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OPTICAL AND X-RAY DATA ON A GROUP OF ISOSTRUCTURAL URANIUM AND PLUTONIUM COMPOUNDS

by

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ABSTRACT

A group of iso-structural compounds of hexavalent and tetravalent uranium and plutonium with tetra-ethyl and tetra-methyl 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 iso-structuralism 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°. The effect of substitutions of Pu for U, UO_2 for U, C_2H_5 for CH_3 on molar refractivities has been investigated.

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I. INTRODUCTION

Di-(tetramethyl ammonium) uranyl tetrachloride and its tetraethyl analogue were described by Rimbach (1904) as isomorphous and tetragonal with ratios a:c = 0.9057 and 0.9094 respectively. These conclusions were derived from morphological measurements by Sachs. While measuring optical properties of these compounds it was noted that while the tetramethyl salt is uniaxial, as required by tetragonal symmetry, the tetraethyl salt is biaxial, the optical axial angle having an appreciable and constant value of 33°. While it is not unusual for substances crystallizing in one of the dimetric systems to exhibit biaxial character due to crystallization strain, such anomalous optic angles are usually smaller and characteristically variable, wide fluctuation of this value being often observed within the same crystal. It was further observed that even conditions of orthorhombic symmetry are not satisfied by the optics of the tetraethyl salt. Only the optic normal is coincident with a principal crystallographic direction [010]; both the bisectrices are inclined by 10 degrees to the crystallographic axes in the optic plane. This indicates a symmetry not higher than monoclinic. On the other hand, the crystals did show a marked similarity of habit to the tetragonal crystals of the ditetramethyl salt, and measurements of interfacial angles on the goniometer left no doubt that they were identical to the crystals described by Rimbach. In order

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to clarify the matter, a study of the two salts by X-ray methods was undertaken which also included some related substances. The following compounds were studied.

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. $\{(C_2H_5)_4N\}_2PuO_2Cl_4$

Preparation of the four uranium compounds is described by Dieke (1949) who also describes the characteristics of their absorption and fluorescence spectra. On the basis of chemical analysis Dieke considers the two uranyl salts to be monohydrates. However, density and cell size determinations leave no doubt that the compounds described in the following are anhydrous, as required by the formulae proposed by Rimbach. Anderson (1949) describes the preparation of di-(tetramethyl ammonium) plutonium hexachloride. A structure analysis of dicesium plutonium hexachloride which is chemically, though not structurally related to the group of compounds studied has been published by Zachariasen (1948).

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II. PREPARATION OF COMPOUNDS

The compounds were prepared by adding ditetramethyl or diethaethyl ammonium chloride, in 30 percent 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 identical morphological and optical properties.

III. PROCEDURES

X-ray diffraction powder diagrams were obtained with compounds 1, 2, and 5. The others were analyzed by single crystal X-ray methods. The 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 petro-

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graphic microscope. Measurements of optic orientation on compound 7 were made with a single circle goniometer equipped with a polarizer and analyzer.

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 Professor 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. (Fig. 3)

(B) Reorienting crystals on a new axis. The scarcity of untwinned crystals in the preparations and the need for knowing precisely 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, 1950) with very small

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quantities of Sauereisen cement serving to bind the two fibers together firmly and quickly. The desired reorientation was generally obtained within 3 degrees on each arc.

IV. EXPERIMENTAL DATA

The data have been summarized in Table I.

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 ± 0.01 kX and the derived densities to ± 0.004. The lattice constants of other compounds were measured from relatively low order reflections and are estimated to be accurate to ± 0.05 kX. Direct densities are believed to be correct to ± 0.001 and the indices of refraction to ± 0.001.

