

## Studies on Transition-metal Oxo and Nitrido Complexes. Part 9.<sup>1</sup> Periodato and Tellurato Oxo-ruthenium Complexes as Organic Oxidants. X-Ray Crystal Structure of *trans*-NaK<sub>5</sub>[RuO<sub>2</sub>(HIO<sub>6</sub>)<sub>2</sub>] $\cdot$ 8H<sub>2</sub>O<sup>†</sup>

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Salts of the anion *trans*-[RuO<sub>2</sub>(HIO<sub>6</sub>)<sub>2</sub>]<sup>6-</sup>, earlier formulated as [Ru(OH)<sub>2</sub>(IO<sub>6</sub>)<sub>2</sub>]<sup>6-</sup>, and of [RuO<sub>2</sub>(H<sub>2</sub>TeO<sub>6</sub>)<sub>2</sub>]<sup>6-</sup> have been prepared, and the X-ray crystal structure of the complex *trans*-NaK<sub>5</sub>[RuO<sub>2</sub>(HIO<sub>6</sub>)<sub>2</sub>] $\cdot$ 8H<sub>2</sub>O determined [monoclinic, space group C2/c, *a* = 26.869(14), *b* = 7.359(2), *c* = 11.471(3) Å,  $\beta$  = 94.47(3)°, *Z* = 4, *R* = 0.059]. Vibrational and electronic spectra for these diamagnetic 'ruthenyl' complexes are also reported. The periodato complexes function as overall six-electron oxidants in aqueous solution, converting primary alcohols to carboxylic acids and secondary alcohols to ketones; such reactions can be rendered catalytic if periodate is used as a co-oxidant. The tellurato complex functions as a two-electron oxidant for alcohols.

In earlier work we described the preparation and characterisation of [RuO<sub>2</sub>(bipy)Cl<sub>2</sub>] (bipy = 2,2'-bipyridyl)<sup>2,3</sup> and of [PPh<sub>4</sub>][RuO<sub>2</sub>Cl<sub>3</sub>]<sup>3</sup> both of which are likely to contain the *trans* O=Ru<sup>VI</sup>=O 'ruthenyl' unit and which function in CH<sub>2</sub>Cl<sub>2</sub> solution as two-electron oxidants, converting primary alcohols to aldehydes and secondary alcohols to ketones.<sup>3</sup> In pursuance of our work on oxo-ruthenium complexes<sup>2</sup> and their utilisation as organic oxidants<sup>3-6</sup> we decided to investigate the nature and possible use as an oxidant of Na<sub>6</sub>[Ru(OH)<sub>2</sub>(IO<sub>6</sub>)<sub>2</sub>] $\cdot$ *n*H<sub>2</sub>O (*n* = 16-19), reported by Mercer and Meyer.<sup>7</sup>

### Results and Discussion

*Salts of [RuO<sub>2</sub>(HIO<sub>6</sub>)<sub>2</sub>]<sup>6-</sup>.*—Although a number of transition-metal periodato complexes have been reported,<sup>8</sup> very little is known about their properties or structures. The periodate ligand (either as [IO<sub>4</sub>]<sup>-</sup>, [IO<sub>6</sub>]<sup>5-</sup>, or [H<sub>*n*</sub>IO<sub>6</sub>]<sup>5-*n*</sup>) seems however to stabilise unusually high oxidation states<sup>8</sup> and is itself an oxidising species (*E*<sup>o</sup> 1.6-0.7 V depending on pH<sup>9</sup>) so that periodato complexes are of potential interest as oxidants. One such reported complex, prepared from a mixture of [RuO<sub>4</sub>]<sup>-</sup> and [RuO<sub>4</sub>]<sup>2-</sup> ‡ with NaIO<sub>4</sub> in NaOH, has been formulated as Na<sub>6</sub>[Ru(OH)<sub>2</sub>(IO<sub>6</sub>)<sub>2</sub>] $\cdot$ *n*H<sub>2</sub>O (*n* = 16-19) on the basis of sodium, ruthenium, iodine, and oxidation state determinations;<sup>7</sup> it is likely<sup>7</sup> that this diamagnetic complex is identical to the species produced by reaction of RuO<sub>2</sub> $\cdot$ *n*H<sub>2</sub>O and periodate.<sup>10</sup> Since we had shown in earlier work<sup>2</sup> that the ruthenate ion [RuO<sub>4</sub>]<sup>2-</sup> reacts with ligands such as ammonia, pyridine, bipyridyl, *etc.* to give octahedral species containing the *trans* O=Ru<sup>VI</sup>=O ruthenyl unit it seemed likely that the anion should be reformulated as *trans*-[RuO<sub>2</sub>(HIO<sub>6</sub>)<sub>2</sub>]<sup>6-</sup> and this was supported by Raman and i.r. data (see below).

We have now isolated, using improved preparative methods,

<sup>†</sup> Pentapotassium sodium *trans*-dioxobis[periodato(4-)-O<sup>1</sup>O<sup>2</sup>]-ruthenate(vi) octahydrate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii-xx.

<sup>‡</sup> Note added at proof: after the proofs of this paper were received a paper appeared which showed that [RuO<sub>4</sub>]<sup>2-</sup> is in fact *trans*-[Ru(OH)<sub>2</sub>O<sub>3</sub>]<sup>2-</sup> (M. O. Elout, W. G. Maise, and W. J. A. Maaskant, *Inorg. Chem.*, 1988, 27, 614).

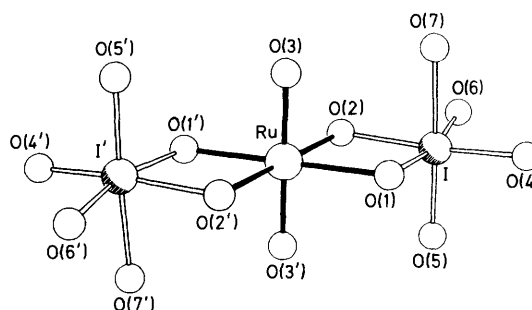


Figure 1. Perspective view of *trans*-[RuO<sub>2</sub>(HIO<sub>6</sub>)<sub>2</sub>]<sup>6-</sup> showing the crystallographic numbering

the salts Na<sub>6</sub>[RuO<sub>2</sub>(HIO<sub>6</sub>)<sub>2</sub>] $\cdot$ 18H<sub>2</sub>O, K<sub>6</sub>[RuO<sub>2</sub>(HIO<sub>6</sub>)<sub>2</sub>] $\cdot$ 6H<sub>2</sub>O, and NaK<sub>5</sub>[RuO<sub>2</sub>(HIO<sub>6</sub>)<sub>2</sub>] $\cdot$ 8H<sub>2</sub>O; the last was the only salt to give crystals suitable for an X-ray crystal structure determination.

