

This study shows that these phases and the compound KTIF₄ described by Hebecker (1975) have the same structural characteristics. But according to Hebecker, KTIF₄ would crystallize with a unit cell three times smaller ($a' = a/\sqrt{3}$, $c' = c$) (see Fig. 1) involving only one Tl₂F₁₂ group per layer.

The larger unit cell of KYF₄ which contains three Y₂F₁₂ groups per layer is to be attributed to the small extent of distortion observed between two adjacent Ln₂F₁₂ groups along the three trigonal directions; as is probably the case with the compounds NaScF₄ (Thomas & Karraker, 1966) and NaNF₄ (Grannec, Champarnaud & Portier, 1970).

To our knowledge, up to now, bipyramidal surroundings have never been reported for Y. Such surroundings have been mentioned only for the lanthanides with the smallest ionic radii: Lu, Yb and Tm, for instance in the compounds β -KYb₂F₇ (Le Fur, Aléonard, Gorius & Roux, 1980), CsYb₃F₁₀ (Aléonard, Roux & Lambert, 1982) and β -RbLu₃F₁₀

(Arbus, Fournier, Cousseins, Védérine & Chevalier, 1982). In these compounds, the bipyramids are always characterized by bond lengths Ln—F_{ax} a little shorter than Ln—F_{eq}, as observed in KYF₄.

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Na₂[Ru(NO₂)₄(NO)(OH)].2H₂O – a Redetermination

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Abstract. Disodium hydroxotetranitro(nitroso)ruthenate(III) dihydrate, $M_r = 414.1$, monoclinic, $C2/m$, $a = 12.8765$ (6), $b = 14.5867$ (9), $c = 7.4478$ (4) Å, $\beta = 121.521$ (3)°, $V = 1192.5$ Å³, $Z = 4$, $D_x = 2.306$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 1.430$ mm⁻¹, $F(000) = 808$, $T = 298$ K, $R = 0.0251$ for 1760 unique observed reflections. We have re-determined the structure of the title compound by single-crystal X-ray diffraction. After recalculation of the bond lengths derived in the neutron diffraction study, the distances involving the non-H atoms show no significant differences between the two determinations.

Introduction. As part of ongoing research related to the geometrical aspects of tetranitro- and hexanitrometallate species, single crystals of Na₂[Ru(NO₂)₄(NO)(OH)].2H₂O were prepared. A crystal structure analysis using neutron diffraction had previously been published (Simonsen & Mueller, 1965), but both the R value of 0.098 and the uncertainties in

the bond lengths of up to 0.007 Å were rather high. In order to improve the accuracy of the structure, a dataset was collected using Mo $K\alpha$ X-radiation. In addition to the expected random errors between the two determinations, there appear to be marked systematic errors.

Experimental. Compound prepared by dissolution of excess NaNO₂ in an aqueous solution of RuCl₃ until colour change observed, crystals obtained by slow evaporation from resulting solution. Yellow columnar crystal, 0.78 × 0.39 × 0.39 mm, Stoe STADI-4 four-circle diffractometer, graphite-monochromated Mo $K\alpha$ X-radiation, cell parameters from 2θ values of 44 reflections measured at $\pm \omega$ ($30 \leq 2\theta \leq 32^\circ$). For data collection $T = 298$ K, ω - 2θ scans using the learnt-profile method (Clegg, 1981), $2\theta_{\text{max}} 60^\circ$, $h -18 \rightarrow 15$, $k 0 \rightarrow 20$, $l 0 \rightarrow 10$, 3 standard reflections, no significant crystal movement or decay, absorption correction using ψ scans (min. and max. transmission factors 0.470 and 0.561, respectively), 1811 unique reflections, giving 1760 with $F \geq 4\sigma(F)$ for structure refinement [using full-matrix least

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Table 1. Atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
Ru	0.261880 (20)	0.0	0.002840 (20)	0.02197 (17)
N(1)	0.42002 (24)	0.0	0.1883 (4)	0.0341 (13)
N(2)	0.23164 (18)	0.10048 (13)	0.1710 (3)	0.0373 (10)
N(3)	0.28348 (17)	0.10222 (13)	-0.1716 (3)	0.0344 (10)
O(11)	0.08720 (18)	0.0	-0.2112 (3)	0.0310 (11)
O(1)	0.5214 (3)	0.0	0.3097 (4)	0.0627 (16)
O(21)	0.13000 (19)	0.11049 (17)	0.1423 (3)	0.0786 (16)
O(22)	0.31505 (20)	0.14796 (11)	0.3020 (3)	0.0654 (13)
O(31)	0.21280 (18)	0.11175 (11)	-0.36157 (22)	0.0556 (10)
O(32)	0.3688 (3)	0.15497 (18)	-0.0857 (3)	0.0919 (18)
O(1W)	0.0136 (3)	0.23163 (19)	0.3047 (4)	0.0617 (13)
Na(1)	0.25	0.25	0.5	0.0724 (19)
Na(2)	0.0	0.10996 (7)	0.5	0.0447 (7)
H(1)	0.046 (5)	0.0	-0.149 (6)	0.06
H(1W)	0.004 (4)	0.2170 (23)	0.211 (5)	0.06
H(2W)	-0.033 (4)	0.274 (3)	0.267 (6)	0.06

