape, and the effect is a geometric function of the diffraction angle, the angular position of the crystal in the beam and the shape of the crystal itself. Various attempts have been made to solve this problem systematically (Howells, 1950) but the solution for a large number of reflections will always be extremely tedious and time consuming.

If the crystal can be ground into the shape of a sphere, as Bond (1951) has recently done, the problem is greatly simplified. In this case, the absorption is a geometric function only of the diffraction angle 2θ, and the radius of the sphere R. This function has now been computed by us and is reported in this paper. The tables below are analogous to those for cylindrical specimens given in the *International Tables for the Determination of Crystal Structures* (1935, vol. 2, p. 581). The present tables were calculated from these data as originally derived by Claasen (1930). The tables for cylinders have been recalculated by Bradley (1935) but his results do not differ in any part from those of Claasen by more than 1% and usually much less. For practical purposes there is no choice between these two sets of tables.

The computation was accomplished by an approximate integration in which the absorption effect was summed over twenty cylindrical elements of the hemisphere, so chosen that the total volume of the elements is to a close approximation the same as that of the sphere, and so that the radii of the elements

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