*X-Ray Crystal Structure of NaK<sub>5</sub>[RuO<sub>2</sub>(HIO<sub>6</sub>)<sub>2</sub>] $\cdot$ 8H<sub>2</sub>O.*—The structure of the anion is shown in Figure 1 together with the atom labelling. Bond lengths and angles are given in Table 1; atomic co-ordinates are given in Table 2, which also includes those for the cations and water molecules. Co-ordination about the ruthenium is distorted octahedral with the ruthenium positioned on a centre of symmetry. That the complex is indeed of the ruthenyl type is shown by the presence of two *trans* terminal oxo ligands; the Ru=O(3) distance of 1.732(8) Å is comparable with those of 1.718(5) and 1.705(7) Å found for ruthenyl groups in the macrocyclic complexes *trans*-[RuO<sub>2</sub>(tmtacpd)][ClO<sub>4</sub>]<sub>2</sub> (tmtacpd = 1,4,8,12-tetramethyl-1,4,8,12-tetra-azacyclopentadecane) and *trans*-[RuO<sub>2</sub>(tmtachd)][ClO<sub>4</sub>]<sub>2</sub> (tmtachd = 1,5,9,13-tetramethyl-1,5,9,13-tetra-azacyclohexadecane) respectively.<sup>11</sup>

The octahedron is completed by two bidentate HIO<sub>6</sub><sup>4-</sup> ligands. The seven-atom unit [I,O(1),O(2),Ru,O(1'),O(2'),I'] is essentially planar (maximum deviation from least-squares plane 0.026 Å for I) with O(4) and O(6) lying 0.16 Å below this plane and O(4') and O(6') a similar distance above. The mean Ru-O(periodate) distances of 2.01 Å are as expected for Ru-O single bonds, and the mean I-O(bridge) distance of 1.95 Å is close to that found for the bridging I-O distance (2.01 Å) in

**Table 1.** Bond lengths (Å) and angles (°)\*

Ru-I	3.093(1)	Ru-O(1)	2.008(8)
Ru-O(2)	2.016(8)	Ru-O(3)	1.732(8)
I-O(1)	1.964(8)	I-O(2)	1.939(8)
I-O(4)	1.795(9)	I-O(5)	1.817(9)
I-O(6)	1.833(10)	I-O(7)	1.990(9)
O(1)-Ru-O(2)	76.0(3)	O(1)-Ru-O(3)	89.3(4)
O(2)-Ru-O(3)	90.4(4)	O(2)-Ru-O(1')	104.0(3)
O(3)-Ru-O(1')	90.7(4)	O(3)-Ru-O(2')	89.6(4)
O(1)-I-O(2)	78.7(3)	O(1)-I-O(4)	93.3(4)
O(2)-I-O(4)	169.4(4)	O(1)-I-O(5)	92.0(4)
O(2)-I-O(5)	92.9(4)	O(4)-I-O(5)	94.3(4)
O(1)-I-O(6)	166.8(4)	O(2)-I-O(6)	90.0(4)
O(4)-I-O(6)	97.0(4)	O(5)-I-O(6)	95.6(4)
O(1)-I-O(7)	86.0(4)	O(2)-I-O(7)	85.6(4)
O(4)-I-O(7)	86.9(4)	O(5)-I-O(7)	177.7(4)
O(6)-I-O(7)	86.2(4)		

\* Primed atoms are generated in the symmetry operation  $\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z$ .

**Table 2.** Atom co-ordinates ( $\times 10^4$ )

Atom	x	y	z
Ru	2 500	2 500	0
I	1 457(1)	2 310(1)	958(1)
O(1)	2 133(3)	3 219(12)	1 388(7)
O(2)	1 806(3)	1 505(12)	-365(7)
O(3)	2 679(3)	498(12)	707(7)
O(4)	1 235(4)	2 926(14)	2 340(8)
O(5)	1 271(3)	4 444(12)	256(7)
O(6)	902(4)	1 041(15)	397(7)
O(7)	1 688(4)	-7(13)	1 712(7)
K(1)	1 755(1)	7 691(4)	-510(3)
K(2)	1 399(1)	6 728(5)	2 642(3)
K(3)	167(3)	2 849(10)	1 158(5)
Na(1)	0	2 237(11)	-2 500
O(8)	2 344(4)	6 838(13)	1 602(7)
O(9)	491(4)	4 475(18)	-1 425(11)
O(10)	618(4)	-35(17)	-1 749(8)
O(11)	560(5)	-2 361(16)	954(11)

$\text{Na}_5\text{HI}_2\text{O}_{10}\cdot 14\text{H}_2\text{O}$ .<sup>12</sup> Of the remaining I-O bonds those at 1.990(9) Å [O(7), O(7')] clearly correspond to the protonated oxo ligand (1.90 Å in  $\text{Na}_5\text{HI}_2\text{O}_{10}\cdot 14\text{H}_2\text{O}$ <sup>12</sup>) while the other six (I=O, av. 1.82 Å, compared with 1.81 Å in  $\text{Na}_5\text{HI}_2\text{O}_{10}\cdot 14\text{H}_2\text{O}$ <sup>12</sup>) correspond to terminal oxo ligands. The slight bending of O(7) towards O(3) [and of O(7') to O(3')] giving an O(7)-O(3) distance of 3.01 Å could be caused by formation of a hydrogen bond involving the hydroxyl hydrogen atoms of I-OH; the corresponding O(5)-O(3') distance, where no protons are likely to be interposed, is 3.11 Å.

The only other X-ray determinations on periodato complexes appear to be those on  $\text{Na}_7\text{H}_4[\text{Mn}(\text{IO}_6)_3]\cdot 17\text{H}_2\text{O}$ , for which only Mn-I, Mn-O, and I-O distances were determined,<sup>13</sup> and for  $\text{Na}_3\text{KH}_3[\text{Cu}(\text{IO}_6)_2]$ , for which data are similarly sparse.<sup>14</sup>

Figure 2(a)-(d) shows the environments of the K and Na cations (see also Experimental section) and Table 3 gives the distances of these cations to the water molecules and the oxygen atoms of the anion. Both the anions and cations are interlinked *via* hydrogen bonding from the water molecules (Table 4).

**Other Physical Data on  $[\text{RuO}_2(\text{HIO}_6)_2]^{6-}$  Salts.**—As reported by Mercer and Meyer,<sup>7</sup> the sodium salt (and also our new salts) are diamagnetic in the solid state; we also find this

**Table 3.** Potassium and sodium ion environments\*

K(1)···O(2)	2.81	K(1)···O(3)	2.82
K(1)···O(4)	2.78	K(1)···O(5)	2.89
K(1)···O(7)	3.08	K(1)···O(8)	2.86
K(1)···O(8')	2.83		
K(2)···O(2)	2.78	K(2)···O(3)	3.13
K(2)···O(4)	2.85	K(2)···O(5)	3.21
K(2)···O(5')	3.17	K(2)···O(7)	2.77
K(2)···O(8)	2.89	K(2)···O(9)	2.88
K(2)···O(11)	2.93		
K(3)···O(4)	3.08	K(3)···O(6)	2.59
K(3)···O(9)	2.68	K(3)···O(10)	3.07
K(3)···O(10')	3.33	K(3)···O(11)	3.01
Na(1)···O(9)	2.39	Na(1)···O(10)	2.46
Na(1)···O(11)	2.42		

\* Distances (Å); estimated standard deviations in all cases 0.01 Å.

