A ^{103}Rh Nuclear Magnetic Resonance Study of Rhodium(III) Bromide Complexes in Aqueous Solution

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The ^{103}Rh NMR signals of all ten monomeric aquabromorhodium(III) complexes, $[RhBr_n(OH_2)_{6-n}]^{3-n}$ with n = 0–6, including the geometric isomers for n = 2–4, have been assigned. The chemical shifts δ_{Rh} of these complexes demonstrate a nephelauxetic dependence, namely a decrease in δ with an increase in the number of bromo ligands. For the geometrical isomers it has been shown that $\delta_{trans} > \delta_{cis}$ and $\delta_{mer} > \delta_{fac}$. Evidence is given for the existence of oligomeric aquabromorhodate(III) species and structural characteristics are proposed consistent with the observed chemical shifts. The ^{103}Rh NMR chemical shift has been measured for the aqueous $[Rh(NH_3)_6]^{3+}$ complex (δ_{Rh} = 4766 at 276 K) and, together with other six-co-ordinated rhodium(III) complexes, correlated with the ligand-field parameter ratio $\beta/\Delta E$, where β is the nephelauxetic ratio and ΔE the electronic transition energy for octahedral complexes, ${}^1A_{1g} \longleftarrow {}^1T_{1g}$. Linear regression gives an estimate of the core-electron diamagnetic shift to $\delta^{d}_{Rh} = -5000(1000)$.

Interest in the solution chemistry of rhodium(III) complexes has grown considerably as a result of the rapid increase in the use of rhodium in catalytic processes and the economic necessity of its recovery. Slow kinetics has often prevented the use of standard equilibrium methods. However, the potential of ^{103}Rh NMR spectroscopy to identify and monitor the distribution of rhodium species in aqueous solution has been demonstrated in recent investigations of the aquachlororhodium(III)[1,2] and the mixed bromochlororhodium(III)[3,4] systems, despite the low sensitivity of the method. In the present study we have investigated the aquabromorhodium(III) system in acidic aqueous solution as a precursor to equilibrium and kinetic investigations. The structural information available from the ^{103}Rh NMR spectra of these complexes is limited to their chemical shifts since no nuclear spin–spin coupling is observed either to the aqua or halide ligands. Assignment of the NMR signals is therefore based on the solution preparation and composition, and in some cases on IR and Raman vibrational spectroscopic results.

It has recently been shown that the metal NMR chemical shifts in octahedral d^6 transition-metal complexes can be correlated to the parameter ratio $\beta/\Delta E$, derived solely from the ligand-field spectrum of the complex.[5,6] In order to verify and extend this correlation for rhodium(III) complexes, δ_{Rh} for $[Rh(NH_3)_6]^{3+}$ was measured.

Experimental

Materials.—The compounds $RhCl_3{\cdot}nH_2O$ ($n \approx 3$) and $RhBr_3{\cdot}nH_2O$ ($n \approx 7$) (Johnson Matthey) were used as the sources of rhodium. A sample of $RhBr_3{\cdot}nH_2O$ was also prepared by dissolving halide-free hydrated rhodium(III) oxide[7] in the stoichiometric amount of concentrated HBr (47%), heating the solution in a closed vessel for 24 h at 50 °C, and evaporating to dryness at 80 °C. The compound $Rh(ClO_4)_3{\cdot}6H_2O$ was synthesised by dissolving halide-free hydrated rhodium(III) oxide in concentrated perchloric acid (*ca.* 70% $HClO_4$), refluxing the solution at 95 °C for 48 h, followed by evaporation under reduced pressure at 60 °C until crystals formed. After cooling to −20 °C, the yellow crystalline product was washed with cold concentrated perchloric acid and dried under vacuum at 80 °C until acid free. **CAUTION**: Perchlorate salts of metal complexes are potentially explosive especially if contaminated with organic material. Precautions should be taken even though we have had no incidents during several preparations as described above.

The salt $K_3[Rh_3Br_9]$ was prepared from an aqueous solution of $RhBr_3{\cdot}nH_2O$ and the stoichiometric amount of KBr in 3 mol dm^{-3} HBr;[8] $[Rh(NH_3)_5Cl]Cl_2$ (0.05 g), synthesised as previously described,[9] was heated with concentrated (25%) ammonia solution (4 cm^3) in a sealed glass container at 100 °C for 72 h to give $[Rh(NH_3)_6]^{3+}$.

Preparation of Rhodium(III) *Bromide Solutions.*—In order to allow observation and identification of as many different rhodium(III) bromide complexes as possible, solutions covering a large range of mole ratios $n_{Br}:n_{Rh}$ and total rhodium(III) concentrations, c_{Rh}, were prepared.

(1) The compound $Rh(ClO_4)_3{\cdot}6H_2O$ was dissolved in 1 mol dm^{-3} $HClO_4$ to give c_{Rh} = 0.1 mol dm^{-3}.

(2) An acidic aqueous solution of $Rh(ClO_4)_3{\cdot}6H_2O$ and LiBr, with a mole ratio $n_{Br}:n_{Rh}$ = 1:1 was heated at 80 °C for 1 h.

(3) Hydrated rhodium(III) oxide was dissolved in concentrated HBr (47%) to give $n_{Br}:n_{Rh}$ = 4:1 and c_{Rh} = 2 mol dm^{-3}. After heating at 50 °C for 24 h the solution was absorbed onto a column of Dowex 50W-X8 cation-exchange resin in the H$^+$ form. After washing off the neutral and anionic species with dilute $HClO_4$ (0.1 mol dm^{-3}) a diffuse orange band, having the UV/VIS characteristics of *trans*-$[RhBr_2(OH_2)_4]^+$ (λ_{max}/nm = 258 and 483),[10] was eluted with 2 mol dm^{-3} $HClO_4$. In order to allow NMR and vibrational spectroscopic measurements, the dilute eluent containing *trans*-$[RhBr_2(OH_2)_4]^+$ (*ca.* 5 mmol dm^{-3}) and $HClO_4$ (*ca.* 1.5 mol dm^{-3}) was concentrated under reduced pressure at 0 °C. During the evaporation the $HClO_4$ content was repeatedly reduced by slow addition of a concentrated KOH solution (5 mol dm^{-3}) with rapid stirring at *ca.* −2 °C. The $KClO_4$ precipitate which formed during this procedure was filtered off.

(4) *and* (5) Solutions of $RhBr_3{\cdot}nH_2O$ in 1 mol dm^{-3} $HClO_4$ with c_{Rh} = 0.7 (Johnson Matthey) and 1.0 mol dm^{-3} [prepared from halide-free hydrated rhodium(III) oxide], respectively, were equilibrated by heating at 100 °C for 24 h.

