

centrifuged with successive portions of distilled water until no odour of ammonia was detectable. The resultant paste was vacuum filtered and dried under vacuum at 298 K.

#### Crystal data

Sn <sub>6</sub> O <sub>4</sub> (OH) <sub>4</sub>	Cu K $\alpha$ radiation
$M_r = 844.16$	$\lambda = 1.54184 \text{ \AA}$
Tetragonal	Cell parameters from 464 reflections
$P4_21c$	$\theta = 5\text{--}55^\circ$
$a = 7.9268 (4) \text{ \AA}$	$\mu = 105.6 \text{ mm}^{-1}$
$c = 9.1025 (5) \text{ \AA}$	$T = 298 \text{ K}$
$V = 571.94 (8) \text{ \AA}^3$	Powder
$Z = 2$	White
$D_x = 4.904 \text{ Mg m}^{-3}$	

#### Data collection

Siemens D-5000 X-ray diffractometer	Step size: $0.02^\circ$
Flat-plate $\theta/2\theta$ scans	Scan time/step: 12 s
Graphite monochromator	Range: $10\text{--}110^\circ 2\theta$

#### Refinement

Refinement on profile intensities	4999 observables
Rietveld method	33 parameters
$R_{wp} = 0.0436$	$(\Delta/\sigma)_{max} = -0.10$
$R_p = 0.0332$	Atomic scattering factors from <i>International Tables for X-ray Crystallography</i> (1974, Vol. IV)
$R_{ex} = 0.0384$	
$\chi^2 = 1.286$	

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$U_{iso}$  for O atoms,  $U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^*$  for Sn atoms.

	$x$	$y$	$z$	$U_{iso}/U_{eq}$
Sn(1)	0.1218 (2)	0.2917 (2)	-0.0038 (6)	0.027 (1)
Sn(2)	0	0	0.2757 (2)	0.032 (3)
O(1)	0.2606 (17)	0.090 (2)	0.1730 (15)	0.019 (3)
O(2)	-0.097 (3)	0.1945 (19)	0.1277 (15)	0.019

Table 2. Bond lengths, significant contact distances ( $\text{\AA}$ ) and angles ( $^\circ$ )

Sn(1)—O(1)	2.52 (2)	Sn(2)—O(1)	2.38 (1)
Sn(1)—O(1 <sup>i</sup> )	2.29 (2)	Sn(2)—O(1 <sup>iii</sup> )	2.38 (1)
Sn(1)—O(2)	2.25 (2)	Sn(2)—O(2)	2.19 (2)
Sn(1)—O(2 <sup>ii</sup> )	1.99 (2)	Sn(2)—O(2 <sup>iii</sup> )	2.19 (2)
O(1)···O(2 <sup>iv</sup> )	2.73 (2)	Sn(2)···Sn(2 <sup>vi</sup> )	4.083 (3)
Sn(1)···Sn(1 <sup>v</sup> )	3.826 (3)		
O(1)—Sn(1)—O(1 <sup>i</sup> )	132.9 (6)	Sn(1 <sup>i</sup> )—O(2)—Sn(2)	114.7 (8)
O(1)—Sn(1)—O(2 <sup>ii</sup> )	75.3 (6)	O(1)—Sn(1)—O(2)	77.3 (6)
O(1 <sup>i</sup> )—Sn(1)—O(2 <sup>ii</sup> )	75.4 (6)	O(1 <sup>i</sup> )—Sn(1)—O(2)	75.8 (6)
O(1)—Sn(2)—O(1 <sup>iii</sup> )	133.7 (7)	O(2)—Sn(1)—O(2 <sup>ii</sup> )	105.1 (8)
O(1)—Sn(2)—O(2)	81.5 (7)	O(1)—Sn(2)—O(2 <sup>iii</sup> )	70.3 (7)
Sn(1)—O(1)—Sn(1 <sup>i</sup> )	94.7 (5)	O(2)—Sn(2)—O(2 <sup>iii</sup> )	104.0 (8)
Sn(1 <sup>i</sup> )—O(1)—Sn(2)	97.9 (6)	Sn(1)—O(1)—Sn(2)	93.6 (5)
Sn(1)—O(2)—Sn(1 <sup>i</sup> )	113.3 (6)	Sn(1)—O(2)—Sn(2)	107.3 (9)

Symmetry codes: (i)  $-y, x, -z$ ; (ii)  $y, -x, -z$ ; (iii)  $-x, -y, z$ ; (iv)  $\frac{1}{2}x, \frac{1}{2}-y, \frac{1}{2}-z$ ; (v)  $-x, 1-y, z$ ; (vi)  $-y, x, 1-z$ .