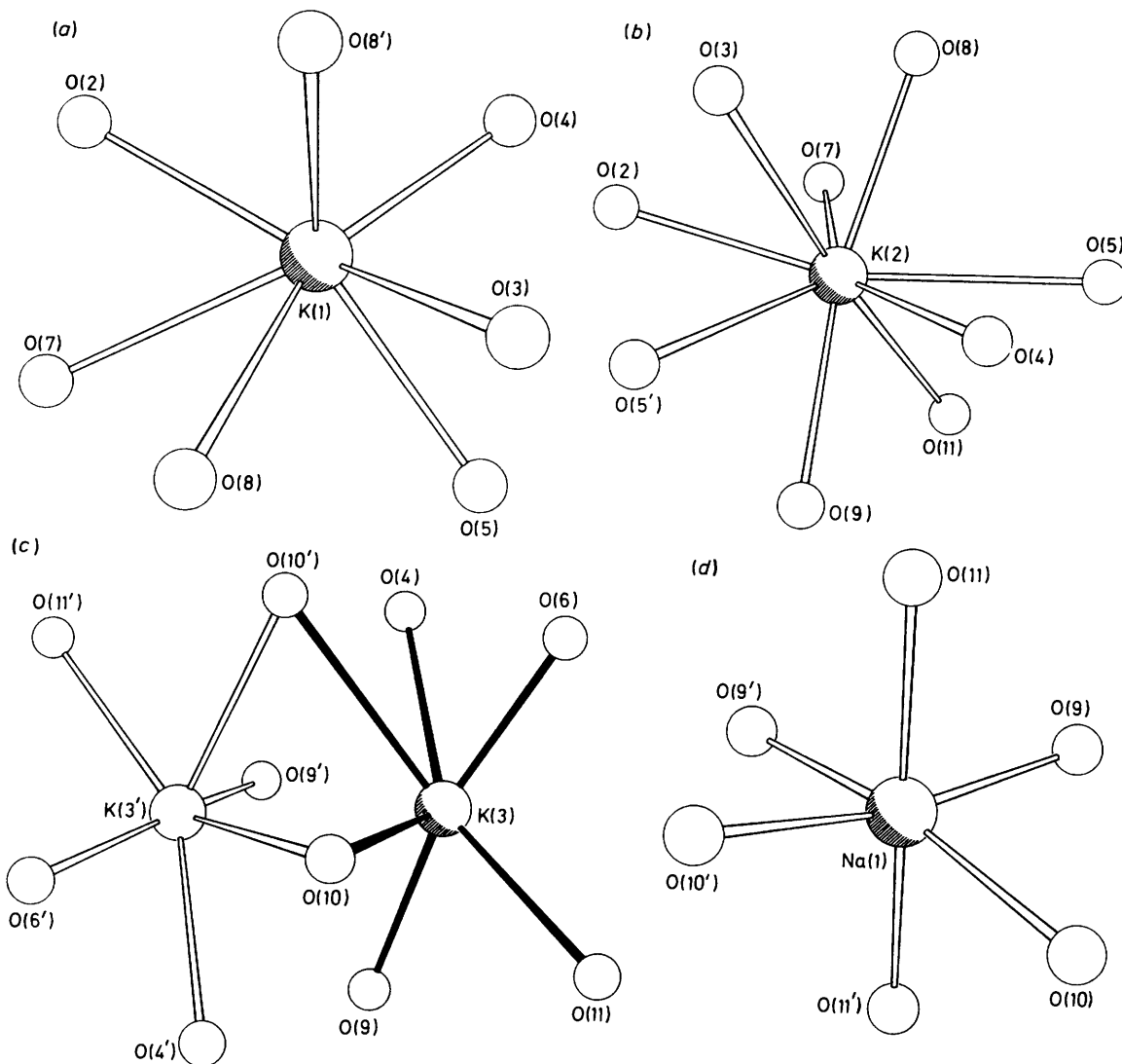
**Table 4.** Hydrogen-bonding interactions <3.0 Å; e.s.d.s  $\pm 0.01$  Å

O(8)···O(1)	2.73	O(8)···O(1')	2.80
O(9)···O(5)	2.73	O(10)···O(6)	2.64
O(10)···O(4')	2.94	O(11)···O(6)	2.76

to be the case for their aqueous solutions using the Evans method.<sup>15</sup> In Table 5 are given Raman and i.r. spectroscopic data for the salts in the solid state (we were unable to record the Raman spectra of the solutions owing to the low solubilities of the salts). We tentatively assign the strong Raman and i.r. bands near 800  $\text{cm}^{-1}$  to the symmetric and asymmetric vibrations  $\nu_{\text{sym}}(\text{RuO}_2)$  and  $\nu_{\text{asym}}(\text{RuO}_2)$  respectively; neither band is shifted on partial deuteration of the complex. These bands are higher in wavenumber than observed for periodates  $[\text{H}_n\text{IO}_6]^{5-n}$ <sup>16</sup> or in periodato complexes.<sup>17-19</sup> In *trans*- $[\text{RuO}_2(\text{NH}_3)_4]\text{Cl}_2$ ,  $\nu_{\text{asym}}(\text{RuO}_2)$  and  $\nu_{\text{sym}}(\text{RuO}_2)$  lie at 845 and 841  $\text{cm}^{-1}$  respectively,<sup>2</sup> while in the macrocyclic complexes *trans*- $[\text{RuO}_2(\text{tmtacpd})][\text{ClO}_4]_2$  and *trans*- $[\text{RuO}_2(\text{tmtachd})][\text{ClO}_4]_2$ ,  $\nu_{\text{asym}}(\text{RuO}_2)$  lies at 855 and 860  $\text{cm}^{-1}$  respectively. In these species however the Ru=O bond distances are slightly shorter than in *trans*- $\text{NaK}_5[\text{RuO}_2(\text{HIO}_6)_2]\cdot 8\text{H}_2\text{O}$  so that the lower wavenumber of *ca.* 820  $\text{cm}^{-1}$  for  $\nu_{\text{asym}}(\text{RuO}_2)$  in the latter seems reasonable. Assignments of the other bands in the salts follow those of Siebert and Weighardt for periodates  $[\text{H}_n\text{IO}_6]^{5-n}$ <sup>16</sup> and of Baran and co-workers<sup>17</sup> for Raman and i.r. spectra of  $[\text{Cu}(\text{HIO}_6)_2]^{5-}$ . Unfortunately the salts are insufficiently soluble for Raman solution data, and we were unable to deuteriate them completely.