(6) Hydrated rhodium(III) oxide was dissolved in concentrated HBr (47%) and heated at 100 °C for 24 h, then diluted with 1 mol dm^{-3} $HClO_4$ to give $n_{Br}:n_{Rh}$ = 4:1 and c_{Rh} = 1.2 mol dm^{-3}.

(7) Hydrated rhodium(III) oxide was dissolved in concen-

trated HBr (47%) and heated at 50 °C for 24 h, giving $n_{Br}:n_{Rh}$ = 4.2:1 and c_{Rh} = 2 mol dm^{-3}.

(8) A saturated solution (c_{Rh} < 1 mol dm^{-3}) of $K_3[Rh_2Br_9]$ in 1 mol dm^{-3} $HClO_4$ was heated at 100 °C for 12 h.

(9) Concentrated HBr (47%) was added to an equilibrated solution with $n_{Br}:n_{Rh}$ = 3:1 and c_{Rh} = 1 mol dm^{-3} to give $n_{Br}:n_{Rh}$ = 5:1. The ^{103}Rh NMR spectrum was recorded without further equilibration.

(10)–(12) Hydrated rhodium(III) oxide was dissolved in HBr (47%) and heated at 50 °C for 24 h, with $n_{Br}:n_{Rh}$ = 8, 17 and 33:1 and c_{Rh} = 1, 0.5 and 0.3 mol dm^{-3}, respectively.

(13) Solutions 1, 4 and 7 were mixed and measured without further equilibration.

Concentrated solutions of the individual aquabromorhodium(III) complexes, $[RhBr_n(OH_2)_{6-n}]^{3-n}$, proved more difficult to prepare by ion-exchange chromatography than their aquachlororhodium(III) analogues.[2] Resolution of the cationic species (n = 0–3) was, however, possible on columns of Dowex 50W-X8(H$^+$) cation-exchange resin using perchloric acid in increasing concentration (0.2–2 mol dm^{-3}) as eluent.[10] The eluted bands were very diffuse and consequently gave dilute solutions which proved difficult to concentrate sufficiently to allow ^{103}Rh NMR measurements. Even during evaporation at low temperature, UV/VIS spectra[10] showed the complex distribution to change to a mixture of species. Attempts to separate the anionic species by ion exchange failed as a result of the large number of species and their relatively rapid interconversion.[11]

NMR, IR and Raman Spectroscopy.—The ^{103}Rh NMR spectra were recorded on a Bruker AM400 spectrometer in unlocked mode at 12.6 MHz, using 10 μs pulses corresponding to a flip angle $\alpha \approx 13°$. Pulse repetition times of 1–2 s were found to give good signal-to-noise ratios. Spectra were normally run for 12 h, accumulating 20 000–40 000 scans. For all measurements the probe was thermostatted to 276 ± 0.5 K. The linewidth of the signals was typically 5 Hz and no broadening due to chemical exchange was found. The chemical shifts were referenced to $\Xi(^{103}Rh)$ = 3.16 MHz,[12] using the high frequency positive convention, and were determined with an accuracy better than 0.1 ppm. To avoid ambiguity in assigning close-lying ^{103}Rh NMR signals, solutions containing several species in detectable concentrations were often used to allow comparison of shift differences between neighbouring signals, which for series of related complexes are less influenced by medium effects than are the absolute chemical shifts.

Far-IR solution spectra were measured on a Digilab FTS-40V spectrometer at a resolution of 2 cm^{-1}. A sample cell with 2 mm silicon windows and a path length of ≈ 12 μm was used. A background spectrum of concentrated HBr (47%) was subtracted from the sample spectrum in order to isolate the spectral features of the rhodium species.

Raman spectra were recorded on a DILOR Z24 triple monochromator, equipped with a single-channel, photon-counting detector. A Coherent Innova 90K krypton-ion laser was used to excite the Raman spectra and plasma lines were removed with an Applied Photophysics 2300 laser filter monochromator. A rotating sample cell was used for the strongly coloured solutions containing the $[RhBr_6]^{3-}$ anion. Spectra were recorded using both the 676.4 and 647.1 nm lines of the krypton laser to allow separation of the weak band at 92 cm^{-1} from residual plasma lines. A background spectrum of concentrated HBr (47%) was subtracted from the sample spectrum. A large spectral band width, *ca.* 7 cm^{-1}, was used in order to achieve an acceptable signal-to-noise ratio. Polarisation measurements were made using a polarisation analyser plate followed by a quarter-wave quartz scrambler in the optical path after the sample. The measurements were calibrated against the depolarised CCl_4.[13]

The UV/VIS measurements were made on a Cary 219 spectrometer with the solutions in quartz cuvettes (10 mm to 10 μm).

Results and Discussion

The ^{103}Rh chemical shifts obtained are summarised in Table 1. Allowing for changes in the shift position due to medium effects, twenty different ^{103}Rh NMR resonances have been observed. Relative intensities are given for each signal though these can only be treated as approximate values since the different species can be expected to have different relaxation times, T_1. The complexity of the spectra for solutions with mole ratios $n_{Br}:n_{Rh}$ = 3–8:1 indicates the presence of oligomeric rhodium(III) bromide complexes. For the analogous aquachlororhodium(III) system only ten ^{103}Rh NMR signals were observed, corresponding to the ten monomeric complexes with formula $[RhCl_n(OH_2)_{6-n}]^{3-n}$ and n = 0–6, including the geometric isomers.[2]

Identification of the Monomeric Complexes $[RhBr_n(OH_2)_{6-n}]^{3-n}$.—Acidic solutions prepared from pure $Rh(ClO_4)_3{\cdot}6H_2O$ (0.1 mol dm^{-3}) in 1 and 10 mol dm^{-3} $HClO_4$ gave single ^{103}Rh NMR signals with shifts of δ 9869 and 9960, respectively. Similarly, at higher concentrations of $Rh(ClO_4)_3{\cdot}6H_2O$ (0.4 mol dm^{-3}) in 1 and 10 mol dm^{-3} $HClO_4$ single resonances were observed with δ_{Rh} = 9865 and 9952, respectively. Despite the large variations in chemical shift all these signals can be assigned to the hexaaquarhodium(III) cation.[2] The increase in shift with increasing concentration of perchlorate probably results from the replacement of rather strongly hydrogen-bonded water molecules in the second hydration sphere of rhodium(III) by weakly hydrogen-bonded perchlorate ions.[14] No ^{103}Rh NMR evidence was found for the formation of polymeric hydrolysis species, even for solutions of $Rh(ClO_4)_3{\cdot}6H_2O$ (1.0 mol dm^{-3}) dissolved in distilled water and stored at 25 °C for 1 month.

