

## Rubidium Tetranitratodioxouranate(VI), $\text{Rb}_2[\text{UO}_2(\text{NO}_3)_4]$

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**Abstract.**  $M_r = 603.52$ , monoclinic,  $P2_1/n$ ,  $a = 6.462$  (1),  $b = 7.885$  (1),  $c = 12.437$  (2) Å,  $\beta = 101.32$  (1)°,  $V = 621.4$  (1) Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 3.22$ ,  $D_x = 3.225$  g cm<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 206.5$  cm<sup>-1</sup>,  $F(000) = 612$ ,  $T = 294$  K, final  $R = 0.032$  for 1194 observed reflections. A new, more precise, determination of the structure of  $\text{Rb}_2[\text{UO}_2(\text{NO}_3)_4]$  has confirmed that the anion contains two mono- and two bidentate nitrate ligands arranged about the linear  $\text{UO}_2$  group so that the eight-coordinated oxygens form an almost regular hexagonal bipyramid. However, significant differences from earlier work are revealed in bond distances, especially those about uranium. The  $\text{O}=\text{U}=\text{O}$  bonds are shorter (by approximately 0.02 Å) than previously reported, and the bidentate nitrates are now seen to be symmetrically bound. The cations are also more precisely located. A reason for conflicting spectroscopic studies is suggested.

**Introduction.** The structures of tetranitratodioxouranates have been studied previously (Staritzky & Walker, 1957; Kapshukov, Volkov, Moskvichev, Lebedev & Yakovlev, 1971) but to low precision. For example, the rubidium salt structure was solved on the basis of less than 500 non-zero reflections to an  $R$  value of 0.148. As part of our ongoing studies on nitrate and related complexes (Rogers, Taylor & Toogood, 1983; Anderson, Chieh, Irish & Tong, 1980) we have reinvestigated the structure of  $\text{Rb}_2[\text{UO}_2(\text{NO}_3)_4]$  in order to complement the recent spectroscopic study by Flint & Sharma (1982) and to resolve some conflicting evidence as to the nature of this material, which has also been reported as containing the trinitrate  $[\text{UO}_2(\text{NO}_3)_3]^-$  ion (Volod'ko, Komyak, Posledovich & Serafimovich, 1969).

**Experimental.** Suitable crystal of title compound grown from a solution containing the appropriate stoichiometric quantities of rubidium and uranyl nitrates. After X-ray work, infrared and Raman spectra were obtained and found to correspond to those published by Flint & Sharma (1982).  $D_m$  by flotation ( $\text{C}_2\text{H}_2\text{Br}_4/\text{CH}_2\text{I}_2$ ). Crystal approximating a sphere of diameter

0.11 (1) mm sealed in epoxy. Syntex  $P2_1$  diffractometer, graphite-monochromatized Mo  $K\alpha$  radiation. Accurate cell constants from positions of 15 well distributed general reflections ( $20 \leq 2\theta \leq 30^\circ$ ). Non-standard setting of  $P2_1/c$ :  $a = 6.462$  (1),  $b = 7.885$  (1),  $c = 12.842$  (2) Å,  $\beta = 108.25$  (1)°. Data collected by  $\theta$ - $2\theta$  scan method using variable scan rates (2.0–29.3° min<sup>-1</sup>), scan width 0.85° below  $K\alpha_1$  to 0.85° above  $K\alpha_2$ ; background counts at beginning and end of each scan for a total time equal to half the scan time. Two standard reflections (006 and 040) monitored every 100 measurements (only  $\pm 2.5\%$  variation) and used to scale data to a common level. 1823 reflections ( $3.2 \leq 2\theta \leq 60^\circ$ ),  $h: 0 \rightarrow 9$ ;  $k: 0 \rightarrow 11$ ;  $l: -17 \rightarrow 16$ ; 1194 with  $I \geq 3\sigma(I)$  considered observed and used in structure determination and refinement. Data corrected for Lorentz and polarization effects and adjusted for spherical absorption effect ( $\mu R = 1.14$ ) applied to  $I_o$ ; correction 1.00–0.92. Structure solved by Patterson and Fourier techniques. With all atoms isotropic, structure refined on  $F$  to  $R = 0.064$ ; refinement with anisotropic temperature factors lowered  $R$  to 0.032,  $wR = 0.036$ .  $w^{-1} = 1.33 - 0.012|F_o| + 0.0001|F_o|^2$  utilized to give constant error throughout various magnitudes of  $F_o$ . Max.  $\Delta/\sigma$  in final LS cycle 0.06; final difference Fourier map residuals in the vicinity of U and Rb: U 1.7(max.), -1.3(min.); Rb 1.1(max.), -1.1(min.) e Å<sup>-3</sup>.† Programs described elsewhere (Taylor, Jacobson & Carty, 1975). Scattering factors, including anomalous-scattering factors for U and Rb, from *International Tables for X-ray Crystallography* (1974).

