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Potassium Double Carbonates of Pentavalent Neptunium, Plutonium, and Americium[1]

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The crystalline compounds $KNpO_2CO_3$ and $KAmO_2CO_3$ were prepared by addition of potassium bicarbonate to an aqueous solution of the pentavalent MO_2^+ ion. They are isostructural with $KPuO_2CO_3$; hexagonal, space group C6/mmc-D^4_{6h}, $Z = 2$, with lattice constants: $KNpO_2CO_3$, $a_0 = 5.120 \pm 0.001$ Å., $c_0 = 9.971 \pm 0.003$ Å.; $KPuO_2CO_3$, $a_0 = 5.093 \pm 0.001$ Å., $c_0 = 9.815 \pm 0.002$ Å.; $KAmO_2CO_3$, $a_0 = 5.112 \pm 0.001$ Å., $c_0 = 9.740 \pm 0.002$ Å.

Introduction

The doubly oxygenated or MO_2^+ configuration of the aqueous pentavalent state for uranium, neptunium, plutonium, and americium has been known for some years.[2] The existence of the MO_2^+ species in certain solid compounds has also been established. Crystal structure data have been reported for three hexagonal double carbonates, $KPuO_2CO_3$, $NH_4PuO_2CO_3$, and $RbAmO_2CO_3$,[3] and for one rhombohedral double fluoride with potassium, $KAmO_2F_2$.[4] Other double carbonates having orthorhombic symmetry, such as $K_5AmO_2(CO_3)_3$, have been reported although no X-ray studies have been published. In no case, however, has a systematic examination of lattice constants been made for a homologous series of pentavalent actinides maintaining the same alkali metal cation while varying the pentavalent actinide constituent.

A steady decrease in cell dimensions has been reported for the trivalent and tetravalent fluorides of uranium, neptunium, plutonium, and americium.[5] The hexavalent states of these elements show a similar decrease, as evidenced in the lattice constants of the double acetates with sodium.[6] Therefore, it seemed of interest to examine a series of pentavalent actinide compounds to determine the extent of the actinide contraction exhibited by this valence state. The 1:1 potassium double carbonates were chosen for this study since the hexagonal symmetry of $KPuO_2CO_3$ would provide straightforward X-ray powder diffraction analysis. The potassium–plutonium compound had been prepared in both the hexagonal $KPuO_2CO_3$ form at pH 7 and the orthorhombic form [presumably $K_5PuO_2(CO_3)_3$][7] at higher carbonate concentrations near pH 12.[8] It was found that the hexagonal 1:1 potassium neptunium or potassium americium[9] carbonates could be prepared by carrying out the precipitation at pH 7 in potassium bicarbonate media.

Experimental

All chemicals were of A.R. grade. The actinide isotopes used were Np^{237}, Pu^{239}, and Am^{243}, each of $\geqslant 99.5\%$ purity.

In all cases, the 1:1 potassium actinide(V) carbonates were prepared by reduction of the actinide(VI) species to the pentavalent state. Solutions of NpO_2^{2+}, PuO_2^{2+}, and AmO_2^{2+} were prepared by ozone oxidation in dilute nitric acid media. A stoichiometric amount of KI was added to the MO_2^{2+} solution to reduce it to the MO_2^+ state. The free iodine liberated by the reduction was extracted with benzene. Potassium bicarbonate was then added to neutralize the acid and to make the final solution 0.1 *M* in bicarbonate. A light-colored precipitate formed immediately (the color was essentially the same for the neptunium, plutonium, and americium compounds) and the temperature was raised to *ca.* 90° for 3–4 hr. to aid digestion. The crystalline precipitate was washed several times with 0.01 *M* $KHCO_3$ during the digestion. The precipitate was then washed first with absolute ethyl alcohol and then with acetone and allowed to dry overnight.

X-Ray capillaries were loaded with the dry material and photographed in a conventional Debeye–Scherrer 114.6-mm. camera, using Ilford "G" film and filtered copper radiation. Both the POWD[10] X-ray powder pattern generating code and a modified MET-124[11] least-squares code were used with an IBM 7094 computer to calculate lattice constants from the observed film data.

Several attempts were made to prepare a corresponding potassium uranium(V) carbonate using the above or similar experimental techniques. No precipitate could be obtained under conditions where $KNpO_2CO_3$, $KPuO_2CO_3$, and $KAmO_2CO_3$ readily formed. In view of the known instability of pentavalent uranium, this aspect of the work was not pursued further.

Results

All three compounds, $KNpO_2CO_3$, $KPuO_2CO_3$, and $KAmO_2CO_3$, are isostructural, hexagonal, space group C6/mmc-D^4_{6h}, two molecules per unit cell. The hexagonal structure was determined for $KPuO_2CO_3$ by Ellinger and Zachariasen.[3] Our preparation confirmed

TABLE I

UNIT CELL DIMENSIONS OF $KNpO_2CO_3$, $KPuO_2CO_3$, AND $KAmO_2CO_3$; ERROR LIMITS ARE STANDARD DEVIATION

	a_0, Å.	c_0, Å.
$KNpO_2CO_3$	5.120 ± 0.001	9.971 ± 0.003
$KPuO_2CO_3$	5.093 ± 0.001	9.815 ± 0.002
$KAmO_2CO_3$	5.112 ± 0.001	9.740 ± 0.002

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(1) This work was done under the auspices of the Atomic Energy Commission.

