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Compounds of Hexavalent and Pentavalent Uranium with the Ordered Perovskite Structure

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Phases with the composition A_2UBO_6 having the ordered perovskite structure have been prepared where A = Ba, Sr and B = various divalent and trivalent cations which can adopt octahedral coördination with oxygen. With the trivalent cations, Cr, In, Sc, Y, and Er, it is assumed that the uranium is in the pentavalent state. The compound Ba_2CuUO_6 is shown to have a tetragonal distortion attributed to the Jahn–Teller effect.

Introduction

The preparation and characterization of numerous compounds of the formula $A_2B'BO_6$ having the ordered perovskite structure have been described in previous publications.[1–7] In these compounds, A represents an alkaline earth ion in 12-fold coördination with oxygen. B′ and B are in 6-fold coördination with oxygen. B′ is in a high oxidation state (5 to 7) and the sum of the oxidation states of B′ and B is eight. The ordering of the B′ and B cations depends largely upon the difference in their oxidation states.

The high oxidation state and coördination requirements for the B′ cation restrict the choice of available elements. Those previously reported are Nb(V), Ta(V), Mo(V), Mo(VI), W(V), W(VI), Re(V), Re(VI), Re(VII), Os(V), Os(VI), Os(VII), and I(VII).

There are sufficient data in the literature to suggest that hexavalent uranium would lend itself to the formation of compounds of this type. In the ideal ordered perovskite structure, there is a rectilinear network of the chains –B–O–B′–O– with three strands intersecting at B and B′. If B′ were hexavalent uranium in this array of atoms, it would seem possible that a distortion could readily occur to a kind of continuous uranyl ion such as was found in the α-UO_3 structure proposed by Zachariasen.[8] The U–O distance was somewhat greater (2.08 Å.) than it is in the uranyl ion (1.91 Å.). The oxygen-deficient phase $UO_{2.82}$ has the ReO_3 structure.[9] It is interesting to note that the number of unpaired electrons per unit cell in this phase is about the same as that in the low-sodium tungsten bronze. In the ternary oxide systems, Rüdorff and Pfitzer[10] demonstrated the existence of compounds A_2UO_6, where A represents one or more alkaline earth ions. These have the cubic ordered perovskite structure and are similar to the tungsten compounds described by Steward and Rooksby.[1] It also has been reported[10] that the oxygen-deficient phase $Ba_3UO_{5.2}$ has the same structure as Ba_3UO_6 but with a larger lattice parameter. The average oxidation state of uranium in the oxygen-deficient phase would be 4.4.

Hoekstra and Katz[11] have shown that the thermal decomposition of some alkaline earth diuranates leads to the formation of non-stoichiometric ternary oxides having the fluorite structure. The magnesium and calcium compounds have a rather narrow homogeneity range and are close to the composition AU_2O_6, indicating pentavalent uranium.[11a] Tetravalent uranium has been reported to give a simple perovskite $BaUO_3$.[10] We were interested to see if hexavalent uranium would give ordered perovskite type compounds with all divalent metal ions and if the pentavalent state could be stabilized by using trivalent B cations.

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[8] W. H. Zachariasen, *Acta Cryst.*, **1**, 265 (1948).

[9] E. Wait, *J. Inorg. Nucl. Chem.*, **1**, 309 (1955).

[10] W. Rüdorff and F. Pfitzer, *Z. Naturforsch.*, **9b**, 568 (1955).

[11] H. R. Hoekstra and J. J. Katz, *J. Am. Chem. Soc.*, **74**, 1683 (1952).

[11a] Similar compounds and also perovskite-type compounds M^IUO_3 (M^I = Na, K, Rb) have been reported by W. Rüdorff, S. Kemmler, and H. Leutner, *Angew. Chem., Intern. Ed.*, **1**, 329 (1962). The existence of these and also of $Rb_{0.85}UO_3$ is postulated by E. A. Ippolitova and L. M. Kovba. (*Proc. Acad. Sci. USSR, Chem. Sect.*, **138**, 521 (1961).)