**Discussion.** Final positional parameters are listed in Table 1. Bond lengths within the anion, contact distances (<4.0 Å) around rubidium and pertinent bond angles are given in Table 2. The structure of the anion represented in the ORTEP plot (Johnson, 1976) in Fig. 1 is basically that previously determined by Kapshukov *et al.*, and predicted by Flint & Sharma

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42129 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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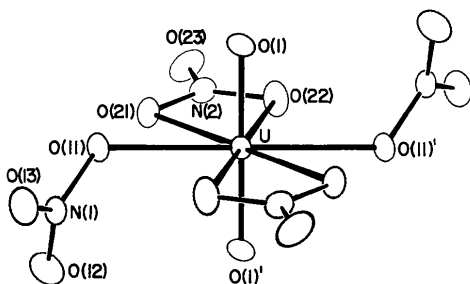
Table 1. Final atomic coordinates (fractional,  $\times 10^4$ ) and isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ )
$$U_{\text{eq}} = (U_{11}U_{22}U_{33})^{1/3}.$$

	x	y	z	$U_{\text{eq}}$
U	5000	5000	5000	22.1
Rb	8419.3 (12)	5179.1 (12)	1587.9 (6)	30.3
O(1)	6663 (9)	5047 (11)	4047 (5)	33
O(11)	3253 (10)	2649 (9)	3974 (6)	33
O(12)	627 (13)	1803 (12)	4695 (6)	45
O(13)	138 (12)	2296 (9)	2961 (6)	37
O(21)	1788 (12)	5805 (9)	3600 (6)	36
O(22)	3581 (10)	7895 (8)	4404 (5)	31
O(23)	669 (13)	8386 (10)	3220 (6)	39
N(1)	1256 (13)	2254 (9)	3886 (6)	27
N(2)	1942 (13)	7402 (10)	3729 (6)	28

Table 2. Bond lengths ( $\text{\AA}$ ), bond angles ( $^\circ$ ) and rubidium-oxygen contacts ( $\text{\AA}$ )

