

## Nitrogenpentammineosmium(II) Complexes

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IN 1965 Allen and Senoff<sup>1</sup> reported the preparation of the first compounds containing molecular nitrogen co-ordinated to a transition metal. Since then several other complexes have been prepared having nitrogen co-ordinated to cobalt,<sup>2</sup> iridium,<sup>3</sup> and rhodium.<sup>4</sup> Recently Borod'ko *et al.*,<sup>5</sup> reported the preparation of an unidentified material containing molecular nitrogen bound to osmium. We now report the preparation of complexes†, general formula  $[\text{Os}(\text{NH}_3)_5\text{N}_2]\text{X}_2$  where  $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{ClO}_4^-$ ,  $\text{BF}_4^-$ , and  $\text{BPh}_4^-$ . The chloride salt precipitates as a pale yellow powder from a solution of ammonium hexachloro-osmate(IV) in hydrazine hydrate under reflux. It is diamagnetic (Found: N, 25.8; H, 4.2; Os, 50.8; Cl, 18.8. Calc. for  $\text{H}_{15}\text{N}_7\text{Cl}_2\text{Os}$ : N, 26.2; H, 4.0; Os, 50.8; Cl, 19.0%).

The chloride and bromide salts are stable in air for extended periods. The other salts decompose slowly in air, especially in strong light. The chloride salt, when decomposed by strong heating *in vacuo*, yielded 87% of the theoretical amount of  $\text{N}_2$ . In neutral aqueous solution slow decomposition is observed but the compounds are stable in strong hydrohalic acids, even under reflux. The conductance of the di-iodide salt in dimethyl sulphoxide is the same as that of  $[\text{Os}(\text{NH}_3)_5\text{I}]\text{I}_2$  over the concentration range  $1-10 \times 10^{-5}$  M.

The infrared spectra of these compounds contain a strong sharp band between 2064—2010  $\text{cm}^{-1}$  (see Table) which in all solid spectra, except that of the tetraphenylborate salt, has a shoulder on the high energy side. This band is not shifted on deuteration and, in analogy with the ruthenium salts, has been assigned to the  $\text{N}_2$  stretching mode. In dimethyl sulphoxide the iodide salt exhibits only one band at 2010  $\text{cm}^{-1}$ , indicating that the splitting observed in the mull spectrum is a crystal effect. Co-ordination to the metal has thus lowered the  $\text{N}_2$  stretching frequency by about 300  $\text{cm}^{-1}$  from that observed for the free  $\text{N}_2$  molecule. This is the largest shift yet observed in complexes containing molecular nitrogen and reflects the strength of the osmium-nitrogen bond. The strength of this bond is also indicated by the stretching frequency of the  $\text{Os}-\text{N}_2$  mode which occurs between 546—520  $\text{cm}^{-1}$ . (See Table.)

The complexes have provided a new and greatly improved synthetic route to the difficult to obtain osmium(III) acidopentammine complexes. Treatment of the iodide salt with hydroiodic acid and a mild oxidizing agent such as iodine gives a high yield of the iodopentammineosmium(III) complex. The chloro- and bromo-pentammines can then be prepared by treatment of the iodopentammine with the appropriate hydrohalic acid.

TABLE

	X	=	$\text{Cl}^-$	$\text{Br}^-$	$\text{I}^-$	$\text{ClO}_4^-$	$\text{BF}_4^-$	$\text{BPh}_4^-$
$\nu(\text{N}_2)$	..	..	2010 vs 2022 sh	2028 vs 2035 sh	2033 vs 2043 sh	2051 vs 2062 sh	2055 vs 2064 sh	2061 vs
$\nu(\text{Os}-\text{N}_2)$	..	..	546	540	533	531	529	520

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† Preliminary reports of the preparation and properties of these compounds were given to the 9th I.C.C.C. Switzerland, September 1966, and the 50th Annual Conference of the C.I.C., Toronto, June 1967.

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