Coordination of Rhodium(III) in Dilute Aqueous Solutions in Presence of Chloride Anion

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Dilute aqueous solutions of Rhodium(III) at the Cl^-/Rh(III) ratios 4.86 and 10.7 have been X-ray examined. Octahedral $Rh(H_2O)_6^{3+}$ and $Rh(H_2O)_3Cl_3$ complexes are the species which are consistent with the correlation functions and the structure functions. The average number of bonded chloride ions per Rhodium atom has been determined and the reliability of the structural information is critically examined.

The influence of the temperature on the substitution of water molecules by chloride ions is confirmed by using Raman spectroscopy.

1. Introduction

For a diluted aqueous $Rh(ClO_4)_3$ solution with added perchlorate acid the presence of the monomeric hexaaquo complex $Rh(H_2O)_6^{3+}$ has recently been established and the structural parameters of the first and second hydration shells of the Rh(III) ion have been determined [1]. Polynuclear Rh(III) complexes were excluded by the acidity conditions [2]. According to [3], $Rh(H_2O)_6^{3+}$ exists in equilibrium with $Rh(H_2O)_{6-y}Cl_y^{3-y}$ ($y = 1-6$) when chloride anions are added and the solution is heated. On the other hand, the hexaaquorhodium(III) complex and its chloride anion substituents are reported to be extremely stable at room temperature [4]. In order to elucidate the situation we have performed X-ray and Raman investigation on this kind of room temperature and heated solutions.

2. Experimental Section

2.1 *X-Ray Measurements and Data Treatment*

A known amount of HCl was added to an aqueous $Rh(ClO_4)_3 + HClO_4$ solution and an aqueous $RhCl_3$ solution. The composition of the two solutions was determined by standard methods. In Table 1 we report the analytical data of the solutions. The temperature of the samples was 19 ± 1 °C. The $\Theta-\Theta$ X-ray diffractometer and technical details of the measurements have previously been described [5]. MoKα radiation with wavelength $\lambda = 0.7107$ Å was used. The measured intensity was recorded in an s range from 0.6 to 15.5 $Å^{-1}$, where $s = (4\pi/\lambda)\sin\Theta$.

Table 1. Composition of the solutions. The concentrations are given in mole/l (upper figures) and by the stoichiometric coefficients in the structural units $[Rh(ClO_4)_3]_{x_1} \cdot [HClO_4]_{2.78\,x_1} \cdot [HCl]_{10.7\,x_1} \cdot [H_2O]_{1-x_1}$ and $[RhCl_3]_{x_1} \cdot [HCl]_{1.86\,x_1} \cdot [H_2O]_{1-x_1}$. The density and the linear absorption coefficient μ calculated for MoKα radiation are also listed.

		$Rh(ClO_4)_3 + HClO_4 + HCl$ Solution **A**	$RhCl_3 + HCl$ Solution **B**
Rh^{3+}	M	0.1870	0.3861
	x_1	0.00359	0.00701
ClO_4^-	M	1.0809	
	x_2	0.02077	
Cl^-	M	2.0000	1.8783
	x_3	0.03844	0.03410
H^+	M	2.5199	0.7200
	x_4	0.04843	0.01307
H_2O	M	51.8468	54.6905
	x_5	0.99641	0.99300
Density ($g \cdot cm^{-3}$)		1.1296	1.0917
(μ) (cm^{-1})		2.8919	2.8456

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The applied correction and normalization process was the same as in [1]. The obtained structure function is

$$i(s) = \left[I_{\mathrm{e.u.}} - \sum_{i=1}^{m} x_i f_i^2 \right], \qquad (1)$$

where f_i are the atomic scattering factors, x_i the stoichiometric coefficients in a structural unit containing m kinds of atoms and $I_{\mathrm{e.u.}}$ is the intensity in electron units.

The correlation functions $G(r)$ were calculated by a Fourier transformation according to

$$G(r) = 1 + \frac{1}{2\pi^2 r \varrho_0} \int_{s_{\min}}^{s_{\max}} \sin(s)\, M(s) \sin(rs)\, \mathrm{d}s, \qquad (2)$$

where r is the interatomic distance, $s_{\min}$ and $x_{\max}$ are the lower and upper limits of the experimental data, ϱ_0 is the bulk number of the stoichiometric units and $M(s)$ a modification function of the form $\left(\sum_{1}^{m} x_i f_i \right)^{-2} \exp(-K s^2)$ with $K = 0.0$ for the solution A ($Rh(ClO_4)_3 + HCl$) and 0.005 for the solution B ($RhCl_3 + HCl$). In B the damping factor ($\exp - 0.005\, s^2$) is introduced in order to reduce termination errors.

In the process of correction of residual systematic errors [6] the peak due to the intramolecular Cl−O distance centered at about 1.45 Å, was also removed. Although less information can be deduced on the geometry of the ClO_4^- ion in such a way, the removal of the peak ensures that the residual peaks in $G(r)$ are real. This procedure has previously been used [1, 7, 8].

2.2 Raman Spectroscopic Measurements

Raman spectra taken at room temperature were performed in 90° scattering geometry using a focussed 632.8 nm He−Ne exciting source (80 mW). Great care was taken to minimize local heating in the solutions. The scattered light was focused onto a slit of a double monochromator equipped with a cooled I.T.T. FW 130 cooled photomultiplier, the nominal resolution was 5 cm^{-1}. The signal was analysed by a standard photon counting system and the data were processed by a digital acquisition system.

3. Analysis of the Results

3.1 X-Ray Data

The experimental functions in the form si$(s)\,M(s)$ and $G(r)$ are shown in Figs. 1 and 2, respectively, for the two solutions studied. In the correlation functions some peaks can be clearly distinguished. From their positions and from earlier results on solutions containing Rh(III), ClO_4^- and Cl^- [1, 9, 10] a rough assignment of interactions to the characteristic distances can be made.

