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PREPARATION, IDENTIFICATION, AND CRYSTAL STRUCTURE OF
A PENTAVALENT AMERICIUM COMPOUND, KAmO_2F_2 . *

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ABSTRACT

A compound that is shown to be KAmO_2F_2 is prepared by the addition of a saturated solution of KF to an acid solution of pentavalent americium. The substance is found to be rhombohedral with one molecule in a unit cell of dimensions $a = 6.78 \text{ \AA}$, $\alpha = 36.25^\circ$. The space group is $\bar{R}3m$, and the atomic positions are: 1 Am in (0,0,0), 1 K in (1/2,1/2,1/2), 2 O in $\pm (u,u,u)$ with $u = 0.102$, 2 F in $\pm (v,v,v)$ with $v = 0.356$. The structure contains radicals $[\text{AmO}_2]^+$ and is built up of layers $(\text{AmO}_2\text{F}_2)^-$ held together by potassium ions. The structure type is that of CaUO_2O_2 . (auth.)

The preparation of double carbonates of alkali with pentavalent trans-uranic elements was recently described by Nigon, et al⁽¹⁾. X-ray diffraction

(1) J. P. Nigon, R. A. Penneman, E. Staritzky, T. K. Keenan, L. B. Asprey, "Alkali Carbonates of Np(V), Pu(V), and Am(V)", *This Journal*, in press.

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studies of the double carbonate preparations led to a determination of the crystal structure of the iso-structural series KPuO_2CO_3 , $\text{NH}_4\text{PuO}_2\text{CO}_3$, and $\text{RbAmO}_2\text{CO}_3$ ⁽²⁾. The present paper gives the results of x-ray diffraction

(2) P. H. Ellinger and W. H. Zachariassen, "The Crystal Structure of KPuO_2CO_3 , $\text{NH}_4\text{PuO}_2\text{CO}_3$, and $\text{RbAmO}_2\text{CO}_3$ ", *This Journal*, in press. *In preparation*

studies of the double fluoride precipitates.

The investigation is based upon two different samples, one being a potassium-ameridium fluoride precipitate, and the other an analogous preparation made with rubidium instead of potassium. It was subsequently found that the commercially supplied rubidium salt which was used in making the latter sample contained considerable amounts of potassium.

PREPARATION OF THE COMPOUNDS

The americium used in this study contained no impurities above the spectroscopic limit of detection.

KAmO_2CO_3 was prepared by OCl^- oxidation of Am(III) in K_2CO_3 solution^(1,3).

(3) L. B. Werner and I. Perlman, *This Journal* 73, 495 (1951).

$\text{RbAmO}_2\text{CO}_3$ was prepared by $\text{S}_2\text{O}_8^{--}$ oxidation of Am(III) in Rb_2CO_3 solution in a similar manner⁽¹⁾.

The alkali- Am(V) carbonate compounds were washed with dilute alkali carbonate solution to reduce alkali carbonate concentration to $<0.1 \text{ M CO}_3^{--}$ and to remove other ions. The solids were then dissolved in 1 M HNO_3 acid in slight excess to give a solution of AmO_2^+ in $<0.1 \text{ M H}^+$.

The solution, containing approximately 10-20 gms./liter of americium as AmO_2^+ , was treated with an equal volume of saturated alkali fluoride. The white precipitate formed was allowed to stand for 5-10 minutes, washed three

times with ca. 10 volumes of water per wash, and slurried into a capillary. The solid, containing ~30 micrograms of americium⁽⁴⁾, was centrifuged into

(4) Excessive film blackening results from the gamma radiation of Am^{241} with larger amounts of sample.

the capillary tip and the supernatant removed by means of a smaller capillary inserted into the larger one. The solid was then washed once with acetone, air-dried, and sealed off preparatory to x-ray examination.

