Potassium Polyuranates

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Dedicated to Professor Walter Feitknecht

Summary

A reinvestigation of the system K_2O–UO_3 by diffraction methods and i.r. spectroscopy shows that there are two well defined polyuranate phases. Both are based structurally on layers of uranium in hexagonal array, as found in U_3O_8 and $K_2U_2O_7$. One polyuranate, isolated in crystalline form is of the diuranate type, with anionic layers 7.045 Å apart, the spacing determined by cation size and packing dimensions of the uranyl group. It has a composition near $K_2O \cdot 3UO_3$, but probably a more complex formula. The second, not isolated pure, has $K_2O : UO_3 < 1 : 8$, with the layers continuously linked through shared uranyl oxygen atoms, as in α-UO_3. The structural principles of these pseudo-hexagonal layer structures are discussed.

Uranium oxides have a twofold interest in solid state chemistry. They display noteworthy topotaxial relationships that have a bearing on the mechanism of solid state reactions. In addition, the variable valence of uranium leads to the possibility of nonstoichiometric behaviour. The ternary uranium (VI) oxides, the uranates, involve both these questions and although much work has been done on the uranates of the Group I and II metals, it can be said that only the monouranates $M^I_2UO_4$ and $M^{II}UO_4$ are both well defined and structurally understood. The polyuranates M_2O, $n\,UO_3$ and MO, $n\,UO_3$ ($n > 1$) present many problems. This paper deals with the potassium polyuranates.

The diuranates $M^I_2U_2O_7$ have long been known[1] and, as has been shown[2] they are invariably formed as a precursor stage, by a typically topochemical mechanism, in the preparation of the monouranates. A partial crystal structure determination by Kovba *et al.*[3] showed that in $K_2U_2O_7$ the uranium atoms occupy positions closely approximating to a planar hexagonal network essentially identical in dimensions with that found in α-UO_3, U_3O_8, $CaUO_4$ and other uranyl derivatives (Figure 1). This structural principle, and the evidence that essentially the same hexagonal array persists through a series of topochemical reactions, is of prime importance, but the positions of the oxygen atoms are not yet known. It is clear that the oxygen atoms are of two structural types: "uranyl" oxygen atoms (designated O_I), with a short U–O bond length, linked in $K_2U_2O_7$ to a single uranium atom, and "equatorial" oxygen atoms (O_{II}) coordinated around the UO_2^{2+} and lying more or less in the plane of the hexagonal array of uranium atoms. Kovba suggested that the O_{II} atoms are distributed statistically over 5/6 of a set of equivalent sites; this is undoubtedly wrong. In the related structure of U_3O_8 it is now established[4] that (in the low temperature orthorhombic structure) the O_{II} atoms are fully ordered in sites that provide two kinds of coordination for the uranium—pentagonal and roughly square. The high temperature modification of U_3O_8 does have the hexagonal symmetry corresponding to a statistical distribution of the O_{II} atoms; there is no long range ordering, but it is by no means certain that there is not a considerable measure of short range order in a structure with so high an apparent defect concentration. In the structurally related Ta_2O_5 and Ta_2O_5–WO_3 system[5] there is complete ordering—at the cost of creating very large unit cells—over a considerable range in the metal : oxygen ratio. It is most improbable that the diuranates are highly defective structures.

Polyuranates $M^I_2U_nO_{3n+1}$, with $n > 2$, exist, but their nature has recently been questioned. In unpublished work carried out some years ago at the University of Melbourne[6,7] it was believed that $K_2U_4O_{13}$ and $K_2U_6O_{19}$, with their rubidium and caesium analogues, had been characterised by their diffraction patterns and infra red spectra, as compounds structurally related to $K_2U_2O_7$. Essentially the same conclusion was reached by Kovba *et al.*[8], who described either a broad range phase or a succession of phases in the range K_2O, 3.1 – 6 UO_3, based on the same hexagonal or pseudo-hexagonal sheets of uranium atoms as are found in $K_2U_2O_7$ and with similar inter-sheet spacings. On that basis, formation of polyuranates would involve a decrease in the number and a change in the coordination, of the in-sheet O_{II} atoms and not, as in typical polyacid systems, a condensation between anionic structural units. A revision of the work, described here, shows that the situation is more complex: the supposed series $K_2U_nO_{3n+1}$ actually involves two distinct phases, of different but related structural types, and shows analogies with recent work on the sodium polyuranates.

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[1] J. L. C. Zimmermann, *Ber. dtsch. chem. Ges. 14* (1881) 140.

[2] J. G. Allpress, J. S. Anderson and A. N. Hambly, *J. Inorg. Nucl. Chem. 30* (1968) 1195.