Electronic spectra showed maxima at 384 and 314 nm, similar to those found for other ruthenyl complexes.<sup>20</sup> The spectra are similar to those of the species studied spectrophotometrically but not isolated by Rozovskii *et al.*,<sup>21</sup> made for  $[\text{RuO}_4]^{2-}$  and  $[\text{IO}_4]^-$  in 1-4 mol  $\text{dm}^{-3}$   $\text{OH}^-$ . They ascribed the formula  $[\text{Ru}^{\text{VII}}\text{O}_2(\text{H}_2\text{IO}_6)_2]^{3-}$  to their species, but our magnetic measurements on our salts in aqueous solution using the Evans method give no evidence of the paramagnetism which could be expected<sup>5</sup> for ruthenium(vii) complexes.

Cyclic voltammetric studies gave quasi-reversible redox couples ( $\Delta E = 60-90$  mV) comparable with those found for *trans*- $[\text{RuO}_2(\text{tmtacpd})][\text{ClO}_4]_2$ ;<sup>22</sup> on the basis of those data and of analysis of our waves we assign the couples at  $E_{\frac{1}{2}} = +0.76$  to  $\text{Ru}^{\text{VI/V}}$ ,  $E_{\frac{1}{2}} = +0.31$  to  $\text{Ru}^{\text{V/IV}}$ ,  $E_{\frac{1}{2}} = +0.13$  to  $\text{Ru}^{\text{IV/III}}$ , and  $E_{\frac{1}{2}} = -0.36$  V to  $\text{Ru}^{\text{III/II}}$  (*vs.* Ag-AgCl electrode; see Figure 3).



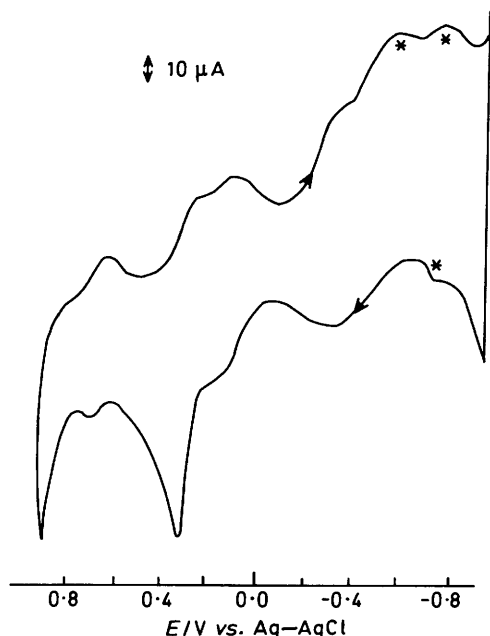
**Figure 2.** Potassium and sodium ion environments: (a) K(1); (b) K(2); (c) the relative dispositions of the two 0.5 occupancy sites for K(3); (d) Na(1), positioned on a crystallographic two-fold axis

**Table 5.** Raman and infrared spectra of ruthenium periodato and tellurato complexes

NaK <sub>5</sub> [RuO <sub>2</sub> (HIO <sub>6</sub> ) <sub>2</sub> ]·8H <sub>2</sub> O		Na <sub>6</sub> [RuO <sub>2</sub> (HIO <sub>6</sub> ) <sub>2</sub> ]·18H <sub>2</sub> O		K <sub>6</sub> [RuO <sub>2</sub> (H <sub>2</sub> TeO <sub>6</sub> ) <sub>2</sub> ]·4H <sub>2</sub> O		Assignment
Infrared	Raman	Infrared	Raman	Infrared	Raman	
3 500—3 000s		3 600—2 800s		3 500—2 900s		v(OH)
1 660s		1 640, 1 600s		1 680—1 627br		δ(HOH)
1 015s		1 080m		1 015m		δ(MOH)*
820s		800s		825s		v <sub>asym</sub> (RuO <sub>2</sub> )
	806s		793		817s	v <sub>sym</sub> (RuO <sub>2</sub> )
750m	753m	750m	752	735m	725m	v <sub>3</sub> (MO <sub>6</sub> )*
720w	716w, 700w	719w	719w, 687w, 670m	680w	647m	
605m	605m	615m	611w	650s	556m	v <sub>1</sub> (MO <sub>6</sub> )
530m	554w, 508w	525m	526w	570s		
455w	464w	450m	493w	515w, 485w		v(RuO)
				455w		
425m	418w		421w	425m	432w	
400w		400s	402w			v <sub>4</sub> (MO <sub>6</sub> )*
			381m			
			367, 358w		397, 306w	

\* M = I or Te.

*Salts of trans-[RuO<sub>2</sub>(H<sub>2</sub>TeO<sub>6</sub>)<sub>2</sub>]<sup>6-</sup>.*—No tellurato complexes of ruthenium have been reported, but the copper(III) and silver(III) species [M(H<sub>2</sub>TeO<sub>6</sub>)<sub>2</sub>]<sup>5-</sup> have been isolated<sup>23</sup> so it seems that [H<sub>2</sub>TeO<sub>6</sub>]<sup>4-</sup>, like its isoelectronic partner [HIO<sub>6</sub>]<sup>4-</sup>, is capable of stabilising relatively high metal oxidation states. We find that reaction of [RuO<sub>4</sub>]<sup>2-</sup> with Te(OH)<sub>6</sub> in aqueous base gives solutions from which the yellow salts K<sub>6</sub>[RuO<sub>2</sub>(H<sub>2</sub>TeO<sub>6</sub>)<sub>2</sub>·4H<sub>2</sub>O and Na<sub>6</sub>[RuO<sub>2</sub>(H<sub>2</sub>TeO<sub>6</sub>)<sub>2</sub>·13H<sub>2</sub>O can be isolated. Although we have been unable to obtain crystals suitable for X-ray structure analysis their formulation



**Figure 3.** Cyclic voltammogram of  $10^{-3}$  mol  $\text{dm}^{-3}$  *trans*-[RuO<sub>2</sub>(HIO<sub>6</sub>)<sub>2</sub>]<sup>6-</sup> in an aqueous solution of 0.1 mol  $\text{dm}^{-3}$  KCl (pH 10.8) using platinum electrodes and scan rate of 50 mV  $\text{s}^{-1}$ . \* Denote irreversible periodate peaks slightly shifted cathodically by 0.01–0.05 V compared to the free ligand, at the same concentration and pH at 25 °C

as 'ruthenyl' complexes is supported by their analyses, diamagnetism, and their reactions (see below) as two-electron oxidants of alcohols. The salts react with concentrated alkali to give [Ru<sup>VI</sup>O<sub>4</sub>]<sup>2-</sup>.