3.1.1 Correlation Functions

Solution A:

The first peak at 2.05 Å is certainly ascribable to $Rh-H_2O_I$ interactions in the first coordination shell, as found in the previous study [1] and in the crystal structure of aquo (HEDTA)rhodium [11]. Obviously,

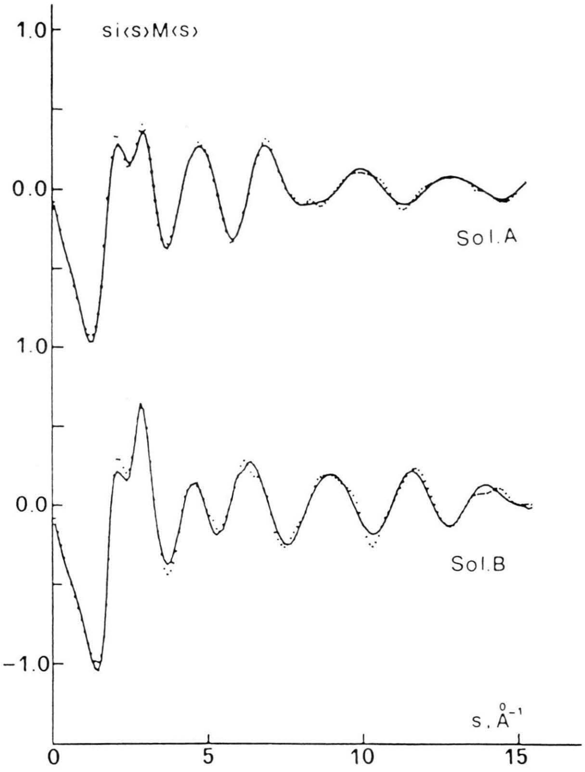


Fig. 1. Experimental (····) and calculated (——) structure functions in the si$(s)\,M(s)$ form. The parameters used for the calculated functions are reported in Table 2 (solution **A**) and in Table 3 (solution **B**).

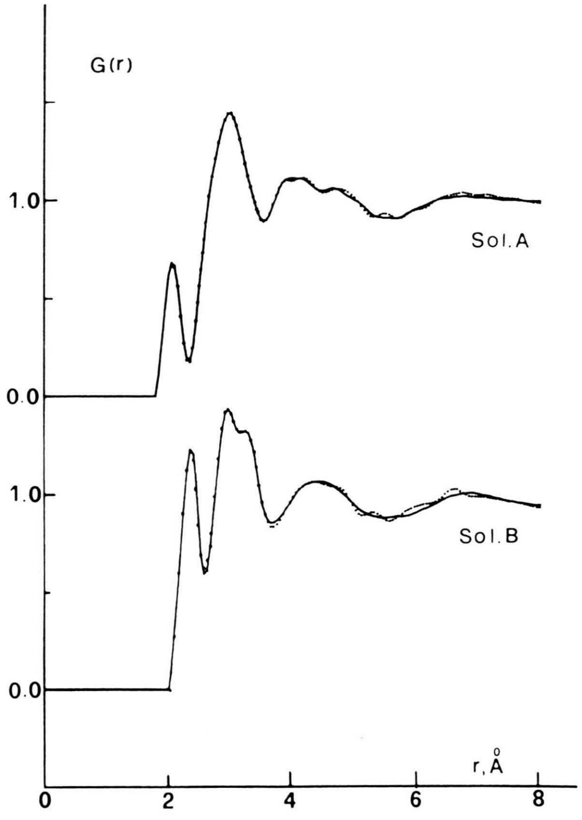


Fig. 2. Experimental (·····) and calculated (——) correlation functions obtained from the si (s) M (s) curves plotted in Figure 1.

in the range 2.35–2.40 Å fall also the $O_{Cl}-O_{Cl}$ distances within the perclorate anion. The second large peak at 3.0 Å is due to different contributions. H_2O-H_2O in the bulk (~ 2.85 Å) and Cl^--H_2O interactions (3.15–3.20 Å) within $Cl(H_2O)_6^-$ octahedral groups are the predominant contributions [1, 9, 10] but other structuring factors will occur in this region: H_2O-H_2O cis interactions from Rh(III) octahedral complexes, water-water distances of two subsequent Rh(III) coordination shells, $O-H_2O$ interactions (with O from perchlorate group) in the hypothesis of contacts ClO_4-H_2O and $H_3O^+(H_2O)_4$ interactions that fall in the range 2.5–2.8 Å [12–14]. To the double peak with two components at about 3.9 Å and 4.2 Å contribute predominantly the $Cl-H_2O$ (Cl from the ClO_4^- group) interactions (these distances fall in the range 3.5–3.9 Å [9, 15] and the $Rh-H_2O_{II}$ (with H_2O_{II} water molecules of the second hydration shell of the Rhodium(III)); H_2O-H_2O trans distances within the octahedral $Rh(H_2O)_6^{3+}$ give small contributions to this peak. The small peak at about 4.5 Å is composite; in it fall the H_2O-H_2O cis distances within the $Cl(H_2O)_6^-$ and the second order water-water distances of the solvent not involved in hydration phenomena.

Solution B

The first peak centered at 2.30 Å is ascribable to $Rh-Cl^-$ interactions in agreement with the value found in the crystal structure of ($NH_4RhCl_5(H_2O)$ [16]. Obviously the $Rh-H_2O_I$ interactions also contribute to this peak, which in the crystal structure [16] has a value of 2.09 Å. This peak is followed by a double peak, having two maxima at about 2.90 Å and 3.20 Å; H_2O-H_2O and Cl^--H_2O pairs are the main components in this region [1, 9, 10]; but also in this solution other structuring factors are present as in A (the Cl^--Cl^- cis distances in the octahedral Rh(III) complexes are new important interactions).

The broad peak around 4–4.60 Å contains several contributions coming from order phenomena beyond the first ion-solvent direct distances. In this range we have $Rh-H_2O_{II}$ distances but also H_2O-H_2O cis distances at about 4.5 Å in the polyhedron $Cl^-(H_2O)_6$ [10] and Cl^--Cl^-, Cl^--H_2O and H_2O-H_2O trans distances in the polyhedron $Rh(H_2O)_{6-y}Cl_y^{3-y}$. Obviously second-order water-water distances in the bulk contribute to this peak.