[3] L. M. Kovba, Yu. P. Simonov, Ippolitova and V. I. Spitsyn, Issled v. Obl. Khim. Urana Sb. Stat. (1961); *Doklady Akad. Nauk* SSSR *120* (1958) 1042.

[4] A. F. Andresen, *Acta Crystallogr. 11* (1958) 612.

[5] R. S. Roth and N. C. Stephenson, *Scotsdale Conference on Extended Defects in Nonmetallic Solids, April 1969*, to be published.

[6] D. J. Kepert, M. Sc. Thesis, University of Melbourne, 1960.

[7] J. G. Allpress, M. Sc. Thesis, University of Melbourne, 1960.

[8] L. M. Kovba and T. I. Churbakova, *Zh. Strukt. Chem. 2* (1960) 585.

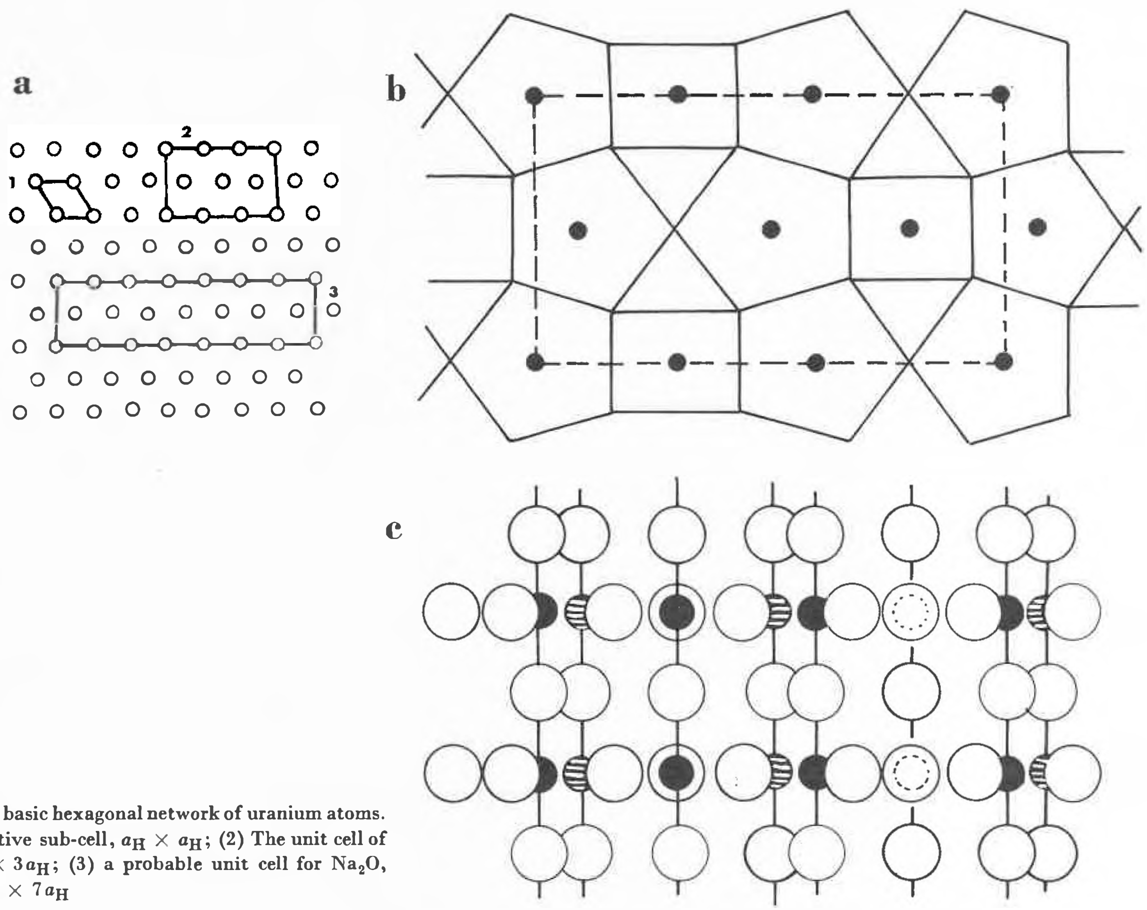

Fig. 1. (a) The basic hexagonal network of uranium atoms. (1) The primitive sub-cell, $a_H \times a_H$; (2) The unit cell of U_3O_8, $\sqrt{3}\, a_H \times 3 a_H$; (3) a probable unit cell for Na_2O, 2.5 UO_3 $\sqrt{3}\, a_H \times 7 a_H$

In this system, hydrated and ill defined sodium polyuranates have been described[9, 10] but no anhydrous compound has been fully characterised. In 1966, however, Carnall, Walker and Neufeld[11] reported that there were three recognisable phases in the system $Na_2O, n UO_3$ ($n > 2$): (i) the diuranate, with a perceptible composition range $2 \leqslant n < 2.1$; (ii) a phase of related structure with n about 2.5; and (iii) a polyuranate with $n \sim 13$, which must, from its c axis spacing, be structurally derived from the U_3O_8 or α-UO_3 type—i.e. with pseudohexagonal sheets directly linked through the uranyl groups, $-U-O_I-U-O_I-$.

