

Nitrogenopentammineruthenium(II) Complexes

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VOL'PIN and SHUR have recently explored the possibility of fixing molecular nitrogen under mild conditions.¹⁻³ We now report that from aqueous solutions of ruthenium trichloride (free from nitric oxide) and hydrazine hydrate at 25° it is possible to isolate complexes which appear to be of the type $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{X}_2$ where $\text{X} = \text{Br}^-$, I^- , BF_4^- ,

and PF_6^- . These salts are the first reported compounds in which N_2 is co-ordinated to a transition metal. The iodide salt is diamagnetic and has the following analysis: N, 20.52; H, 3.96; NH_3 , 17.84; I, 54.05%. (Calc. for $\text{H}_{15}\text{N}_7\text{I}_2\text{Ru}$: N, 20.94; H, 3.21; NH_3 , 18.16; I⁻, 54.27%). The complexes are only moderately stable towards air

¹ M. E. Vol'pin and V. B. Shur, *Doklady Akad. Nauk S.S.S.R.*, 1964, **156**, 1102.

² M. E. Vol'pin and V. B. Shur, *Vestnik Akad. Nauk S.S.S.R.*, 1965, 51.

³ M. E. Vol'pin, V. B. Shur, and L. P. Bichin, *Izvest. Akad. Nauk S.S.S.R., Ser. Khim.*, 1965, 720.

and decompose fairly rapidly in water. The conductance of solutions of the di-iodide salt in dimethyl sulphoxide is exactly the same as solutions of the reference compound $[\text{Ru}^{\text{III}}(\text{NH}_3)_5\text{I}]_2\text{I}_2$ over the concentration range measured ($1-10 \times 10^{-5}$ M).

The infrared spectra of these compounds contain a strong, sharp, band between $2170-2115$ cm^{-1} (see Table) which is assigned to the N_2 stretch. Upon co-ordination to the metal the N_2 stretching mode has undergone a shift to lower frequency of about 200 cm^{-1} from that observed for molecular nitrogen (2331 cm^{-1}).⁴ It is not possible at present to ascertain whether co-ordination occurs through the lone pair of electrons on one of the nitrogen atoms or through the π -electron system of the molecule, but the crystal structure of these compounds is being investigated.

If the iodide salt is treated with 20% aqueous NaBH_4 solution and 40% NaOH solution the amount of ammonia evolved corresponds to 24%, compared with 18% found on normal treatment with alkali, indicating that nearly all of the co-ordinated nitrogen is converted into ammonia by the action of the borohydride ion.¹⁻³

When the fluoborate salt is treated with 95% sulphuric acid under high vacuum the non-condensable gas (77° K) that is liberated was shown to be nitrogen by mass spectrometry. A maximum of about 40% of the theoretical amount of nitrogen has been obtained in this way, and it is thought that the remaining nitrogen may have been converted into ammonia or oxidized by

the acid. The complexes, $[\text{Ru}(\text{NH}_3)_6](\text{BF}_4)_2$, $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$, and $\text{FeCl}_2 \cdot 2\text{N}_2\text{H}_4$ were treated with sulphuric acid in a similar manner. No nitrogen was evolved, indicating that the source of the nitrogen is not hydrazine or ammonia.

We have considered the possibility that the complex contains a co-ordinated di-imide molecule, *i.e.*, $[\text{Ru}^{\text{II}}(\text{NH}_3)_5, \text{NH}=\text{NH}]^{2+}$. Evidence against this is (a) that the $\nu_{\text{N}=\text{N}}$ frequency should be at about 1400 cm^{-1} ,⁵ (b) that the n.m.r. spectrum in dimethyl sulphoxide contains no bands other than those attributed to the ammonia hydrogens, and (c) that the gas liberated on treatment with sulphuric acid contains no hydrogen.

Because of the lability of the N_2 ligand these complexes are ideal starting materials for the preparation of a number of ruthenium(II) and ruthenium(III) complexes. Mild treatment with the hydrohalic acids leads to the formation of the corresponding halogenopentammineruthenium(III) salts. The following ruthenium(II) complexes have also been prepared by the reaction of the nitrogenopentamine complexes with the appropriate ligand: $[\text{Ru}(\text{NH}_3)_6]\text{X}_2$, $[\text{Ru}(\text{NH}_3)_4\text{py}_2]\text{X}_2$, $[\text{Ru}(\text{NH}_3)_2\text{py}_4]\text{X}_2$, $[\text{Ru}(\text{NH}_3)_5\text{DMSO}]\text{X}_2$ where $\text{X} = \text{I}^-$, BF_4^- , PF_6^- , and $\text{DMSO} =$ dimethyl sulphoxide.

TABLE

X =	Br^-	I^-	BF_4^-	PF_6^-
ν_{N_2}	2118s	2129s	2154s	2167s

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⁴ K. Nakamoto, "Infrared Spectra of Inorganic and Co-ordination Compounds," Wiley, New York, 1963, p. 72.

⁵ E. J. Blau, B. F. Hochheimer, and H. J. Unger, *J. Chem. Phys.*, 1961, **34**, 1060.