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^{103}Rh Chemical Shifts of $[RhCl_{6-n}Br_n]^{3-}$

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All ten compounds $[RhCl_{6-n}Br_n]^{3-}$ have been prepared in solution in mixtures of concentrated HCl and HBr and identified by ^{103}Rh NMR spectroscopy. The ^{103}Rh chemical shifts are in the range δ7985 for $[RhCl_6]^{3-}$ to δ7077 for $[RhBr_6]^{3-}$ {reference Ξ (^{103}Rh) = 3.16 MHz}.

The recent observation of all ten compounds $[RhCl_n(OH_2)_{6-n}]^{3-n}$ by ^{103}Rh NMR spectroscopy has demonstrated the power of ^{103}Rh NMR spectroscopy to identify rhodium containing compounds in solution [1]. Before ^{103}Rh NMR spectroscopy becomes a useful technique to identify species in solution, it is necessary to build up a library of ^{103}Rh chemical shifts containing compounds which cannot be identified in easier ways, *e.g.*, ^{1}H, ^{13}C, or ^{31}P NMR spectroscopy. The series of compounds $[RhCl_{6-n}Br_n]^{3-}$ provides a good example as it yields the substituent parameters for replacing Cl^- by Br^- and checks for any of the anomalous substitution effects found in the series $[RhCl_n(OH_2)_{6-n}]^{3-n}$ where replacement of OH_2 by Cl^- could produce shifts between +64 and –585 ppm.

Solutions containing $[RhCl_{6-n}Br_n]^{3-}$ were prepared by dissolving *ca.* 400 mg of commercial hydrated rhodium trichloride in *ca.* 0.5 ml D_2O and *ca.* 5 mg hydrated chromic chloride was added. This solution was diluted to 2 ml with varying mixtures of concentrated HCl and concentrated HBr. The solutions were kept at *ca.* 80 °C for 30 minutes to complete the reaction to the hexahalo complexes. The ^{103}Rh NMR spectra were recorded in 10 mm tubes at 12.6 MHz using a Bruker WH400 NMR spectrometer. The samples were thermostatted at a nominal 313 K to minimise broadening due to overnight temperature changes as a temperature dependence of the ^{103}Rh chemical shift of up to 1 ppm/°C is anticipated [2].

All ten expected compounds were detected in the various HCl/Br solutions, although the chemical shifts were somewhat (10 p.p.m.) dependent on solvent composition. There are in effect seven different chemical shift areas due to the seven possible values of n in $[RhCl_{6-n}Br_n]^{3-}$, n = 0 to 6, each value of n being separated by *ca.* 150 ppm making it a trivial exercise to assign the signals to a value of n. In the cases of n = 2, 3, and 4, the signals are doublet due to *cis-trans* or *mer-fac* isomerism. The signals were assigned to the relevant isomer by both statistical probability of formation and analogy to known compounds. Thus statistically, in the absence of electronic factors, *cis*-isomers are more probable than *trans*-isomers by a factor of four, while the *mer*-isomer is more probable than the *fac*-isomer by a factor of three, and the ratios of the intensities of the ^{103}Rh NMR signals are in agreement with these ratios within experimental error. It is also known that *cis*- and *fac*-isomers give signals to lower frequency of *trans*- and *mer*-isomers [2]. The results are collected in Table I.

TABLE I. ^{103}Rh Chemical Shifts for $[RhCl_{6-n}Br_n]^{3-}$ in Mixtures of Concentrated Hydrochloric and Hydrobromic Acid.

Compound	$\delta(^{103}Rh)$/ppm[a]
$[RhCl_6]^{3-}$	7985
$[RhCl_5Br]^{3-}$	7848
cis-$[RhCl_4Br_2]^{3-}$	7707
trans-$[RhCl_4Br_2]^{3-}$	7712
fac-$[RhCl_3Br_3]^{3-}$	7556
mer-$[RhCl_3Br_3]^{3-}$	7561
cis-$[RhCl_2Br_4]^{3-}$	7403
trans-$[RhCl_2Br_4]^{3-}$	7409
$[RhClBr_5]^{3-}$	7243
$[RhBr_6]^{3-}$	7077

[a] Reference to Ξ (^{103}Rh) = 3.16 MHz, using the sign convention that high frequency is positive.

Examination of the results in the Table show that as Cl^- is replaced by Br^- the stepwise decrease in ^{103}Rh chemical shift changes from –136 ppm to –166 ppm and is not significantly dependent on the *trans*-ligand. This series provides yet another example of the so-called 'inverse halogen effect' [3]. This effect can be explained in terms of the Ramsey equation

$$\delta(^{103}\text{Rh}) = \frac{A\langle r_d^{-3}\rangle}{\Delta E} + C$$

where A and C are constants, ΔE is the energy difference between the highest occupied and lowest empty d-orbital, and $\langle r_d^{-3}\rangle$ is (the average radius of the d-orbital)$^{-3}$. When the normal halogen effect

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applies the ΔE term is dominant, with the weaker Br^- producing a smaller ΔE term than the Cl^- ligand. When the inverse halogen effect applies the $\langle r_d^{-3} \rangle$ term is dominant with the more covalent Br^- increasing the size of the d-orbitals more effectively than is found for the Cl^- ligand.

References

1 B. E. Mann and C. Spencer, *Inorg. Chim. Acta, 65,* L57 (1982).

2 See for example R. G. Goodfellow, in 'N.M.R. and the Periodic Table', ed. R. K. Harris and B. E. Mann, Academic Press, 1979, p. 248.

3 See for example R. G. Kidd, ref. 2, p. 208.