X-RAY DIFFRACTION DATA AND CHEMICAL COMPOSITION

The x-ray diffraction data for the pure potassium preparation as obtained with Cu K α radiation are given in Table I. All the observed diffraction lines can be ascribed to a single phase with a rhombohedral unit cell of dimensions⁽⁵⁾: $a = 6.78 \pm 0.01 \text{ \AA}$, $\alpha = 36.25^\circ \pm 0.05^\circ$. The second sample,

(5) The hexagonal cell has dimensions $a_1 = 4.22 \text{ \AA}$, $a_3 = 18.99 \text{ \AA}$.

the rubidium preparation made with appreciable potassium content, gave unit cell dimensions: $a = 7.03 \pm 0.01 \text{ \AA}$, $\alpha = 35.11 \pm 0.05^\circ$. The sample was found to contain a small amount of rubidium-silico-fluoride and traces of an unknown phase. The considerable increase in cell dimensions of the second sample over the first is proof that the alkali atoms are constituents of the structure. In view of the impure nature of the second sample, the crystal structure determination is based upon the diffraction data of the pure potassium preparation.

According to the method of chemical preparation, the cation constituents of the structure are K^+ and Am^{+5} . It is generally supposed, and indeed directly verified for the double carbonates, that the pentavalent state of

TABLE I. X-RAY DIFFRACTION DATA, Cu K α

Observed Intensity	Observed $\sin^2\theta$	Rhombohedral H ₁ H ₂ H ₃	Calculated $\sin^2\theta$
80	0.0148	111	0.0149
50	0.0467	100	0.0462
100	0.0516	110	0.0511
30	0.0594	222	0.0594
40	0.0714	211	0.0709
15	0.0860	221	0.0858
10	0.1256	322	0.1255
60	0.1340	{ 10 $\bar{1}$ 333	0.1335 0.1341
60	0.1492	{ 210 332	0.1484 0.1501
15	0.1802	11 $\bar{1}$	0.1797
25	0.1853	200	0.1846
40	0.1935	321	0.1929
15 diffuse	0.2064	{ 220 433	0.2044 0.2095
10 diffuse	0.2385	{ 444 443	0.2376 0.2441
5	0.2611	331	0.2590
20	0.2671	432	0.2676
15	0.2827	422	0.2836
35 diffuse	0.3170	{ 20 $\bar{1}$ 21 $\bar{1}$	0.3132 0.3181

TABLE I, continued

20	0.3379	$\left\{ \begin{array}{l} 310 \\ 442 \end{array} \right.$	0.3379 0.3430
10	0.3547	320	0.3528
20 diffuse	0.3700	$\left\{ \begin{array}{l} 554 \\ 543 \\ 555 \\ 533 \end{array} \right.$	0.3685 0.3711 0.3717 0.3776
10	0.3919	421	0.3925
15	0.4004	211	0.4005
35	0.4156	$\left\{ \begin{array}{l} 300, 22\bar{1} \\ 431 \end{array} \right.$	0.4154 0.4171
20	0.4593	$\left\{ \begin{array}{l} 553 \\ 411, 330 \end{array} \right.$	0.4569 0.4599

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americium involves radicals $[AmO]^+$. The conceivable anion constituents other than the oxygen atoms of the possible radicals $[AmO_2]^+$ are fluoride and nitrate ions.

It has been amply demonstrated for compounds of the heavy elements that it is possible to assign fixed volume requirements to the various ions, V_i , so that the volume of the unit cell is given (usually to better than 5 percent) by the sum $\sum V_i^{(6)}$. Small, high charged cations like Am^{+5} and N^{+5}

(6) See for instance W. H. Zachariasen, This Journal 70, 2117 (1948).

have negligible volume requirements, since they fit into the interstices between the anions. The experimental values for the volume requirements of the pertinent ions are listed in Table II.

TABLE II. VOLUME REQUIREMENTS

Ion	Volume Requirement in A^3
K^+	21
Am^{+5}	0
$[AmO_2]^+$	38*
O^{-2}	19
F^-	18
N^{+5}	0
$[NO_3]^{-1}$	57*

*The values for the oxygen radicals are determined by the number of oxygen atoms.

The volume of the unit cell is $98 A^3$. Accordingly the unit cell contains a total of five potassium plus oxygen plus fluorine atoms, and at least one of them is a potassium atom. In addition, there must be at least

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one americium atom per unit cell. It is easily seen that there is one and only one way of balancing valences subject to the necessary boundary conditions deduced from volume considerations, and this is by having a unit cell content corresponding to the formula: KAmO_2F_2 . The presence of two oxygen atoms per americium atom strongly suggests the existence of radicals $[\text{AmO}_2]^+$ as previously observed in $\text{Rb}[\text{AmO}_2]\text{CO}_3$.