Experimental

Reagents.—The oxides of manganese, iron, cobalt, nickel, zinc, cadmium, chromium, scandium, and the alkaline earths were similar to those described previously.[3-5] Uranyl nitrate was C.P.; uranium trioxide was prepared by heating the uranyl nitrate at 400°, and uranium dioxide was prepared by heating the trioxide at 1000° under 1 atm. of hydrogen. Indium sesquioxide was prepared by dissolving indium metal in nitric acid, evaporating to dryness, and heating to decompose the nitrate. Copper oxide was reagent grade. Yttrium sesquioxide was 99.0%, erbium sesquioxide 99.9%.

Procedures for Preparations.—The reactions represented by eq. 1–3 were carried out by heating at 1000° intimate mixtures of the solid reagents in zirconium silicate boats placed in electric muffle furnaces for approximately 20 hr. The samples (about 0.5 g.) were exposed to the air during the heating period. The products were examined microscopically and by X-rays.

$$2ACO_3 + BO + UO_2(NO_3)_2 \cdot 6H_2O \longrightarrow A_2BUO_6 + 2CO_2 + 6H_2O + 2NO_2 + {}^1/_2O_2 \qquad (1)$$

when A = Ba; B = Mg, Ca, Sr, Ba, Co, Ni, Cu, Zn, Cd
when A = Sr; B = Mg, Ca, Sr, Co, Ni, Cd

$$3CaO + UO_2(NO_3)_2 \cdot 6H_2O \longrightarrow Ca_3UO_6 + 6H_2O + 2NO_2 + {}^1/_2O_2 \qquad (2)$$

$$3BaCO_3 + B_2O_3 + UO_2(NO_3)_2 \cdot 6H_2O \longrightarrow Ba_3B_2UO_9 + 6H_2O + 2NO_2 + {}^1/_2O_2 \qquad (3)$$

B = Sc, In, Rh, Y

If it was desired to have uranium in an oxidation state lower than six or when iron, chromium, or manganese were to be used, stoichiometric mixtures of compounds were heated in a closed system. Equations 4–9 represent reactions with pelleted mixtures in evacuated silica capsules at 1000°.

$$4AO + B_2O_3 + UO_2 + UO_3 \longrightarrow 2A_2BUO_6 \qquad (4)$$

when A = Ba; B = Cr, Mn, Fe, In, Sc, Er, Y, Rh
when A = Sr; B = Cr, Mn, Fe, In

$$2AO + BO_2 + UO_2 \longrightarrow A_2BUO_6 \qquad (5)$$

A = Ba or Sr B = Cr or Mn

$$6BaO + Cr + Cr_2O_3 + 3UO_3 \longrightarrow 3Ba_2CrUO_6 \qquad (6)$$

$$3BaO + B_2O_3 + UO_3 \longrightarrow Ba_3B_2UO_9 \qquad (7)$$

B = Fe or Cr

$$4BaO + In_2O_3 + 2UO_2 \longrightarrow 2Ba_2InUO_{5.5} \qquad (8)$$

$$2BaO + MgO + UO_2 \longrightarrow Ba_2MgUO_5 \qquad (9)$$

In general the reactions were complete after 20 hr. at 1000°. When $Ba_3In_2UO_9$ was prepared according to eq. 3 but at 800°, the reaction was very slow (approximately 5 days for completion). Periodic examination of the reaction mixture by means of X-ray powder diffraction tracings revealed that the reaction proceeds as

$$3BaO + In_2O_3 + UO_3 \xrightarrow{\text{(fast)}} Ba_3UO_6 + In_2O_3 \xrightarrow[\text{1000° (fast)}]{\text{800° (slow)}} Ba_3In_2UO_9$$

The same mechanism was observed in the case of the preparation of $Ba_3Sc_2UO_9$; however, this reaction proceeded slowly even at 1000°.

