EXAFS Investigation of Inner- and Outer-Sphere Chloroaquo Complexes of Cr^{3+} in Aqueous Solutions

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Abstract: The structure of four solutions containing the isolated chromochloroaquo complexes, $[CrCl_n(H_2O)_{6-n}]^{(3-n)+}$ ($n = 1-3$), have been investigated with the aid of EXAFS. Synthesis and isolation processes are described. In the inner-sphere complexes, Cr^{3+} ions are surrounded by $5H_2O + 1Cl^-$ (species [I], 1 *m*), $4H_2O + 2Cl^-$ (species [II], 1 and 0.005 *m*), and $3H_2O + 3Cl^-$ (species [III], 0.005 *m*), with Cr−O and Cr−Cl average distances of 2.00 and 2.30 Å, respectively. In the four solutions a second coordination sphere is detected between 3.9 and 4.5 Å. In solution containing species [I], this sphere is formed by water molecules (∼14) at 3.97 Å, whereas for solutions containing [II] and [III], several outer-sphere chloride anions are detected. For species [II] the second coordination sphere is formed by 3.3 (1 *m*) or 4.9 (0.005 *m*) chloride ligands, depending upon concentration of the complex, at around 4.4 Å and by 8.0 (1 *m*) or 7.2 (0.005 *m*) water molecules at 3.9 Å. For species [III], where [HCl] = 12 M, this sphere is formed exclusively by seven chloride ligands at 4.3 Å.

1. Introduction

During the last 20 years X-ray absorption spectroscopies, XANES (X-ray absorption near edge structure), and EXAFS (extended X-ray absorption fine structure) have been powerful tools for analyzing systems exhibiting only short-range order.[1] In a first stage attention was mainly focused on the domain of solid state, amorphous solids and catalysts,[2] and bioinorganic substances containing heavy metals.[3] The widespread use of these techniques to elucidate solvation and complex structures of ions in aqueous and nonaqueous solvents has appeared during the last decade,[4−7] although during the first period there were a few studies concerning the structure of metal aquo complexes in water.[8]

Within this framework, using the EXAFS technique we have reported evidence of the existence of the second hydration shell in dilute $Cr(NO_3)_3$ aqueous solutions.[9] In this case the high stability of the $[Cr(H_2O)_6]^{3+}$ hydrated cation allows a close examination by EXAFS of its second hydration shell. Moreover, we have carried out a detailed study of the structure beyond the first solvation shell of cations, investigating the effect of concentration,[10] charge of the central ion (Zn^{2+} vs Cr^{3+}),[10] and kinetic stability of the first sphere complexes (Zn^{2+}, Ga^{3+}, Cr^{3+}, and Rh^{3+}).[11] We have observed no change in the first hydration sphere within a wide range of concentrations, although some changes have been detected in the second hydration shell for highly diluted (10^{-2} M) or highly concentrated (>1 M) solutions. The second hydration shell has shown to be extremely sensitive to the kinetic stability of the first sphere complex.[11]

In the present work we continue using the EXAFS technique to determine the solvation structure in ionic solutions studying the inner-sphere chromochloroaquo complexes and searching for ordering beyond the first coordination sphere. To achieve these aims, we have undertaken a set of experiments in which we have changed the charge of the hydrated cation, not by substituting the central atom, as in ref 11, but rather by replacing water molecules by chloride ions in the first shell of the hexaaquocomplex of Cr^{3+}. Therefore, we have obtained complexes with total charge 2+, $[CrCl(H_2O)_5]^{2+}$, 1+, $[CrCl_2(H_2O)_4]^+$, or zero, $[CrCl_3(H_2O)_3]$. Related studies of solutions containing the three chromochloroaquo complexes in different percentages have been carried out by Magini[12] using XRD, who obtains average values of the structural parameters for the first sphere of all the involved species. We have analyzed solutions containing only one of these species to simplify the experimental conditions in determining the structural parameters by EXAFS. To isolate and identify each species, a careful study of the equilibrium reactions and conditions involving all these species was carried out. At the level of the first coordination sphere it is also of interest to examine the changes of the XANES spectrum induced by substitution of water molecules by chloride anions.