The diuranates are well known. Our own observations and those of Carnall, Walker and Neufeld raise the question of the stoichiometric variability of the diuranate phase. Table 1 lists the cell dimensions of the alkali diuranates, indexed on an orthorhombic pseudo-hexagonal basis for comparison with other phases. The Na, K and Rb compounds share essentially the same basic hexagonal network (Figure 1a) of uranium atoms lying in the a–b plane; the Na and K compounds are a superstructure attributable to a slight displacement of the U atoms from the ideal hexagonal positions of this basic unit; the Rb compound can be indexed as truly hexagonal, but in terms of a hexagonal network of the same dimensions. This network is slightly contracted as compared with the basic hexagonal network of α-UO_3 and U_3O_8. With change in the alkali cation, the intersheet spacing increases progressively. $Cs_2U_2O_7$ has not yet been indexed on the same basis.

Table 1. Cell dimensions of alkali metal diuranates, Å

	a	b	c	Z
$Na_2U_2O_7$ [11]	6.812 $\sqrt{3} \times 3.930$	11.790 3×3.930	17.742 3×5.914	9
$K_2U_2O_7$ [6]	6.902 $\sqrt{3} \times 3.985$	7.971 2×3.985	19.643 3×6.548	3
$Rb_2U_2O_7$ [7]	$24,0^0$ 6×4.00	13.86 $2\sqrt{3} \times 4.00$	20.57 3×6.86	36

Carnall, Walker and Neufeld found that in $Na_2U_2O_7$ the main antisymmetric uranyl stretching frequency shifted progressively from 860 cm^{-1} for samples prepared at low temperatures to 820 cm^{-1} for material annealed at 800 °C. We have also observed a variability of the uranyl stretching frequency depending

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[9] C.A. Wamser, J. Belle, E. Bernsohn and B. Williamson, *J. Amer. Chem. Soc. 74* (1952) 1020.

[10] J. Maly and V. Vesely, *J. Inorg. Nucl. Chem. 7* (1958) 119.

[11] W.T. Carnall, A. Walker and S.J. Neufeld, *Inorg. Chem. 5* (1966) 2135.

on the method of preparation and thermal history of the sample and have found furthermore that the frequency can be smoothly correlated with variations in the inter-sheet spacing (Table 2). When well crystallised $Na_2U_2O_7$ was heated for 220 hours at 850°C in air, it lost 1.1% of its weight. The colour of the material darkened only slightly, whereas the mixed uranium (VI)-uranium (V) ternary oxides are black. Hence the loss of weight must be attributed to a small volatilisation of Na_2O, rather than to loss of oxygen, giving a final composition around $Na_{1.85}U_2O_{6.93}$. The cell dimensions of the product (a 11.76_6, b 6.87_0, c 17.86_0 Å) show little change from those of the original $Na_2U_2O_7$, but the infra red spectrum showed considerable changes in the uranyl stretching region. The basic uranium hexagonal network therefore remains unchanged, as it does also in Na_2O, 2.1 UO_3, reported in [11]. In order to preserve the relation of the formula to the basic structure of uranium atoms, the latter compound may better be formulated as $Na_{1.90}U_2O_{6.95}$, a composition close to that reached in the volatilisation of Na_2O from the diuranate.

Table 2. Correlation of uranyl stretching frequency with inter-sheet spacing in $Na_2U_2O_7$

Material	cm^{-1}	Cell Dimensions, Å			
		a	b	c	$\frac{1}{3}c$
From hydrolysis of β-Na_2UO_4	826	diffuse		18.27	6.09
Thermal decomposition of β-Na_2UO_4	822	6.90	11.73	17.99	6.00
Thermal decomposition of α-Na_2UO_4, 950°	834	6.90	11.73	17.94	5.98
Recrystallised from fused NaCl	851	6.89_5	11.72_9	17.86_0	5.95_6

In an unpublished study of the mixed uranium (V, VI) ternary oxides[6] we have found that $Na_2U_2O_7$ gives rise to a series of oxygen-deficient compounds $Na_2U_2O_{7-x}$ ($x < 0.5$), with the $Na_2U_2O_7$ structure. Thus the $Na_2U_2O_7$ phase has a significantly broad phase field in the ternary Na–U–O phase diagram.

