

Hydridopentamine- and Hydridoquotetrammine-rhodium(III) Sulphates

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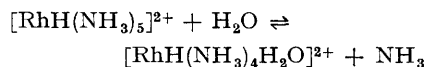
THE only hydrido-complexes of transition metals with non- π -bonding ligands are the hydridoamine-rhodium(III) species, but these have been characterised primarily by spectroscopic methods (i.r., n.m.r.) and only impure tetraphenylborate salts could be precipitated.^{1,2} We now report the isolation of the first two pure hydrido-complex salts, namely the hydridopentamine sulphate, $[\text{RhH}(\text{NH}_3)_5]\text{SO}_4$, and the hydridoquotetrammine, $[\text{RhH}(\text{H}_2\text{O})(\text{NH}_3)_4]\text{SO}_4$. The pentamine

is obtained by treatment of the chloropentamminerhodium(III) sulphate with metallic zinc in ammoniacal solution, a method originally developed³ for the preparation of ruthenium(II) ammines. The hydrido-complex is precipitated as a white crystalline solid on addition of excess of concentrated ammonia. Remarkably, the salt is stable in air indefinitely; its i.r. has an intense band at 2073 cm.^{-1} ($\nu_{\text{Rh-H}}$) while the electronic absorption spectrum shows a band at $307 \text{ m}\mu$ confirming our

previous conclusions² (based on solution spectra) regarding the position of the hydride ion in the spectrochemical series for rhodium(III) amine complexes and thus eliminating any possibility that the solution spectra were due to hydrolysed species.

The addition of acetone to dilute solutions of the pentammine salt in water precipitates the white, air-stable hydrido-aquotetrammine; the i.r. spectrum of this salt shows bands due to bound water while $\nu_{\text{Rh-H}}$ is 2145 cm.^{-1} . Dissolution of the hydridopentammine in D_2O followed by precipitation with acetone shows that exchange with hydride and bound water occurs much faster than the exchange with ammonia. The n.m.r. in H_2O has τ 32.0 , ^{103}Rh splitting 25 c./sec. , and if one drop of concentrated ammonia is added, the spectrum of the hydridopentammine, τ 27.1 , splitting

14.5 c./sec. , appears. Hence there is in solution the equilibrium



The ready loss of one ammonia molecule is a striking example of the strong *trans*-labilizing effect of the hydride ion; the resulting aquotetrammine is clearly the *trans*-isomer⁴ (cf., *trans*- $[\text{RhH}(\text{H}_2\text{O})(\text{CN})_4]^{2-}$).

The species in solution undergo a variety of ligand replacement and insertion reactions, giving for example an ethyl complex with ethylene and on oxidation with molecular oxygen, a purple-blue peroxo-complex.

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¹ R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 1963, 3594.

² J. A. Osborn, R. D. Gillard, and G. Wilkinson, *J. Chem. Soc.*, 1964, 3168.

³ F. M. Lever and A. R. Powell, International Conference on Co-ordination Chemistry, *Chem. Soc. Special Publ.* No. 13, p. 135.

⁴ D. N. Lawson, M. J. Mays, and G. Wilkinson, *J. Chem. Soc. (A)*, 1966, 52.