Peaks from larger intermolecular distances are absent; as in previous investigations the order phenomena observable in the correlation curves concern ionic hydration exclusively. Polynuclear Rh(III) complexes were excluded in our solutions. The comparison between these solutions and the previously studied solution [1] shows that the addition of HCl acid in A produces only the shift of the peak at about 2.85 Å because in this region fall now the Cl^--H_2O interactions (3.15–3.20 Å). No evidence for Rh–Cl direct interactions is present in A; these interactions are present in B.

A quantitative description of the possible structure in the solutions is treated with the help of the model hypothesis in Sect. 3.1.2 and 3.1.3.

3.1.2 Model Interpretation of the X-ray Structure Function

For a quantitative analysis, a theoretical structure function according to the well-known formula proposed by Narten and Levy [17] was evaluated and systematically refined by least-squares. The least-squares refinements were carried out using the total s interval, the function

$$U = \sum_{0}^{s_{\max}} [i(s)_{\exp} - i(s)_{\mathrm{calc}}]^2 \qquad (3)$$

being minimized by means of the previously used LSHS program [1].

For calculating the theoretical $i(s)$ we used a structural model based on the hypothesis that the water molecules and the chloride anions which are nearest neighbours, and the water molecules which are second neighbours to cation, have a discrete structure described by appropriate hydration geometries; the Cl^- not bonded to Rhodium(III) ion is presented as $Cl(H_2O)_6^-$. The perchlorate anion has twelve bonded water molecules. The hydrated ions were considered spatially non-correlated and a uniform distribution of distances (continuum) was assumed. According to experimental observations, the model used has the following features:

Solution A ($Rh(ClO_4)_3 + HClO_4 + HCl$)

1) The Rh(III) ion is surrounded by six first-shell water molecules;
2) the complex $Rh(H_2O)_6^{3+}$ is surrounded by a second shell formed by twelve water molecules;
3) interactions between oxygen atoms (O_{Cl}) within the perchlorate anion, namely $O_{Cl}-O_{Cl}$ interactions, are introduced;
4) each H_3O^+ is tetrahedrally coordinated with four water molecules;
5) the Cl^- anion is surrounded by six water molecules;
6) the ClO_4^- anion is surrounded by twelve water molecules;
7) the residual water molecules not involved in hydration phenomena were assumed to retain the structure they have in pure water and their contribution was introduced into the model $i(s)$ function by appropriately weighting experimental $i(s)$ obtained from pure water;
8) in addition to discrete-structure interactions, a continuum region was introduced around each species to account for absence of positional correlation at larger distances.

The independent structural parameters introduced in the least-squares procedure are:

Cation

$r_{Rh-H_2O_I} = Rh-H_2O_I$ distance; $\sigma_{Rh-H_2O_I}$ = rms deviation of the distance $Rh-H_2O_I$; $\sigma_{H_2O_I-H_2O_I}$ = ms deviation of the $H_2O_I-H_2O_I$ distances in the octahedral geometry of the complexes $Rh(H_2O)_6^{3+}$. The $H_2O_I-H_2O_I$ are related to the $Rh-H_2O_I$ distance by the adopted geometry. $r_{Rh-H_2O_{II}} = Rh-H_2O_{II}$ distance (with H_2O_{II} water in a second hydration shell; $\sigma_{Rh-H_2O_{II}}$ = its rms deviation; $r_{H_2O_I-H_2O_{II}} = H_2O_I-H_2O_{II}$ distance between water molecules pertaining to two subsequent hydration shells of the cation; $\sigma_{H_2O_I-H_2O_{II}}$ = rms deviation of the distance. Obviously the coordination number $n_{H_2O_I-H_2O_{II}}$ is equal $(1/6)\, n_{Rh-H_2O_{II}}$ that is two. No fixed orientation was chosen for H_2O_{II} molecules.

Perchlorate group

$r_{O_{Cl}-O_{Cl}}$ = distance $O_{Cl}-O_{Cl}$ in the perchlorate anion; $\sigma_{O_{Cl}-O_{Cl}}$ = rms deviation of the distance. r_{O-H_2O} = oxygen atom (from perchlorate group) – water molecules distance; σ_{O-H_2O} = rmsd of the distance. r_{Cl-H_2O} = distance chloro atom – water molecules; σ_{Cl-H_2O} = its rms deviation. Each oxygen atom from perchlorate group has bonded three water molecules.

Chloride Anion

$r_{Cl^--H_2O} = Cl^--H_2O$ distance; $\sigma_{Cl^--H_2O}$ = rms deviation of the distance Cl^--H_2O. $\sigma_{H_2O-H_2O}$ = rms deviation of the H_2O-H_2O distances in the octahedral geometry of the complex $Cl(H_2O)_6^-$. The H_2O-H_2O are related to the Cl^--H_2O distance by the adopted geometry.

$H_3O^+(H_2O)_4$

$r_{H_3O^+-H_2O}$ = distance $H_3O^+-H_2O$; $\sigma_{H_3O^+-H_2O}$ = rms deviation of the distance. $\sigma_{H_2O-H_2O}$ = rms deviation of the H_2O-H_2O distances; these distances are related to the $H_3O^+-H_2O$ distance by the adopted tetrahedral geometry.

Solution B ($RhCl_3 + HCl$)

1) The Rh(III) ion surrounded by three water molecules and three chloride anions. This point is discussed in detail in Section 3.1.3;
2) the complex $Rh(H_2O)_3Cl_3$ is surrounded by a second shell formed by 15 water molecules (two

for each water molecule and three for each chloride anion);

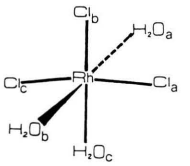
3) each H_3O^+ is tetrahedrally coordinated with four molecules;
4) the Cl^- anion not bonded to Rh(III) ion is surrounded by six water molecules;
5) the residual water molecules not involved in hydration phenomena are treated as described in the previous point 7;
6) a continuum region was introduced also in this case.

