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^{103}Rh NMR Chemical Shifts of All Ten $[RhCl_n(OH_2)_{6-n}]^{3-n}$ Complexes in Aqueous Solution

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The slow kinetics of the $[RhCl_n(OH_2)_{6-n}]^{3-n}$ system allows separation of all the ten possible species with the use of ion-exchange techniques [1, 2]. A combined Raman and X-ray diffraction study on such separated solutions, each containing a single dominating Rh–Cl complex, has recently been performed [3]. Each Rh complex gives a separate signal in ^{103}Rh NMR spectroscopy, which therefore is an excellent tool to identify the complexes and follow the separation procedures. However, previous ^{103}Rh NMR studies on this system [4, 5] do not fully agree with our assignments reported here.

A Bruker AM400 NMR spectrometer was used in an unlocked mode, with the samples in 10 mm tubes. The chemical shifts are referenced to $\Xi(^{103}Rh) = 3.16$ MHz, as proposed by Goodfellow [6]. The high-frequency positive-shift convention was used. Approximately 40° pulses were applied with a pulse-repetition time of 8 s.

In order to unambigously assign the resonances, ^{103}Rh NMR spectra were recorded for acidic aqueous solutions normally with a single dominating Rh complex, Cl^- and ClO_4^- ions, *cf.* Table I, except for the *cis*- and *trans*-$[RhCl_4(OH_2)_2]^-$ isomers, which were less stable in separated solutions.

Finally a non-equilibrium 0.5 M Rh solution containing all ten $[RhCl_n(OH_2)_{6-n}]^{3-n}$ isomers in significant amounts was prepared by mixing the appropriate separated solutions and adding excess HCl to 1 M. This unusual solution allows direct comparisons to be performed of experimental NMR parameters such as linewidths and chemical shifts, because environmental effects are the same for all the Rh(III) species. Its ^{103}Rh NMR spectrum was recorded first at 3 °C for 12 h (Fig. 1A), then (after keeping it one day at 3 °C) at 35 °C for another 12 h (Fig. 1B). The comparison of the two spectra shows the strong temperature dependence of the chemical shifts of all Rh species (from 1.7 to 2.3 ppm/degree, Table I) and also that some changes in the chemical composition have occurred. The latter spectrum shows an increase in the concentration of the $[RhCl_5(OH_2)]^{2-}$ complex, which is the thermodynamically most stable of the chloro-complexes at $[Cl]^-_{free} = 1$ M [7], while the amounts of the neighbouring $[RhCl_6]^{3-}$ and *cis*-$[RhCl_4(OH_2)_2]^-$ complexes have decreased. The concentration of the *trans*-$[RhCl_2(OH_2)_4]^+$ complex has increased, which is consistent with the anation scheme given by Palmer and Harris [1], in which this complex is obtained by a slow exchange of the water ligand *trans* to Cl in $[RhCl(OH_2)_5]^{2+}$. The *trans*-effect is also evident in the increase in the concentration of *trans*-$[RhCl_4(OH_2)_2]^-$, produced by anation of *mer*-$[RhCl_3(OH_2)_3]$, and in the disappearance of the *fac*-$[RhCl_3(OH_2)_3$ isomer (Fig. 1B), which gives *cis*-$[RhCl_4(OH_2)_2]^-$ upon anation.

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TABLE I. Chemical Shifts $\delta(^{103}Rh)$ (ppm) for the Non-equilibrium Solution Mixture at 3 °C (Fig. 1A) and 35 °C (Fig. 1B), and for some Other Solutions used for the Assignments

Complex	A (3 °C)	B (35 °C)	Other solutions
$[Rh(OH_2)_6]^{3+}$	9866	9931	9862^a, 9896^b
$[RhCl(OH_2)_5]^{2+}$	9445	9503	9435^c
trans-$[RhCl_2(OH_2)_4]^+$	9153	9208	9144^c, 9160^d
cis-$[RhCl_2(OH_2)_4]^+$	9088	9142	9077^c, 9094^d, 9097^d
mer-$[RhCl_3(OH)_2)_3]$	8817	8870	8831^e, 8829^f, 8836^g
fac-$[RhCl_3(OH_2)_3]$	8753		8770^e, 8776^f, 8773^g
trans-$[RhCl_4(OH_2)_2]^-$	8561	8620	8578^f, 8585^g
cis-$[RhCl_4(OH_2)_2]^-$	8486	8541	8481^h, 8507^e, 8503^f, 8510^g
$[RhCl_5(OH_2)]^{2-}$	8235	8298	8228^h, 8258^f, 8264^g
$[RhCl_6]^{3-}$	8001	8075	7997^h, 7946^i

