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Crystal Structure of $K[UO_2(NO_3)_3]$ and Some Features of Compounds $M[UO_2(NO_3)_3]$ (M = K, Rb, and Cs)

S. V. Krivovichev* and P. C. Burns**

* *St. Petersburg State University, St. Petersburg, Russia*
** *University of Notre Dame, Notre Dame, Indiana, the United States*

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Abstract—Greenish-yellow transparent crystals of $K[UO_2(NO_3)_3]$ were prepared from aqueous solutions as by-product in synthesis of potassium chromatouranylates. The crystal structure was solved by the direct methods and refined to $R_1 = 0.037$ ($wR_2 = 0.070$) for 1452 reflections with $|F_{hkl}| \geq 4\sigma|F_{hkl}|$. Monoclinic system, space group $C2/c$, $a = 13.4877(10)$, $b = 9.5843(7)$, $c = 7.9564(6)$ Å, $\beta = 116.124(2)°$, $V = 923.45(12)$ Å^3. The structure of $K[UO_2(NO_3)_3]$ contains isolated complex ions $[UO_2(NO_3)_3]^-$ whose uranyl groups are aligned parallel to the $[\bar{1}01]$ plane. The K^+ cations, coordinated by twelve oxygen atoms, are located between the complex anions. Comparison of the structure with known data on $M[UO_2(NO_3)_3]$ compounds (M = K, Rb, Cs) suggests the possibility of phase transitions due to relatively small displacements of $[UO_2(NO_3)_3]^-$ anions and K^+ cations, retaining the general structural motif.

Alkali metal nitratouranylates with the general formula $M[UO_2(NO_3)_3]$ (M = K, Rb, Cs) are of great interest in the context of their specific optical characteristics [1], caused by the features of their crystal structure. For example, in rhombohedral rubidium nitratouranylate $Rb[UO_2(NO_3)_3]$ the linear uranyl groups UO_2^{2+} are aligned parallel to the threefold axis, which accounts for the sharp dichroism of this compound: in plane-polarized light with orientation of the polarization plane parallel to the threefold axis, the crystals are colorless, while with the polarization in the perpendicular direction the color of the crystals is yellow-green, characteristic of uranyl compounds [1, 2]. It should be noted that, although the compounds $[M[UO_2(NO_3)_3]$ (M = K, Rb, Cs) were known even in the 19th century [3], their crystal chemistry was not adequately studied. In particular, the structure of $K[UO_2(NO_3)_3]$ was not completely solved up to now. This gap is filled by our study.

EXPERIMENTAL

The $K[UO_2(NO_3)_3]$ crystals were prepared from aqueous solutions as a by-product in synthesis of potassium chromatouranylates [4]. A 3-ml portion of a 0.1 M $UO_2(NO_3)_2 \cdot 6H_2O$ solution was mixed with 1 ml of a 0.05 M K_2CrO_4 solution. The resulting mixture was placed in a vent hood and allowed to stand until the solvent completely evaporated. Among the crystals formed at the bottom of the crystallizer, we found greenish-yellow transparent crystals of $K[UO_2(NO_3)_3]$.

A single crystal of $K[UO_2(NO_3)_3]$ was studied on a Bruker SMART diffractometer equipped with a planar CCD (charge coupled device) detector in the laboratory of the University of Notre Dame (Indiana, the United States). The data set on the intensities of the diffraction maxima was obtained from a 0.12 × 0.08 × 0.04-mm single crystal. The exposure time for each reflection was 10 s. A total of 1200 reflections were obtained in scanning along the ω axis with a step of 0.3°, which corresponds to more than a half of the diffraction sphere. The unit cell parameters were calculated by the least-squares method from 2174 intense reflections: $a = 13.4877(10)$, $b = 9.5843(7)$, $c = 7.9564(6)$ Å, $\beta = 116.124(2)°$, $V = 923.45(12)$ Å^3. The data set on the structural factors was obtained using the SAINT software after making appropriate corrections. The correction for absorption was made by the semiempirical method of pseudo-ψ-scanning using 778 reflections with $I > 15\sigma(I)$ by simulation of the crystal as an ellipsoid. Averaging of symmetrically equivalent reflections resulted in the index $R_{\text{int}} = 0.065$.