The Raman and i.r. spectra (Table 5) also support a 'ruthenyl' structure; as with the periodato salts the i.r. band at 825  $\text{cm}^{-1}$  and the Raman band at 817  $\text{cm}^{-1}$  lie too high to arise from the tellurato ligands<sup>18,23,24</sup> and we assign them to  $\nu_{\text{asym}}(\text{RuO}_2)$  and  $\nu_{\text{sym}}(\text{RuO}_2)$  respectively. The other bands in the i.r. and Raman spectra are assigned according to the nomenclature adopted for Na<sub>5</sub>[Cu(H<sub>2</sub>TeO<sub>6</sub>)<sub>2</sub>·10H<sub>2</sub>O].<sup>18</sup>

*Organic Oxidations by trans-[RuO<sub>2</sub>(HIO<sub>6</sub>)<sub>2</sub>]<sup>6-</sup> and trans-[RuO<sub>2</sub>(H<sub>2</sub>TeO<sub>6</sub>)<sub>2</sub>]<sup>6-</sup>.*—We have shown in earlier work that the [RuO<sub>4</sub>]<sup>2-</sup> ion in aqueous base functions as an overall four-electron oxidant, converting primary alcohols to carboxylic acids and secondary alcohols to ketones; peroxydisulphate, [S<sub>2</sub>O<sub>8</sub>]<sup>2-</sup>, can be used as a co-oxidant to render the system catalytic.<sup>3,4</sup> In non-aqueous solution the ruthenyl species [RuO<sub>2</sub>(bipy)Cl<sub>2</sub>], [RuO<sub>2</sub>Cl<sub>3</sub>]<sup>-</sup>, and *trans*-Ba[RuO<sub>3</sub>(OH)<sub>2</sub>] function as two-electron oxidants,<sup>3</sup> converting primary alcohols to aldehydes and secondary alcohols to ketones.

In Table 6 we give some typical oxidations of alcohols carried out by *trans*-[RuO<sub>2</sub>(HIO<sub>6</sub>)<sub>2</sub>]<sup>6-</sup> and *trans*-[RuO<sub>2</sub>(H<sub>2</sub>TeO<sub>6</sub>)<sub>2</sub>]<sup>6-</sup> in aqueous solution. The tellurato complex appears to function in a similar fashion to *trans*-Ba[RuO<sub>3</sub>(OH)<sub>2</sub>], oxidising activated alcohols only. With benzyl alcohol, 1 mmol of the complex oxidises 0.75 mmol of the alcohol to 0.50 mmol of benzaldehyde and 0.25 mmol of benzoic acid, giving RuO<sub>2</sub> as the product, so clearly this is a weak two-electron oxidant {very similar to *trans*-Ba[RuO<sub>3</sub>(OH)<sub>2</sub>]<sup>3</sup>}. The periodato complex is more interesting, however. Stoichiometric oxidations in aqueous solutions using normal and substituted benzyl alcohols and benzaldehyde shows it to function as an overall six-electron oxidant, Ru<sup>VI</sup> being reduced to Ru<sup>IV</sup> and I<sup>VI</sup> to I<sup>V</sup>. At pH 12 it was possible to isolate the ruthenium as RuO<sub>2</sub> and the iodine as [IO<sub>3</sub>]<sup>-</sup> after such oxidations. The participation of co-ordinated periodate in these oxidations is surprising since, although H<sub>5</sub>IO<sub>6</sub> in 1 mol  $\text{dm}^{-3}$  H<sub>2</sub>SO<sub>4</sub> will oxidise primary alcohols to aldehydes it does so only very slowly at pH 12, the pH at which our oxidations were carried out. Blank experiments using the substrates listed in Table 6 with [IO<sub>4</sub>]<sup>-</sup> at pH 12

**Table 6.** Organic oxidations by *trans*-[RuO<sub>2</sub>(HIO<sub>6</sub>)<sub>2</sub>]<sup>6-</sup> and *trans*-[RuO<sub>2</sub>(H<sub>2</sub>TeO<sub>6</sub>)<sub>2</sub>]<sup>6-</sup>

	<i>trans</i> -[RuO <sub>2</sub> (HIO <sub>6</sub> ) <sub>2</sub> ] <sup>6-</sup>					<i>trans</i> -[RuO <sub>2</sub> (H <sub>2</sub> TeO <sub>6</sub> ) <sub>2</sub> ] <sup>6-</sup>		
	Product <sup>c</sup>	Stoichiometric <sup>a</sup> oxidation		Catalytic <sup>b</sup> oxidation		Product <sup>c</sup>	Stoichiometric <sup>a</sup> oxidation	
		Yield (%)	Time (h)	Yield (%)	Time (h)		Yield (%)	Time (h)
Benzyl alcohol	A	96	1	95	1.5	A	35	24
						D	65	
4-Methoxybenzyl alcohol	A	97	1	99	1.5	A	33	48
						D	65	
2-Chlorobenzyl alcohol	A	94	1	96	1.5	A	30	24
						D	68	
Benzaldehyde	A	95	1	96	1	A	45	96
Cyclobutanol <sup>d</sup>	K	70	1					
PhCH(OH)CH(OH)Ph	A	80	2.5					
Cyclohexanol	K	—	—	75	2			
Tetrahydronaphthol	K	65	1.5	85	2	K	40	24
Diphenylmethanol	K	—	—	40	2			
Lanost-8-en-3β-ol	K	55	2	64	4			

<sup>a</sup> In saturated aqueous solution. <sup>b</sup>  $6 \times 10^{-4}$  mol Ru, 0.25 mol  $\text{dm}^{-3}$  OH<sup>-</sup>, 0.15 mol  $\text{dm}^{-3}$  [IO<sub>4</sub>]<sup>-</sup>; 0.05 mol  $\text{dm}^{-3}$  primary alcohol, 0.03 mol  $\text{dm}^{-3}$  secondary alcohol. <sup>c</sup> A = Corresponding acid, D = corresponding aldehyde, K = corresponding ketone. <sup>d</sup> As for *b* but with 1 mol  $\text{dm}^{-3}$  OH<sup>-</sup>.

gave only traces of acid or aldehyde at the stated times. It seems that the metal centre activates the periodato ligand; a similar phenomenon has been noted for peroxodisulphate which, while inactive alone, will cleave cyclic diols in the presence of silver(I)<sup>25</sup> and will oxidise alcohols in the presence of ruthenium(VI).<sup>3,4</sup> We find that other periodato complexes behave in similar fashion; thus  $[\text{Mn}(\text{HIO}_6)_3]^{8-}$  functions as an overall six-electron oxidant towards benzylic alcohols, and oxidation of alcohols by  $[\text{Cu}(\text{HIO}_6)_2]^{5-}$  has been noted.<sup>26</sup>