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(11) M. H. Mueller and L. Heaton, Argonne National Laboratory Report ANL-6176 (1961). That portion of this code dealing with the standard deviation of the fitted constants was revised by F. H. K.

Table II

		$KNpO_2CO_3$		$KAmO_2CO_3$	
hkl	*I* obsd.	*d* calcd., Å.	*d* obsd., Å.	*d* calcd., Å.	*d* obsd., Å.
002	s	4.99	5.01	4.87	4.87
100	m	4.43	4.44	4.43	4.43
101	vs	4.05	4.06	4.03	4.03
102	s	3.31	3.31	3.28	3.28
103	m	2.66	2.66	2.62	2.62
110	s	2.56	2.56	2.56	2.56
004	m	2.49	2.49	2.44	2.44
112	m	2.28	2.28	2.26	2.26
200	w	2.22	2.22	2.21	2.21
201	s	2.16	2.16	2.16	2.16
104		2.17		2.13	2.13 w
202	m	2.03	2.02	2.02	2.01
203	mw	1.844	1.846	1.829	1.828
105	mw	1.819	1.821	1.783	1.785
114	m	1.786	1.787	1.763	1.764
211	ms	1.653	1.653	1.649	1.649
204		1.657		1.638	. . .
006		1.662		1.623	1.618
212	w	1.589	1.588	1.582	1.584
105	vw	1.556	1.557	1.524	1.525
213	w	1.496	1.496	1.487	1.488
300	w	1.478	1.480	1.476	1.476 w
205		1.483		1.462	1.463 w

the values initially reported for $KPuO_2CO_3$. Unit cell dimensions are given in Table I.

A listing of portions of the observed and calculated X-ray powder diffraction patterns for $KNpO_2CO_3$ and $KAmO_2CO_3$ is given in Table II. The corresponding data for $KPuO_2CO_3$ are given in ref. 3.

Discussion

As pointed out by Ellinger and Zachariasen,[3] the structure of these complexes consists of $[MO_2CO_3]^-$ layers held together by the K^+ cations. In addition, the MO_2^+ portion is linear and is parallel to the c_0 axis. The anticipated actinide contraction is evidenced by the decrease in the c_0 axis length. A lack of decrease in the a_0 dimension is not surprising since the carbonate oxygens are loosely coordinated to the actinide(V) central atom at 2.55 Å. as opposed to the 1.94 Å. bond length estimated for the Pu–O bond in the PuO_2^+ species.[3] Assuming the change in the c_0 axis length is due to change in the M–O bond length, Np–O would be *ca.* 1.98 Å. and Am–O would be *ca.* 1.92 Å. The observed difference in the c_0 dimension is four times that in the M–O bond distance, since each unit cell contains two MO_2^+ groups or four M–O bonds.

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The Preparation and Reactions of Some Tungsten(II) and Tungsten(IV) Halides[1-3]

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A method for the preparation of the tungsten(IV) halides WCl_4 and WBr_4 by aluminum reduction of WCl_6 and WBr_5, respectively, has been developed. The reactions are carried out in sealed, evacuated tubes under a controlled temperature gradient and afford virtually quantitative yields of the crystalline tetrahalides, which are deposited from the vapor phase. The solids WCl_4, WBr_4, and the corresponding chlorides and bromides of tantalum(IV) and niobium(IV) form an isomorphous series. A convenient synthesis of WCl_2 and WBr_2 in high purity results from the disproportionation of WCl_4 and WBr_4, respectively, at 450 to 500°. It is shown that the reactions of WCl_6 and WBr_5 lead to the dipyridine adducts of the respective tungsten(IV) halides also obtained by direct reaction between the tetrahalides and pyridine.

Introduction

The following methods for the preparation of WCl_4 have been reported: (1) reduction of WCl_6 with hydrogen,[4,5] (2) chlorination of WO_2 with CCl_4 in a sealed tube,[6] and (3) reduction of WCl_6 with red phosphorus.[7] Because each of these methods suffers at least one serious disadvantage (*e.g.*, high pressure reaction for (1) and (2) and difficulty in purification of product for (1) and (3), a more convenient method for the synthesis of the compound was sought.

Although a method for the preparation of WBr_4 by reduction of WBr_5 with tungsten had been previously reported by us,[8] the reaction gave low yields and was very slow. Substitution of aluminum for the tungsten has resulted in a much more rapid reaction and very good yields; the method has been applied to the preparation of WCl_4 with equal success.

Hydrogen reduction[9] of the higher halides has also

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(2) Presented in part before the Division of Inorganic Chemistry, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963.

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