The independent structural parameters introduced in the least-squares procedure are:

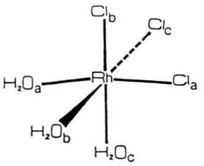
(i) $Rh(H_2O)_3Cl_3$ complex:

$r_{Rh-Cl_b^-} = Rh-Cl_b^-$ distance (with Cl_b^- chloride anion bonded to Rhodium), $\sigma_{Rh-Cl_b^-}$ = its rmsd, $r_{Rh-H_2O_I} = Rh-H_2O_I$ distance, $\sigma_{Rh-H_2O_I}$ = its rmsd, $\sigma_{complex}$ = rms deviation for all the distances $H_2O_I-H_2O_I$, $H_2O_I-Cl_b^-$, $Cl_b^--Cl_b^-$ within the complex $Rh(H_2O)_3Cl_3$.

Obviously the chlorine atoms in the octahedron can take up two different arrangements as shown in scheme 1 (configuration mer) and 2 (configuration fac). Both models have been tested. Moreover for both models a slight distortion in the octahedron has also been introduced in order to adjust the separation (from each other) of the chlorine atoms bonded to the rhodium ion.



Scheme 1



Scheme 2

(ii) Cation-second hydration shell:

$r_{Rh-H_2O_{II}} = Rh-H_2O_{II}$ distance; $\sigma_{Rh-H_2O_{II}}$ = its rmsd; $r_{H_2O_I-H_2O_{II}} = H_2O_I-H_2O_{II}$ distance between water molecules pertaining to two subsequent hydration shell of the Rhodium; $\sigma_{H_2O_I-H_2O_{II}}$ = rms deviation of the preceding distance.

The coordination number $n_{H_2O_I-H_2O_{II}}$ is equal to two. $r_{Cl_b^--H_2O_{II}} = Cl_b^--H_2O_{II}$ distance (H_2O_{II} are the second shell water molecules of the Rhodium and Cl_b^- are the chloride anions bonded to Rhodium); $\sigma_{Cl_b^--H_2O_{II}}$ = its rmsd; $n_{Cl_b^--H_2O_{II}}$ = is equal to three for each chloride anion.

(iii) Chloride anion and $H_3O^+(H_2O)_4$

The same parameters as used for A.

3.1.3 Computation Procedure

Solution A

Preliminarly we have carried out a calculation, inserting only the $Rh-H_2O_I$ and $O_{Cl}-O_{Cl}$ interactions. The relative parameters are: $r_{Rh-H_2O_I}$, $\sigma_{Rh-H_2O_I}$, $n_{Rh-H_2O_I}$, $r_{O_{Cl}-O_{Cl}}$ and $\sigma_{O_{Cl}-O_{Cl}}$. The least-squares refinement was made using the s interval 7–15.28 Å^{-1}. In Table 2 we report the obtained parameters and in Fig. 3c the obtained structure function (solid line) and also the structure functions calculated with only the $Rh-H_2O_I$ contribution (Fig. 3a) and with only the $O_{Cl}-O_{Cl}$ contribution (Figure 3b).

The features of the experiment structure function were very well reproduced in the range 7–15.28 Å^{-1}. The predominant contribution is due to $Rh-H_2O_I$ interactions. The values of the parameters are in agreement with those found in the previous study [1]. The $n_{Rh-H_2O_I}$ is very close to 6, so the assumption for an octahedral $Rh(H_2O)_6^{3+}$ is rather convincing. With the model described in Sect. 3.1.2 we have carried out numerous least-squares refinements cycles to obtain the best agreement with the experimental structure function. We have tested also a model omitting the $ClO_4^--H_2O$ interactions (point 6 in the Sect. 3.1.2) but the agreement was worse.

In Table 3 we report the structural parameters obtained with the complete model and in Figs. 1 and 2 (solid line) the calculated structure function and the theoretical $G(r)$, respectively. In Fig. 4a–g we show the calculated structure functions deriving from the different contributions of the model. The good reliability of the parameters (r, σ, n) of the interaction $r_{Rh-H_2O_I}$ is evident, in fact this contribution is the only important one in the range 7–15.28 Å^{-1}, so that this range is sufficient to determine these parameters. The sum of free water, continuum and long distances in the proposed model reproduces the 0–7 Å^{-1}s interval of the si(s) function (Figure 3g).

Solution B

Also for this solution we have carried out a preliminary calculation with a model, in which we have inserted only the parameters regarding the