The ^{103}Rh chemical shift for the $[RhBr_6]^{3-}$ complex has previously been reported as δ 7077[3] at 313 K and 6924[4] at 243 K [for rhodium(III) complexes the increase in δ_{Rh} with increasing temperature is *ca.* 2 ppm K^{-1} [2,6]]. We have assigned the single resonances at δ 6993 and 6981 (276 K) in the spectra of solutions 11 and 12, respectively, to $[RhBr_6]^{3-}$. In these equilibrated solutions the mole ratio of bromide to rhodium is high, $n_{Br}:n_{Rh}$ = 17 and 33:1 and the total rhodium concentration fairly low, c_{Rh} = 0.5 and 0.3 mol dm^{-3}, respectively. Thus, it is reasonable to expect a dominating monomeric hexabromo species. Moreover, the Raman spectrum of solution 11 showed a polarised band at 187 cm^{-1}, a depolarised band at 172 cm^{-1}, and a broad band at 92 cm^{-1}, Fig. 1. In the far-IR

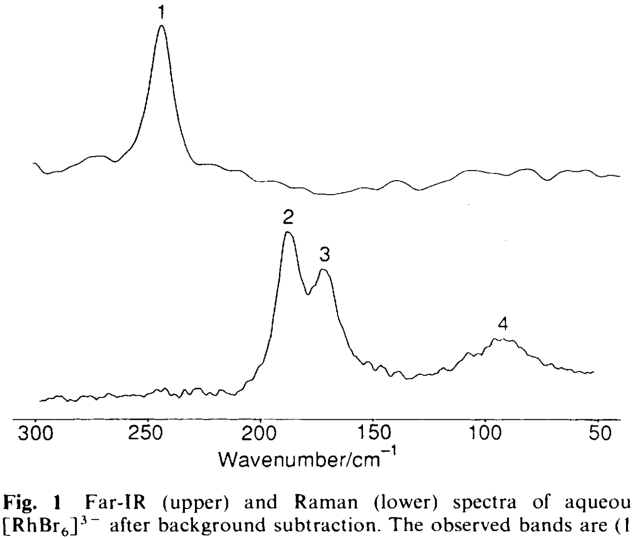

Fig. 1 Far-IR (upper) and Raman (lower) spectra of aqueous $[RhBr_6]^{3-}$ after background subtraction. The observed bands are (1) $\nu_3(T_{1u})$ 244 cm^{-1}, (2) $\nu_1(A_{1g})$ 187 cm^{-1}, (3) $\nu_2(E_g)$ 172 cm^{-1} and (4) $\nu_5(T_{2g})$ 92 cm^{-1}

Table 1 Summary of observed chemical shifts, δ_{Rh}, with their approximate relative intensities (in %) within parentheses* for acidic aqueous rhodium(III) bromide solutions at 276 K. Assignments are given for the complexes $[RhBr_n(OH_2)_{6-n}]^{3-n}$ (n = 0–6), and the dimeric species in groups A–C (see text)

Solution	1	2	3	4	5	6	7	8	9	10	11	12	13	Mean shift	
$n_{Br}:n_{Rh}$	0	1	2	3	3	4	4.2	4.5	5	8	17	33	2.4	$\bar{\delta}_{Rh}$	Assignment
	9870(100)	9860(37)	9922(8)				9878						9871	9880	0
		9327(19)	9301(8)		9339(5)				9340					9327	1
		8926(39)	8888(84)		8938(31)	8942	8930(22)		8937(24)				8938(16)	8928	2t
		8838		8850	8847								8847	8846	2c
		8440		8453(13)	8449(12)				8445				8449	8447	3m
				8349(8)	8345									8347	3f
					8062		8043	8070	8056(12)	8035			8062	8056	4t
					7962		7957		7963				7965	7962	4c
				7930(25)	7924(10)	7928		7936(11)					7923(5)	7928	A
				7512(5)		7507	7473(6)	7517(13)	7493(10)	7450			7502(8)	7493	5
				7387	7382	7386(9)		7390(11)	7378(5)				7383(6)	7384	B
				7376(10)	7372(6)	7375	7368(6)	7380					7372	7373	B
				7352	7347	7352		7357					7349	7351	B
				7340(6)	7336	7340		7341					7337	7339	B
							7064		7067				7080	7070	C
							7041(8)			7013(85)	6993(100)	6981(100)		7007	6
				6932	6926	6929(9)	6908(6)	6934(11)	6921(5)				6926	6925	C
									6893				6898	6896	C
				6808(10)	6802(13)	6806(62)	6782(46)	6807(47)	6799(31)	6780			6803(42)	6798	C
				6744	6738	6743							6740	6741	C

* Not given for minor species with relative intensities < 5%.