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Table 1. Experimental Conditions Required to Isolate Each Complex and the Band Position in the UV−Vis Spectrum

	species	starting salt	time of stability/media	UV−vis (nm)	[*m*]
$[CrCl_3(H_2O)_3]$	[III]	$CrCl_3{\cdot}6H_2O$	indefinite/[HCl] $\simeq$ 12 M	475, 665	0.005
$[CrCl_2(H_2O)_4]^+$	[II]	$CrCl_3{\cdot}6H_2O$	1 h/[HCl] $\geq$ 0.1 M	450, 635	0.005, 1
$[CrCl(H_2O)_5]^{2+}$	[I]	$[CrCl(H_2O)_5]SO_4$	1 h/H_2O	430, 605	1
$[Cr(H_2O)_6]^{3+}$	[0]	$Cr(NO_3)_3{\cdot}6H_2O$	indefinite pH $\simeq$ 2	407, 575	

To keep the concentration of one of the haloaquo complexes considerably higher than the others (typically more than 95%), different quantities of hydrochloric acid are needed. This suggested to us that it would be interesting to use EXAFS to study the presence of outer-sphere chloride anions in the set of chloroaquo complexes. The existence of this type of outer-sphere complexes was postulated in the 1950s,[13,14] but only in the 1990s has been proved by means of XRD.[15,16]

The objective of this study was to determine separately the structure of the three inner-sphere chromochloroaquo complexes and to identify the type (water molecules and/or chloride ions), distances, and number of ligands in the second coordination sphere of these complexes.

2. Experimental Section

2.1. Preparation and Isolation of Chloroaquo Complexes of Cr^{3+}. The *trans*-dichlorotetraaquochromiun ion, $[CrCl_2(H_2O)_4]^+$, is the chromium species in the commercially available salt, $CrCl_3{\cdot}6H_2O$.[17] This species is the main one in the dark-green solution obtained just after dissolving the above salt in water. This solution gradually becomes pale due to the replacement of the chloride ligands by water molecules, generating $[CrCl(H_2O)_5]^{2+}$ (light green) and $[Cr(H_2O)_6]^{3+}$ (violet), the latter being the dominant species after equilibrium is reached. Nevertheless, the concentration ratio of these species depends on Cl^- and Cr^{3+} absolute concentrations and ratio, as well as on the pH of the solution.[18,19]

When the $CrCl_3{\cdot}6H_2O$ salt is dissolved in concentrated HCl solution (*ca.* 12 M), the neutral complex $[CrCl_3(H_2O)_3]$ is obtained. This species transforms easily into the dichloro complex, this transformation being partially inhibited by acidic media.[13]

All these processes can be summarized by the following reactions in which chloride ligands are substituted by water molecules:

$$CrCl_3{\cdot}6H_2O(s) + H_2O \rightleftharpoons [CrCl_2(H_2O)_4]^+_{aq} + Cl^-_{aq} + 2H_2O$$

$$[CrCl_2(H_2O)_4]^+_{aq} + H_2O \rightleftharpoons [CrCl(H_2O)_5]^{2+}_{aq} + Cl^-_{aq}$$

$$[CrCl(H_2O)_5]^{2+}_{aq} + H_2O \rightleftharpoons [Cr(H_2O)_6]^{3+}_{aq} + Cl^-_{aq}$$

$$CrCl_3{\cdot}6H_2O(s) + HCl_{aq} \rightleftharpoons [CrCl_3(H_2O)_3]_{aq} + HCl_{aq} + 3H_2O$$

Each chloroaquocomplex has characteristic spectroscopic properties that permits its identification and isolation.[13] The most suitable technique is UV−vis spectroscopy. Each spectrum consists of three bands: one band appearing in the far UV is due to electronic transitions between metal and ligand and extends beyond the ultraviolet limit of the spectrometer at 200 nm. The other two bands, responsible for the color of the complexes, are due to d−d transitions within the metal ion. They appear between 400 and 475 nm and between 575 and 650 nm. There is a regular shift of about 30 nm for the long-wavelength band for each chloride ligand added to the inner-sphere complex. The solutions follow Beer's law for low concentrations (<0.1 M).