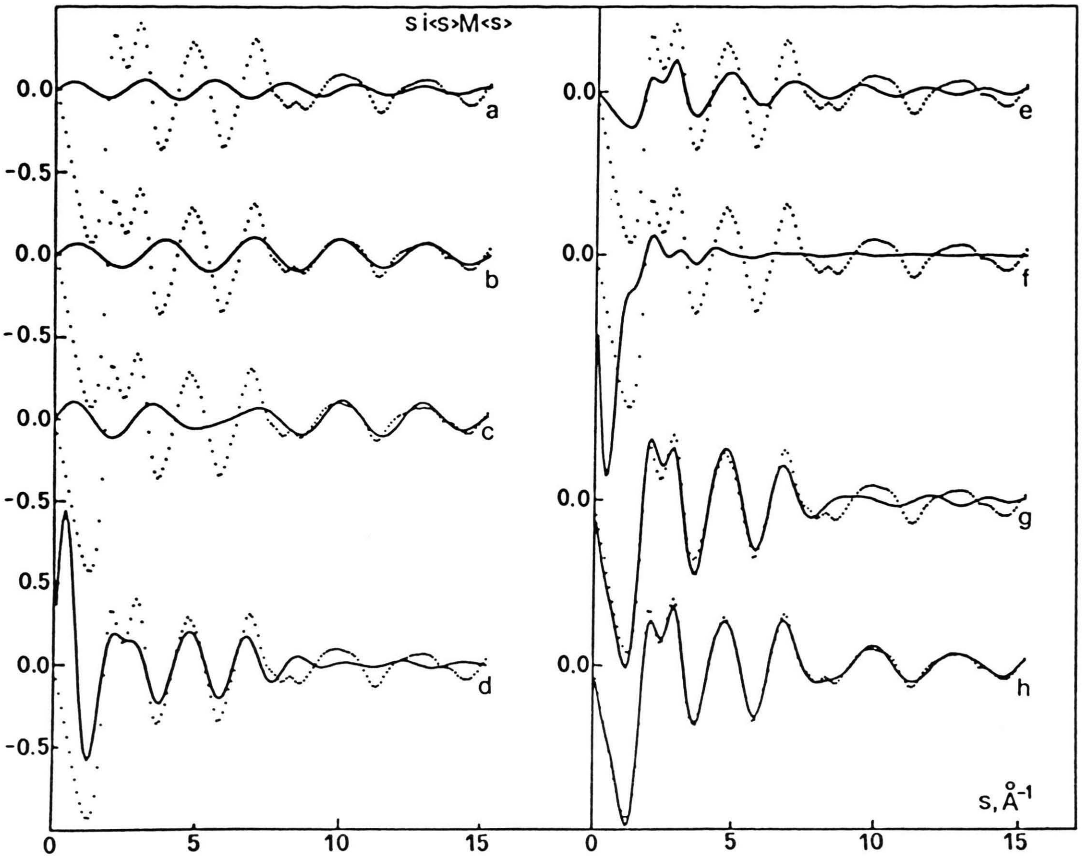


Fig. 3. Solution **A**. (h) si$(s)\,M(s)$ structure functions, experimental (····) and calculated from model (——). The si$(s)\,M(s)$ partial structure functions are calculated with: (a) only the contribution due to $O_{Cl}-O_{Cl}$ distances inside the ClO_4^- group; (b) only the contribution of the $Rh-H_2O_I$ interactions; (c) the sum of the two preceding contributions; (d) the sum derived from all the contributions of the complete model except the terms (a) and (b); (e) the contribution from free water; (f) the contribution from the continuum; (g) the sum of the contributions (d), (e), and (f).

Table 2. Solution **A**. Distances r (Å), root mean square deviations σ (Å) and frequency factors (n) for the interactions. Best Fit Values for the independent parameters of the complete model (b) and these used in the calculation of the partial structure functions plotted in Figures 3a–c (a). Standard errors in parentheses. In the last line is reported the agreement factor R, defined by the formula $R^2 = \sum(\mathrm{si}(s)_{exp} - \mathrm{si}(s)_{calc})^2 / \sum(\mathrm{si}(s))^2$.

	Parameters	(a)	(b)		Parameters	(a)	(b)
Cation	$r_{Rh-H_2O_I}$	2.0846(4)	2.062(4)	Group ClO_4^-	$r_{O_{Cl}-O_{Cl}}$	2.41(2)	2.38(1)
	$\sigma_{Rh-H_2O_I}$	0.08(1)	0.079(5)		$\sigma_{O_{Cl}-O_{Cl}}$	0.146(8)	0.101(9)
	$\sigma_{H_2O_I-H_2O_I}$	–	0.112(5)		$n_{O_{Cl}-O_{Cl}}$	6	6
	$n_{Rh-H_2O_I}$	6.5(7)	6		$r_{O_{Cl}-O_{Cl}}$	–	2.965(5)
	$r_{Rh-H_2O_{II}}$	–	4.07(2)		$\sigma_{O_{Cl}-H_2O}$	–	0.095(6)
	$\sigma_{Rh-H_2O_{II}}$	–	0.22(1)		r_{Cl-H_2O}	–	3.76(1)
	$n_{Rh-H_2O_{II}}$	–	12		σ_{Cl-H_2O}	–	0.265(8)
	$r_{H_2O_I-H_2O_{II}}$	–	2.72(2)		n_{Cl-H_2O}	–	12
	$\sigma_{H_2O_I-H_2O_{II}}$	–	0.08(2)	Anion Cl^-	r_{Cl-H_2O}	–	3.185(5)
					σ_{Cl-H_2O}	–	0.171(4)
$H_3O^+(H_2O)_4$	$r_{H_3O^+-H_2O}$	–	2.75(1)		$\sigma_{H_2O-H_2O}$	–	0.38(2)
	$\sigma_{H_3O^+-H_2O}$	–	0.096(7)				
	$\sigma_{H_2O-H_2O}$	–	0.52(4)		$[H_2O]_{free}$		13.433 M
					R		9.23%