Table 2. Bond lengths (\AA) and angles ($^\circ$) for $\text{Na}_2[\text{Ru}(\text{NO})(\text{NO}_2)_4(\text{OH})] \cdot 2\text{H}_2\text{O}$

The values in the column headed *X* refer to the present X-ray study; those under *N1* are the original values (Simonsen & Mueller, 1965); those under *N2* are derived from Simonsen and Mueller's published coordinates but using the accurate unit cell obtained in the course of the X-ray structure determination.

	<i>X</i>	<i>N1</i>	<i>N2</i>
Ru—N(1)	1.7641 (25)	1.748 (4)	1.757 (4)
Ru—N(2)	2.0923 (21)	2.078 (3)	2.095 (3)
Ru—N(3)	2.0894 (19)	2.080 (3)	2.097 (3)
Ru—O(11)	1.9619 (25)	1.950 (5)	1.961 (3)
N(1)—O(1)	1.135 (3)	1.127 (7)	1.133 (7)
N(2)—O(21)	1.219 (4)	1.213 (5)	1.222 (5)
N(2)—O(22)	1.220 (4)	1.212 (5)	1.218 (5)
N(3)—O(31)	1.2265 (19)	1.211 (4)	1.219 (5)
N(3)—O(32)	1.2135 (20)	1.207 (5)	1.213 (5)
O(11)—H(1)	0.86 (3)	0.921 (9)	0.931 (9)
O(1W)—H(1W)	0.68 (5)	0.929 (16)	
O(1W)—H(2W)	0.81 (5)	0.911 (14)	
Na(1)—O(22)	2.527 (2)	2.505 (4)	2.528 (4)
Na(1)—O(31)	2.424 (2)	2.413 (4)	2.429 (4)
Na(1)—O(1W)	2.611 (3)	2.613 (6)	2.629 (6)
Na(2)—O(11)	2.437 (2)	2.430 (7)	2.446 (7)
Na(2)—O(31)	2.369 (2)	2.345 (5)	2.361 (5)
Na(2)—O(1W)	2.359 (3)	2.335 (8)	2.352 (8)

Bond angles from the X-ray study

N(1)—Ru—N(2)	91.75 (10)	Ru—N(1)—O(1)	179.14 (23)
N(1)—Ru—N(3)	90.75 (10)	Ru—N(2)—O(21)	119.83 (19)
N(1)—Ru—O(11)	178.05 (11)	Ru—N(2)—O(22)	121.01 (19)
N(2)—Ru—N(2')	88.94 (8)	O(21)—N(2)—O(22)	119.1 (3)
N(2)—Ru—N(3)	89.95 (8)	Ru—N(3)—O(31)	122.61 (13)
N(2)—Ru—N(3')	177.29 (9)	Ru—N(3)—O(32)	120.15 (13)
N(2)—Ru—O(11)	89.64 (9)	O(31)—N(3)—O(32)	117.23 (16)
N(3)—Ru—N(3')	91.06 (9)	Ru—O(11)—H(1)	108.92 (25)
N(3)—Ru—O(11)	87.89 (9)	H(1W)—O(1W)—H(2W)	101 (6)

squares on *F* (SHELX76; Sheldrick, 1976)]. Initial coordinates were taken from the published values obtained after refinement against neutron data (Simonsen & Mueller, 1965). In the early stages of refinement the H-atom positions were fixed, but in the final cycles they were allowed to refine freely with a common, fixed U_{iso} of 0.06\AA^2 . Anisotropic thermal

parameters for the non-H atoms, secondary-extinction parameter refined to $1.11(3) \times 10^{-6}$. At final convergence, $R = 0.0251$, $wR = 0.0398$, $S = 1.698$ for 106 parameters, $(\Delta/\sigma)_{\text{max}}$ in final cycle 0.05, max. and min. residues in final ΔF synthesis 0.64 and -0.77 e \AA^{-3} , respectively. The weighting scheme $w^{-1} = \sigma^2(F) + 0.0005F^2$ gave satisfactory agreement analyses. Scattering factors were inlaid (Sheldrick, 1976) except for Ru (Cromer & Mann, 1968). Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1, while selected bond lengths and angles appear in Table 2.* The atom-

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54852 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