The structure of the title compound was refined by Rietveld analysis. A starting model based on the isostructural lead compound in space group  $P4_21c$  was used. The scale factor, three background parameters and pseudo-Voigt peak-shape parameters were refined first, followed by unit-cell and zero-point-correction parameters. Refinement continued with variation of

the atomic and displacement parameters. Anisotropic displacement parameters were refined for Sn atoms only and the O-atom isotropic displacement parameters were tied. A fully absorbing flat-plate sample was assumed and no preferred orientation correction was found to be necessary. The H atom was not located and attempts to refine the H-atom position from the neutron study of the lead analogue were unsuccessful.

Program(s) used to refine structure: *GSAS* (Larson & Von Dreele, 1987). Molecular graphics: *SNOOPI* (Davies, 1983).

We gratefully acknowledge the SERC for an award to SRJ, and Professor J. D. Donaldson for helpful discussions.

Lists of powder diffraction data, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1120). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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#### Sodium Hexanitroruthenate(II) Monohydrate

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#### Abstract

Crystals of sodium hexanitroruthenate(II) monohydrate, Na<sub>4</sub>[Ru(NO<sub>2</sub>)<sub>6</sub>].H<sub>2</sub>O, are composed of [Ru(NO<sub>2</sub>)<sub>6</sub>]<sup>4-</sup> complex anions, Na<sup>+</sup> cations and water molecules. The structure is compared with those of other hexanitroruthenate(II) complexes.

### Comment

A procedure for the synthesis of ruthenium(II) hexanitrite compounds from aqueous solutions was developed by us previously (Emelyanov *et al.*, 1992). We have determined the crystal structures of  $\text{Na}_4[\text{Ru}(\text{NO}_2)_6] \cdot 2\text{H}_2\text{O}$ ,  $\text{Li}_4[\text{Ru}(\text{NO}_2)_6] \cdot 12\text{H}_2\text{O}$  and  $\text{K}_4[\text{Ru}(\text{NO}_2)_6]$  (Gromilov, Baidina, Emelyanov, Alekseev & Belyaev, 1993; Gromilov, Emelyanov, Alekseev, Baidina & Belyaev, 1994) and now present that of sodium hexanitro-ruthenate(II) monohydrate, (I).

The structure of (I) is composed of exactly centrosymmetric  $[\text{Ru}(\text{NO}_2)_6]^{4-}$  complex anions,  $\text{Na}^+$  cations and water molecules, which lie on crystallographic diad axes (Fig. 1). The Ru atoms have nearly ideal octahedral coordination involving six N atoms of the nitro groups. The average Ru—N and N—O bond lengths are 2.060 and 1.246 Å, respectively; the average O—N—O angle is 116.2°. The complex anions are linked by  $\text{H} \cdots \text{O}$  hydrogen bonds of 2.03 Å (Fig. 2). The two crystallographically independent Na atoms have different coordination environments. The coordination polyhedron around Na1 is formed by seven O atoms. The Na2 ion is coordinated by six O atoms, one of which

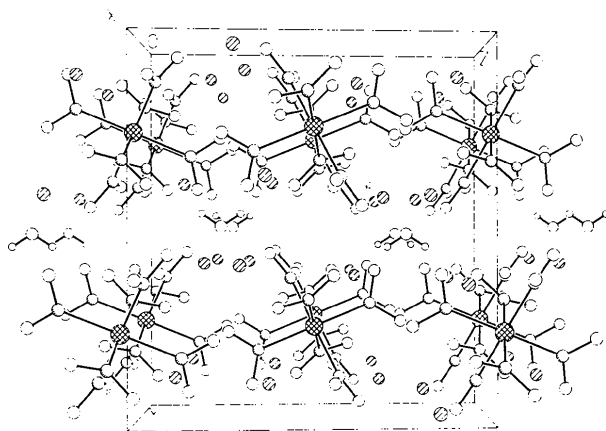


Fig. 1. The structure of  $\text{Na}_4[\text{Ru}(\text{NO}_2)_6] \cdot \text{H}_2\text{O}$  viewed down the  $a$  axis.