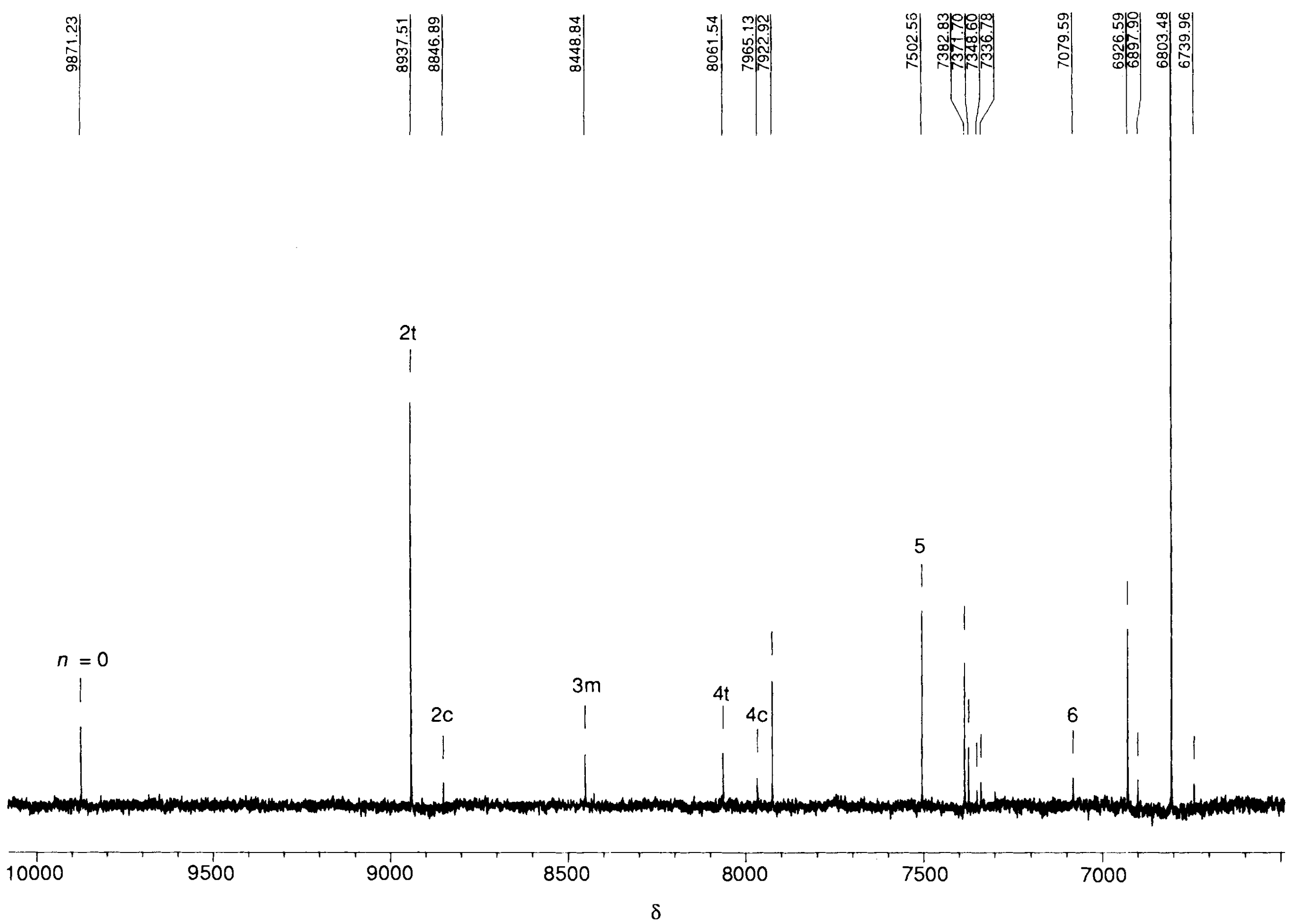

Fig. 2 12.64 MHz ^{103}Rh NMR spectrum of a non-equilibrium rhodium(III) bromide solution (13) recorded at 276 K. The assignments given are for species of type $[RhBr_n(OH_2)_{6-n}]^{3-n}$, with n = 0–6

spectrum a single absorption band was observed at 244 cm^{-1}. Vibrational spectra have recently been reported for solid $Cs_3[RhBr_6]$ with Raman bands at 190 (A_{1g}), 173 (E_g) and 113 (T_{2g}) cm^{-1}, and an IR absorption at 244 (T_{1u}) cm^{-1}.[15] The assignments are based on a normal coordinate analysis of a $[RhBr_6]^{3-}$ complex in O_h symmetry in a general valence force field. Spoonhower[16] has previously tentatively assigned Raman bands at 187 and 175 cm^{-1} to the symmetric A_{1g} and the antisymmetric E_g stretching modes, respectively, of $[RhBr_6]^{3-}$ in solution. The similarities with our solution spectra confirm the ^{103}Rh NMR assignment. In solutions containing a mixture of species the identification of the ^{103}Rh NMR resonance for the monomeric $[RhBr_6]^{3-}$ complex can, however, often be ambiguous due to the variations in its chemical shift with solution composition. For example, for solution 7 two possible signals are observed with shifts of δ 7064 and 7041, Table 1. For electrostatic reasons it is likely that the variation in δ_{Rh} of $[RhBr_6]^{3-}$ is pH dependent, as a result of the expected increase in the hydrogen bonding to the bromide ligands when water molecules in the hydration sphere of the anion are replaced by oxonium ions.

Having established the shifts for the complexes $[RhBr_n(OH_2)_{6-n}]^{3-n}$ with n = 0 and 6, it was possible to assign the remaining species with n = 1–5, assuming a stepwise decrease in the ^{103}Rh chemical shift with the number of bromo ligands n. The assignment is straightforward for n = 1–3, but for n = 4 three signals were observed as possible candidates for the *cis* and *trans* isomers. The assignment made (Table 1) is based on comparisons with the corresponding aquachlororhodium(III) system in which the shift difference, $\Delta\delta_{Rh}$, for each pair of geometric isomers was found to be relatively constant. For the geometric isomers of the $[RhCl_n(OH_2)_{6-n}]^{3-n}$ complexes, $\delta_{trans} - \delta_{cis}$ = 65 and 75 for n = 2 and 4, respectively, and $\delta_{mer} - \delta_{fac}$ = 64 for n = 3.[2] Our assignments for the aquabromorhodium(III) system give, *e.g.* for solution 5 where all such shifts are observed under the same conditions, $\delta_{trans} - \delta_{cis}$ = 91 and 100 for n = 2 and 4, respectively, and $\delta_{mer} - \delta_{fac}$ = 104 for n = 3. The alternative assignments of the isomers for n = 4 (Table 1) would give $\delta_{trans} - \delta_{cis}$ = 38 or 138.

The assignment of the signals with a mean δ_{Rh} = 7493 (Table 1) to the monoaquapentabromorhodate(III) anion is based mainly on the more regular variation of δ with the number of bromo ligands, than the alternative assignment of signals having a mean shift of δ 7384.

The assignment of the *cis* and *trans* isomers of $[RhBr_2(OH_2)_4]^+$ was assisted by Raman spectroscopy. Solution 3, prepared by ion-exchange chromatography, was found to contain a dominant species with δ_{Rh} = 8888. The Raman spectrum of this solution showed a single polarised band at 190 cm^{-1} in the Rh–Br stretching region. The depolarisation ratio $\rho = 0.3 \pm 0.1$ showed this to be a symmetric stretching mode, consistent with the symmetric stretch of the linear Br–Rh–Br unit of a *trans*-$[RhBr_2(OH_2)_4]^+$ complex. The *cis* isomer would be expected to give rise to two Raman-active Br–Rh–Br stretching vibrations, as observed for the solid *cis*-$Cs_3[RhCl_4Br_2]$ with two strong Raman bands at 234 and 223 cm^{-1}, assigned as the symmetric and antisymmetric stretching vibrations of the non-linear Br–Rh–Br entity, respectively.[15]

The ^{103}Rh NMR spectrum of solution 13 is shown in Fig. 2, with assignments for the species $[RhBr_n(OH_2)_{6-n}]^{3-n}$, with n = 0, 2-*trans*, 2-*cis*, 3-*mer*, 4-*trans*, 4-*cis*, 5 and 6. This non-

