

Quinquevalent Rhodium Compounds: RhF_5 and CsRhF_6

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THREE binary fluorides of rhodium have been reported: a trifluoride,¹ a tetrafluoride,² and a hexafluoride.³ Ruff and Ascher¹ obtained the trifluoride, plus a small amount of red-brown sublimate, by the fluorination of rhodium at 500–600°, and suggested that the sublimate was either a tetrafluoride or a pentafluoride. Sharpe, in his report² of the tetrafluoride, concluded that this was identical with Ruff and Ascher's sublimate. The

$95.5 \pm 0.5^\circ$. Rhodium was determined as the metal, and fluorine as lead chloride fluoride, following sodium carbonate fusion [Found: F, 47.3; Rh 52.4. RhF_5 requires: F, 48.0; Rh, 52.0%].

The magnetic properties of the compounds are consistent with the d^4 non-bonding electron configuration expected for Rh^V . The magnetic susceptibility data for the temperature range 77–293°K are given in Table I. The susceptibility

TABLE I. Magnetic susceptibility—temperature data for rhodium pentafluoride

Temp. (°K)	77	87.6	101	112.9	130.6	148.8	166.5
$10^6 \chi_A$ (c.g.s. units)	5895	5757	5553	5299	5230	5054	4947
Temp. (°K)	191.3	210.8	226.7	247.4	267.4	283.2	293
$10^6 \chi_A$ (c.g.s. units)	4644	4409	4235	4235	3873	3726	3669

existence of a pentafluoride was again indicated, however, by the observations of Chernick, Claassen, and Weinstock. They noted³ that the hexafluoride, in its rapid decomposition at room temperature, liberates half a mole of fluorine for each mole of hexafluoride decomposed:



We have prepared material of empirical formula RhF_5 , and have established the rhodium to be quinquevalent. The compound has been prepared by the action of gaseous fluorine, at 90 lb./sq.in. on the trifluoride at 400°. It has also been identified, together with the hexafluoride and trifluoride, as a product of the combustion of rhodium wire in fluorine. The compound is a dark red solid, m.p.

variation with temperature is greater than in the case of $[\text{RuF}_5]^{3-}$ salts,⁴ where the susceptibility is approximately temperature-independent, but is not as extreme as in the case of ruthenium tetrafluoride.⁵ The temperature-dependence of the susceptibility of RhF_6 may be due to the lower symmetry of the ligand environment in this compound, compared to the $[\text{RuF}_6]^{2-}$ ion.

Rhodium pentafluoride is isomorphous with its ruthenium,^{6,7} osmium,⁷ and iridium analogues,⁸ the crystal data being: a , 12.28; b , 9.85; c , 5.48 Å; β , 99.2°; $U_{\text{obs.}}$, 654.2 Å³; $Z = 8$. Presumably the structural unit of this compound is a fluorine-bridged tetramer, as in ruthenium pentafluoride.⁷ It is noteworthy that the unit-cell volume is smaller than in the ruthenium analogue, possibly as a

¹ O. Ruff and E. Ascher, *Z. anorg. Chem.*, 1929, **183**, 206.

² A. G. Sharpe, *J. Chem. Soc.*, 1950, 3444.

³ C. L. Chernick, H. H. Claassen, and B. Weinstock, *J. Amer. Chem. Soc.*, 1961, **83**, 3165.

⁴ A. Earnshaw, B. N. Figgis, J. Lewis, and R. D. Peacock, *J. Chem. Soc.*, 1961, 3132.

⁵ J. H. Holloway and R. D. Peacock, *J. Chem. Soc.*, 1963, 3892.

⁶ J. H. Holloway and R. D. Peacock, *J. Chem. Soc.*, 1963, 527.

⁷ J. H. Holloway, R. D. Peacock, and R. W. H. Small, *J. Chem. Soc.*, 1964, 644.

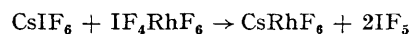
⁸ N. Bartlett and P. R. Rao, *Chem. Comm.*, 1965, 252.

consequence of the greater polarizing power of Rh^{V} compared to Ru^{V} .

The pentafluoride is a powerful oxidizing and fluorinating agent. It reacts violently with water to give ozone-smelling gases, and fluorinates carbon tetrachloride, chlorine monofluoride being among the products.

Cæsium fluoride and rhodium pentafluoride in

1:1 stoichiometry react in iodine pentafluoride solution to yield cæsium hexafluororhodate(v):]



The red-brown salt is isomorphous and almost isodimensional with CsPtF_6 .⁹ Hexafluororhodates(v) were previously unknown.

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⁹ N. Bartlett and N. K. Jha, in H. H. Hyman, ed., "Noble Gas Compounds," Chicago University Press, Chicago and London, 1963, p. 27.