$K_2U_2O_7$ also shows the same kind of variability in the peak position and shape of the uranyl stretching region (Table 3).

It is not clear whether the changes in i.r. frequencies arise from changes in crystal perfection, as suggested by Carnall, Walker and Neufeld[12] or from changes in stoichiometry, which can certainly occur. It is likely, but it is not proven, that the variations in O : U ratio arise from abstraction of O_{II} atoms from the basic sheets rather than from loss of the more tightly bound uranyl oxygen atoms O_I, since the same kind of stoichiometric variability is found in α-UO_3 and the U_3O_8 phase, in which the basic hexagonal sheets are linked by continuous strings of $-U-O_I-U-O_I-U-$ bonds along the c direction. Variation in the O_{II} : U ratio could arise in two kinds of deviation from ideal stoichiometry: (a) In a structure with a constant ratio of M^+ cations : U, by a change in the uranium valence, or (b) by a variation in the M^+ : U ratio without any change in the oxidation state of uranium. In this way the diuranate phase can cover a significantly broad phase field.

Table 3. Dependence of uranyl stretching frequency on thermal history for $K_2U_2O_7$

Material	cm^{-1}	Cell dimensions, Å			
		a	b	c	$\frac{1}{3}c$
Recrystallised from KCl	866, 777	6.90_2	7.97_1	19.64_3	6.548
U_3O_8 + excess KCl reacted below the melting point	838, 777	6.90	7.97	19.76	6.59
U_3O_8 + excess KCl at 500°	825, 777	6.90	7.97	19.76	6.59
Intermediate stage in preparation of K_2UO_4	848, masked	–			
$K_2U_2O_7$ heated at 920° *in vacuo*	816, 773	6.90	7.98_4	19.73_4	6.57_8

The structural problem of the diuranates and polyuranates is the manner of coordination of uranium by the O_{II} atoms. In U_3O_8 (Figure 1b), which is idealised, it has been established[4] that the O_{II} atoms provide mixed square and pentagonal in-plane coordination of uranium. By analogy with the recent work of Roth and Stephenson[5] on the remarkable and structurally similar Ta_2O_5–WO_3 system, it can be seen that a decrease in the O_{II} : U ratio could be accommodated by a higher proportion of square to pentagonal coordination polyhedra. O_{II} atoms in these systems appear to be relatively mobile and if the changes in relative numbers of the two coordination sites can be associated with the development of long range order, it is possible that the apparently continuous phase field may, in fact, be resolved into a large number of discrete phases, with very large cell dimensions in the a–b plane. In the ideal diuranate structure there are two O_I atoms per uranium, leaving 1.5 O_{II} atoms per uranium to be disposed in the basal plane. The continuous linkage of polyhedra requires that each oxygen atom be linked to three uranium atoms, so that the mean coordination number of uranium atoms is 4.5, suggesting an equal number of square and pentagonal sites. Plausible configurations for such a structure can be worked out, but remain speculative until a full crystal structure has been performed.

The polyuranates

If the hexagonal array of uranium atoms persists as a structural motif in the polyuranates, two obvious

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[12] W. T. Carnall, A. Walker and S. J. Neufeld, *Inorg. Chem. 4* (1965) 1808.

possibilities are open. (i) The lowered O : U ratio may be accommodated by condensation between sheets, to give a series of possible compounds $M_2U_{2n}O_{7n-1}$. α-UO_3 then appears as the end member of this series, with $n = \infty$, and infinite strings of $-U-O_I-U-$ bonds. The *c* axis spacing of α-UO_3 (4.149 Å) and of U_3O_8 (2 × 4.135 Å) then fixes the characteristic spacing between linked sheets. Polyuranates with $n = 2, 3 \ldots$ etc. would then be built up from slabs approximately $n \times 4.15$ Å thick, separated by spacings characteristic of the diuranate structure, with their singly linked O_I atoms and cations packed between the anionic slabs. The dimensions of the repeating unit along the direction of stacking is thereby predictable. (ii) By retention of the distinct diuranate-like sheets, at a spacing characteristic of the cations as found in the diuranates, but with a decrease in the number, and therefore in the coordination, of the in-sheet O_{II} atoms. In the first case the i.r. spectrum should show frequencies characteristic of two distinct $U-O_I$ linkages, as found in (e.g.) α-UO_3 and in $M_2U_2O_7$ respectively; in the second case, although the proportion of uranyl groups in different site symmetries is changed, so that a different band contour would be expected, the total change should be less in extent. A third possibility, which must be considered, is that finite slabs or blocks of diuranate-like structure are fused together at regular intervals by shared O_I atoms, to give what is effectively a crystallographic shear structure.