U—O(1)	1.749 (6)	U—O(11)	2.403 (7)
U—O(21)	2.515 (8)	U—O(22)	2.517 (7)
N(1)—O(11)	1.311 (11)	N(1)—O(12)	1.210 (11)
N(1)—O(13)	1.233 (11)	N(2)—O(21)	1.271 (11)
N(2)—O(22)	1.276 (10)	N(2)—O(23)	1.215 (11)
O(1)—U—O(1 <sup>h</sup> )	180.0 (2)	O(1)—U—O(11)	86.8 (2)
O(1)—U—O(11 <sup>h</sup> )	93.2 (2)	O(1)—U—O(21)	93.4 (2)
O(1)—U—O(21 <sup>h</sup> )	86.6 (2)	O(1)—U—O(22)	91.0 (2)
O(1)—U—O(22 <sup>h</sup> )	89.0 (2)	O(11)—U—O(11 <sup>h</sup> )	180.0 (2)
O(11)—U—O(21)	65.8 (2)	O(11)—U—O(21 <sup>h</sup> )	114.2 (2)
O(11)—U—O(22)	115.9 (2)	O(11)—U—O(22 <sup>h</sup> )	64.1 (2)
O(21)—U—O(21 <sup>h</sup> )	180.0 (2)	O(21)—U—O(22)	50.5 (2)
O(21)—U—O(22 <sup>h</sup> )	129.5 (2)	O(22)—U—O(22 <sup>h</sup> )	180.0 (2)
U—O(11)—N(1)	125.5 (3)	U—O(21)—N(2)	97.4 (3)
U—O(22)—N(2)	97.2 (3)	O(11)—N(1)—O(12)	119.0 (5)
O(11)—N(1)—O(13)	117.3 (4)	O(12)—N(1)—O(13)	123.6 (5)
O(21)—N(2)—O(22)	114.8 (4)	O(21)—N(2)—O(23)	122.6 (5)
O(22)—N(2)—O(23)	122.6 (4)		
Rb...O(1 <sup>l</sup> )	3.467 (6)	Rb...O(1 <sup>ll</sup> )	3.917 (6)
Rb...O(11 <sup>ll</sup> )	3.082 (7)	Rb...O(11 <sup>lll</sup> )	3.926 (7)
Rb...O(12 <sup>ll</sup> )	3.094 (8)	Rb...O(12 <sup>lv</sup> )	3.063 (8)
Rb...O(13 <sup>lv</sup> )	2.982 (7)	Rb...O(13 <sup>v</sup> )	2.928 (7)
Rb...O(21 <sup>v</sup> )	3.018 (8)	Rb...O(22 <sup>vl</sup> )	3.132 (7)
Rb...O(22 <sup>vl</sup> )	3.076 (7)	Rb...O(23 <sup>v</sup> )	3.387 (8)
Rb...O(23 <sup>vl</sup> )	3.047 (8)		

Symmetry code: (i)  $x, y, z$ ; (ii)  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ ; (iii)  $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$ ; (iv)  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ ; (v)  $1 + x, y, z$ ; (vi)  $\frac{1}{2} + x, \frac{3}{2} - y, -\frac{1}{2} + z$ ; (vii)  $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$ ; (viii)  $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$ ; (ix)  $-x, -y, -z$ .

Fig. 1. The structure of the  $[\text{UO}_2(\text{NO}_3)_4]^{2-}$  anion, showing the numbering scheme used in the tables.

who apparently were unaware that it had been determined by X-ray methods. However, the bond parameters in the present study are considerably different from those reported by Kapshukov *et al.* and reflect the significant improvement in the current data set. For example, the uranyl,  $\text{O}=\text{U}=\text{O}$ , bond distances are found to be some  $0.02 \text{ \AA}$  shorter than in the Russian work. Even larger discrepancies occur for other bond lengths especially in the nitrate groups. It is now clear that the bidentate nitrate groups are similar to those in other symmetrically bound bidentate nitrate ligands (e.g. Rogers *et al.* and references therein) and analogous to those in  $[\text{UO}_2(\text{CO}_3)_3]^{4-}$  (Anderson *et al.*, 1980). Likewise the distances and angles within the monodentate nitrate ligands are similar to those compiled by Addison, Logan, Wallwork & Garner (1971).

Rubidium ions occupy sites in which there are 13 neighbouring oxygens within  $3.93 \text{ \AA}$ , at distances ranging from  $2.9\text{--}3.0 \text{ \AA}$  (two contacts) through  $3.0\text{--}3.2 \text{ \AA}$  (seven contacts), with four other longer contacts. Here again significant differences from the earlier work are apparent, both in the number of contacts and in their distances.

As a postscript we believe that the reason why Volod'ko *et al.* (1969) concluded that their material  $[\text{UO}_2(\text{NO}_3)_4]^{2-}$  contained  $[\text{UO}_2(\text{NO}_3)_3]^-$  and  $\text{NO}_3^-$  may be connected with the fact that we found it possible to produce the trinitrate complex (together with free rubidium nitrate), in addition to the tetranitrate complex, from solutions of the correct stoichiometry for preparation of the tetranitrate complex — a phenomenon also observed by Flint (1984).

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