^{a}1 M Rh^{3+} in 1.9 M $HClO_4$, 3 °C. ^{b}1 M Rh^{3+} in 1.9 M $HClO_4$, 25 °C. ^{c}0.6 M $RhCl^+$ in 1.6 M $HClO_4$, 3 °C. ^{d}0.3 M $RhCl_2^+$ in 0.7 M $HClO_4$, 3 °C. ^{e}0.6 M $RhCl_3$ in 0.1 M $HClO_4$, 3 °C. ^{f}0.6 M $RhCl_3$ + conc. HCl to 1 M excess, 3 °C. ^{g}0.6 M $RhCl_3$ in 1 M HCl after heating 20 h at 85 °C, 3 °C. ^{h}0.9 M Li_3RhCl_6 in 0.5 M HCl, 3 °C. ^{i}0.9 M Li_3RhCl_6 in conc. HCl, 25 °C.

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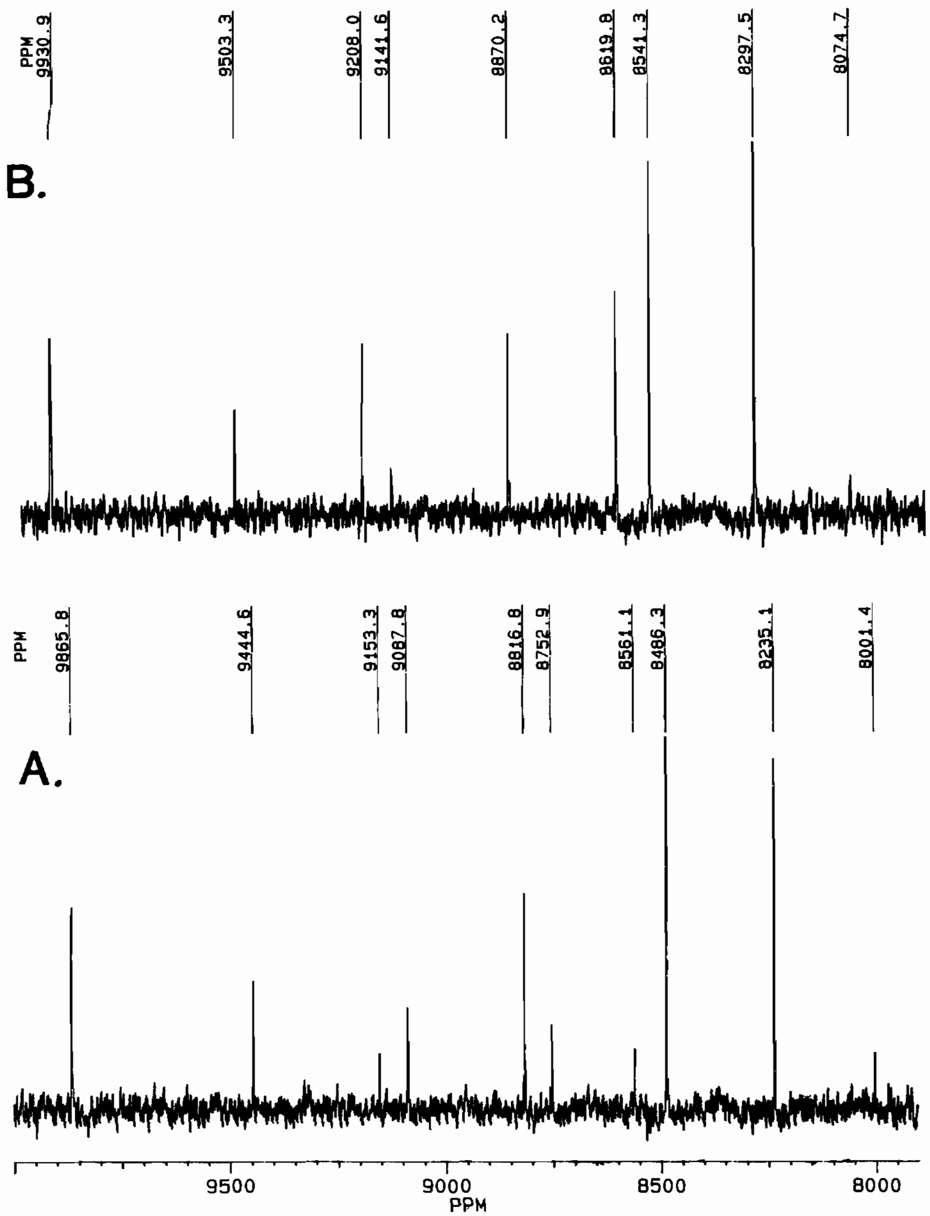