It is interesting that several of the compounds (Ba_2CrUO_6, $Ba_3Cr_2UO_9$, and Ba_2RhUO_6) adopt the hexagonal barium titanate structure. Ba_2CrUO_6 could be prepared both as a brown cubic phase and a black hexagonal phase. The mixture of reagents indicated by eq. 4 leads to the hexagonal phase, that by eq. 5 and 6 lead to the cubic phase. When the preparation of $Ba_3Rh_2UO_9$ was attempted, the X-ray pattern of the product was nearly identical with the pattern for Ba_2RhUO_6. This system would have to be more completely investigated in order to define the possible Rh/U ratios.

The preparation of oxygen-deficient phases is illustrated by eq. 8 and 9. One could propose as a general formula Ba_2MgUO_{6-x} where x might range from 0 to 1. When a preparation of a compound with $x = 0.5$ was attempted, however, two ordered perovskite phases were observed in the X-ray diffraction pattern of the product. A complete range of homogeneity was not then obtained under the experimental conditions.

X-Ray Identification.—All preparations were examined on a General Electric XRD-5 diffractometer using CuKα radiation. Intensity calculations were carried out for the compound Ba_2ZnUO_6. Space group no. 225, Fm3m, was used: 8Ba in *c*, 4Zn in *b*, 4U in *a*, and 24O in *d* with x equal to 0.25. Corrections for anomalous scattering were made.[12] The observed intensities were measured by cutting out the peaks and weighing. The data given in Table I give a reliability index of 6.3%.

$$R = [\Sigma \left| I_o^{1/2} - I_0^{1/2} \right| / \Sigma I_0^{1/2}]$$

The lattice constants in Table II were generally obtained by extrapolation of a_0 *vs.* $^1/_2 (\cos^2 \theta/\sin \theta + \cos^2 \theta/\theta)$. The slope of the line was positive in all cases and approximately equal to 0.09 for A_2BUO_6 type compounds. In cases where no back reflections were obtained, the lattice constant corrections were made in an arbitrary fashion assuming the above slope.

Although most of the compounds were indexed on the basis of the cubic unit cell, many of these had line splitting in the back reflections indicating lower symmetry. Where three indices are given, the compound was indexed on the basis of an orthorhombic unit cell. The original *a*, *b*, and *c* are still equal within experimental error, but β is no longer equal to 90°. Thus, the original ordered perovskite unit cell is pseudo-monoclinic, but is better indexed on the basis of a smaller orthorhombic unit cell.

Compounds of the type $A_2B_2UO_9$ cannot have the ordered perovskite arrangement previously described since the B-to-U ratio is not unity. However, it was necessary to use the doubled unit cell to index all observed lines. The type of order in these compounds is currently under study.

Discussion

The compounds containing colorless B cations were yellow to orange powders. They were not luminescent under exposure to ultraviolet radiation as all uranyl compounds seem to be. The ex-

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(12) C. H. Dauben and D. H. Templeton, *Acta Cryst.*, 8, 841 (1955).