The absorption spectrum of the dark-green solution we obtained just after dissolving the $CrCl_3{\cdot}6H_2O$ salt showed bands at 450 and 635 nm in the region between 200 and 800 nm, that can be assigned to $[CrCl_2(H_2O)_4]^+$, species [II], in solution. After about 1 h, the absorption bands in the spectra were displaced to lower wavelengths due to the appearance of other species in solution, species [I], $[CrCl(H_2O)_5]^{2+}$, and species [0], $[Cr(H_2O)_6]^{3+}$. By following the evolution of the UV−vis spectrum of species [II] we observed that the reaction rate for its decomposition in species [I] and [0] decreased by decreasing the pH. For this reason we added HCl to the solution containing species [II] to obtain a pH $\leq$ 1. In this condition the spectrum did not show changes in maxima position for 1 h. Additional amounts of free chloride ions were present in this solution, already containing 1 mol of chloride ions/mol of complex since the hydrated salt can be formulated as $[CrCl_2(H_2O)_4]Cl{\cdot}2H_2O$. Keeping similar values of pH by adding hydrogen chloride, the ratio $[Cl^-]$/[II] decreased with the increase in the concentration of the salt.

The absorption spectrum of the solution containing species [0], hexaaquocomplex of Cr^{3+}, shows bands at 407 and 575 nm. It is obtained when a Cr^{3+} salt for which the anion does not show a tendency to form complexes, like nitrate, is dissolved in water. The solution has to be acidulated to avoid hydrolysis and polymerization processes.[10]

The chloropentaaquochromiun complex, species [I], was obtained in solution from the salt $[CrCl(H_2O)_5]SO_4(s)$ by Weinland's method.[20] To prepare this salt, a saturated solution of $CrCl_3.6H_2O(s)$ in water was kept at room temperature for 24 h. Afterward, a slight excess of 70% sulfuric acid was added and the salt $[CrCl(H_2O)_5]SO_4$ was obtained as a green precipitate that was separated by filtration. When this precipitate was dissolved in water, a light-green solution was obtained, showing bands at 430 and 605 nm, ascribed to species [I]. This color and the spectrum was maintained for 1 h. After this period of time, the spectra showed a bathochromic shift, which was due to the presence of more than one species in solution.

There is a fourth complex of chromium in solution: $[CrCl_3(H_2O)_3]$, species [III], but it is formed only at high concentrations of HCl.[13] When $CrCl_3{\cdot}6H_2O$ salt was dissolved in 12 M HCl, at first the solution showed a dark-green color and contained species [I] and [II]. The solution color changed gradually toward yellow-green, and maximum positions in the spectrum shifted toward higher wavelengths. After 2 hours, the spectrum was stabilized and showed bands at 475 and 665 nm, ascribed to species [III], $[CrCl_3(H_2O)_3]$.[13]

The experimental conditions required to isolate each complex as well as band position in the UV−vis region are given in Table 1. The different starting species were prepared using $CrCl_3{\cdot}6H_2O$ from Merck reagents p.a., as received.

2.2. Measurements of X-ray Absorption Spectra and Data Analysis. X-ray absorption measurements were recorded at the K-absorption edge of Cr (edge position 5989 eV) at the EXAFS station 8.1 (dipole radiation, focusing optics) of the Synchrotron Radiation Source (Daresbury Laboratory, U.K.) with ring energy of 2 GeV and ring current of 200 mA. The station operated with a double-crystal monochromator Si [220] which was detuned 30% in intensity to minimize the presence of higher harmonics. Calibration of the monochromator was carried out using a Cr foil. Resolution was estimated to be about 1.0 eV by the sharp pre-edge peak of the spectrum of chromate ions.

Optimized ion chambers, filled with the appropriate He/Ar mixtures to absorb 20% intensity in I_o (15 Torr of Ar) and 80% intensity in I_t (109 Torr of Ar), were used as detectors in the transmission experiments. Each datum point was collected for 1 s and several scans were averaged,

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thus minimizing high- and low-frequency noise. The most dilute solutions (0.005 *m*) were recorded in fluorescence mode using a solid state detector, a Canberra 13-elements formed by high-purity germanium array, the output being fed via shaping amplifier to a multichannel analyzer.