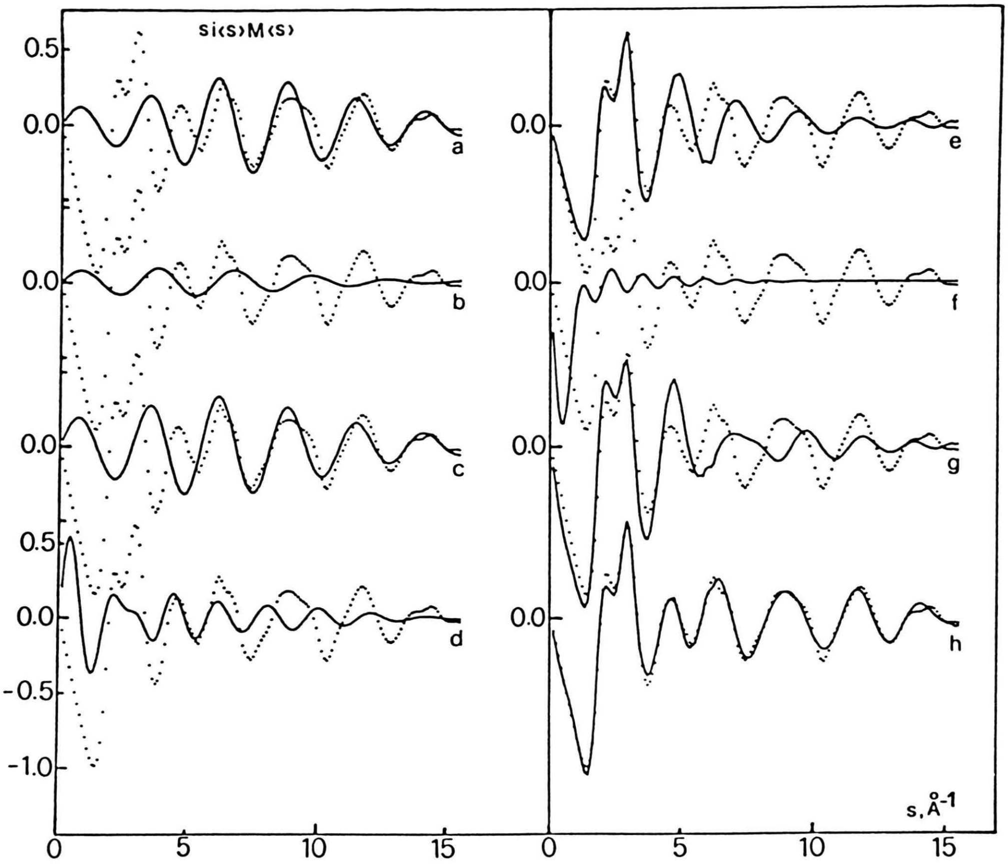


Fig. 4. Solution **B**. (h) si(s) $M(s)$ structure functions, experimental (····) and calculated from model fac (——). The si(s) $M(s)$ partial structure functions are calculated with: (a) only the contribution due to the Rh$-$Cl$^-$ distances; (b) only the contribution of the Rh$-$H$_2$O$_\mathrm{I}$ interactions; (c) the sum of the preceding contributions; (d) the sum derived from all the structural contributions of the complete model except the terms (a) and (b); (e) the contribution from free water; (f) the contribution from the continuum; (g) the sum of the contributions (d), (e), and (f).

direct distances Rh$-$Cl$_\mathrm{b}^-$ and Rh$-$H$_2$O$_\mathrm{I}$. Only five parameters are refined; namely $r_{\mathrm{Rh-Cl_b^-}}$, $\sigma_{\mathrm{Rh-Cl_b^-}}$, $n_{\mathrm{Rh-Cl_b^-}}$, $r_{\mathrm{Rh-H_2O_I}}$, $\sigma_{\mathrm{Rh-H_2O_I}}$; obviously $n_{\mathrm{Rh-H_2O_I}}$ is equal to $6-n_{\mathrm{Rh-Cl_b^-}}$. The s intervall used in the refinement was 7$-$15.58 Å^{-1}. $n_{\mathrm{Rh-Cl_b^-}}$ resulted to be 2.8 ± 0.2; in this case the approximation that in the s intervall used the other contributions are completely negligible proved to be incorrect; in fact the two contributions reproduce the features of the experimental structure function well but not entirely. In Table 3 we report the parameters obtained and in Fig. 4c the obtained structure function (solid line) and also the structure functions calculated with only the Rh$-$Cl$_\mathrm{b}^-$ contribution (Fig. 4a) and with only the Rh$-$H$_2$O$_\mathrm{I}$ contribution (Fig. 4b). The $n_{\mathrm{Rh-Cl_b^-}}$ is very close to 3, so the assumption for on octahedron Rh(H$_2$O)$_3$Cl$_3$ is rather convincing. With the complete model described in the preceding Sect. 3.1.2 we have carried out a great many refinements' cycles until to obtain the best agreement between the calculated and experimental structure functions. It has been not possible distinguish between the different models for the position of the chlorine atoms in the first coordination shell of the rhodium since the agreement factor R (defined as $R=[\sum(\mathrm{si}(s)_{\mathrm{exp}}-\mathrm{si}(s)_{\mathrm{calc}})^2/\sum(\mathrm{si}(s))^2]^{1/2}$ resulted substantially equal in the four cases (fac, mer and fac and mer distorted). For this reason in Table 3 we report only the structural parameters obtained with the complete model fac not distorted and in Figs. 1 and 2 (solid line) the calculated structure function and the theoretical $G(r)$, respectively. Also

Table 3. Solution **B**. Distances r (Å), root mean square deviations σ (Å) and frequency factors n for the $Rh-Cl^-$ and $Rh-H_2O_I$ interactions. Best-Fit values for the independent parameters of the model (b) and those used in the calculations of the partial structure functions plotted in Figures 3a–c. Standard errors in parentheses. $[H_2O]_{free}$ is the concentration of water treated as pure water and R is the agreement factor R, as defined in Table 2.

Parameters		(a)	(b)			
Cation	r_{Rh-Cl^-}	2.30 (1)	2.33 (1)	$Cl(H_2O)_6^-$	$r_{Cl^--H_2O}$	3.23 (2)
	σ_{Rh-Cl^-}	0.05 (1)	0.05 (1)		$\sigma_{Cl^--H_2O}$	0.14 (2)
	n_{Rh-Cl^-}	2.8 (2)	3		$\sigma_{H_2O-H_2O}$	0.28 (7)
	$r_{Rh-H_2O_I}$	2.06 (1)	2.09 (1)			
	$\sigma_{Rh-H_2O_I}$	0.11 (2)	0.13 (2)			
	$n_{Rh-H_2O_I}$	3.2 (2)	3			
	$\sigma_{complex}$	–	0.26 (2)	$H_3O^+(H_2O)_4$	$r_{H_3O^+-H_2O}$	2.70 (3)
	$r_{Rh-H_2O_{II}}$	–	4.11 (2)		$\sigma_{H_3O^+-H_2O}$	0.08 (3)
	$\sigma_{Rh-H_2O_{II}}$	–	0.51 (3)		$\sigma_{H_2O-H_2O}$	0.4 (3)
	$r_{H_2O_I-H_2O_{II}}$	–	2.70 (4)			
	$\sigma_{H_2O_I-H_2O_{II}}$	–	0.08 (3)	$[H_2O]_{free}$	40.521 M	
	$r_{Cl_b^--H_2O_{II}}$	–	3.32 (2)			
	$\sigma_{Cl_b^--H_2O_{II}}$	–	0.14 (2)	R	12.13%	