It should be emphasized that a consideration of diffraction intensities independently leads to the conclusion of one potassium atom and one americium atom per unit cell.

The chemical identity of the phase having been established, the density can be calculated, and the result is: $\rho = 5.96 \text{ g/cm}^3$.

DETERMINATION OF THE STRUCTURE

Since there is only one americium atom in the rhombohedral cell, the coordinate origin is conveniently laid in this atom, i.e., 1 Am in (0,0,0). The intensity distribution is predominantly determined by the strongly scattering americium atom, but the effect of the other atoms is readily discernible. This is seen from Table III, where column 5 gives the observed intensities and column 2 those calculated on the basis of the americium contribution alone. Reflections with odd values of $\sum H_i$ appear much weaker and reflections with even $\sum H_i$ ($\sum H_i = 4$ being an exception) much stronger than can be accounted for by the americium contribution. This feature of the intensity distribution necessitates placing the potassium atom in the position (1/2, 1/2, 1/2).

The position deduced for the potassium atom strongly suggests the presence of an inversion center and hence equivalence between the two oxygen atoms and between the two fluorine atoms. Assuming such equivalence, the

space group symmetry becomes $R\bar{3}m$ with the atomic positions: 1 Am in (0,0,0), 1 K in (1/2,1/2,1/2), 2 O in $\pm(u,u,u)$, 2 F in $\pm(v,v,v)$.

With the small scattering powers of oxygen and fluorine, it is not possible to locate these atoms with any degree of accuracy from the rather crude intensity data. Approximate values of the parameters u and v can, however, be found. In column 3 of Table III are given the intensities calculated on the basis of the americium and potassium scattering. Comparison of columns 3 and 5 shows that the observed intensities of reflections for which $\sum H_i = 4, 5$ and 7 are considerably weaker than can be accounted for in terms of americium and potassium atoms. The parameter values u and v are accordingly such as to give large negative contributions to the structure factor for these reflections, and this requirement gives: $u \approx 0.10$, $v \approx 0.34$.

With the deduced parameter values, each americium atom forms two short bonds with oxygen atoms giving a collinear radical $[AmO_2]^+$ (the possibility $u \approx 0.34$, $v \approx 0.10$ is rejected, since it corresponds to the unreasonable conclusion of radicals $[AmF_2]^{+3}$) and six long bonds to fluorine atoms. Each potassium atom is bonded to two fluorine atoms and to six oxygen atoms.

The only accurate determination of the size of an XO_2 -radical is for $[UO_2]^{+2}$ in $MgUO_2O_2$, and this gave $U-O = 1.93 \pm 0.03 \text{ \AA}^{(7)}$. For the $[UO_2]^+$

(7) W. H. Zachariasen, unpublished work.

group a reasonable estimate is $U-O = 1.96 \text{ \AA}$, which with a $0.03 \text{ \AA}$ contraction in going from uranium to americium gives $1.93 \text{ \AA}$ as an expected value for $Am-O$ in $[AmO_2]^+$ and a parameter value $u = 0.102$.

In KF the distance $K-F = 2.66 \text{ \AA}$. Potassium has coordination number eight in the present structure. The anticipated K-F distance in $KAmO_2F_2$ is therefore $2.74 \text{ \AA}$ requiring $v = 0.356$.