In our earlier work it had been concluded[2, 3, 6, 7] that $K_2U_4O_{13}$ and $K_2U_6O_{19}$ existed as distinct compounds, with reproducible infra red spectra that suggested more than one environment for the uranyl group. A material of the composition $K_2U_5O_{16}$ could be interpreted as a mixture of these two phases. The diffraction patterns were partially indexed analytically, but not completely satisfactorily, and appeared to be related to $K_2U_2O_7$. The inter-sheet spacing (whether the *c* axis spacing of a hexagonal structure or the *c** spacing of a monoclinic or triclinic distortion) seemed unambiguously recognizable, and very similar to that of $K_2U_2O_7$. Hence the conclusion was drawn that these were also single sheet structures, involving only a change in the number of O_{II} atoms. Such a change, however, poses a serious problem, in that the O_{II} : U ratio becomes 5 : 4 in $K_2U_4O_{13}$ and 7 : 6 in $K_2U_6O_{19}$. It is difficult to fit such numbers of O_{II} atoms into square or pentagonal coordination in a manner compatible with the fixed geometry of the uranium sub-lattice and the usual $U-O_{II}$ interatomic distances.

The question has accordingly been reinvestigated by preparing a series covering the composition range $K_2U_3O_{10}$ to $K_2U_8O_{25}$. As was found by Carnall, Walker and Neufeld, the i.r. spectrum is more sensitive as a diagnostic technique than the X-ray diffraction patterns. These showed remarkable similarity throughout the series, with very small changes in the positions of the strongest lines, as would indeed be expected if the polyuranates were based on similar sheet structures in the *a–b* plane and similar inter-sheet spacings along the *c* axis. There were progressive changes in the intensity of lines, and the large number of closely spaced lines in the diffraction patterns suggested a structure or structures with a large unit cell. The i.r. spectra (Figure 2, Table 4) make it evident that the whole series is, however, a mixture of two phases that are nearly indistinguishable by powder diffraction methods.

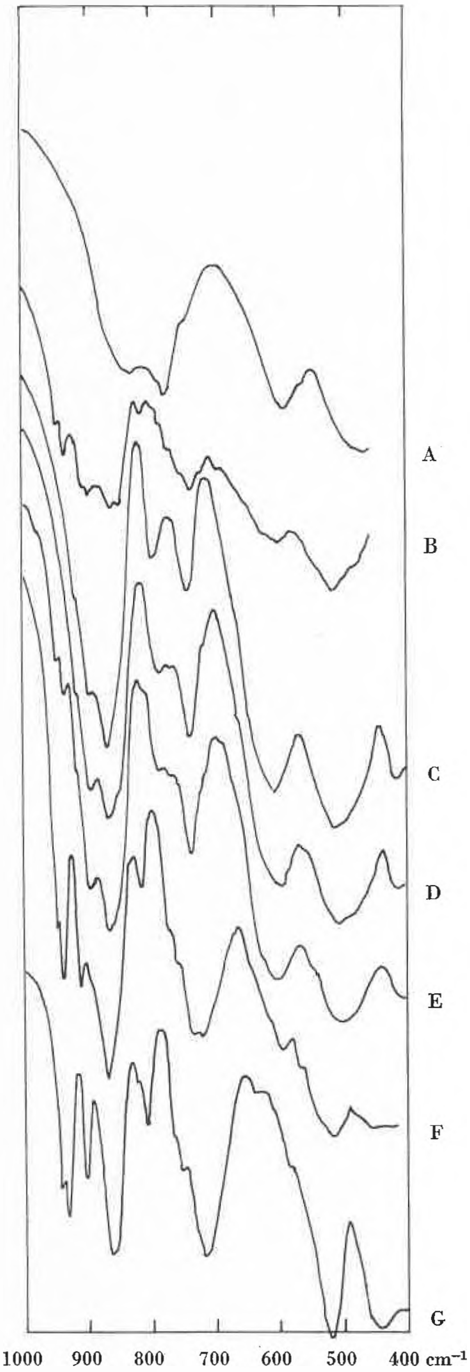

Fig. 2. I.r. absorption spectra of the series K_2O, nUO_3 (n = 2 to 8). *A*: $K_2U_2O_7$, *B*: n = 3.03, *C*: n = 4, *D*: n = 5, *E*: n = 5.58, *F*: n = 6, *G*: n = 7.97