The structure was solved by the direct method and refined to $R_1 = 0.037$ ($wR_2 = 0.070$) for 1452 reflections with $|F_{hkl}| \geq 4\sigma|F_{hkl}|$. The final model included the coordinates and anisotropic thermal parameters for all the atoms (Table 1). The interatomic distances are given in Table 2. The table of measured and evaluated structural amplitudes can be submitted by S.V. Krivovichev on request.

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Table 1. Atomic coordinates and thermal parameters (Å^2) in the $K[UO_2(NO_3)_3]$ structure

Atom	x	y	z	U_{iso}	U_{11}
U	0	0.76173(2)	0.25	0.03365(12)	0.0308(2)
K	–0.25	0.75	0.5	0.0527(5)	0.0527(12)
N(1)	–0.1615(4)	0.9170(5)	–0.0693(7)	0.0425(10)	0.037(3)
N(2)	0	0.4576(7)	0.25	0.051(2)	0.061(5)
O(1)	–0.0955(4)	0.7608(3)	0.3447(7)	0.0442(9)	0.039(2)
O(2)	–0.0952(4)	0.9771(4)	0.0820(6)	0.0495(10)	0.056(3)
O(3)	–0.1493(4)	0.7852(4)	–0.0734(6)	0.0492(10)	0.046(3)
O(4)	–0.0698(4)	0.5289(4)	0.1156(6)	0.0502(10)	0.047(3)
O(5)	–0.2310(4)	0.9791(4)	–0.1980(7)	0.0591(12)	0.043(3)
O(6)	0	0.3320(6)	0.25	0.074(2)	0.123(7)

Atom	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U	0.0384(2)	0.0347(2)	0	0.0171(1)	0
K	0.0652(12)	0.050(1)	–0.0036(8)	0.0315(10)	–0.0073(8)
N(1)	0.051(3)	0.043(3)	0.003(2)	0.022(2)	–0.003(2)
N(2)	0.052(4)	0.047(4)	0	0.030(4)	0
O(1)	0.055(2)	0.047(2)	–0.001(2)	0.026(2)	–0.001(2)
O(2)	0.048(2)	0.043(3)	0.003(2)	0.021(2)	0.003(2)
O(3)	0.047(2)	0.048(3)	–0.007(2)	0.015(2)	0.003(2)
O(4)	0.052(2)	0.045(3)	–0.005(2)	0.014(2)	0.001(2)
O(5)	0.062(3)	0.060(3)	0.018(2)	0.013(2)	0.001(2)
O(6)	0.036(3)	0.070(5)	0	0.048(5)	0

RESULTS AND DISCUSSION

The structure of $K[UO_2(NO_3)_3]$ consists of isolated complex ions $[UO_2(NO_3)_3]^-$ shown in Fig. 1. The uranyl cation UO_2^{2+} is coordinated by three NO_3^- groups in the equatorial plane. The average bond length $\langle U–O_{Ur}\rangle$ in the uranyl cation and the average length of the equatorial bond $\langle U–O_{eq}\rangle$ are 1.755 and 2.482 Å, respectively. The N–O bond lengths for bridging oxygen atoms are in the range from 1.269 to 1.278 Å, while the N–O bonds for the terminal oxygen atoms (not bonded to uranium atoms) are significantly shorter (1.198–1.204 Å). The similar distortions are observed for alkali metal carbonatouranylates, e.g., $Cs_4[UO_2(CO_3)_3]$ [5].

The structure contains one symmetrically independent K atom coordinated with twelve oxygen atoms. The coordination of the K atom with respect to the twelve neighboring oxygen atoms approximately corresponds to coordination of a sphere in the closest cubic packing of equal-sized spheres. Since the ionic radius of the K^+ cation (1.64 Å for coordination number 12 [6]) somewhat exceeds the ionic radius of the O^{2-} anion (1.35–1.42 Å [6]), the resulting configuration is not quite closely packed, which can cause possible phase transitions (see below).