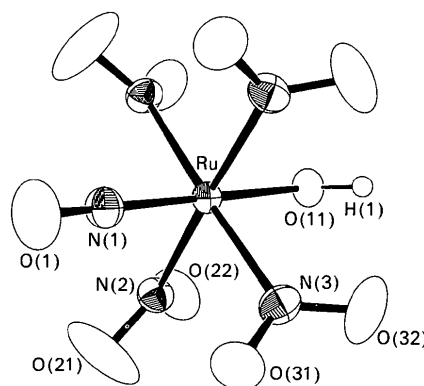


Fig. 1. A general view of the $[\text{Ru}(\text{NO}_2)_4(\text{NO})(\text{OH})]^{2-}$ anion showing the atom-numbering scheme: thermal ellipsoids are drawn at the 30% probability level, excepting those of H which have artificial radii of 0.10\AA for clarity. The anion lies across a crystallographic mirror plane which passes through O(1), N(1), Ru, O(11) and H(1).

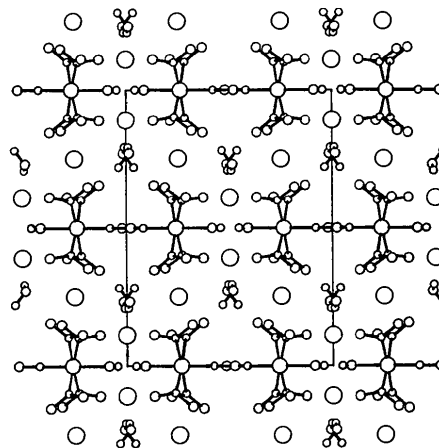


Fig. 2. A view along the *c* axis showing the packing of anions, sodium cations and water molecules.

numbering scheme for the molecule is shown in Fig. 1, which was generated using *ORTEP* (Mallinson & Muir, 1985). The packing within the crystal lattice is shown in Fig. 2 (Motherwell & Clegg, 1978). Molecular geometry calculations were performed using *CALC* (Gould & Taylor, 1985).

Discussion. Although the positions of the H atoms are given considerably more accurately, uncertainties involving the non-H atoms are approximately twice as large in the neutron study (Simonsen & Mueller, 1965). The gross structure of the anion is as described for the previous determination, with octahedral coordination of the Ru centre by one OH, one NO and four NO₂ ligands. The metal and the NO and OH groups lie on a crystallographic mirror plane. The distances between the Ru and its ligating atoms are consistently longer (by an average of 0.01 Å) than the distances obtained in the neutron diffraction study. A qualitatively similar trend is observed for N—O distances. Although the six-coordination about the Na⁺ ions is similar to that described in the earlier work, the distances to the apical atoms are again somewhat larger (by 0.015–0.025 Å) in our study: only the Na(1)—O(water) and Na(2)—O(hydroxo) distances are in good agreement.

The systematically shorter bond lengths in the neutron study do not arise from differences in the

radiation used or in the temperature at which data were collected: the discrepancies arise solely from systematic errors in the unit-cell edges ($a = 12.75$, $b = 14.52$, $c = 7.37$ Å) used in the earlier derivation. We have therefore recalculated the bond lengths for the neutron diffraction study from the published fractional coordinates, but using the accurate unit cell obtained in the course of the X-ray structure determination. The three sets of bond distances are listed for comparison in Table 2 and, although our values are significantly more accurate in respect of the non-H atoms, there are no significant differences between these and the corrected values for the neutron study.

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Structure of Ba₃(AsS₄)₂·7H₂O at 125 K

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Abstract. Diarsenic tribarium octasulfide–water (1/7) Ba₃As₂S₈·7H₂O, $M_r = 944.45$, monoclinic, $P2_1/n$, $a = 12.450$ (2), $b = 12.727$ (3), $c = 12.694$ (2) Å, $\beta = 97.99$ (1)°, $V = 1991.8$ (8) Å³, $Z = 4$, $D_x = 3.149$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 99.9$ cm⁻¹, $F(000) = 1728$, $T = 125$ K, final $R = 0.019$ for 5215 unique observed reflections. The structure, known already from a room-temperature study, has been reinvestigated at 125 K in order to clarify hydrogen bonding. It consists of a framework of BaS₄(H₂O)₄/BaS₆(H₂O)₄ polyhedra and AsS₄ tetrahedra that is reinforced by two O—H···O, eleven O—H···S and one bifurcated O—H···S,S hydrogen bonds. Many of the hydrogen bonds are severely

bent. The O···S distances of the eight most linear respective hydrogen bonds measure on average 3.24 (8) Å, which is relatively short in comparison to a large number of other thiosalt hydrates.

Introduction. In connection with structural and spectroscopic investigations of hydrogen bonds between water molecules as donor and S atoms as acceptor (Mikenda, Mereiter & Preisinger, 1989) the crystal structure of Ba₃(AsS₄)₂·7H₂O became of interest. The structure of this salt had previously been determined at room temperature by Cordier, Schwidetzky & Schäfer (1985) and refined to $R = 0.076$ for 5904 reflections. Since no information on H-atom posi-