Table 4. Infra red frequencies of potassium polyuranate preparations

Material	ν, cm^{-1}										
K_2O, 3.03 UO_3	946 (w)	933 (w)	900 (s)	860 (s)	848	814 (w)	773 (s, br)	735	720 (s, br)	594 (s)	
K_2O, 3,68 UO_3	895 (vw)	870 (s)	791 (w)	745 (w)	602 (s)	502 (s, br)	412				
K_2O, 4 UO_3	900 (vw)	872 (s)	817 (w)	770 (s, br)	725 (s)	600 (s)	520 (s, br)	450			
K_2O, 5.58 UO_3	946 (vw)	936 (w)	900 (w)	868 (s)	790 (w)	775 (w)	605 (s)	505 (s, br)			
K_2O, 6 UO_3	947	936 (s)	900 (w)	870 (s)	830 (s, br)	817	770 (s, br)	760 (s, br)	725 (s)	520 (s)	450 (br)
K_2O, 7.97 UO_3	942 (w)	930 (s)	906 (m)	810 (mw)	755 (s, br)	720 (s)	520 (s)	446 (s)			
Hand picked red polyuranate crystals	910 (w)	898	882 (w)	866 (s)	787 (m)	736 (s)	598 (s, br)				

s strong, m medium, w weak intensity, br broad.

The lambent red-orange preparation K_2O, 3.03 UO_3 already shows a quite different i.r. spectrum from that of $K_2U_2O_7$. Hence there is at least one defined phase with $n > 2$, and probably around 3, in the potassium polyuranate system. With increase in the $UO_3 : K_2O$ ratio, from 3.03 to 6, a shoulder at 910 cm^{-1} and peak at 898 cm^{-1} grow progressively and the supposed $K_2U_4O_{13}$ shows no distinctive features other than those of the mixture. The very sharp peaks at 943 cm^{-1}, 936 cm^{-1} and 910 cm^{-1} increase progressively up to $K_2O : 7.97\ UO_3$, when they are the strongest features in the uranyl stretching region and there are only vestiges of the spectrum associated with "$K_2U_3O_{10}$". There are also marked and consistent changes, concurrently, in the 400–750 cm^{-1} region that has been assigned to O_{II} vibrational modes.

There is thus evidence for two, and only two, polyuranates in the composition range $3 < n < 8$. One of these has $n > 8$ and is present in very small amount in K_2O, 3.03 UO_3. If it can be assumed that this sample had reached an equilibrium phase composition in the solid state reaction by which it was prepared, the red polyuranate has $n < 3$. For reasons considered below, it is likely that this phase cannot be assigned a simple formula $K_2U_3O_{10}$.

As prepared, all the samples were microcrystalline, but long annealing of "$K_2U_4O_{13}$" and "$K_2U_6O_{19}$" at 900 °C in air gave crystals visible under the microscope. It was subsequently established by microscopy that all the series contained two components of the same physical appearance. Reflected light microscopy of a polished compact, and microprobe analysis, indicated that the two phases were apparently intergrown, pointing to some topotaxial relation between them. One phase consisted of dull red crystals, ultimately obtained in laths up to 0.005–0.010 cm in length; the other was darker in colour, with more nearly isometric habit and much smaller particles. Since all these materials have similar high densities, selective flotation is impossible, but the difference in size and habit of the crystals made it possible to effect a partial separation by elutriation with toluene into a coarse fraction, enriched in the red phase, and a fine particle fraction enriched in the higher polyuranate. These differed in i.r. spectrum, that of the fines (Figure 3) showing considerable enhancement of the peak assigned to the high polyuranate. The diffraction patterns of the two fractions showed that the strong lines must nearly coincide; these include reflections most directly related to the simple hexagonal sub-cell, which is thus probably a common structural motif, with small dimensional differences between the two phases, leading to imperfect superposition of lines in the mixed reaction

