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The Identification of All Ten $[Rh(OH_2)_{6-n}Cl_n]^{3-n}$ Isomers by ^{103}Rh NMR Spectroscopy

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Hydrated rhodium trichloride is the most common starting material for the preparation of rhodium containing compounds. We have examined three commercial samples which all were found to give several ^{103}Rh NMR signals, but the ratios of the signal intensities varied markedly from one sample to another, see Fig. 1. Clearly all three samples contain a number of different rhodium complexes, and the proportions vary between the samples. The full characterisation of 'hydrated rhodium trichloride' is of considerable interest to preparative rhodium chemistry especially as the yield of a sensitive rhodium complex is often dependent on the particular batch of hydrated rhodium trichloride.

When solutions of each sample are heated overnight at 80 °C, they give the same spectrum, showing that this heat treatment produces an equilibrium mixture. The ^{103}Rh NMR spectra of two equilibrated samples of hydrated rhodium chloride, differing in concentration by a factor of three, are identical showing that the four signals do arise from monomers rather than dimers. Progressive addition of LiCl followed by equilibration at 80 °C after each addition, caused the signals* at δ9115 and δ8794 to decrease in intensity relative to the signals at δ8858 and δ8545. At higher LiCl concentration two new signals appeared at δ8605 and δ8295 and increased together in intensity as more LiCl was added. Further LiCl produced signals at δ8238 and δ8009. Addition of further LiCl caused the precipitation of a rose-red solid. Finally in 80% concentrated hydrochloric acid/ 20% D_2O the major signal was at δ7950 although the signal at δ8233 was still present. It has been previously shown that $[RhCl_6]^{3-}$ is the major species present in concentrated hydrochloric acid. These observations also correlate well with the electrophoretic behaviour of the $[Rh(OH_2)_{6-n}Cl_n]^{3-n}$ system where the charges on the species were determined but differentiation between *cis*- and *trans*- and *mer*- and *fac*-isomers was not possible [2].

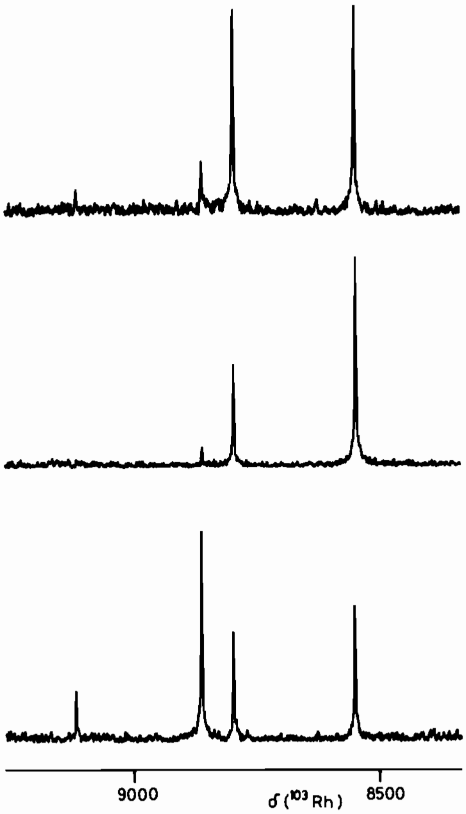

Fig. 1. The 12.64 MHz ^{103}Rh NMR spectrum of three commercial samples of hydrated rhodium trichloride, (400 mg), containing *ca.* 8 mg of hydrated chromic trichloride in *ca.* 1.6 ml D_2O.

A chloride free solution containing $[Rh(OH_2)_6]^{3+}$ was obtained by adding base to an aqueous solution of 'hydrated rhodium trichloride' to give a solution at *ca.* pH 14. Hydrated rhodium oxide was then precipitated by adjusting to pH 7, with perchloric acid. The hydrated rhodium oxide was dissolved in perchloric acid/D_2O to give a ^{103}Rh signal at δ9992. Heating this solution at 80 °C with ½ equivalent of LiCl gave signals at δ9991, δ9819 and δ9479. These observations lead to the assignment of the signals as $[Rh(OH_2)_6]^{3+}$ δ9992; $[Rh(OH_2)_5Cl]^{2+}$ δ9479; *cis*- and *trans*-$[Rh(OH_2)_4Cl_2]^+$ δ8794 and δ9115; *fac*- and *mer*-$Rh(OH_2)_3Cl_3$ δ8545 and δ8858; *cis*- and *trans*-$[Rh(OH_2)_4Cl_2]^-$ δ8295 and δ8605; $[Rh(OH_2)$-

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*The ^{103}Rh NMR signals were measured at 12.6 MHz using a Bruker WH-400 NMR spectrometer. The chemical shifts are referenced to − 3.16 MHz *via* the ^{2}H lock, and use the IUPAC [1] recommended sign convention of high frequency being positive. Usually solutions were made up in D_2O using 'hydrated rhodium trichloride' (300 to 400 mg), $CrCl_3$ (5 to 10 mg), and other solvents and additives are noted in the text. The ^{103}Rh chemical shifts were found to be significantly sensitive to temperature and added LiCl, changing by up to 20 ppm over the range of conditions used.

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$Cl_5]^{2-}$ δ8233; and $[RhCl_6]^{3-}$ *ca.* δ7975**. The additional signal at δ9819 is believed to be $[Rh(OH_2)_5(OClO_3)]^{2+}$. The *cis-/trans-* and *mer-/fac-* assignments are not proven by the above approach, but are made on the basis that in other similar rhodium chloro complexes the *cis-* or *fac-*isomer occurs at lower frequency [3] than the corresponding *trans-* or *mer-*isomer.

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References

1 Recommendation for the presentation of NMR data for publication in chemical journals, *Pure Appl. Chem., 29,* 627 (1972);
45, 217 (1976).
2 E. Blasius and W. Preetz, *Z. anorg. allg. Chem., 335,* 1 (1965).
3 See for example, R. G. Goodfellow, in 'N.M.R. and the Periodic Table', p. 244, ed. by R. K. Harris and B. E. Mann, Academic Press (1979).

**Average value for LiCl addition and in 80% concentrated hydrochloric acid.