Three solutions containing species [I], [II], or [III] were prepared following the procedures described above, and monitorized by UV−vis spectroscopy before and after the recording of the spectra to ensure that no significant amounts of the other species were present in the solution. The concentration of the investigated species in the measured solution was conditioned by the synthesis method for species [I] and [III]. Thus we had to measure diluted (0.005 *m*) or concentrated (1 *m*) solutions, containing species [III] and [I], respectively. Since there were no restrictions in the concentration for aqueous solutions of [II], we measured solutions with both concentrations to check if this magnitude had some influence on the coordination parameters. The X-ray absorption spectra of the four solutions were recorded in specially designed metal-free EXAFS cells.[21,22] In the fluorescence mode depth of the liquid vein was kept constant at 2.5 mm. For transmission experiments the pathlength was selected according to the concentration of the solution being measured. The spectra of solids crystalline compounds $CrCl_3.H_2O$, $Cr(NO_3)_3{\cdot}9H_2O$, and anhydrous $CrCl_3$ were measured as obtained from Merck reagents p.a., under He in a solid EXAFS cell that allows "in situ" measurements under controlled atmosphere and/or temperature.[23] Detailed information about experimental procedures for measuring liquid and solid samples can be found in refs 10 and 23, respectively.

Standard procedures were used to perform pre-edge and background removal.[24] Inner potential was determined as the maximum of the first derivative at the edge region in the absorption spectrum. The EXAFS spectra were analyzed by using the function given by Stern et al.,[25] with the program XDAPS, from the University of Utrecht,[26] that carries out a nonlinear least squares fit. Errors in the structural parameters were calculated from the covariance matrix taking into account the statistical noise in the experimental EXAFS spectra and the correlation between the refined parameters. The quality of the fit was quantitatively determined by the goodness of fit value (ϵ_v^2) calculated as outlined in the workshop for "Standard and criteria for EXAFS data analysis".[27]

Phase shifts and backscattering amplitude functions for the Cr−O pair were determined from the experimental spectrum of the crystalline hydrate $Cr(NO_3)_3{\cdot}9H_2O$, and for the Cr−Cl pair from the algorithm of McKale,[28] taking $S_o^2 = 0.7$, $\sigma = 0.0$. The suitability of this reference was checked in the fit of the EXAFS spectrum of anhydrous $CrCl_3$ solid salt. In this compound the first polyhedron around Cr^{3+} ions is formed by six chloride ions forming a distorted octahedron.[29] Due to this distortion, the EXAFS spectrum cannot be used to obtain the phase shifts and backscattering amplitude functions of Cr−Cl contributions (see Appendix).

3. Results

3.1. XANES Spectra. Figure 1 includes the XANES spectra of the solids chromium nitrate crystalline hydrate, $Cr(NO_3)_3{\cdot}9H_2O$ (Figure 1a), chromium chloride crystalline hydrate, $CrCl_3.6H_2O$ (Figure 1b), and anhydrous chromium chloride, $CrCl_3$ (Figure 1c). The local structure of each compound can be described as an octahedron formed by six oxygen atoms at 2.0 Å in $Cr(NO_3)_3{\cdot}9H_2O(s)$; four oxygen atoms at 2.0 Å and two chlorine atoms at 2.3 Å in $CrCl_3{\cdot}6H_2O(s)$ and six chlorine atoms, between 2.33 and 2.36 Å, in anhydrous $CrCl_3(s)$. These environments, will be called hereafter hexahydrate, dichlorotetrahydrate and hexachloro, respectively. The first two are very similar to the local structures of species [0] and [II] in solution.

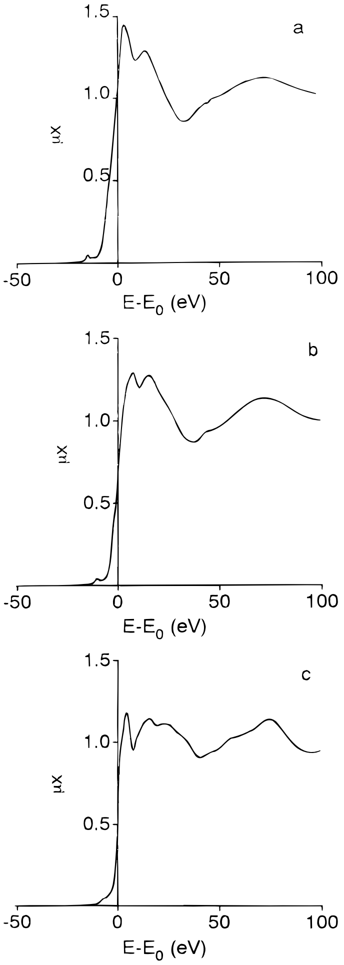

Figure 1. Normalized absorption spectra at the Cr−K edge, XANES region, of the following solid compounds: (a) $Cr(NO_3)_3{\cdot}9H_2O$, (b) $[CrCl_2(H_2O)_4]Cl{\cdot}2H_2O$, (c) $CrCl_3$.