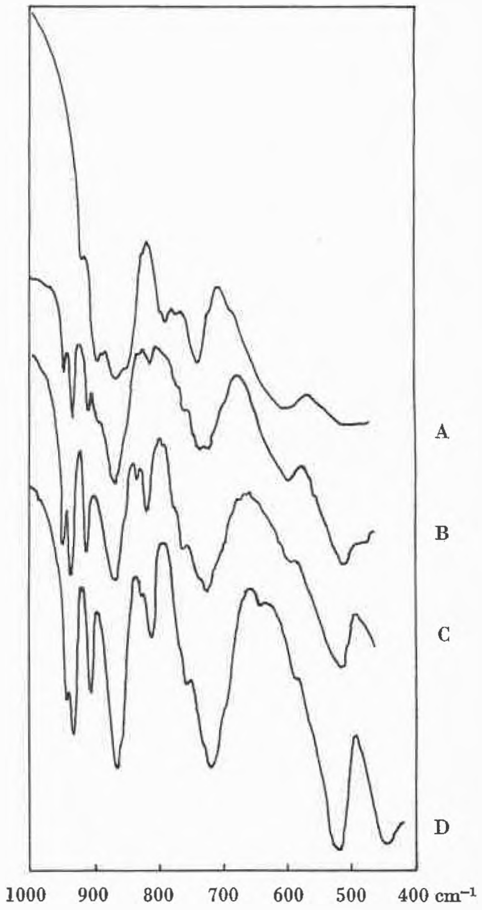

Fig. 3. I.r. absorption spectra of the components of polyuranate preparations. *A* Hand picked crystal of lower polyuranate. *B* Coarse particle fraction, enriched in lower polyuranate. *C* Fine particle fraction, enriched in higher polyuranate. *D* K_2O, 7.97 UO_3

products. X-ray diffractometry showed that the strong lines differed in contour as between the two fractions, and this change in line contour is responsible for the small and rather erratic changes in the measured position of the diffraction lines as the whole composition series is traversed. In addition, the diffraction pattern of the fine fraction is rich in closely spaced lines at fairly low Θ, indicative of at least one long spacing.

Sufficient single crystals of the red "triuranate" could be picked out by hand for i.r. spectroscopy, electron diffraction and single crystal X-ray work. The i.r. spectrum (Figure 3, Table 4) agrees closely with that of the K_2O, 3.03 UO_3 preparation, confirming that the compound is close to the triuranate composition. The small peak at 910 cm^{-1} may be a vestige of the strong absorption at 910–946 cm^{-1} characteristic of the higher polyuranate, and arising from inclusions or small overgrowths of the latter. The strongest absorption is in the region characteristic of the asymmetric stretch of the "simply linked" uranyl group, but at a higher frequency (i.e. rather shorter bond length) than in $K_2U_2O_7$. The complex profile may indicate that more than one site symmetry is involved.

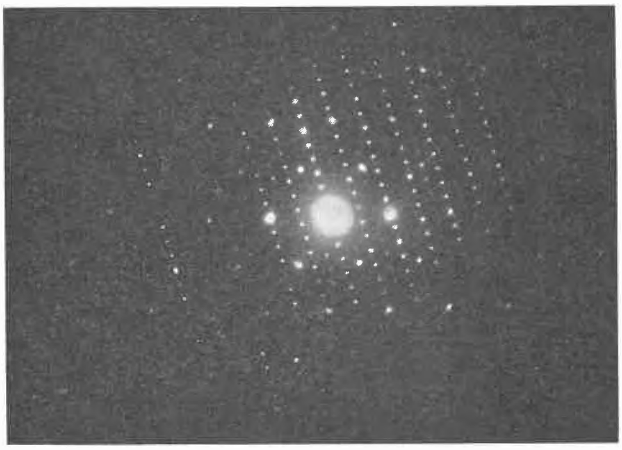

Fig. 4. Electron diffraction pattern of potassium polyuranate ($n \sim 3$). Near-basal plane section of reciprocal lattice, showing the prominent U_3O_8-like sub-cell

A single crystal X-ray examination is at a very preliminary stage, only tentative conclusions can be drawn. However; electron diffraction (kindly carried out by Dr. R. J. D. Tilley) revealed several cross sections of the reciprocal lattice (Figure 4), one of which displayed perfect hexagonal symmetry and was assigned to a hexagonal lattice of side a approximately 12.35 Å. In Figure 4, the most intense spots correspond in position to the (200) reflections of the recurrent hexagonal uranium network, as indexed (e.g. in the high temperature modification of U_3O_8) for a cell of side $\sqrt{3}\ a_H$, where a_H is the U–U distance in the basic network. These spots grew in intensity during observation, and close examination showed that they were then double. Their enhanced intensity is probably due in part to some decomposition in the electron beam to form U_3O_8 (or possibly $K_2U_2O_7$) of very slightly different cell dimensions, but in perfect epitaxy with the red polyuranate. The latter can thus be assigned basically the same pseudohexagonal arrangement of uranium atoms. The relation between structures is that the (200) sub-cell spots translate into (310) of the true reciprocal lattice net: a (polyuranate) $= \frac{\sqrt{39}}{2}\ a_H$. Preliminary work on Weissenberg and oscillation photographs shows that the third axis is orthogonal to this hexagonal sheet, with $c = 14.09$ Å. The strongest X-ray reflections can be indexed in terms of a smaller sub-cell, with $a = 6.90$, $c = 7.045$ Å. As in other compounds of this series, the superstructure must arise from small displacements of the uranium atoms from the idealized hexagonal positions.