The projection of the $K[UO_2(NO_3)_3]$ structure onto the (010) plane is shown in Fig. 2. The linear uranyl groups of the $[UO_2(NO_3)_3]^-$ ions are parallel to the $[\bar{1}01]$ direction. The K^+ cations are located between the complex anions.

Table 2. Interatomic distances (Å) in $K[UO_2(NO_3)_3]$

Bond	Length	Bond	Length
U–O(1)^a	1.755(4) × 2	N(1)–O(5)	1.198(6)
U–O(4)^a	2.475(4) × 2	N(1)–O(3)	1.276(5)
U–O(3)^a	2.483(5) × 2	N(1)–O(2)	1.278(6)
U–O(2)^a	2.487(4) × 2	$\langle$N(1)–O$\rangle$	1.25
$\langle U–O_{Ur}\rangle$	1.755		
$\langle U–O_{eq}\rangle$	2.482	N(2)–O(6)	1.204(8)
		N(2)–O(4)^a	1.269(5) × 2
K–O(1)^b	2.854(4) × 2	$\langle$N(2)–O$\rangle$	1.25
K–O(3)^{c,d}	3.069(5) × 2		
K–O(5)^{e,f}	3.105(4) × 2		
K–O(6)^{g,h}	3.168(1) × 2		
K–O(5)^{c,d}	3.181(4) × 2		
K–O(2)^{e,f}	3.229(4) × 2		
$\langle$K–O$\rangle$	3.10		

Note: Symmetry transformations: (*a*) (–*x*, *y*, –*z* + 1/2); (*b*) (–*x* – 1/2, –*y* + 3/2, –*z* + 1); (*c*) (*x*, *y*, *z* + 1); (*d*) (–*x* – 1/2, –*y* + 3/2, –*z*); (*e*) (*x*, –*y* + 2, *z* + 1/2); (*f*) (–*x* – 1/2, *y* – 1/2, –*z* + 1/2); (*g*) (*x* – 1/2, *y* + 1/2, *z*); (*h*) (–*x*, –*y* + 1, –*z* + 1).

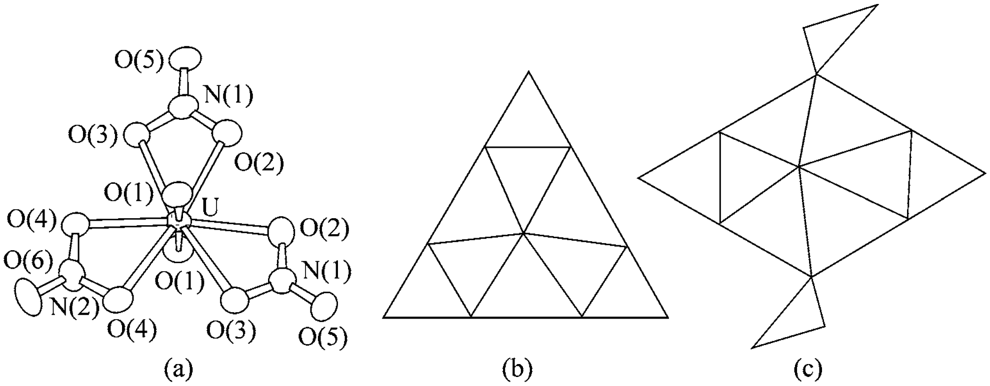

Fig. 1. Complex anion $[UO_2(NO_3)_3]^-$ in the $K[UO_2(NO_3)_3]$ structure, shown (a) with the ellipsoids of thermal vibrations of atoms and (b) in the polyhedral form; (c) $[UO_2(NO_3)_4]^{2-}$ anion in the $Rb_2[UO_2(NO_3)_4]$ structure.