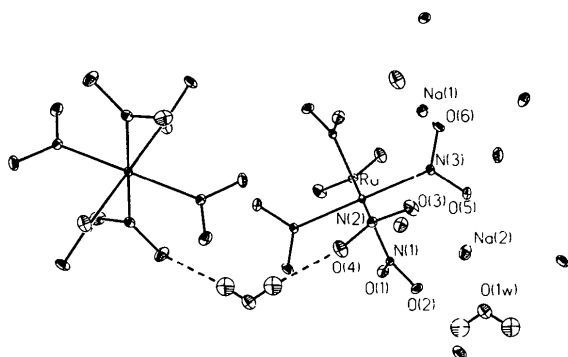


Fig. 2. A fragment of the structure, the hydrogen bonding, Na polyhedra and the atom-numbering scheme with 50% probability displacement ellipsoids.

belongs to the water molecule. These polyhedra are connected by a common edge, the  $\text{Na1} \cdots \text{Na2}$  distance being 3.926 (1) Å.

On comparing the structures of the known ruthenium(II) hexanitrite complexes, we can conclude that the nitrite groups have virtually the same geometry: the N—O distances vary between 1.196 (7) and 1.316 (7) Å, and the O—N—O angles lie in the range 112.9 (8)–117.4 (8)°. In the coordination polyhedron around the Ru atom, the mean distance decreases from 2.10 Å in the lithium salt to 2.05 Å in the potassium salt; deviations from ideal octahedral coordination at Ru are slight in all cases but, nevertheless, are most pronounced in (I).

### Experimental

Crystals of the title compound were prepared from an aqueous solution of  $\text{Na}_2[\text{RuNO}(\text{NO}_2)_4\text{OH}] \cdot 2\text{H}_2\text{O}$ ,  $\text{NaNO}_2$  and  $\text{NaOH}$  (Emelyanov *et al.*, 1992). The density  $D_m$  was measured by flotation in bromoform/toluene.

#### Crystal data

$\text{Na}_4[\text{Ru}(\text{NO}_2)_6] \cdot \text{H}_2\text{O}$   
 $M_r = 487.11$   
 Monoclinic  
 $C2/c$   
 $a = 7.920 (2) \text{ \AA}$   
 $b = 12.929 (3) \text{ \AA}$   
 $c = 12.177 (2) \text{ \AA}$   
 $\beta = 94.86 (3)^\circ$   
 $V = 1242.4 (5) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 2.604 \text{ Mg m}^{-3}$   
 $D_m = 2.600 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation  
 $\lambda = 0.71069 \text{ \AA}$   
 Cell parameters from 24 reflections  
 $\theta = 6.39\text{--}8.73^\circ$   
 $\mu = 1.496 \text{ mm}^{-1}$   
 $T = 293 (2) \text{ K}$   
 Prism  
 $0.6 \times 0.3 \times 0.2 \text{ mm}$   
 Yellow

#### Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction:  $\psi$  scans (North, Phillips & Mathews, 1968)  
 $T_{\min} = 0.78$ ,  $T_{\max} = 1.00$   
 3403 measured reflections  
 1748 independent reflections

1518 observed reflections  
 $[I > 2\sigma(I)]$   
 $R_{\text{int}} = 0.0168$   
 $\theta_{\max} = 30.06^\circ$   
 $h = -11 \rightarrow 10$   
 $k = -18 \rightarrow 18$   
 $l = 0 \rightarrow 17$   
 3 standard reflections  
 frequency: 60 min  
 intensity decay: none

#### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.0179$   
 $wR(F^2) = 0.0433$   
 $S = 0.960$   
 1748 reflections  
 117 parameters  
 All H-atom parameters refined  
 $w = 1/[\sigma^2(F_o^2) + (0.0238P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.062$

$\Delta\rho_{\max} = 0.79 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -1.33 \text{ e \AA}^{-3}$   
 Extinction correction: SHELXL93 (Sheldrick, 1993)  
 Extinction coefficient: 0.0020 (2)  
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