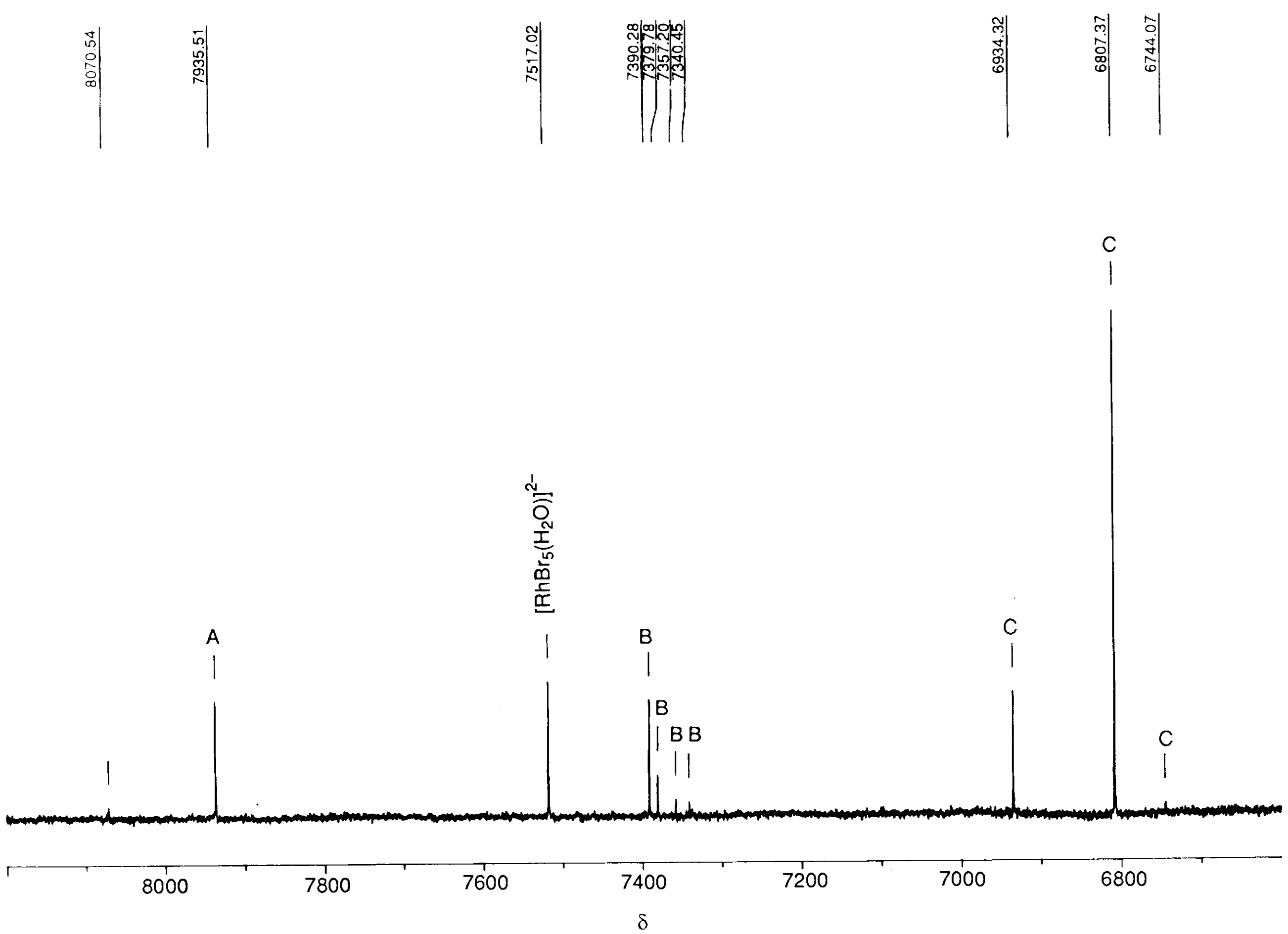

Fig. 3 12.64 MHz ^{103}Rh NMR spectrum of an equilibrated solution (8) of $K_3[Rh_2Br_9]$ (c_{Rh} < 1 mol dm^{-3}) in 1 mol dm^{-3} $HClO_4$ recorded at 276 K. Assignments are given for the proposed dimeric aquabromorhodate(III) species and $[RhBr_5(OH_2)]^{2-}$

equilibrium mixture was prepared to allow observation of a large number of species under the same experimental conditions.

Polynuclear Aquabromorhodate(III) *Complexes.*—After the identification of the ^{103}Rh NMR signals for the monomeric complexes $[RhBr_n(OH_2)_{6-n}]^{3-n}$, ten resonances remained unassigned (see Table 1). These are observed in the region δ_{Rh} = 7923–6740, partly within the chemical shift range for the mixed bromochlororhodium(III) complexes.[3] However, since the majority of solutions were prepared from halide-free hydrated rhodium(III) oxide, these peaks do not originate from chloride contamination. It was found for equilibrated solutions with similar mole ratios ($n_{Br}:n_{Rh} \approx 4:1$) by means of ^{103}Rh NMR measurements that the complex distribution was dependent on the total rhodium concentration. Upon dilution the monomeric complexes $[RhBr_n(OH_2)_{6-n}]^{3-n}$ were favoured, thus indicating the presence of polynuclear rhodium(III) bromide complexes.

The ^{103}Rh NMR spectrum of a saturated solution of $K_3[Rh_2Br_9]$ in 1 mol dm^{-3} $HClO_4$ (solution 8) is given in Fig. 3. Here we note that $[RhBr_5(OH_2)]^{2-}$ is the only mononuclear complex observed together with the proposed polynuclear species, with practically no $[RhBr_4(OH_2)_2]^-$ or $[RhBr_6]^{3-}$ present in this solution for which the mole ratio $n_{Br}:n_{Rh}$ = 4.5:1. Solutions prepared from $K_3[Rh_2Br_9]$ were found to equilibrate rapidly to a mixture of species, thus preventing determination of the ^{103}Rh chemical shift for the $[Rh_2Br_9]^{3-}$ ion.

The observation of bromide-bridged polynuclear complexes is expected in solutions of sufficient concentration to allow measurement of ^{103}Rh NMR resonances since the dimeric triply and doubly bridged species $[Rh_2Br_9]^{3-}$ and $[Rh_2Br_{10}]^{4-}$, respectively, have been proposed to exist in aqueous solution and the kinetics of their interconversion has been investigated.[17,18] However, from the NMR spectra it seems likely that the aquation in acidic solution of the $[Rh_2Br_9]^{3-}$ complex, by dissolution of $K_3[Rh_2Br_9]$, eventually proceeds to monomeric $[RhBr_5(OH_2)]^{2-}$ species. Thus, triply and doubly bromide-bridged aquated species of types $[Rh_2Br_n(OH_2)_{9-n}]^{6-n}$ and $[Rh_2Br_n(OH_2)_{10-n}]^{6-n}$, respectively, and possibly also singly bridged $[Rh_2Br_n(OH_2)_{11-n}]^{6-n}$, may exist in the equilibrium mixture, accounting for the unassigned ^{103}Rh NMR signals for such solutions. Although the proposed dimeric aquabromorhodate(III) species have not previously been reported in the literature, the alternative explanation involving polynuclear bromorhodate(III) species is unlikely considering the large number of unassigned ^{103}Rh NMR signals in solutions prepared from $K_3[Rh_2Br_9]$, containing no excess of bromide. No nuclear spin–spin coupling was found between ^{103}Rh nuclei to support the existence of asymmetric dimeric aquabromorhodate(III) complexes. However, such two-bond couplings may not be resolved in our ^{103}Rh NMR spectra where the observed linewidths are 3–7 Hz. The reported one-bond coupling constants are in the range $^1J(^{103}Rh-^{103}Rh)$ = 4–17 Hz, and the ^2J coupling constants are probably significantly smaller.[19] For example, we have recently measured $^2J(^{103}Rh-^{103}Rh)$ = 1.6 Hz in the hydroxo-bridged linear trimer $[(H_2O)_4Rh(\mu-OH)_2Rh(OH_2)_2(\mu-OH)_2Rh(OH_2)_4]^{5+}$.