The local valence balance for the $K[UO_2(NO_3)_3]$ structure was analyzed using the known equation $s_{ij} = \exp[(r_0 - d_{ij})/b]$, where d_{ij} and s_{ij} are the length and multiplicity of the bond between *i*th and *j*th atoms, respectively, and r_0 and b are empirical parameters for a given pair cation–anion. The latter parameters were taken from [7] for the N(V)–O (r_0 = 1.432 Å; b = 0.37 Å) and K(I)–O (r_0 = 2.132 Å; b = 0.37 Å) bonds and from [8] for the U(VI)–O bonds (r_0 = 2.042 Å; b = 0.506 Å for the six-coordinate uranyl ion). The sums of multiplicities of the bonds with cations are 6.04, 4.92, 4.96 and 0.93 valence units (v.u.) for U, N(1), N(2), and K(1), respectively. The sums of multiplicities of the bonds with the oxygen atoms are in the range 1.90–2.02 v.u.

The crystallographic characteristics of $M[UO_2 \cdot (NO_3)_3]$ for M = Rb, Cs in comparison with $K[UO_2 \cdot (NO_3)_3]$ are listed in Table 3. It is interesting that $Rb[UO_2(NO_3)_3]$ and $Cs[UO_2(NO_3)_3]$ are isostructural and have trigonal (rhombohedral) symmetry. However, the relative position of the $[UO_2(NO_3)_3]^-$ clusters and M^+ cations in the structures of these compounds is identical to that in the $K[UO_2(NO_3)_3]$ structure. In the latter structure, a pseudorhombohedral cell with the size close to that in $Rb[UO_2(NO_3)_3]$ and $Cs[UO_2 \cdot (NO_3)_3]$ can be found (with a correction for the ionic radii of cations). The transition of the true monoclinic cell of $K[UO_2(NO_3)_3]$ (given by the vectors **a**, **b**, and **c**) to the pseudo-rhombohedral subcell (in the hexagonal coordinates $\mathbf{a}_R$, $\mathbf{b}_R$, $\mathbf{c}_R$) is given by the following system of equations: $\mathbf{a}_R = \mathbf{b}$, $\mathbf{b}_R = 1/2(\mathbf{a} - \mathbf{b} + 2\mathbf{c})$, and $\mathbf{c}_R = \mathbf{a} - \mathbf{c}$. The corresponding transformation is shown geometrically in Fig. 3. The pseudo-rhombohedral subcell in the $K[UO_2(NO_3)_3]$ structure has the following parameters: a_R = 9.584, b_R = 9.192, c_R = 18.432 Å, α_R = 90°, β_R = 88.64°, and γ_R = 121.42°. These values are in agreement with the parameters of true rhombohedral cells in $Rb[UO_2(NO_3)_3]$ and $Cs[UO_2(NO_3)_3]$ (a = 9.35–9.65 Å, c = 18.9–19.5 Å), considering the difference in the sizes of alkali metal cations.

For $K[UO_2(NO_3)_3]$, the following crystallographic characteristics were determined: space group *Pbca*, a = 9.34, b = 12.46, c = 15.95 Å [11]. These data disagree with our data confirmed by solving the crystal structure. However, the unit cell volume of 1856.2 Å obtained previously [11] agrees well with our value of 1846.9 Å. Presumably, there are two polymorphous modifications of $K[UO_2(NO_3)_3]$, monoclinic and rhombic. Transition from the monoclinic unit cell to the rhombic cell (given by the vectors $\mathbf{a}_O$, $\mathbf{b}_O$, $\mathbf{c}_O$) can be given by the equations $\mathbf{a}_O = \mathbf{b}$, $\mathbf{b}_O = 1/2(2\mathbf{a} + \mathbf{c})$, and $\mathbf{c}_O = -2\mathbf{c}$ (Fig. 3). The phase transition from the monoclinic to rhombic modification may involve relatively small shifts of $[UO_2(NO_3)_3]^-$ anions and K^+ cations, retaining the general structural motif. The prerequisite for the transition (e.g., with temperature variation) can be a change in potassium coordination,