B. Morphological and Optical Data

The crystal habit of all compounds under consideration is cubooctahedral or pseudo-cubooctahedral, which is consistent with the close similarity of structures indicated by other evidence. Figure 2 shows the crystal habit of di-(tetraethyl ammonium) uranium hexachloride which is typical of the four compounds of the tetravalent metals. Figure 3 referring to di-(tetraethyl ammonium) uranyl tetrachloride may be considered representative of the habit of the four compounds with the XO_2 group. In the case of the

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TABLE I

Compound	Symmetry, Space Group, and Lattice Constants	Density Meas. (d) X-ray (ρ)	No. of Molecules Per Unit Cell	Crystal Habit, Twinning	Optic Char. Axial Angle Dispersion	Optic Orientation	Refractive Indices n (5893)	Color and Absorption
1. $\{(CH_3)_4N\}_2UCl_6$	Isometric Face centered cubic $a_o = 13.03$	$d = 1.791$ $\rho = 1.788$	4	$\{100\}, \{111\}$	Isotropic		1.511	green
2. $\{(CH_3)_4N\}_2PuCl_6$	Isometric Face centered cubic $a_o = 12.94$	$\rho = 1.830$	4	$\{100\}, \{111\}$	Isotropic		1.526	orange yellow
3. $\{(C_2H_5)_4N\}_2UCl_6$	Orthorhombic $Fmmm\ (D_{2h}^{23})$ $a_o = 14.2,\ b_o = 14.7$ $c_o = 13.3$	$d = 1.693$ $\rho = 1.69$	4	$\{111\}, \{100\}$ $\{010\}, \{001\}$	Negative $2V = 35^o$	$X = c$ $Y = a$ $Z = b$	1.548 1.555 1.556	light green $Z = Y > X$
4. $\{(C_2H_5)_4N\}_2PuCl_6$	Orthorhombic $Fmmm$ $a_o = 14.2,\ b_o = 14.5$ $c_o = 13.5_6$		4	$\{111\}, \{100\}$ $\{010\}, \{001\}$	Negative $2V = 24^o$ $r > v$ 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 $I/4m$ $a_o = 9.12$ $c_o = 11.77$	$d = 1.889$ $\rho = 1.889$	2	$\{001\}, \{110\}$ $\{101\}$,	Positive Uniaxial	O E	1.516 1.526	yellow $E > O$
6. $\{(CH_3)_4N\}_2PuO_2Cl_4$	Tetragonal $I/4m\ (C_{4h}^5)$ $a_o = 9.2$ $c_o = 11.9$		2	$\{001\}, \{110\}$ $\{101\}$	Positive Uniaxial	O E	1.526 1.541	yellow $E > O$
7. $\{(C_2H_5)_4N\}_2UO_2Cl_4$	Monoclinic $a_o = 16.3_0,\ b_o = 10.0,$ $c_o = 12.9_0,\ \beta = 142^o$ [geometrically equivalent to an orthorhombic I_{mmm} with $\{a = 9.96,\ b = 10.07,\ c = 12.9\}$]	$d = 1.723$ $\rho = 1.71_5$	2	$\{001\}, \{110\}$ $\{010\}, \{101\}$ $\{\bar{1}01\}$	Negative $2V = 33^o$ $r > v$ mod.	$X\wedge C = 10^o$ $Y = b$ Z	1.531 1.558 1.559	yellow $Z = Y > X$
8. $\{(C_2H_5)_4N\}_2PuO_2Cl_4$	Tetragonal $a_o = 10.0$ $c_o = 12.9$ $I/4m\ (C_{4h}^5)$		2	$\{001\}, \{110\}$ $\{101\}$	Negative Uniaxial	E O	1.539 1.566	yellow $O > E$

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Fig. 1: Crystal habit and optic orientation of $\left\{(C_2H_5)_4N\right\}_2UCl_6$.
Projected parallel to [001]