We propose the following explanation for the unassigned ^{103}Rh NMR signals based on the assumptions: (*i*) dimeric bromide-bridged aquabromorhodate(III) complexes exist in

Table 2 Summary of ^{103}Rh chemical shift and optical data for rhodium(III) complexes in O_h and C_{3v} symmetry

Complex	δ	$10^5\Delta E'^{-1}$/cm	β	Ref.
$[RhF_6]^{3-}$	—	4.70	0.64	24
$[Rh(OH_2)_6]^{3+}$	9880[a]	3.95	0.71	6
fac-$[RhCl_3(OH_2)_3]$	8817	4.71	0.53	2, 6
$[RhCl_6]^{3-}$	8001	5.18	0.48	2, 6
$[RhBr_6]^{3-}$	7007[a]	5.55	0.39	6
$[Rh(NO_2)_6]^{3-}$	5580	3.35	0.59[b]	5, 25
$[Rh(NH_3)_6]^{3+}$	4766[a]	3.05	0.60	26

[a] This work. [b] Estimated value, see ref. 5.

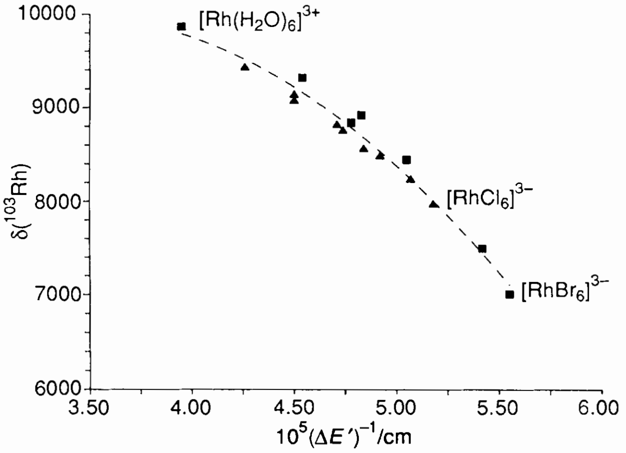

Fig. 4 Dependence of δ_{Rh} of the species $[RhCl_n(OH_2)_{6-n}]^{3-n}$ (▲) and $[RhBr_n(OH_2)_{6-n}]^{3-n}$ (■), n = 0–6, on $1/\Delta E'$, the reciprocal of the lowest d–d transition energy for each complex

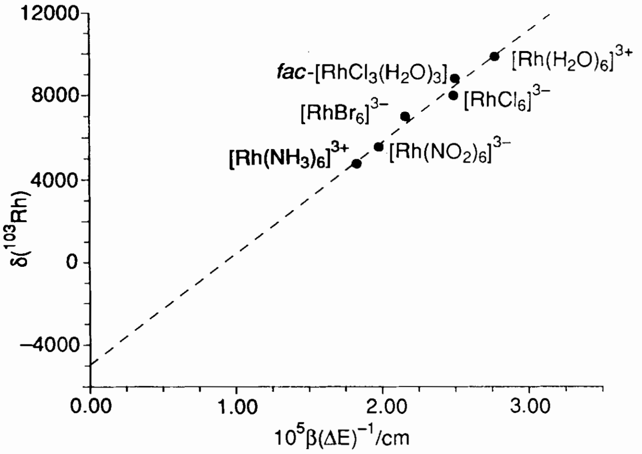

Fig. 5 Dependence of δ_{Rh} for octahedral rhodium(III) species (Table 2) on the ligand-field parameter ratio $\beta/\Delta E$. The least-squares fitted line shows the extrapolation giving δ^{d}_{Rh} = −5000 (1000) at $\beta/\Delta E$ = 0

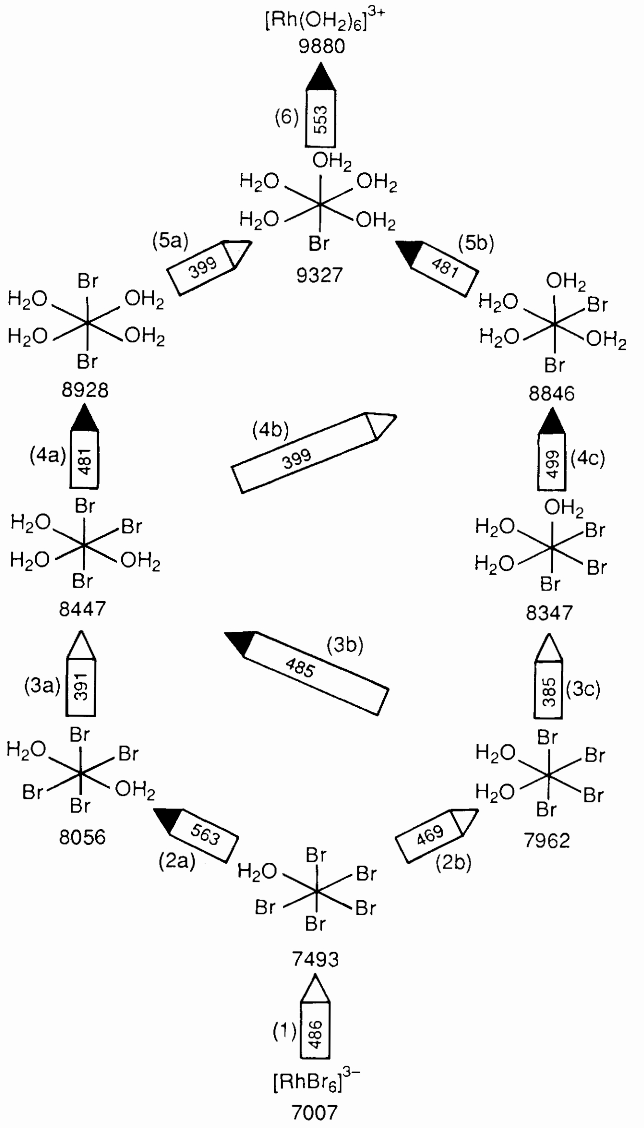

Fig. 6 Metal chemical shift substitution scheme showing the two types of *trans* substitution: hetero (black arrows) and homo (white arrows). Mean chemical shifts $\bar{\delta}_{Rh}$ and shift differences (inside arrows) are given for the system $[RhBr_n(OH_2)_{6-n}]^{3-n}$. The figures in parentheses identify the substitution steps in the general case of substitution of MA_6 by B (see Table 3)