The *trans*- $[\text{RuO}_2(\text{HIO}_6)_2]^{6-}$  ion resembles  $[\text{RuO}_4]^{2-}$  in that, in aqueous base (pH 12), it oxidises primary alcohols to carboxylic acids and secondary alcohols to ketones. Like ruthenate too it can be made to function catalytically, as indicated in Table 6, with turnover times of up to 85. Large-scale oxidations can also be accomplished: thus, 10.8 g of benzyl alcohol are converted to 10.1 g of benzoic acid (83% yield) over a period of 3 h by  $9.5 \times 10^{-4}$  mol of  $\text{Na}_6[\text{RuO}_2(\text{HIO}_6)_2] \cdot 18\text{H}_2\text{O}$ ,  $0.33 \text{ mol dm}^{-3}$   $\text{NaIO}_4$ , and  $0.25 \text{ mol dm}^{-3}$   $\text{NaOH}$ , a turnover of 105. In more concentrated base ( $>1 \text{ mol dm}^{-3}$   $\text{OH}^-$ ), the electronic spectra show that *trans*- $[\text{RuO}_2(\text{HIO}_6)_2]^{6-}$  is converted to  $[\text{RuO}_4]^{2-}$ , and higher yields and turnovers can be achieved with such solutions using  $[\text{IO}_4]^-$  as co-oxidant [thus 12.6 g of benzyl alcohol are converted to 14.1 g of benzoic acid (98% yield) using  $4.8 \times 10^{-4}$  mol Ru,  $1 \text{ mol dm}^{-3}$   $\text{OH}^-$ , and  $0.23 \text{ mol dm}^{-3}$   $\text{NaIO}_4$  corresponding to a turnover of 245].

We find that *trans*- $[\text{RuO}_2(\text{HIO}_6)_2]^{6-}$  cleaves diols (e.g., hydrobenzoin) or double bonds (e.g., cinnamyl alcohol), both reactions typical of periodate.<sup>27,28</sup> Although  $[\text{IO}_4]^-$  has been used previously with ruthenium complexes as a co-catalyst<sup>29,30</sup> the solutions were either neutral or acid, in which case  $\text{RuO}_4$  rather than *trans*- $[\text{RuO}_2(\text{HIO}_6)_2]^{6-}$  will have been formed.

## Experimental

Hydrated ruthenium trichloride,  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ , was supplied by Johnson-Matthey.

**Preparations.**—*Hexasodium trans-dioxobis(periodato)ruthenate(VI)*,  $\text{Na}_6[\text{RuO}_2(\text{HIO}_6)_2] \cdot 18\text{H}_2\text{O}$ . This method avoids the use of hypochlorite which is involved in the literature preparation of  $\text{Na}_6[\text{Ru}(\text{OH})_2(\text{IO}_6)_2] \cdot n\text{H}_2\text{O}$ .<sup>7</sup> Hydrated ruthenium trichloride (0.5 g, 1.9 mmol) was dissolved in 2 mol  $\text{dm}^{-3}$   $\text{NaOH}$  solution (20  $\text{cm}^3$ ) with stirring. A saturated solution of  $\text{NaIO}_4$  (0.94 g, 4.4 mmol) was prepared; half was added to the alkaline ruthenium solution with stirring until a red-brown solution was obtained, and the rest of the  $\text{NaIO}_4$  solution was then added to give a red-brown precipitate of the complex. This was filtered off, washed with  $0.01 \text{ mol dm}^{-3}$   $\text{NaOH}$  solution and dried (2 g of product). It was recrystallised by forming a saturated solution in  $0.01 \text{ mol dm}^{-3}$   $\text{NaOH}$  and precipitation by addition of an equal volume of  $0.75 \text{ mol dm}^{-3}$   $\text{NaOH}$ . The material was washed with a small volume of  $0.001 \text{ mol dm}^{-3}$   $\text{NaOH}$ . Yield 1.5 g, 1.6 mmol (85%) (Found: H, 3.2; I, 24.0; Na, 13.4; Ru, 9.7.  $\text{H}_{38}\text{I}_2\text{Na}_6\text{O}_{32}\text{Ru}$  requires H, 3.6; I, 24.4; Na, 13.2; Ru, 9.7%).

*Hexapotassium trans-dioxobis(periodato)ruthenate(VI)*,  $\text{K}_6[\text{RuO}_2(\text{HIO}_6)_2] \cdot 6\text{H}_2\text{O}$ . A saturated aqueous solution of potassium hypochlorite (4  $\text{cm}^3$ ) was made by the method of Audette and Quail.<sup>31</sup> This solution was mixed with aqueous 2 mol  $\text{dm}^{-3}$   $\text{KOH}$  (6  $\text{cm}^3$ ) and hydrated ruthenium trichloride (0.5 g, 1.9 mmol) added with stirring. The mixture was stirred overnight to give a brown solution to which solid periodic acid ( $\text{H}_5\text{IO}_6$ , 0.8 g, 3.5 mmol) was then added over a 15-min period with continual stirring. The red-brown precipitate was filtered off, washed with a little cold water, and dried *in vacuo* over  $\text{KOH}$ . Yield 1.4 g, 1.5 mmol (80%). Molar conductance of  $10^{-3}$  mol  $\text{dm}^{-3}$  aqueous solution  $890 \Omega^{-1} \text{ cm}^2$  at 25 °C (Found: H,

1.8; I, 28.0; K, 24.8; O, 34.0.  $\text{H}_{14}\text{I}_2\text{K}_6\text{O}_{20}\text{Ru}$  requires H, 1.5; I, 27.5; K, 25.4; O, 34.6%).

*Pentapotassium sodium trans-dioxobis(periodato)ruthenate(VI)*,  $\text{NaK}_5[\text{RuO}_2(\text{HIO}_6)_2] \cdot 8\text{H}_2\text{O}$ . Dried ruthenium dioxide (0.5 g, 3.8 mmol) was added to aqueous 2 mol  $\text{dm}^{-3}$   $\text{KOH}$  (4  $\text{cm}^3$ ) and aqueous  $\text{KOC}$  (4  $\text{cm}^3$ , prepared as described above) and stirred until a red-brown solution was obtained. An aqueous solution of  $\text{NaOH}$  (0.3 g, 7.5 mmol, in 2  $\text{cm}^3$  of water) was then added with stirring to  $\text{H}_5\text{IO}_6$  (1.7 g, 7.5 mmol, in 3  $\text{cm}^3$   $\text{H}_2\text{O}$ ). This solution was added dropwise to the above red-brown solution with continual stirring for 1 h, a little diethyl ether (1  $\text{cm}^3$ ) added and the mixture left for 2 h. The red-brown crystals were filtered off and dried *in vacuo* over  $\text{KOH}$  (yield 2.1 g, 2.3 mmol, 60%). Molar conductance of  $10^{-3}$  mol  $\text{dm}^{-3}$  aqueous solution  $880 \Omega^{-1} \text{ cm}^2$  at 25 °C (Found: H, 1.8; K, 21.0; Na, 2.2.  $\text{H}_{18}\text{I}_2\text{K}_5\text{NaO}_{22}\text{Ru}$  requires H, 1.9; K, 20.7; Na, 2.4%).