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

	x	y	z	U <sub>eq</sub>
Ru	1/4	1/4	1/2	0.01092 (6)
N1	0.1147 (2)	0.12689 (11)	0.43237 (11)	0.0163 (3)
O1	-0.03967 (15)	0.11649 (11)	0.44357 (11)	0.0256 (3)
O2	0.1817 (2)	0.06029 (10)	0.37562 (11)	0.0275 (3)
N2	0.4770 (2)	0.17510 (11)	0.48434 (12)	0.0168 (3)
O3	0.5600 (2)	0.19351 (12)	0.40373 (13)	0.0340 (3)
O4	0.5423 (2)	0.11408 (12)	0.55309 (12)	0.0338 (3)
N3	0.2668 (2)	0.30940 (11)	0.34399 (11)	0.0154 (3)
O5	0.2069 (2)	0.26448 (10)	0.25960 (11)	0.0290 (3)
O6	0.3431 (2)	0.39278 (10)	0.32902 (11)	0.0254 (3)
O1W	1/2	-0.0097 (2)	1/4	0.0288 (4)
Na1	0.65317 (9)	0.37543 (6)	0.38096 (6)	0.0232 (2)
Na2	0.74110 (9)	0.08617 (6)	0.30610 (6)	0.0271 (2)

Table 2. Selected geometric parameters (Å, °)

Ru—N1	2.0518 (15)	O2—Na2 <sup>iii</sup>	2.369 (2)
Ru—N2	2.0649 (14)	O2—Na1 <sup>iv</sup>	2.402 (2)
Ru—N3	2.0639 (14)	O3—Na1	2.488 (2)
N1—O1	1.249 (2)	O3—Na2	2.385 (2)
N1—O2	1.250 (2)	O4—Na1 <sup>v</sup>	2.481 (2)
N2—O3	1.250 (2)	O5—Na2 <sup>iii</sup>	2.486 (2)
N2—O4	1.232 (2)	O5—Na1 <sup>iii</sup>	2.557 (2)
N3—O5	1.239 (2)	O6—Na1	2.493 (2)
N3—O6	1.257 (2)	O6—Na1 <sup>iii</sup>	2.569 (2)
O1—Na2 <sup>i</sup>	2.341 (2)	O6—Na2 <sup>vi</sup>	2.635 (2)
O1—Na1 <sup>ii</sup>	2.390 (2)	O1W—Na2 <sup>iii</sup>	2.3300 (15)
N1—Ru—N2	91.62 (6)	O2—N1—O1	116.83 (15)
N1—Ru—N3	89.51 (6)	O4—N2—O3	115.94 (14)
N2—Ru—N3	87.99 (6)	O5—N3—O6	115.91 (14)

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

Data collection: CAD-4 Software (Enraf-Nonius, 1989). Cell refinement: CAD-4 Software. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: ORTEPII (Johnson, 1976). Software used to prepare material for publication: SHELXL93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU193). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Diphosphorus Tetraiodide at 120 K

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### Abstract

The structure of the title compound, P<sub>2</sub>I<sub>4</sub>, was determined at 120 K. The structure is composed of isolated P<sub>2</sub>I<sub>4</sub> molecules each lying on crystallographic symmetry centres. There are no apparent intermolecular contacts between the molecules. The bond distances are P—I 2.472 (2) and 2.475 (2) Å, P—P 2.230 (3) Å.

### Comment

The structure was originally determined at ambient temperature from photographic data estimated visually; the structure was solved from two Patterson projections on the (100) and (010) planes (Yuen Chu Leung & Waser, 1956). Having suitable crystals of P<sub>2</sub>I<sub>4</sub> on hand, we considered it useful to redetermine the structure from accurate diffractometer data collected at low temperature.

Despite an absorption correction, there are rather high residual electron densities in the vicinity of the I

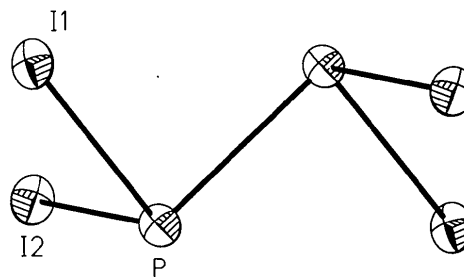


Fig. 1. Molecule of P<sub>2</sub>I<sub>4</sub> showing 50% probability displacement ellipsoids.