acidic aqueous solution; (*ii*) the chemical shift for a ^{103}Rh nucleus present in a dimer is additive with the number of directly co-ordinated bromide ligands, as is the case for monomeric aquabromorhodium(III) complexes; and (*iii*) the shift is not strongly dependent on the environment of the neighbouring ^{103}Rh nuclei. The 10 unassigned ^{103}Rh NMR signals (Table 1) can be divided into three distinct groups with chemical shifts similar to those of the monomeric complexes $[RhBr_4(OH_2)_2]^-$, $[RhBr_5(OH_2)]^{2-}$ and $[RhBr_6]^{3-}$, respectively, each group representing ^{103}Rh nuclei present in either mono-, di- or tri-μ-bromo-bridged dimers with the same number of directly co-ordinated Br^- ligands as in the 'parent' monomeric species: (*a*) group A, with one signal at $\bar{\delta}_{Rh}$ = 7928, corresponding to a bridged diaquatetrabromorhodate(III) structural entity; (*b*) group B, with signals at $\bar{\delta}_{Rh}$ = 7384, 7373, 7351 and 7339, each corresponding to a bridged aquapentabromorhodate(III) structural unit; and (*c*) group C, $\bar{\delta}_{Rh}$ = 7070, 6925, 6896, 6798 and 6741, each corresponding to a bridged hexabromorhodate(III) entity.

The relatively small differences in the ^{103}Rh chemical shifts within each group are probably caused by differences in the neighbouring groups, in the multiplicity of the bromide bridge, and the existence of geometric isomers of the bridged complexes. For example, the aqua ligands in the aquapentabromo species of group B can be either axial or equatorial with respect to a di-μ-bromo bridge.

Hexaamminerhodium(III).—The UV/VIS spectrum of the solution prepared by treatment of $[Rh(NH_3)_5Cl]Cl_2$ with concentrated ammonia was characteristic of the hexaamminerhodium(III) ion in aqueous solution (λ_{max}/nm = 256 and 306).[20] The ^{103}Rh NMR spectrum contained a single signal with δ_{Rh} = 4766, which we thus assigned to $[Rh(NH_3)_6]^{3+}$.

Table 3 Comparison of metal chemical shift differences for stepwise hetero and homo substitution of the ligands in an MA_6 species with B (see substitution scheme, Fig. 6)

$[MA_nB_{6-n}]$		$[PtBr_nCl_{6-n}]^{2-}$		$[PtCl_n(OH_2)_{6-n}]^{2-}$		$[PtCl_n(OH)_{6-n}]^{2-}$		$[RhBr_nCl_{6-n}]^{3-}$		$[RhCl_n(OH_2)_{6-n}]^{3-}$		$[RhBr_n(OH_2)_{6-n}]^{3-}$	
Homo	Hetero	Homo < Hetero[a]		Homo > Hetero[b]		Homo < Hetero[c]		Homo > Hetero[d]		Homo > Hetero[e]		Homo > Hetero[f]	
6		277				453		138		421		553	
	5a		301				500		136		292		399
5b		289				476		141		357		481	
4a		300		605		509		151		336		481	
	4b		313		522		533		146		271		399
4c		299		625		510		151		335		499	
	3a		327		477		568		153		256		391
3b		313		598		550		158		331		485	
	3c		327		495		573		153		267		385
2a		323		622		597		166		326		563	
	2b		338		501		615		160		251		469
	1		350		504		666		166		234		486

[a] $\delta_{trans} < \delta_{cis}$ and $\delta_{mer} < \delta_{fac}$, ref. 30. [b] $\delta_{trans} > \delta_{cis}$ and $\delta_{mer} > \delta_{fac}$, ref. 31. [c] $\delta_{trans} < \delta_{cis}$ and $\delta_{mer} < \delta_{fac}$, ref. 31. [d] $\delta_{trans} > \delta_{cis}$ and $\delta_{mer} > \delta_{fac}$, ref. 4. [e] $\delta_{trans} > \delta_{cis}$ and $\delta_{mer} > \delta_{fac}$, ref. 2. [f] $\delta_{trans} > \delta_{cis}$ and $\delta_{mer} > \delta_{fac}$ (this work).

Correlations of δ_{Rh} *with Ligand-field Parameters.*—Juranić[5,6] has shown that for d^6 transition-metal complexes the paramagnetic contribution to the nuclear shielding (σ^p) in the Ramsey equation can be described in terms of the ligand-field parameters β, the nephelauxetic ratio, and ΔE, the ${}^1A_{1g} \longleftarrow {}^1T_{1g}$ electronic transition energy for octahedral complexes, equation (1), where μ_0 is the vacuum permeability, μ_B the Bohr magneton and $\langle r_d^{-3}\rangle_F$ the expectation value of the inverse cube distance of a d electron in the free ion/atom. If the diamagnetic (σ^d) contribution to the nuclear shielding is assumed to be constant[6] the metal chemical shift (δ_{tot}) can be approximated by equation (2) where K is a positive constant.

$$\sigma^p = -8\frac{\mu_0\mu_B^2}{\pi}\langle r_d^{-3}\rangle_F \frac{\beta}{\Delta E} \quad (1)$$

$$\delta_{tot} = \delta_d + K(\beta/\Delta E) \quad (2)$$

The variation of the metal chemical shift of the aquabromorhodium(III) and aquachlororhodium(III) complexes with the reciprocal transition energy $1/\Delta E'$ is given in Fig. 4. The transition energy $\Delta E({}^1A_{1g} \longleftarrow {}^1T_{1g})$ has been approximated by $\Delta E'$, the energy of the first d–d absorption band,[10,17,21–23] for species of symmetry lower than O_h. For these complexes substitution of aqua ligands by halide leads to a decrease in the transition energy $\Delta E'$, as predicted by the spectrochemical series. Fig. 4 shows that δ_{Rh} decreases with an increase in the number of halide ligands, indicating that the decrease of the nephelauxetic ratio β more than outweighs the decrease in ΔE, see equation (2).