Fig. 1. The 12.6 MHz ^{103}Rh NMR spectrum of a non-equilibrium 0.5 M Rh(III) solution with $[Cl]^-_{tot}$ = 2 M, $[H]^+$ = 1 M, and $[ClO_4]^-$ = 0.5 M at 3 °C (A) and subsequently at 35 °C (B).

Most of the resonances in Table I could be identified directly by information obtained previously on the dominating species from the preparation procedures and from their Raman and electronic spectra [3]. For the *cis*- and *trans*-$[RhCl_4(OH_2)_2]^-$ isomers the assignment is based on the criteria given in ref. 8, where an analogous study of the solvolysis products of $[PtCl_6]^{2-}$ has been made by ^{195}Pt NMR spectroscopy. The scheme in Fig. 2 confirms the tendency found for the $[PtCl_n(OH_2)_{6-n}]^{2-n}$ system that each substitution of H_2O (or OH^-) for a Cl atom *trans* to Cl, in all cases causes a smaller positive change in the chemical shift than that of Cl *trans* to H_2O (or OH^-). It also shows that this change smoothly increases for both these types of aquation in the $[RhCl_n(OH_2)_{6-n}]^{3-n}$ complexes when the number of Cl ligands, n, decreases.

The assignment of the tetrachloro isomers is also consistent with the reported aquation and anation schemes [1, 9] as applied on the changes in the ^{103}Rh NMR spectra, Table I, upon partial equilibration of the separated solutions.

An apparent increase of the linewidths of the ^{103}Rh NMR resonances was observed with increasing

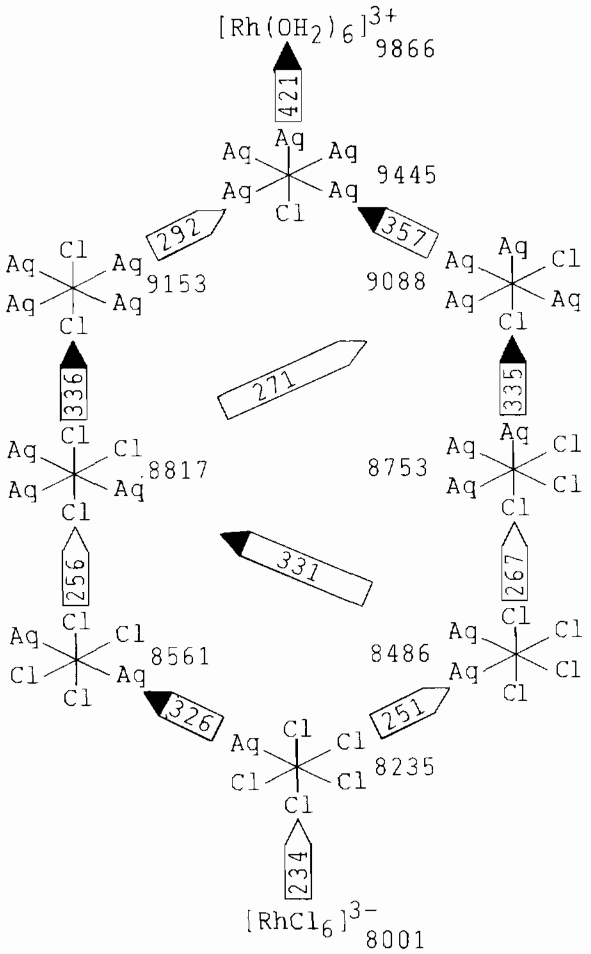

Fig. 2. The scheme shows the chemical shifts δ(Rh) in ppm of the species formed, and the stepwise changes in δ(Rh) (numbers inside arrows), upon aquation of $[RhCl_6]^{3-}$. The arrows with black tip denote substitution for H_2O of a Cl atom *trans* to H_2O, and the others of a Cl atom *trans* to Cl.