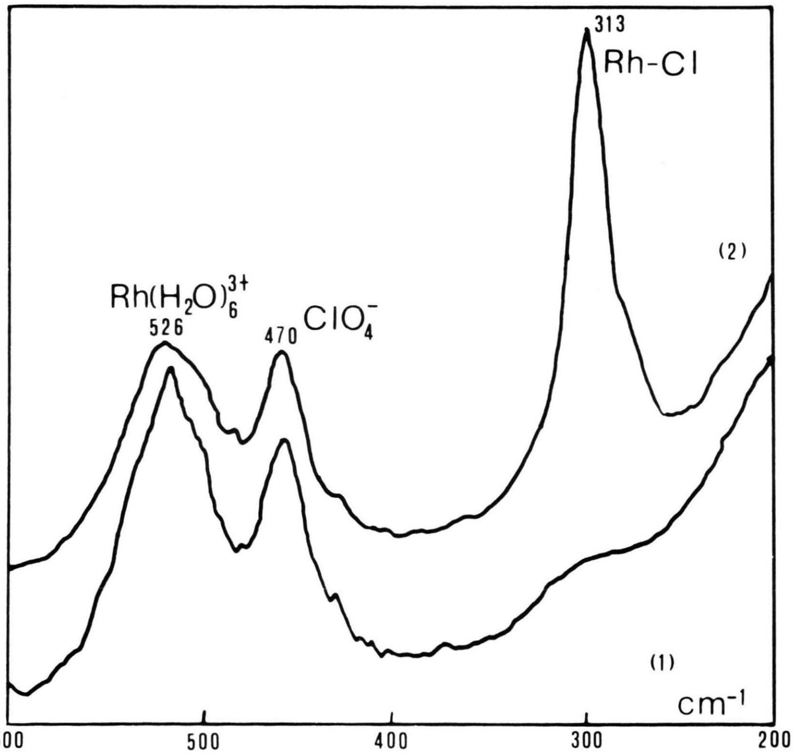


Fig. 5. Raman spectra of the solution **A** (1) before the heating; (2) after the heating.

in this case it is useful to analyse the partial contribution deriving from the different contributions of the model. They are reported in Figure 4a–g. It is evident that the predominant partial structure function is that deriving from the $Rh-Cl_b^-$ interactions (Figure 4a); on the contrary the partial structure function due to $Rh-H_2O_I$ interactions (Fig. 4b) is negligible. The sum of free water, continuum and long distances in the model reproduces the features of the 0–6 Å^{-1} s interval of the si(s) function (Fig. 4g) but contributes also in the 7–15.58 Å^{-1} s interval. According to these considerations the parameters regarding the Rh$-$Cl$_b^-$ interactions (r, σ, n) are well defined while the parameters regarding the Rh$-$H$_2$O$_I$ interactions (r, σ) have a larger imprecision.

3.2 Raman Data

The spectra obtained for A are shown in Fig. 5, in the range 200$-$600 cm^{-1}. The first one is obtained before heating. The second after heating for 40 minutes at 120 °C. A new Raman band appears to 313 cm^{-1}, while the two bands presented at 470 and 526 cm^{-1} remain in the same position; they are due to ClO_4^- group and to $Rh(H_2O)_6^{3+}$ in the octahedral configuration, respectively. The presence of bands in the frequency range 100$-$400 cm^{-1} is a confirmation of the existence of metal-chloride contacts. The spectral features of Cl$^-$ containing solutions have been analyzed [18$-$22]. For a detailed attribution of the bands to different complexes Me$-$Cl$_y$ (with $y = 1, 6$) it is necessary to have a detailed analysis of solutions with different Cl$^-$/Me ratios. In the present analysis the Raman spectra serve only to confirm the presence or the absence of these complexes and to show the temperature effect on the substitution processes of water molecules by chloride anion in the first hydration shell of the rhodium. For this reason we have collected the Raman spectrum of B only once, since the Raman bands present at 305 and 350 cm^{-1} (Fig. 6) show the presence of Rh$-$Cl contacts in the solution. In **A** and **B** we have, obviously, bands in different position (cm^{-1}), because a different number of Cl$^-$ anions enter into the first coordination sphere of the Rh(III) ion, according to the Cl/Rh ratio in the two solutions. The spectra, at room temperature, were unchanged for months. We intend to start a detailed Raman analysis of the different complexes $Rh(H_2O)_{6-y}Cl_y^{3-y}$ ($y = 1, 6$) since this technique has shown, with this preliminary study, to be of value in studying the temperature effects on the Cl$-$H$_2$O substitution processes.

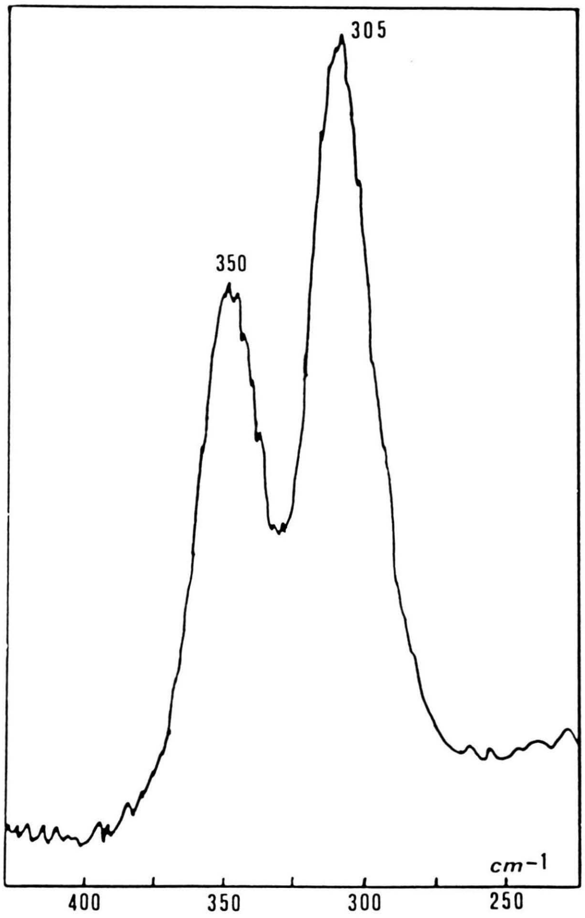


Fig. 6. Raman spectrum of the solution **B**.