*Hexapotassium trans-dioxobis(tellurato)ruthenate(VI)*,  $\text{K}_6[\text{RuO}_2(\text{H}_2\text{TeO}_6)_2] \cdot 4\text{H}_2\text{O}$ . The method was that used for preparation of  $\text{K}_6[\text{RuO}_2(\text{HIO}_6)_2] \cdot 6\text{H}_2\text{O}$ , with  $\text{H}_6\text{TeO}_6$  (1.7 g, 7.4 mmol) replacing  $\text{H}_5\text{IO}_6$ . The orange-yellow material was filtered off, washed, and dried. Yield 0.9 g, 1 mmol (55%). Molar susceptibility,  $\chi_M = -0.8 \times 10^{-8} \text{ m}^3 \text{ mol}^{-1}$  (Found: H, 1.4; K, 26.3; Ru, 11.8; Te, 28.8.  $\text{H}_{16}\text{K}_6\text{O}_{18}\text{RuTe}_2$  requires H, 1.4; K, 26.3; Ru, 11.3; Te, 28.6%).

*Hexasodium trans-dioxobis(tellurato)ruthenate(VI)*,  $\text{Na}_6[\text{RuO}_2(\text{H}_2\text{TeO}_6)_2] \cdot 13\text{H}_2\text{O}$ . Hydrated ruthenium trichloride (0.5 g, 1.9 mmol) was dissolved in 2 mol  $\text{dm}^{-3}$  aqueous  $\text{NaOH}$  (20  $\text{cm}^3$ ) and sodium peroxodisulphate ( $\text{Na}_2\text{S}_2\text{O}_8$ , 2.38 g, 10 mmol) added with continual stirring of the mixture for 20 min until a clear red solution of  $[\text{RuO}_4]^{2-}$  was obtained. An aqueous solution of  $\text{H}_6\text{TeO}_6$  (0.87 g, 3.8 mmol in 5  $\text{cm}^3$  of water) was then added dropwise over 2 h with stirring, by which time a bulky yellow precipitate appeared. This was filtered off, washed with a little water, and dried over  $\text{P}_2\text{O}_5$ . Yield 1.6 g, 1.6 mmol (86%). Molar susceptibility,  $\chi_M = -0.6 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$  (Found: H, 2.9; Na, 14.1; Ru, 10.2; Te, 26.7.  $\text{H}_{38}\text{Na}_6\text{O}_{27}\text{Ru}$  requires H, 3.1; Na, 14.4; Ru, 10.6; Te, 26.7%).

**Oxidations.**—(a) *Stoichiometric.* Reactions were carried out using  $\text{Na}_6[\text{RuO}_2(\text{HIO}_6)_2] \cdot 18\text{H}_2\text{O}$  or  $\text{Na}_6[\text{RuO}_2(\text{H}_2\text{TeO}_6)_2] \cdot 13\text{H}_2\text{O}$  in saturated aqueous solutions, typically 1 mmol of periodato complex with 1 mmol of alcohol in 10  $\text{cm}^3$  of water, or for the tellurato complex 0.75 mmol of alcohol in 7  $\text{cm}^3$  of water. The mixture was stirred until the red (periodato) or yellow (tellurato) colours become black due to formation of  $\text{RuO}_2$ . The  $\text{RuO}_2$  was filtered off, washed with  $1 \text{ mol dm}^{-3}$   $\text{NaOH}$  ( $3 \times 5 \text{ cm}^3$ ) and the combined filtrates washed with diethyl ether ( $3 \times 10 \text{ cm}^3$ ). The ethereal layer was dried with  $\text{Na}_2\text{SO}_4$  and the aldehyde or ketone content quantified with 2,4-dinitrophenylhydrazine. The alkaline aqueous layer was acidified with  $5 \text{ mol dm}^{-3}$   $\text{H}_2\text{SO}_4$  to pH 2, extracted with ether ( $3 \times 20 \text{ cm}^3$ ), and dried to give the acid.

(b) *Catalytic.* The catalyst  $\{\text{Na}_6[\text{RuO}_2(\text{HIO}_6)_2] \cdot 18\text{H}_2\text{O}; 0.03 \text{ g}, 0.028 \text{ mmol}\}$  was dissolved in  $0.25 \text{ mol dm}^{-3}$  aqueous  $\text{NaOH}$  solution (20  $\text{cm}^3$ ) and  $\text{NaIO}_4$  (1.4 g, 6.6 mmol) added. The alcohol (2 mmol) was then added [in the case of secondary alcohols, 0.043 g (0.04 mmol) of catalyst was used]. The pale yellow solution was stirred for the time stipulated in Table 6. The mixture was then filtered and extracted with ether ( $3 \times 10 \text{ cm}^3$ ) and the extract treated as above.

**General Characterisation.**—The melting points,  $^1\text{H}$  n.m.r. and i.r. spectra of the acids were compared with the literature values,<sup>32</sup> and the aldehydes or ketones identified similarly by isolation or as their 2,4-dinitrophenylhydrazone derivatives. Raman spectra were measured on a Spex Ramalog 5 instrument with a CRL Innova krypton ion laser with excitation at 6 471 or 5 682 Å as discs or i.r. spectra were run as liquid paraffin

mulls and as KBr discs on a Perkin-Elmer R32 instrument. Cyclic voltammograms were measured on a Princeton Research model 174A instrument. Molar conductances were measured on a Digital Conductivity Meter PT1-18 at 25 °C. Potassium was determined gravimetrically as the tetraphenylborate and sodium by atomic absorption; in *trans*-NaK<sub>5</sub>[RuO<sub>2</sub>(HIO<sub>6</sub>)<sub>2</sub>]·8H<sub>2</sub>O the alkali metals were analysed on a Dionex ion-exchange column. Ruthenium was estimated by atomic absorption and also by conversion of the complexes to [RuO<sub>4</sub>]<sup>2-</sup> by boiling with 2 mol dm<sup>-3</sup> aqueous KOH solution followed by spectrophotometric determination using the band at 460 nm.<sup>33</sup> Iodine analyses were carried out by F. Pascher, Munich, and hydrogen by the microanalytical department at Imperial College. Tellurium was estimated gravimetrically as the element after removal of ruthenium as RuO<sub>4</sub> by boiling with NaIO<sub>4</sub>.

*X-Ray Crystal Structure of trans-NaK<sub>5</sub>[RuO<sub>2</sub>(HIO<sub>6</sub>)<sub>2</sub>]·8H<sub>2</sub>O.*—Crystal data. H<sub>18</sub>I<sub>2</sub>K<sub>5</sub>NaO<sub>22</sub>Ru, *M* = 943.5, monoclinic, *a* = 26.869(14), *b* = 7.359(2), *c* = 11.471(3) Å, β = 94.47(3)°, *U* = 2 261 Å<sup>3</sup>, space group *C2/c*, *Z* = 4, *D*<sub>c</sub> = 2.77 g cm<sup>-3</sup>, very thin unstable orange-red interpenetrating platelets (100) prominent; crystal coated with epoxy resin, crystal dimensions 0.12 × 0.07 × 0.01 mm, μ(Cu-K<sub>α</sub>) = 370 cm<sup>-1</sup>, λ = 1.541 78 Å, *F*(000) = 1 776.