Although the three spectra are quite similar, some differences can be observed between them, due to the inclusion of chloride ligands in the first coordination polyhedra, which generates new Cr−Cl distances and structural changes in the higher shells. In all the spectra appear small pre-edge features that are similar, although less intense, than those observed in other transition metal compounds presenting distorted octahedral symmetry, *e.g.* the TiO_2 crystalline forms anatase and rutile.[30] In the anhydrous chloride, these features are not a separate peak, but a small shoulder.

The edge, itself, does not show any shoulder nor inflexion points. In the hexahydrate (Figure 1a) and dichlorotetrahydrate (Figure 1b) two peaks appear just after the edge, at approximately 5 and 15 eV, having the same intensity the second peak for both species, whereas the peak at 5 eV is more intense in the hexahydrate. For the hexachloro (Figure 1c), an additional peak is observed at 25 eV, wider and less intense than the other two. Another effect of the increasing number of chloride ions is the decrease in the intensity of the edge peaks, as compared to the intensity in the EXAFS region.

The XANES spectra for species [0], [I], [II], and [III] in solution are plotted in Figure 2. The main tendencies observed

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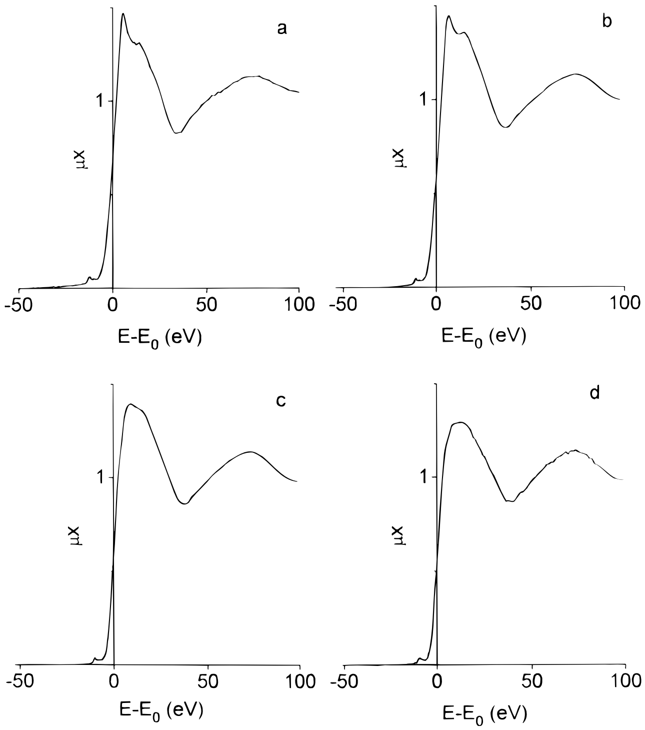

Figure 2. Normalized absorption spectra at the Cr−K edge, XANES region, of the following species in aqueous solution (a) $[Cr(H_2O)_6]^{3+}$ (0.01 *m*); (b) $[CrCl(H_2O)_5]^{2+}$ (1 *m*); (c) $[CrCl_2(H_2O)_4]^+$ (0.005 *m*); (d) $[CrCl_3(H_2O)_3]$ (0.005 *m*).

in the spectra of the solid compounds are maintained in the spectra of the chloroaquo complexes in aqueous solutions, although the features after the edge are less resolved in this case. Moreover the minimum after the edge, appearing in the solids at around 35−40 eV, is more pronounced in solution. The small prepeaks appear in the four species, and the peaks after the edge at around 5 and 15 eV present different intensities in the hexaaquo and monochloro species [0] and [I] (Figure 2, parts a and b), respectively, and are merged in the dichloro and trichloro species [II] and [III] (Figure 2, parts c and d), respectively.