Table 3. Crystallographic characteristics of $M[UO_2(NO_3)_3]$ (M = K, Rb, Cs, NH_4)

Formula	Space group	*a*, Å	*b*, Å	*c*, Å	β, deg	References
$K[UO_2(NO_3)_3]$	*C*2/*c*	13.4877	9.5843	7.9564	116.124	This work
$Rb[UO_2(NO_3)_3]$	$R\bar{3}c$	9.384	–	18.899	–	[2, 9]
$Cs[UO_2(NO_3)_3]$	$R\bar{3}c$	9.64	–	19.509	–	[10]

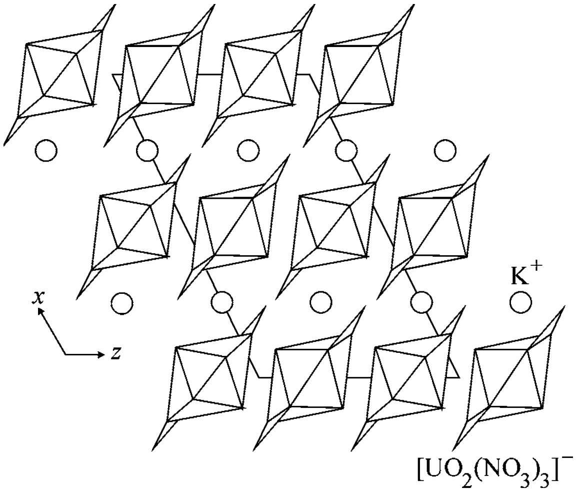

Fig. 2. Projection of the $K[UO_2(NO_3)_3]$ crystal structure onto the (010) plane.

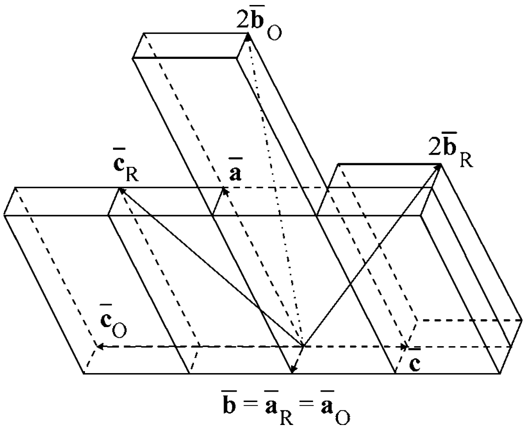

Fig. 3. Scheme of transition from the true monoclinic cell of $K[UO_2(NO_3)_3]$ given by the vectors **a**, **b**, and **c** to the pseudo-rhombohedral subcell ($\mathbf{a}_R$, $\mathbf{b}_R$, $\mathbf{c}_R$) and pseudo-rhombic cell ($\mathbf{a}_O$, $\mathbf{b}_O$, $\mathbf{c}_O$).

from close-packed to more open configurations. In this case, with heating, the lower coordination numbers are more preferable because of the difference in the radii of alkali metal cations and O^{2-} anions. Curiously, for $Rb[UO_2(NO_3)_3]$ the monoclinic C-unit was determined in [12]. Zalkin and co-workers [2] criticized these data, not considering the possibility of existence of polymorphous modifications of this compound. The pattern of phase transitions in the series $M[UO_2(NO_3)_3]$ (M = K, Rb, Cs) is interesting but yet poorly understood.

The complex anion $[UO_2(NO_3)_3]^-$ observed in the $K[UO_2(NO_3)_3]$ occurs less frequently than the $[UO_2 \cdot (CO_3)_3]^{4-}$ anion having the similar structure, which suggests its lower stability [13]. It is interesting that the trinitrate anion is not unique anion for alkali metal nitratouranylates. For example, the structure of $Rb_2[UO_2(NO_3)_4]$ [14, 15] contains the tetranitrate complex ion $[UO_2(NO_3)_4]^{2-}$, shown in Fig. 1c.

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