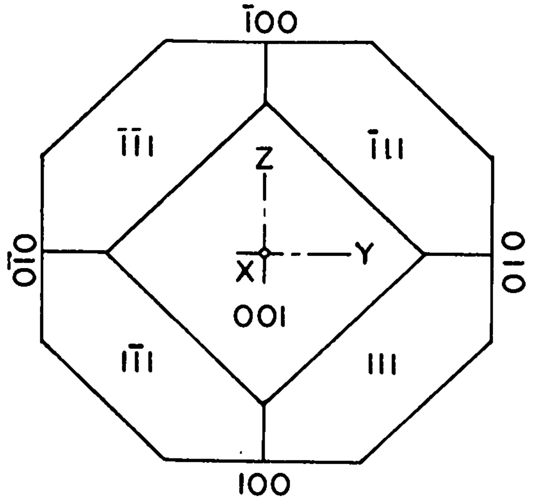
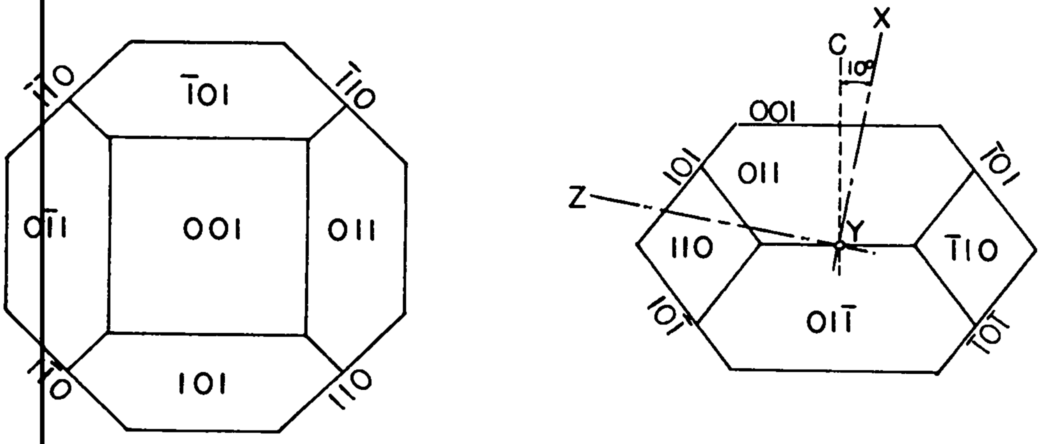


Fig. 2: Crystal habit and optic orientation of $\left\{(C_2H_5)_4N\right\}_2UO_2Cl_4$.



(a) Projected parallel to [001]. (b) Projected parallel to [010] .

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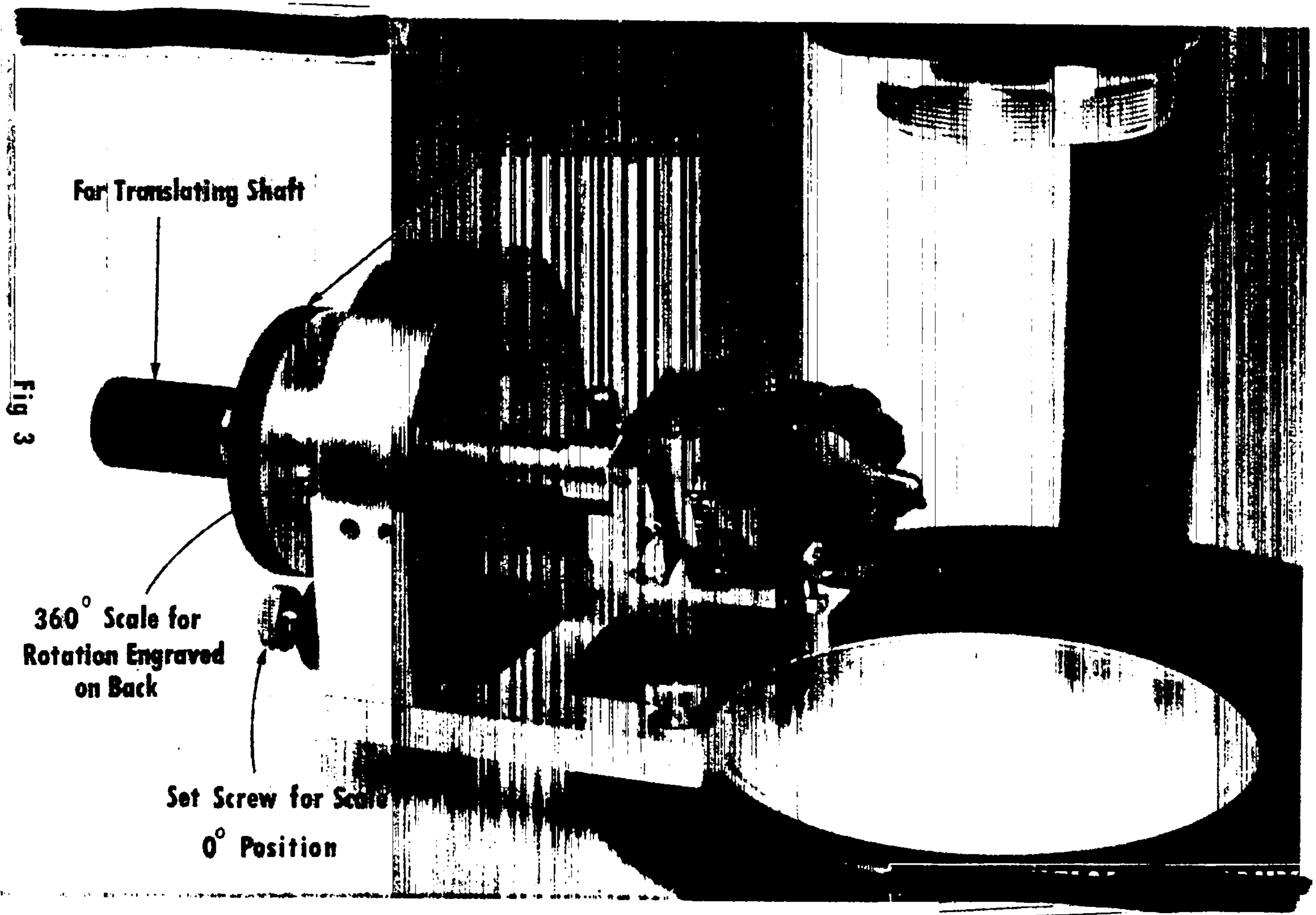
For Translating Shaft
360° Scale for Rotation Engraved on Back
Set Screw for Scale 0° Position