3.2. EXAFS Spectra. The EXAFS data of the solid samples containing hexahydrate, dichlorotetrahydrate, and hexachloro entities are plotted in Figure 3, while the corresponding spectra of the solutions containing species [I] (1 *m*), [II] (1 and 0.005 *m*), and [III] (0.005 *m*) appear in Figure 4.

As can be seen in both figures, the inclusion of chloride ions induces changes both in node position and backscattering amplitude of the EXAFS functions. Figure 5, including the magnitude of the uncorrected Fourier transform (FT) of the EXAFS spectra of species [I]−[III] in solution, shows that increasing the number of inner-shell chloride ligands produces a widening and a shift to larger distances of the main peak in the FT. Another significant change is observed in these FT's: the shift to higher R values of the peak corresponding to a second coordination/hydration sphere and the increase in intensity of this peak in species [III]. (The word *sphere* will be used here to define a complete coordination environment, while the word *shell* will be used when referring to a separate contribution to the EXAFS spectrum. Thus, in the chloropentaaquo the first coordination *sphere* is formed by two *shells* in the EXAFS spectrum, one shell formed by five Cr−O contributions and the other shell by one Cr−Cl contribution.)

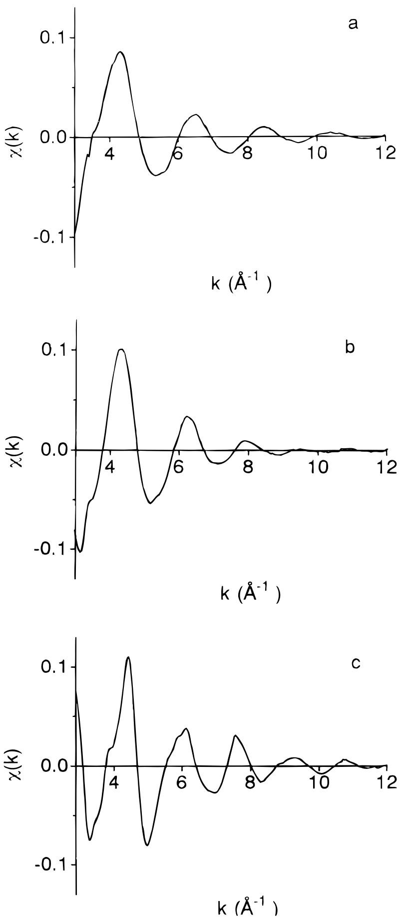

Figure 3. Raw EXAFS spectra of the Cr−K edge of the following crystalline solids: (a) $Cr(NO_3)_3{\cdot}9H_2O$, (b) $[CrCl_2(H_2O)_4]Cl{\cdot}2H_2O$, (c) $CrCl_3$.

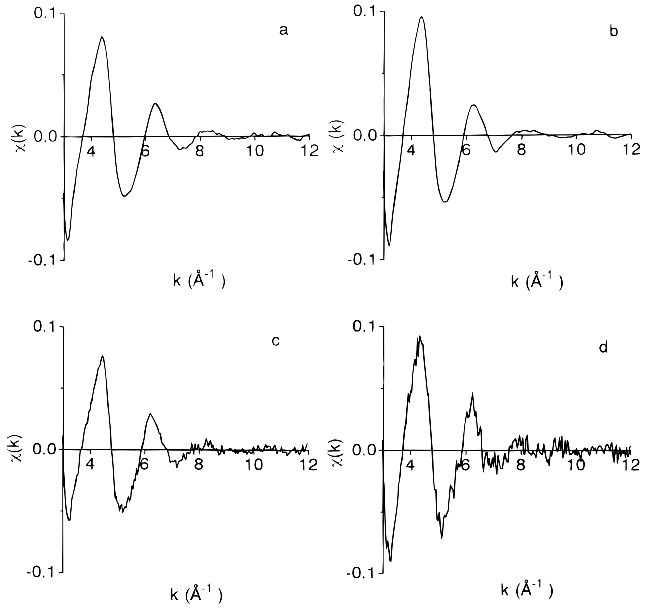

Figure 4. Raw EXAFS spectra of the Cr−K edge of the aqueous solutions containing the following species: (a) $[CrCl(H_2O)_5]^{2+}$ (1 *m*); (b) $[CrCl_2(H_2O)_5]^+$ (1 *m*); (c) $[CrCl_2(H_2O)_4]^+$ (0.005 *m*); (d) $[CrCl_3(H_2O)_3]$ (0.005 *m*).

