405. *Iodides of Osmium and Rhenium.*

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The new osmium and rhenium iodides, OsI_3, OsI_2, OsI, and ReI_2, have been prepared. They have been characterised by analysis, *X*-ray powder photography, and magnetic measurements. The ready formation of these lower iodides supports the view that the iodine can participate in π-bonding and thereby stabilise low oxidation states.

A survey of the known halides of the transition metals indicates a predominance of iodides in low oxidation states, although there appear to be many gaps to be filled. The known iodides of rhenium and osmium are the tetra-,[1] tri-,[2] and mono-compounds [1] of the former and tetra-[3a,b] and di-iodides [3a,4] of the latter. In the present investigation, osmium tri-, di-, and mono-iodide and rhenium di-iodide have been prepared and characterised.

The existence of osmium tetraiodide could not be confirmed. The black crystalline compound obtained by reaction of hydriodic acid with osmium dioxide was dihydroxonium hexaiodo-osmate(IV). This compound is isomorphous with, and has similar cell dimensions to, diammonium hexaiodo-osmate(IV), and its composition, as a dibasic acid, accords with the formulation as a structurally similar hydroxonium compound $(H_3O)_2OsI_6$.

Thermal degradation of this hexaiodo-osmic(IV) acid gave rise to three new compounds, osmium tri-, di-, and mono-iodide which are obtained successively. This process can only be reversed for the di-iodide, *i.e.*, heating it with iodine gives the tri-iodide. For preparative purposes the products can be obtained more satisfactorily by other methods, as, for example, by heating the acid in a sealed tube to give osmium tri-iodide, or treating osmium tetroxide with hydriodic acid for varying times to give the di- and the mono-compound.

The compounds, which are black or grey and are insoluble in most solvents, were identified by analysis and, where possible, *X*-ray powder photography. The tri- and the mono-iodide appear to be amorphous. The earlier mention of osmium di-iodide [4] is not based on experimental evidence and it seems that the compound has not been obtained previously. Magnetic moments (Table 1) support the analytical evidence on the oxidation states, except that for osmium monoiodide the unexpected low moment for a d^7-configuration suggests the presence of an Os–Os interaction. Since spin pairing always occurs for the heavy transition metals the value of 1·8 B.M. for osmium tri-iodide is in agreement with the value expected for one unpaired electron in a d^5-spin-paired compound. The low moment for osmium di-iodide is in agreement with the diamagnetism expected for

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[1] Peacock, Welch, and Wilson, *J.*, 1958, 2901.

[2] Freni and Valenti, *Gazzetta*, 1960, **90**, 1436.

[3] (*a*) Moracht and Wischin, *Z. anorg. Chem.*, 1893, **3**, 174; (*b*) Roseinheim and Sasserath, *ibid.*, 1899, **21**, 122.

[4] Alvarez, *Chem. News*, 1905, 172.

TABLE 1.

Properties of osmium and rhenium iodides.

Compound[a]	Valency	*d*-Electron config.	Colour	Magnetic moment[b] (B.M.)		Remarks
				Found	Calc. (spin only)	
$(NH_4)_2OsI_6$ ...	4	d^4	Blue-black	1·3[c]	2·83	Isomorphous.
$(H_3O)_2OsI_6$[d]	4	d^4	Blue-black	2·2[c]	2·83	
OsI_3	3	d^5	Black	1·8	1·73	
OsI_2	2	d^6	Black	0·6	0·0	
OsI	1	d^7	Metallic grey	0·5	1·73	Possible Os–Os interaction.
ReI_4[1]	4	d^3	Black	0·9	3·88	
ReI_3[2]	3	d^4	Violet black	—		
ReI_2............	2	d^5	Grey-black	0·5	1·73	Possible Re–Re interaction.
ReI[1]	1	d^6	Black	0·6	0·0	Cubic structure, see ref. 1.

[a] Infrared spectra were run on all compounds (2·5—15 mμ), to show absence of metal double-bond oxygen[6] and freedom from solvent. [b] Magnetic moments measured by the Gouy method at 20°. [c] Large spin–orbit coupling present. [d] Molar conductivity in dimethylformamide (25°) 108 ohm^{-1} mole^{-1} cm.^{2}.

a d^6-spin-paired compound. The actual value of 0·6 B.M. may be due to some temperature-independent paramagnetism.

A thermal degradation of rhenium tetraiodide, to give the monoiodide, according to the method of Peacock *et al.*,[1] gave first an intermediate phase, identified as rhenium di-iodide. This compound was also prepared by heating the tetraiodide in a sealed tube. The magnetic moment indicates the absence of unpaired electrons, which is unexpected for a d^5-configuration and therefore suggests a metal–metal interaction. *X*-Ray powder data (Table 2) show conclusively that the compound is not a mixture of the monoiodide and a higher compound.

TABLE 2.

d-Values for *X*-ray powder series.[a]

ReI_2		ReI		OsI_2		$(H_3O)_2OsI_6$		$(NH_4)_2OsI_6$	
3·43m	2·16m	5·18m	2·21m	3·09s	1·83vw	6·28w	2·14w	6·32w	2·14w
2·95w	2·02s	3·43m	2·15m	2·31m	1·67w	5·47m	1·97s	5·44m	1·97s
2·81w	1·81s	3·14s	1·83w	2·01m	1·51w	3·19s	1·86m	3·19s	1·85m
2·73m	1·72m	2·88w	1·77m			2·77m	1·68vw	2·76m	1·68w
2·38m	1·28s	2·54m	1·58m			2·48m	1·61m	2·48m	1·61m

[a] OsI_3 and OsI appear to be amorphous, the powder photographs containing only indistinct haloes.