TABLE I

X-RAY POWDER DIFFRACTION DATA FOR Ba_2ZnUO_6

hkl	$\sin^2\theta$ obsd.	$\sin^2\theta$ calcd.	*I* obsd.	*I* calcd.
111	0.0256	0.0252	18.2	16.0
200	.0337	.0336	1.8	0.9
220	.0672	.0673	100.0	100.0
311	.0922	.0925	10.0	9.8
222	.1014	.1008	0.8	0.9
400	.1345	.1345	29.4	29.6
331	.1599	.1597	5.2	4.6
420	.1683	.1681	0.4	0.2
422	.2018	.2018	41.2	41.1
511, 335	.2271	.2271	4.5	3.6
440	.2709	.2690	15.9	17.8
531	.2945	.2942	3.8	3.6
600, 442	.3027	.3027	0.3	0.8
620	.3361	.3363	16.1	17.6
533	.3619	.3615	1.9	1.4
622	...	.3699	0.0	0.1
444	.4034	.4035	5.7	3.7
711, 551	.4287	.4288	2.7	2.1
640	.4372	.4372	0.2	0.3
642	.4708	.4708	18.8	21.3
731, 553	.4960	.4960	2.9	2.7
800	.5384	.5380	3.1	3.1
733	.5633	.5633	1.2	0.8
820, 644	.5717	.5717	0.5	0.5
822, 660	.6055	.6053	11.2	13.1
751, 555	.6308	.6309	1.9	1.9
662	...	.6393	0.0	0.02
840	.6726	.6730	9.6	11.4
911, 753	.6983	.6982	2.7	2.5
842	.7066	.7066	0.3	0.5
664	.7399	.7403	7.7	9.1
931	.7655	.7655	2.7	1.8
844	.8068	.8076	11.3	13.3
933, 771, 755	.8327	.8328	3.0	3.2
10.00, 860	...	.8412	0.0	0.1
10.20, 862	.8751	.8748	28.9	37.6
951, 773	.9000	.9001	5.0	4.0
953	.9673	.9674	6.2	5.0

TABLE II

LATTICE CONSTANTS OF COMPOUNDS OF THE TYPE A_2BUO_6 AND $A_3B_2UO_9$

Compound	*a*	*b*	*c*
Ba_2MgUO_6	8.381		
Ba_2CaUO_6	8.67^a		
Ba_2SrUO_6	8.84^a		
Ba_3UO_6	8.89^a		
Ba_2MnUO_6	8.52		
Ba_2FeUO_6	8.312		
Ba_2CoUO_6	8.374		
Ba_2NiUO_6	8.336		
Ba_2CuUO_6	8.18	(tet.)	8.84
Ba_2ZnUO_6	8.397		
Ba_2CdUO_6	6.13	8.64	6.07
Ba_2CrUO_6	8.297		
Ba_2ScUO_6	8.49		
Ba_2InUO_6	8.521		
Ba_2ErUO_6	8.67^a		
Ba_2YUO_6	8.69^a		
Ba_2CrUO_6	5.83	(hex.)	14.4
Ba_2RhUO_6	5.84	(hex.)	14.9
$Ba_3Cr_2UO_9$	5.82	(hex.)	14.6
$Ba_3Fe_2UO_9$	8.232		
$Ba_3Sc_2UO_9$	8.49		
$Ba_3In_2UO_9$	8.512		
$Ba_3Y_2UO_9$	8.70^a		
$Ba_2InUO_{5.5}$	8.551		
$(BaSr)SrUO_6$	6.26	8.76	6.13
Sr_2MgUO_6	8.19^a		
Sr_2CaUO_6	6.06	8.46	5.93
Sr_3UO_6	6.22	8.65	6.01
Sr_2MnUO_6	8.28^a		
Sr_2FeUO_6	8.11^a		
Sr_2CoUO_6	8.19^a		
Sr_2NiUO_6	8.15^a		
Sr_2CdUO_6	6.03	8.42	5.91
Sr_2CrUO_6	8.09^a		
Sr_2InUO_6	8.33^a		
$Sr_3Cr_2UO_9$	8.00^a		
$(SrCa)CaUO_6$	6.01	8.36	5.83
Ca_3UO_6	5.95	8.26	5.73

[a] Slightly distorted.

cellent agreement between the observed and calculated intensities in the X-ray powder pattern of the compound Ba_2ZnUO_6 indicates that the cation positions are close to those of the ideal ordered perovskite structure. The lattice constants of the cubic and near cubic compounds vary in the expected way with the radius of the B cation. All of these observations are compatible with the assumption of an essentially regular octahedral environment for the B cation and the uranium ion.

Many of the compounds listed in Table II are, however, slightly distorted from the cubic perovskite, causing the splitting of some of the back-reflection lines in the X-ray powder diffraction tracings. A tolerance factor expression using the average radius of the B cations would be $t = (R_A + R_O)/\sqrt{2}[(R_U + R_B)/2 + R_O]$. For the barium compounds, the numerator is large enough so that many of the compounds are cubic, but with the strontium compounds the numerator is always too small. All of the strontium compounds are distorted. The only calcium compound obtained was Ca_3UO_6.