4. Discussion and Conclusions

The present study on two very dilute aqueous solutions of Rhodium (III) has given useful information about the coordination of this metal in different chemical conditions. The species $Rh(H_2O)_6^{3+}$ is present in solution of $Rh(ClO_4)_3$ with added $HClO_4$ and HCl if the solution is prepared but not heated (solution **A**). The structural parameters' values obtained in this case are, within the precision of the method, very close to those previously obtained in the study [1] on a solution of $Rh(ClO_4)_3$ with added $HClO_4$. The good reliability of the parameters regarding the first hydration shell of the Rhodium (III) has been shown; we wish to emphasize that they are obtained in spite of the very low concentration of Rhodium (< 0.2 M), unusual in diffractometric studies on solutions. As far as regards the average number of chloride anions bonded to the Rhodium (III), in the solution **B**, the least-squares refinement procedure gives a value of about three. This value is in agreement with information in the literature. The Rh$-$Cl$_b^-$ distance is very close to that found in solid $(NH_4)_2RhCl_5H_2O$ [16]. The reliability of these parameters has already been discussed. The parameters regarding the contacts $ClO_4^- - H_2O$ are in good agreement with those obtained in the study [9] on a solution of $Mg(ClO_4)_2$; also the $Cl^- - H_2O$ interactions are defined in spite of the low concentration of Cl^- and the parameters' values are within the range obtained in a great many of studies on solutions [10, 23–26] containing Cl^-.

In conclusion the qualitative analysis of the $G(r)$ correlation functions has shown differences between the two solutions (shift of the first peak from 2.05 Å to 2.3 Å) due to the presence in **B** of Rh–Cl contacts in the first hydration shell; the comparison of the experimental $G(r)$ of **A** with the previously studied solution [1] of $Rh(ClO_4)_3 + HClO_4$ shows only differences in the r interval at about 3 Å; those differences are due to the presence in our solution of $Cl^- - H_2O$ contacts. The Raman spectra confirm the result obtained with the X-ray diffraction technique and allow verification of the effect of the temperature on the substitution processes of water molecules with chloride anion.

The quantitative analysis of the structure functions gives reliable structural parameters of the different species existent in our solutions.

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[1] R. Caminiti and P. Cucca, Chem. Phys. Lett. **88,** 51 (1984).

[2] J. S. Forrester and G. H. Ayres, J. Phys. Chem. **63,** 1979 (1959).

[3] W. C. Walsey, C. A. Reynolds, and J. Kleinberg, Inorg. Chem. 2, n° 3, 463 (1963).

[4] K. Swaminathan and G. H. Harris, J. Amer. Chem. Soc. **83,** 4411 (1966).

[5] R. Caminiti, G. Licheri, G. Piccaluga, and G. Pinna, J. Chem. Phys. **65,** 3134 (1976).

[6] H. A. Levy, M. D. Danford, and A. H. Narten, Oak Ridge National Laboratory, Rep. n° 3960 (1966).

[7] R. Caminiti, J. Mol. Liquids **28,** 191 (1984).

[8] R. Caminiti, P. Cucca, and T. Radnai, J. Phys. Chem. **88,** 2382 (1984).

[9] R. Caminiti, G. Cerioni, P. Cucca, and G. Crisponi, J. Chem. Phys., submitted.

[10] R. Caminiti, A. Musinu, G. Paschina, and G. Pinna, J. Appl. Cryst. **15,** 482 (1982).

[11] G. H. Y. Lin, J. D. Legget, and R. H. Wing, Acta Cryst. **B 29,** 1023 (1973).

[12] R. Triolo and A. H. Narten, J. Chem. Phys. **63,** 3624 (1975).

[13] N. Ohtomo, K. Arakawa, M. Takenchi, T. Yamagychi, and H. Ohtaki, Bull. Chem. Soc. Japan **54,** 1314 (1981).

[14] R. Caminiti, Chem. Phys. Lett. **96,** 390 (1983).

[15] M. Magini, J. Inorg. Nucl. Chem. **40,** 43 (1978).

[16] G. Bugli and C. Potvin, Acta Cryst. **B 37,** 1394 (1981).

[17] A. H. Narten and H. A. Levy, Scienze **165,** 447 (1969).

[18] C. H. Huang and M. H. Brooker, Chem. Phys. Lett. **43,** 180 (1976).

[19] Y. M. Bosworth and R. J. H. Clark, J. Chem. Soc. Dalton **1974,** 1749.

[20] M. P. Fontana, G. Maisano, P. Migliardo, and F. Wanderlingh, Solid State Commun. **23,** 489 (1977).

[21] M. P. Fontana, G. Maisano, P. Migliardo, and F. Wanderlingh, J. Chem. Phys. **69,** 676 (1978).

[22] S. K. Sharma, J. Chem. Phys. **60,** 1368 (1974).

[23] R. Caminiti, G. Licheri, G. Piccaluga, and G. Pinna, J. Appl. Cryst. **12,** 34 (1979).

[24] M. Magini and T. Radnai, J. Chem. Phys. **71,** 4255 (1979).

[25] R. Caminiti, G. Licheri, G. Paschina, G. Piccaluga, and G. Pinna, Rend. Sem. Fac. Sci. Cagliari **50,** 367 (1980).

[26] A. Musinu, G. Paschina, G. Piccaluga, and M. Magini, J. Chem. Phys. **80,** 2772 (1984).