The orthorhombic cell tentatively assigned would contain 26 uranium atoms in the basal plane. Whether it be a 1- or a 2-layered structure, the probable formula of this compound must reflect this, and is likely to be of the general type $K_{2x}U_{26}O_{78+x}$, with $2x : 26 \sim 1 : 3$. On this basis the simplest possibilities would appear to be $K_8U_{13}O_{43}$ (K_2O, 3.25 UO_3) or $K_2U_{26}O_{87}$ (K_2O, 2.89 UO_3) or $K_{10}U_{13}O_{49}$ (K_2O, 2.6 UO_3). The spacing between layers appears to be about 7% greater than in $K_2U_2O_7$. Much the same increase of spacing can be recognised in the sodium polyuranate reported by Carnall, Walker and Neufeld. New experiments have completely confirmed their findings, except that additional low angle lines found in Guinier camera diffraction patterns suggest that their unit cell is a submultiple of the true cell. In all compounds of this type, the underlying nearly hexagonal network of uranium atoms at 3.90–3.96 Å spacing prescribes certain metrical relations between the axes in the basal plane of any orthorhombic cell. It may be noted that their assignment, $a = 6.68$, $b = 12.50$, $c = 9.18$ Å contains the relations $a = \sqrt{3} \times 3.854$ Å, $3c = 7 \times 3.933$ Å. It is therefore probable that the c axis should be tripled, and the assignment of b and c axes interchanged for homology with other compounds in this series, giving a unit cell $a = 6.68$, $b = 27.54$, $c = 12.50$ Å, corresponding to a cell $\sqrt{3}a_H \times 7a_H$, with layers $\frac{1}{2}c = 6.25$ Å apart. This inter-sheet spacing is 5.5% larger than that (5.91$_4$ Å) in $Na_2U_2O_7$. Since the cohesive forces along the c axis are chiefly the electrostatic interactions between the alkali metal cations and the anionic sheets, the decreased alkali metal : uranium ratio may well account for the observed small expansion. An inference from this is that the change in U : O ratio, from diuranate to polyuranate, does arise from a decrease in the number and a change in the coordination of the O_{II} atoms.

The second constituent of the polyuranate preparations is that characterised by very strong and sharp i.r. absorption at 946, 936 and 910 cm^{-1}. This has not yet been obtained pure or macrocrystalline; it is, however, the major component of K_2O, 7.97 UO_3. The diffraction pattern has not yet been indexed, but reflections associated with the small hexagonal sub cell are present. The i.r. absorption can be compared with the strong, sharp peaks found by Carnall, Walker and Neufeld at 920 cm^{-1} for the higher sodium polyuranate to which, on cogent grounds, they assign the composition Na_2O, 12.7 UO_3. For this, they give the cell dimensions $a = 6.807$, $b = 15.934$, $c = 8.254$ Å—i.e. $a = \sqrt{3} \times 3.931$, $b = 4 \times 3.983$ Å, or a structure with sheets $\sqrt{3}\,a_H \times 4\,a_H$, 4.127 Å apart. This inter-sheet spacing is characteristic of that between layers in continuously linked $-O_I-U-O_I-U-$ structures (e.g. in U_3O_8, 4.149 Å) and it may be inferred that the higher sodium polyuranate has this structure. It is very probable that K_2O, $n\,UO_3$ ($n \geqslant 8$) is also of the same type.

Two unanswered questions follow from this inference. The continuous linkage of sheets through O_I atoms appears to fix the $U-O_I$ bond length unambiguously at 2.07 Å—a long $U-O_I$ bond, for which a low asymmetric stretching frequency would be predicted. A similar high frequency is found in α-UO_3, but there is no absorption in this region from U_3O_8. Carnall, Walker and Neufeld have discussed this problem; the higher potassium polyuranate adds another example of the anomaly. The second question is the location of the cations in these structures. With normal interionic distances they cannot be accommodated between the layers. In unpublished work we have found a considerable number of phases derived directly from U_3O_8 by the introduction of alkali metal cations and large divalent cations (e.g. Ba^{2+}, Pb^{2+}) into the U_3O_8 structure. These are mixed valence phases with at least an observable composition range, $M_xU_3O_{8\pm y}$. The sodium and potassium polyuranates appear to be analogous, but are uranium(VI) compounds. Until a complete structure determination has been made, their constitution remains obscure, but it would appear inescapable that other cations can occupy uranium atom sites in the basic hexagonal network.

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