One of the most interesting compounds is Ba_2CuUO_6. It is perhaps the only instance of the introduction of copper(II) into an oxide with the perovskite structure. The tetragonal distortion would be expected from the Jahn–Teller effect if the copper were assumed to be in the octahedral sites. Since divalent copper has nine d electrons, one d orbital must be only half-filled. In general it is the $d_{x^2-y^2}$ orbital which is half-filled.[13] This causes interionic distances along the x and y axes to be less than those along the z axis. In the compound Ba_2CuUO_6 c is 0.66 Å. longer than a, which indicates that the radius of Cu^{+2} is 0.33 Å. longer along the z axis than along the x and y axes. In the only other case reported for Cu^{+2} in a perovskite ($KCuF_3$; $a = 4.140$, $c = 3.922$),[14] the $d_{x^2-y^2}$ orbital appears to be completely filled while the d_{z^2} orbital is now only half-filled.

Although the compound Ba_2ZnUO_6 could be prepared without difficulty by the procedure indicated in eq. 1, the preparation of the strontium analog Sr_2ZnUO_6 was not accomplished. A mixture of oxides with $Ba/U = 2$ gives a mixture of $BaUO_4$ and Ba_3UO_6. The strontium–uranium–oxygen system, on the other hand, yields the compounds $SrUO_4$, Sr_3UO_6, and an intermediate one, presumably Sr_2UO_5. The latter always was present in the products obtained by heating the stoichiometric mixtures in which the proportions were $Sr:U:Zn = 2:1:1$. It is not clear why this phase should be so strongly competitive in the reactions involving zinc compounds. The ordered perovskite phase was readily obtained with B cations smaller and larger than zinc.

The diffraction pattern of Ba_2ZnUO_6 did not show the presence of any impurities. The corresponding magnesium compound (Ba_2MgUO_6), on the contrary, was contaminated with both $BaUO_4$ and Ba_3UO_6. An attempt to make the oxygen-deficient compound $Ba_2MgUO_{5.5}$ led to a product containing two ordered perovskite phases, one of which was Ba_2MgUO_6. The other had a larger lattice constant (8.48 Å.). A mixture of oxides intended to give the compound Ba_2MgUO_5 led to the formation of yet another ordered perovskite phase ($a = 8.545$ Å.). The superlattice reflections, however, were very weak compared to the other phases. The large lattice constant and the low degree of ordering lead to the conclusion that the composition of the phase was not the expected one.

The compounds with a trivalent B cation (Ba_2CrUO_6, Ba_2ScUO_6, Ba_2YUO_6, Ba_2ErUO_6, Ba_2InUO_6, Sr_2CrUO_6, and Sr_2InUO_6) would appear to contain pentavalent uranium. The composition of these phases, however, is assumed from the cation ratios in the mixtures from which they were prepared and the relative intensities of ordering lines. Variation of the composition can readily give hexavalent uranium. This is found in the phase $Sr_3Cr_2UO_9$ which still has the ordered perovskite structure although the diffraction pattern shows much fainter superlattice lines. The lattice constant of this phase, however, is definitely smaller than that of the compound Sr_2CrUO_6. This would be expected with the substitution of chromium for uranium.

It is noteworthy that some of the compounds adopt the hexagonal barium titanate structure and that the compound Ba_2CrUO_6 could be obtained either in the hexagonal or in the cubic form depending apparently upon the ingredients of the mixture used for the reaction. The evidence suggests that the achievement of a particular crystal form depends to some extent on the kinetics of the reaction and not altogether upon the thermodynamically favored species.

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(14) K. Knox, *Acta Cryst.*, **14**, 583 (1961).

(15) Undergraduate research participant, N.S.F. summer program, 1961.