TABLE III. Calculated Intensities

$H_1H_2H_3$	Calculated Intensity			Observed Intensity
	Am Atoms	K + Am Atoms	All Atoms	
111	89	59	77	80
100	73	50	53	50
110	70	98	100	100
222	21	30	27	30
211	50	72	42	40
221	43	28	20	15
322	28	20	12	10
101	29	39	60)	60
333	10	7	9)	
210	51	36	42)	60
332	25	34	42)	
111	20	15	16	15
200	20	27	27	25
321	38	51	50	40
220	18	23	16)	15 diffuse
433	17	23	23)	
311	16	12	9	-
444	5	6	6)	10 diffuse
443	14	10	12)	
331	13	9	6	5
432	26	19	25	20
422	12	16	20	15
201	22	16	17)	35 diffuse
211	22	29	28)	
544	11	8	6	-

TABLE III (continued)

310	20	26	19)	20
442	10	13	14)	
320	20	15	11	10
551	10	11	12)	20 diffuse
513	19	25	25)	
555	3	2	3)	
533	10	7	9)	
421	17	13	9	10
211	9	12	17	15
300, 221	17	12	14)	35
431	17	22	27)	
553	8	6	5)	20
411, 330	15	22	20)	

The parameter values $u = 0.102$, $v = 0.356$ will be used in preference to the direct result $u = 0.10$, $v = 0.34$. The calculated intensities, with all atoms considered, are listed in column 4 of Table 3. The following intensity formula is used throughout the article:

$$I \propto |F|^2 = \frac{p \cdot \cos^2 \theta}{\sin^2 \theta \cos \theta} A.$$

p is the multiplicity factor, and A is the absorption factor for a cylindrical sample with $\mu R = 3.0$.

DISCUSSION OF THE STRUCTURE

The structure found for KAmO_2F_2 is of the CaUO_2O_2 type⁽⁸⁾. The inter-

(8) W. H. Zachariasen, Acta Cryst. 1, 281 (1948).

atomic distances are:

$$\begin{aligned} \text{Am} - 2 \text{ O} &= (1.93 \text{ \AA}) \\ \text{Am} - 6 \text{ F} &= 2.47 \text{ \AA} \\ \text{K} - 6 \text{ O} &= 2.73 \text{ \AA} \\ \text{K} - 2 \text{ F} &= (2.71 \text{ \AA}) ; \end{aligned}$$

the values in parenthesis being assumed. The Am-F and K-O distances are not much affected by moderate variations in the parameter values u and v , and are therefore quite accurate. The great difference between the primary Am-O bond length and the secondary Am-F bond length is worthy of notice. The following table gives results for primary and secondary bond lengths of XO_2 radicals in various crystals.

<u>Compound</u>	<u>Radical</u>	<u>Primary Bond Length</u>	<u>Secondary Bond Length</u>
UO ₂ F ₂ (9)	[UO ₂] ⁺²	U - 2 O = (1.91 Å)	U - 6 F = 2.50 Å
KAmO ₂ F ₂	[AmO ₂] ⁺¹	Am - 2 O = (1.93)	Am - 6 F = 2.47
MgUO ₂ O ₂ (10)	[UO ₂] ⁺²	U - 2 O = 1.93 ± 0.03	U - 4 O = 2.18
CaUO ₂ O ₂	[UO ₂] ⁺²	U - 2 O = 1.91 ± 0.10	U - 6 O = 2.29
KPuO ₂ CO ₃ (11)	[PuO ₂] ⁺¹	Pu - 2 O = (1.94)	Pu - 6 O = 2.55

(9) W. H. Zachariasen, *Acta Cryst.* 1, 277 (1948).

(10) " " " ", unpublished result.

(11) F. H. Ellinger and W. H. Zachariasen, *op. cit.*

In KPuO_2CO_3 , the six secondary bonds all lie in a plane, and the bond length is for this reason longer than otherwise might be expected. This substance apart, the experimental results indicate that the secondary X-F bonds are appreciably longer than the secondary X-O bonds, and this in turn suggests that the primary bond lengths in UO_2F_2 and KAmO_2F_2 may be somewhat smaller than assumed.

The KAmO_2F_2 structure is built up of hexagonal layers $[\text{AmO}_2\text{F}_2]^-$ held together by the potassium ions. These layers are isostructural with the UO_2F_2 layers in uranyl fluoride and with the $[\text{UO}_2\text{O}_2]^{-2}$ layers in CaUO_2O_2 . The period is 4.22 Å for the $[\text{AmO}_2\text{F}_2]^-$ layer and 4.20 Å for the UO_2F_2 layer as against 3.87 Å for the $[\text{UO}_2\text{O}_2]^{-2}$ layer.

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