Fig 3

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tetragonal members of this group we may, by choosing the orientation used by Sachs, re-index the forms {101}, {110}, to {111}, {100} which brings out the close relation to the group of compounds represented by Figure 1. This is equivalent to the substitution of the larger face-centered for the body-centered tetragonal cell. In case of the monoclinic compound illustrated, however, the directions of crystallographic axes are fixed uniquely by optical symmetry.

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}, $\{\bar{1}01\}$, equally well developed. Compounds 5, 6, and 7 commonly form twins, either simple or repeated with {110} as the twinning plane in all cases.

Table II

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

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

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light. (Table II).

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:

$$R = \frac{M}{d} \cdot \frac{n^2 - 1}{n^2 + 2},$$

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 and Heigl (1931).

Table III

Compound	Molar Refractivity
1. $\{(CH_3)_4N\}_2UCl_6$	100.2
2. $\{(CH_3)_4N\}_2PuCl_6$	100.6
3. $\{(C_2H_5)_4N\}_2UCl_6$	134.
5. $\{(CH_3)_4N\}_2UO_2Cl_4$	90.0
7. $\{(C_2H_5)_4N\}_2UO_2Cl_4$	124.1

V. 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 face-centered cubic cell with a 13A edge, which contains four molecules of the double chlorides of ditetramethyl ammonium with tetravalent uranium or

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plutonium.

Substitution of ethyl for the methyl groups lowers the symmetry to that of the orthorhombic space group Fmmm. The cell edge lengths differ by several percent from one another and the orthorhombic symmetry was shown unambiguously by the single crystal X-ray data. It is apparent also from optical examination; both salts are biaxial with an appreciable optic angle, and the plutonium compound exhibits, in addition, extreme dispersion of optic axes giving rise to striking abnormal interference colors in views inclined to a symmetry plane.

The two di-(tetramethyl ammonium) compounds of hexavalent U and Pu are body centered tetragonal with space group I/4m 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, F 4/m, with a cell of double volume which, in the case of the uranyl methyl compounds, would have the lattice constants $a_o = 12.90$, $c_o = 11.77$.

As already mentioned, di-(tetraethyl ammonium) uranyl tetrachloride has been reported as tetragonal and isomorphous with the corresponding methyl salt on the basis of morphological measurements, while optical measurements indicate much lower (e.g. monoclinic) symmetry. Weissenberg X-ray diagrams resolved a one-percent difference between the a and b cell edges, indicating orthorhombic symmetry. Sixth layer

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Weissenberg patterns about the 12.9A 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 = 9.9_6, b = 10.0_7, c = 12.9_0 which brings out the relation to the tetragonal cells of the compounds, discussed previously. In view of the optical evidence we may regard this compound as having a monoclinic space group. For instance C 2/m retains two of the cell edges of the above orthorhombic cell.