The features of iodine which probably acount for these compounds, with the metals in low oxidation states, are (*a*) the ease of oxidation of iodide to the free element, which gives access to the low valency states by thermal degradation, and (*b*) the ability of iodine to participate in π-bonding,[5] which would tend to stabilise the compounds formed.

EXPERIMENTAL

Preparation of Dihydroxonium Hexaiodo-osmate(IV).—Osmium dioxide (0·68 g.) was heated under reflux with 55% hydriodic acid (25 ml.) for 48 hr. The hot solution was filtered and evaporated to dryness over potassium hydroxide *in vacuo* [Found: Os, 18·7; I, 77·5. $(H_3O)_2OsI_6$ requires Os, 19·2; I, 77·1%]. A potentiometric titration of the *compound* in dry alcohol with sodium ethoxide gave 2·2 equiv. of acid per mol. This figure is high, perhaps

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[5] Chatt, *J. Inorg. Nuclear Chem.*, 1958, **8**, 515.

[6] Barraclough, Lewis, and Nyholm, *J.*, 1959, 3552.

owing to a slow decomposition of the compound in alcohol, indicated by the formation of a slight precipitate. The compound loses hydrogen iodide very slowly when kept in a vacuum-desiccator; after 10 weeks the osmium content had increased to 23·2%.

Diammonium Hexaiodo-osmate(IV).—The salt $(NH_4)_2OsCl_6$ was heated under reflux with hydriodic acid in the presence of ammonium iodide (2 mol.). The iodo-compound which crystallised was filtered off and dried [Found: Os, 19·0; I, 78·3; N, 2·6. Calc. for $(NH_4)_2OsI_6$: Os, 19·2; I, 77·1; N, 2·8%].

Osmium Tri-iodide.—The hexaiodo-acid (0·12 g.) was heated in a sealed tube (25 ml. capacity) for 6 hr. at 250° in an atmosphere of nitrogen. Free iodine was removed by washing with carbon tetrachloride and ethanol, and the *product* dried (Found: Os, 33·05; I, 66·1. OsI_3 requires Os, 33·3; I, 66·7%).

Osmium Di-iodide.—Osmium tetroxide (1 g.) was heated with 55% hydriodic acid (20 ml.) and ethanol (2 ml.) for 3 hr. on a water-bath and then boiled gently for 15 min. The solution was filtered and evaporated to dryness over potassium hydroxide *in vacuo.* The *product* was washed free from iodine and dried (Found: Os, 42·5; I, 57·5. OsI_2 requires Os, 42·8; I, 57·2%). It is slightly soluble in 55% hydriodic acid.

Osmium Monoiodide.—Osmium tetroxide (1 g.), dissolved in 55% hydriodic acid (10 ml.) and ethanol (2 ml.), was heated on a water-bath for 48 hr. in an atmosphere of oxygen-free carbon dioxide. The precipitated *monoiodide* was collected, washed as above, and dried (Found: Os, 60·6; I, 39·5, 40·2. OsI requires Os, 59·9; I, 40·1%).

Rhenium Tetraiodide.—This was prepared according to the method of Peacock *et al.*[1] (Found: Re, 26·5; I, 73·3. Calc. for ReI_4: Re, 26·8; I, 73·2%). Its magnetic moment was 0·9 B.M., in disagreement with a value for three unpaired electrons said to be obtained by Colton and Wilkinson.[7]

Rhenium Monoiodide.—This was prepared according to the method of Peacock *et al.*,[1] a temperature of 130° being used for 100 hr. (Found: I, 39·8. Calc. for ReI: I, 40·5%). The magnetic moment for this compound was 0·5 B.M., as expected for a spin-paired d^6-configuration.

Rhenium Di-iodide.—Rhenium tetraiodide (0·5 g.) was heated for 6 hr. at 350° in a sealed tube (capacity 25 ml.) under an atmosphere of carbon dioxide. The *product* was washed free from iodine and dried (Found: Re, 42·6; I, 57·3, 57·9. ReI_2 requires Re, 42·3; I, 57·7%). A less pure product was obtained when a mixture of perrhenic acid (1 g.), 55% hydriodic acid (15 ml.), and ethanol (15 ml.) was evaporated nearly to dryness; the product was washed with ethanol and dried (Found: Re, 43·2; I, 58·3%).

Analyses.—Osmium and rhenium were determined spectrophotometrically by the absorption of the thiourea complex at 540 μ [8] and the α-furil dioxime complex at 532 μ,[9] respectively. Iodine was determined by the method of Peacock *et al.*[1] or gravimetrically by the Carius method.

X-*Ray Powder Photographs.*—These were obtained by using Mo-K_α radiation for osmium di-iodide and Cu-K_α radiation for the remaining compounds, with a Philips's Debye–Scherrer camera of diameter 11·48 cm. The results are given in Table 2.

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[7] Colton and Wilkinson, *Chem. and Ind.*, 1959, 1314.

[8] Dwyer and Gibson, *Analyst*, 1951, **76**, 104.

[9] Meloche, Martin, and Webb, *Analyt. Chem.*, 1957, **29**, 527.