*Data collection and processing.* Nicolet R3m diffractometer, ω-scan method (2θ ≤ 116°), graphite-monochromated Cu-K<sub>α</sub> radiation; 1 363 independent reflections measured, 1 220 observed [*I*<sub>o</sub> > 3σ(*I*<sub>o</sub>)], corrected for Lorentz and polarisation factors; empirical absorption correction (thin plate) based upon 366 azimuthal measurements, maximum and minimum transmission factors 0.48 and 0.07.

*Structure analysis and refinement.* The structure was solved by the heavy-atom method, the positions of the Ru and I atoms being determined from a sharpened vector map and the remaining atoms derived from subsequent Δ*F* maps. These unambiguously established the ruthenium periodate core and the presence of eight water molecules (four of these crystallographically independent). The positions of two of the K atoms were clearly identified but the identities of the atoms associated with the remaining principal residual peaks in a Δ*F* map computed at this stage were unclear. The residual electron density was in each case equivalent to approx. 0.5 of a K atom. Both ion exchange and atomic absorption measurements confirmed that the crystalline sample contained Na as well as K. Refinement of the two unidentified sites as Na atoms gave satisfactory convergence and thermal parameters comparable to those for the K atoms. However, this ratio of Na to K atoms was incompatible with the results of the ion exchange, atomic absorption, and gravimetric analyses which gave an unambiguous 1:5 ratio. Inspection of the environments of these two 'Na' atoms and their distances to neighbouring oxygen atoms suggested that whilst one of the positions was compatible with an Na atom, the other appeared to be more consistent with a K atom. Treating this site as a 0.5 weight K atom instead of a full weight Na atom resulted in no change in *R* and equally acceptable thermal parameters. This also now gave the desired ratio of Na to K atoms in the crystal.

The structure was refined anisotropically by block-cascade full-matrix least squares to give *R* = 0.059, *R'* = 0.063 [*w*<sup>-1</sup> = σ<sup>2</sup>(*F*) + 0.001 *F*<sup>2</sup>]. The maximum residual electron density in the final Δ*F* map was 2.1 e Å<sup>-3</sup> in the region of the I atoms (reflecting the difficulty in applying an adequate absorption correction) and the mean and maximum shifts/error in the final refinement cycle were 0.002 and 0.007 respectively. The hydrogen atoms were not located and no contribution was computed. Computations were carried out on an Eclipse S140 computer using the SHELXTL program system.<sup>34</sup>

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

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### References

- Part 8, W. P. Griffith, N. McManus, and A. D. White, *J. Chem. Soc., Dalton Trans.*, 1986, 1035.
- W. P. Griffith and D. Pawson, *J. Chem. Soc., Dalton Trans.*, 1973, 1315.
- G. Green, W. P. Griffith, D. M. Hollinshead, S. V. Ley, and M. Schröder, *J. Chem. Soc., Perkin Trans. 1*, 1984, 681.
- M. Schröder and W. P. Griffith, *J. Chem. Soc., Chem. Commun.*, 1979, 58.
- A. C. Dengel, W. P. Griffith, and R. A. Hudson, *Transition Met. Chem.*, 1985, **10**, 98.
- W. P. Griffith, S. V. Ley, and A. D. White, *J. Chem. Soc., Chem. Commun.*, 1987, 1625.
- E. E. Mercer and S. M. Meyer, *J. Inorg. Nucl. Chem.*, 1972, **34**, 777.
- B. K. Chaudhuri and H. G. Mukherjee, *J. Indian Chem. Soc.*, 1979, **56**, 1098; H. Siebert, *Fortschr. Chem. Forsch.*, 1967, **8**, 470.
- 'Standard Potentials in Aqueous Solution,' eds. A. J. Band, R. Parsons, and J. Jordan, M. Dekker, New York, 1985.
- L. Jenovsky, *Omagiu Raluca Ripan*, 1966, 293.
- T. C. Mak, C. M. Che, and K. Y. Wong, *J. Chem. Soc., Chem. Commun.*, 1985, 986.
- K. M. Tobias and M. Jansen, *Z. Anorg. Allg. Chem.*, 1986, **538**, 159.
- A. Linek, *Czech. J. Phys.*, 1963, **B13**, 398.
- I. Hadinec, L. Jenovsky, A. Linek, and V. Synecek, *Naturwissenschaften*, 1960, **16**, 377.
- D. F. Evans, *J. Chem. Soc.*, 1959, 2003; D. F. Evans and T. A. James, *J. Chem. Soc., Dalton Trans.*, 1974, 765.
- H. Siebert and G. Weighardt, *Z. Naturforsch., Teil B*, 1972, **27**, 1299; *Spectrochim. Acta, Part A*, 1971, **27**, 1677.
- A. H. Jubert, E. J. Baran, A. L. Diez, and O. Sala, *J. Raman Spectrosc.*, 1987, **18**, 23.
- A. L. Diez, R. L. Grassi, C. I. Cabello, and E. J. Baran, *Acta Sud Am. Quim.*, in the press.
- H. G. Mukherjee, S. B. Sarkar, B. Mandal, and B. K. Chaudhuri, *J. Indian Chem. Soc.*, 1984, **56**, 628.
- C. M. Che, K. Y. Wong, and C. K. Poon, *Inorg. Chem.*, 1985, **24**, 1797.
- G. I. Rozovskii, Z. A. Poshkute, A. Y. Prokopchik, and P. K. Norkus, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1973, **18**, 1432.
- C. M. Che and K. Y. Wong, *J. Chem. Soc., Chem. Commun.*, 1986, 229.
- A. Balikungeri, M. Pelletier, and D. Monnier, *Inorg. Chim. Acta*, 1977, **22**, 7.
- J. Hauck, *Z. Naturforsch., Teil B*, 1970, **25**, 647; H. Siebert, *Z. Anorg. Allg. Chem.*, 1959, **301**, 161.
- E. S. Huyser and L. G. Rose, *J. Org. Chem.*, 1972, **37**, 851.
- W. G. Movil, *Inorg. Chem.*, 1973, **12**, 31.
- B. H. Sklarz, *Q. Rev. Chem. Soc.*, 1967, **21**, 3.
- F. Sondheimer, R. Mechoulam, and M. Sprecher, *Tetrahedron*, 1964, **20**, 2473.
- E. S. Gore, *Platinum Met. Rev.*, 1983, **27**, 111 and refs. therein.
- P. H. J. Carlsen, *Synth. Commun.*, 1987, **17**, 19.
- R. J. Audette and J. W. Quail, *Inorg. Chem.*, 1972, **11**, 1904.
- 'Dictionary of Organic Compounds,' 5th edn., Chapman and Hall, London, 1982, vol. 1, pp. 560, 1061; vol. 4, p. 3692 and refs. therein.
- R. E. Connick and C. R. Hurley, *J. Am. Chem. Soc.*, 1952, **74**, 5012.
- G. M. Sheldrick, SHELXTL, 'Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data,' University of Göttingen, Federal Republic of Germany, 1978; revised version, 1984.