The validity of equation (1) has been demonstrated for a range of d^6 metal-ion complexes,[6] particularly cobalt(III), of type MA_6 (O_h) and *fac*-MA_3B_3 (C_{3v} symmetry). The scarcity of data (see Table 2) for rhodium(III) complexes prompted us to measure δ_{Rh} for $[Rh(NH_3)_6]^{3+}$, the complex which could be predicted to have the lowest metal chemical shift of those for which $\beta/\Delta E$ is known. The linear dependence of the available ${}^{103}Rh$ chemical shifts on the ligand-field parameter ratio $\beta/\Delta E$ is depicted in Fig. 5. The extrapolated metal chemical shift at $\beta/\Delta E = 0$ gives an estimate of the core-electron diamagnetic shift for the free rhodium atom, provided that the diamagnetic shielding is unaffected at the ligand-field strengths present in the experimental data and the medium effects in the δ_{Rh} and ΔE values are similar (or negligible).[6] A linear regression (Fig. 5) of the data points in Table 2 gave $\delta^d_{Rh} = -5000$, with a standard error of 1000 ppm, a value in agreement with a previous estimation.[5]

Magnetochemical Ligand Series.—Using the optical data available for $K_3[RhF_6]$ (s)[24] we predicted δ_{Rh} for $[RhF_6]^{3-}$ to be *ca.* 11 000 ppm from equation (2). Attempts to measure this by dissolving $K_3[RhF_6]$ in concentrated HF (40%) failed as $[RhF_6]^{3-}$ was rapidly aquated giving a range of complexes of type $[RhF_n(OH_2)_{6-n}]^{3-n}$. However, δ_{Rh} of $[RhF(OH_2)]^{2+}$ was determined to 10 524 ppm at 298 K,[27] which is the largest S_{Rh} reported, as expected for a complex involving the weakly nephelauxetic fluoride ligand.[23] For qualitative purposes, the following magnetochemical ligand series for rhodium(III) in which the ligands are ordered according to decreasing total magnetic shielding of the metal nucleus, can be derived:[6] $NH_3 > NO_2^- > Br^- > Cl^- > H_2O > F^-$.

Chemical Shift Order for Geometric Isomers.—The ligand-field approach[5,6,28] has also been used to predict the relative order of metal chemical shifts for the geometric isomers in octahedral complexes of type MA_nB_{6-n}, where n = 2–4. For a series of complexes in which the variation in the d^6 metal chemical shift is governed by the nephelauxetic properties of the ligands, it is predicted that $\delta_{cis} > \delta_{trans}$ and $\delta_{fac} > \delta_{mer}$,[28] with the opposite shift order for a spectrochemical behaviour. However, the rhodium(III) complexes $[RhBr_n(OH_2)_{6-n}]^{3-n}$, $[RhCl_n(OH_2)_{6-n}]^{3-n}$ and $[RhBr_nCl_{6-n}]^{3-}$ all exhibit nephelauxetic behaviour of their metal chemical shifts,[2,4] but $\delta_{trans} > \delta_{cis}$ and $\delta_{mer} > \delta_{fac}$ for the geometric isomers, contrary to prediction.[28] Other exceptions to the predicted behaviour are found for complexes involving aqua or sterically demanding ligands, and are proposed to result from mutual ligand interactions or special properties of the aqua ligand.[29] Even if the presence of the aqua ligand can explain the observed behaviour in the first two systems, the bromochlororhodate(III) series remains anomalous since good quantitative agreement between the observed and derived metal chemical shifts has been found for the analogous $[PtBr_nCl_{6-n}]^{2-}$ complexes, for the same ligand pair.[30] It is interesting that, where data are available,[12] octahedral rhodium(III) complexes with spectrochemical behaviour of their ${}^{103}Rh$ chemical shifts follow predictions. This is found for $[RhX_2(AsMe_3)_4]^+$ and $[RhX_4L_2]^-$ (X = Cl or Br, L = SMe_2 or $SOMe_2$) with $\delta_{trans} > \delta_{cis}$ and for $[RhX_3L_3]$ (L = PMe_3, $AsMe_3$, SMe_2 or SMePh) with $\delta_{mer} > \delta_{fac}$.[28]

Empirical trans-*Substitution Schemes.*—Correlations of chemical shift with ligand-replacement schemes (see Fig. 6) have also been used[31] to rationalise the metal chemical shift assignment for the geometric isomers of octahedral MA_nB_{6-n}

species. In the stepwise substitution of a ligand A with B, two distinct types of substitution can be distinguished: (*a*) *homo* in which substitution of A for B leads to a *trans* B–M–B pair; (*b*) *hetero* in which substitution of A for B leads to a *trans* A–M–B pair.

The two substitution types are depicted in Fig. 6 for the $[RhBr_n(OH_2)_{6-n}]^{3-n}$ system with the black-tipped arrows representing homo and the white-tipped arrows hetero substitution. If $\delta_{trans} > \delta_{cis}$ (for both $n = 2$ and 4) and $\delta_{mer} > \delta_{fac}$ then obviously the homo type substitution leads, in all cases, to a greater change in the metal chemical shift than the hetero, and *vice versa*. Chemical shift differences for the aquabromorhodium(III) species and other MA_nB_{6-n} systems, for which the metal chemical shifts for some of the geometrical isomers have been assigned by independent methods, are summarised in Table 3. For the given assignments we see that for each system one of the substitution types gives consistently greater changes in the metal chemical shift than the other by an approximately constant amount. Furthermore, the magnitude of the change usually varies in a continuous manner for each substitution type. Reversing the assignments for the geometric isomers leads to erratic variations in the magnitude of the shift change.

Although empirical correlations of this type are not sufficient on their own to assign geometric isomers in MA_nB_{6-n} systems, they can be used in conjunction with other experimental data to rationalise the assignments for the present system and for several other 'anomalous' systems, *e.g.* $[RhCl_n(OH_2)_{6-n}]^{3-n}$ and $[RhBr_nCl_{6-n}]^{3-}$.

Conclusion

Rhodium-103 NMR spectroscopy has been used to identify the ten monomeric aquabromorhodium(III) species, $[RhBr_n(OH_2)_{6-n}]^{3-n}$ (n = 0–6), in aqueous solution. For solutions with a total rhodium concentration $c_{Rh} > 0.5$ mol dm^{-3}, and with mole ratios $n_{Br}:n_{Rh}$ = 3–8 : 1, a complex equilibrium of oligomeric aquabromorhodate(III) species is found to exist. It is possible, however, to rationalise the ^{103}Rh chemical shifts observed for the bromide-bridged complexes into groups of close-lying signals, each representative of rhodium nuclei with the same ligand stoichiometry $RhBr_n(OH_2)_{6-n}$, n = 4–6. Further work is required for detailed assignments of the ^{103}Rh NMR resonances of these species.

The metal chemical shifts of rhodium(III) species in O_h and C_{3v} symmetry have been used to extend the correlation range with the ligand-field parameter ratio $\beta/\Delta E$. The theoretical ligand-field approach is, however, less successful in assigning the geometric isomers in octahedral RhA_nB_{6-n} complexes. Empirical *trans*-substitution schemes have been used to rationalise the metal chemical shifts for the present aquabromorhodium(III) and the bromochlororhodium(III) systems.

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