number of chloro ligands, from about 2.5 Hz for $[Rh(OH_2)_6]^{3+}$ to about 10 Hz for $[RhCl_6]^{3-}$. Closer scrutiny revealed, however, splitting of the resonances, as exemplified in Fig. 3 for the *cis*-$[RhCl_4(OH_2)_2]^-$ complex. For all the chloro complexes where the signal to noise level allowed estimation of the relative peak height ratios, these were in approximate agreement with the calculated abundance of the naturally occurring ^{35}Cl, ^{37}Cl isotopomers*. In the cases where the splitting of the peaks was sufficiently resolved the linewidth of each isotopomer was estimated to *ca.* 2.5 Hz. Each substitution of ^{35}Cl for the heavier ^{37}Cl isotope gives a frequency shift of *ca.* –0.3 ppm (3.5 to 4 Hz), analogously to the –0.17 ppm shift observed in 86 MHz ^{195}Pt NMR spectra of $PtCl_6^{2-}$ isotopomers [11].

*The relative abundance of the isotopomers $[Rh^{35}Cl_k{}^{37}Cl_{n-k}(OH_2)_{6-n}]^{3-n}$ is given by the binominal probability distribution function $P(k) = \binom{n}{k} p_{35}{}^k p_{37}{}^{n-k}$, for k = 1,2,..., n, where $p_{35} = 0.755$ and $p_{37} = 0.245$ are the natural abundances of the ^{35}Cl and ^{37}Cl isotopes, respectively (for the theory see ref. 10).

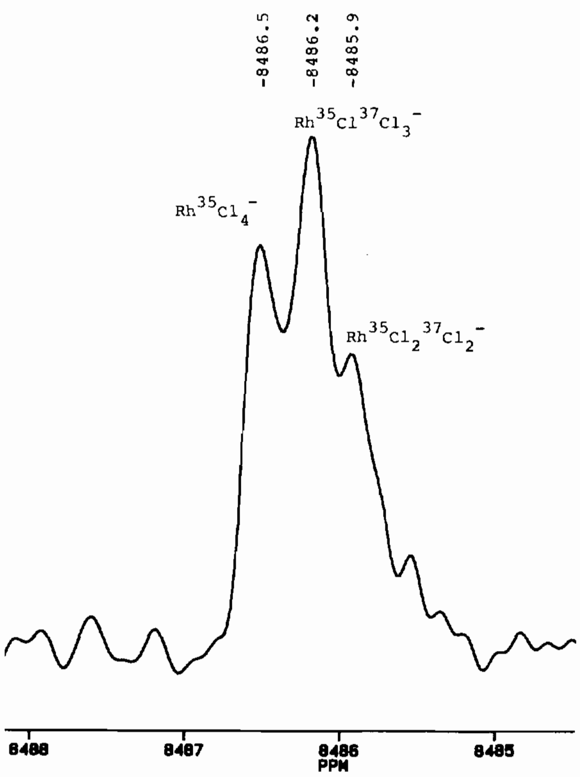

Fig. 3. The observed isotopic splitting of the ^{103}Rh NMR resonance of the *cis*-$[RhCl_4(OH_2)_2]^-$ complex in Fig. 1A. The calculated natural abundances [10] are: $[Rh^{35}Cl_4(OH_2)_2]^-$ = 32%, $[Rh^{35}Cl_3{}^{37}Cl(OH_2)_2]^-$ = 42%, $[Rh^{35}Cl_2{}^{37}Cl_2(OH_2)_2]^-$ = 21% and $[Rh^{35}Cl^{37}Cl_3(OH_2)_2]^-$ = 4.5%, in fair agreement with the peak height ratios obtainable from the Figure.

The dependence of the ^{103}Rh chemical shift on the solution composition and acidity is large (Table I), and when comparing spectra from different solutions care has to be taken so that one signal, shifted by changed conditions, is not assigned to a different species. In combination with a missing signal for the *trans*-$[RhCl_2(OH_2)_4]^+$ complex this seems to be the reason for the partly different assignments made in ref. 4. Moreover, the signals reported at 9992 and 9819 ppm, which were proposed to originate from $[Rh(OH_2)_6]^{3+}$ and a perchlorate complex [4], are probably due to hydrolysis complexes. We have investigated some solutions prepared by dissolving hydrated rhodium oxide in perchloric acid, as in ref. 4, and found that several oligomeric hydrolysis species having ^{103}Rh resonances in this range persist in appreciable amounts even in strongly acid solutions. A further, more detailed study of the Rh(III) hydrolysis is in progress.

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