By way of a possible explanation of the failure of the X-ray analysis to detect deviations from orthorhombic symmetry, it might be suggested that in a compound of this type the heavy atoms contribute almost exclusively to X-ray reflections. It is conceivable that the disposition of the heavy ions, U, Pu and even Cl, may conform to orthorhombic symmetry, deviations from which are due solely to positions of light ions.

The compounds of these tetravalent metals are similar in many respects to corresponding compounds of Pt(IV) and Sn(IV). Results of early morphological investigations have been summarized by Groth (1906). Di-(tetramethyl ammonium) platinum hexachloride is isometric with octahedral habit and cleavage. The corresponding tetraethyl compound is described as monoclinic with pseudo-octahedral development by lamellar twinning. The stannic compound is similar. Both undergo reversible transformation to an isotropic form on heating. Groth

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also describes intermediate compounds: $\{(CH_3)_3(C_2H_5)N\}_2PtCl_6$; $\{(CH_3)_2(C_2H_5)_2N\}_2PtCl_6$ which was observed in an isometric (high temperature), tetragonal (room temperature) and a low symmetry form; and $\{(CH_3)(C_2H_5)_3N\}_2PtCl_6$ which is described as "probably monoclinic" at room temperature, cubic at high temperature.

X-ray studies of $\{(CH_4)N\}_2PtCl_6$ were made by Huggins (1926). Wyckoff and Corey (1929, 1929a) reported on $\{(CH_3)_4N\}_2SnCl_6$, $\{(CH_3)_3(C_2H_5)N\}_2SnCl_6$, $\{(CH_3)_2(C_2H_5)_2N\}_2SnCl_6$.

From all this work it appears that there exists a group of isostructural crystals, approximating to cubic morphology, whose composition can be represented by

$$\{(R')_n(R'')_{4-n}N\}_2M^{IV}X_6 \quad \text{or}$$

$$(R')_n(R'')_{4-n}N_2M^{VI}O_2X_4$$

R' and R'' can represent at least CH_3^- and $C_2H_5^-$, and apparently also $C_3H_7^-$. The alkyl radicals may be partially replaced by hydrogen. The ammonia nitrogen may be substituted by phosphorus, arsenic, and antimony. We have encountered tin, platinum, uranium, plutonium and silicon, as well as the uranyl and plutonyl groups, in place of M. The halogens, chlorine and fluorine, have appeared for X, and presumably so could bromine and iodine.

The structural similarity of compounds studied in the present work

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affords the opportunity to investigate the effect of some substitutions on molar refractivities. Thus from data given in Table III for compounds 1 and 2 we find that substitution of a Pu(IV) ion for U(IV) increases the molar refractivity by 0.4 cm^3. This difference is of the order of the combined error of measurements on which the calculations were based and indicates that any difference which may exist between the polarizibility of the two ions is very small.

From molar refractivities of compounds 1, 5, 3, and 7 respectively, we obtain: $R(U) - R(UO_2) - 2R(Cl) = -10.2$ or -10.3. If we accept the value of 8.7 given by Smythe (1931) for R(Cl) we find that the additive effect due to substitution of UO_2 for U(IV) is 7.1 or 7.2.

The effect of substituting a C_2H_5 group for CH_3 is one-eighth of the difference between molar refractivities of compounds 3, 1 and 7, 5. The two sets of figures give 4.26 and 4.27 cm^3, respectively. As expected, this value is somewhat lower than the difference due to a similar substitution in the series of saturated hydrocarbons given as 4.8 by Fajans (1945).

VI. ACKNOWLEDGEMENTS

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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VIII-APPENDIX "A"

The following observations were made on some of the compounds studied after the main body of the report was written:

(1) 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.

(2) Similar reversible transformations were observed with $\{(C_2H_5)N\}_2PuCl_6$. Decrease of birefringence occurred at 87°C and the crystals became isotropic at 97°C.

(3) The optic axial angle of $\{(C_2H_5)_4N\}_2UO_2Cl_4$, measured at room temperature, was found to vary between 28 and 36 degrees in different crystals. There appeared to be no correlations 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°.

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(4) 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°. The following values of the two angles were determined at different temperatures:

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

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