Good reproductions of the EXAFS data in species [I], [II], and [III] are obtained with three or four shell fits. These shells have been included gradually according to the quality of the fits and to the amplitude of the residuals. No restrictions were imposed during the fitting procedure, *i.e.* four parameters were varied freely within each coordination shell, and thus, the analysis produced spontaneously the values described below. Fitting parameters and standard deviations of species [I], [II],

Table 2. EXAFS Coordination Parameters[a]

species	shell	N	R/Å	$\Delta\sigma^2$/Å^2	ΔE_o/eV
$[CrCl(H_2O)_5]^{2+}$, 1 *m*, [I]	Cr–O_1	5.1 ± 0.9	1.98 ± 0.04	0.0012 ± 0.001	4.9 ± 3.1
	Cr–Cl_1	1.2 ± 0.5	2.26 ± 0.05	0.0039 ± 0.003	−1.1 ± 2.0
	Cr–O_2	13.9 ± 0.8	3.97 ± 0.02	0.0090 ± 0.002	3.8 ± 0.5
$[CrCl_2(H_2O)_4]^{+}$, 1 *m*, [II]	Cr–O_1	4.2 ± 0.7	1.99 ± 0.03	0.0001 ± 0.001	3.5 ± 2.9
	Cr–Cl_1	2.3 ± 0.5	2.30 ± 0.03	0.0070 ± 0.002	−2.9 ± 0.9
	Cr–O_2	8.0 ± 1.6	3.89 ± 0.06	0.0040 ± 0.004	7.6 ± 2.0
	Cr–Cl_2	3.3 ± 0.7	4.36 ± 0.07	0.0100 ± 0.005	−1.4 ± 1.4
$[CrCl_2(H_2O)_4]^{+}$, 0.005 *m*, [II]	Cr–O_1	4.0 ± 0.5	1.99 ± 0.02	0.0001 ± 0.001	7.9 ± 3.4
	Cr–Cl_1	1.9 ± 0.5	2.31 ± 0.02	0.0075 ± 0.003	−6.6 ± 1.7
	Cr–O_2	7.2 ± 1.6	3.88 ± 0.04	0.0035 ± 0.005	8.7 ± 2.4
	Cr–Cl_2	4.9 ± 0.6	4.43 ± 0.02	0.0087 ± 0.004	−5.7 ± 0.8
$[CrCl_3(H_2O)_3]$, 0.005 *m*, [III]	Cr–O_1	3.2 ± 0.9	1.98 ± 0.07	0.0015 ± 0.002	10.0 ± 6.0
	Cr–Cl_1	3.0 ± 0.5	2.29 ± 0.03	0.0058 ± 0.001	−3.1 ± 1.2
	Cr–Cl_2	7.0 ± 0.5	4.29 ± 0.02	0.0069 ± 0.002	−1.0 ± 0.4
$[Cr(H_2O)_6]^{3+}$, 0.01 *m*, [0][b]	Cr–O_1	6.0 ± 0.11	2.00 ± 0.01	0.000 ± 0.0004	1.05 ± 0.3
	Cr–O_2	13.5 ± 1.16	4.02 ± 0.08	0.011 ± 0.003	1.00 ± 0.71

		N_{min}	N_{max}	R_{min}	R_{max}	$\Delta\sigma^2_{min}$	$\Delta\sigma^2_{max}$	$(\Delta E_o)_{min}$	$(\Delta E_o)_{max}$
$[Cr(H_2O)_6]^{3+}$, 0.005–2.5 *m*,[0][b]	Cr–O_1	6.0	6.4	2.00	2.01	0.0000	0.002	−0.8	1.05
	Cr–O_2	13.1	13.6	3.95	4.02	0.0083	0.014	−0.04	1.00

[a] *N*, coordination number; *R*, coordination distance; $\Delta\sigma^2$, Debye-Waller factor; ΔE_o, inner potential correction. Standard deviations were calculated from the covariance matrix and estimates of the noise level in the scans. [b] Data taken from ref 10.

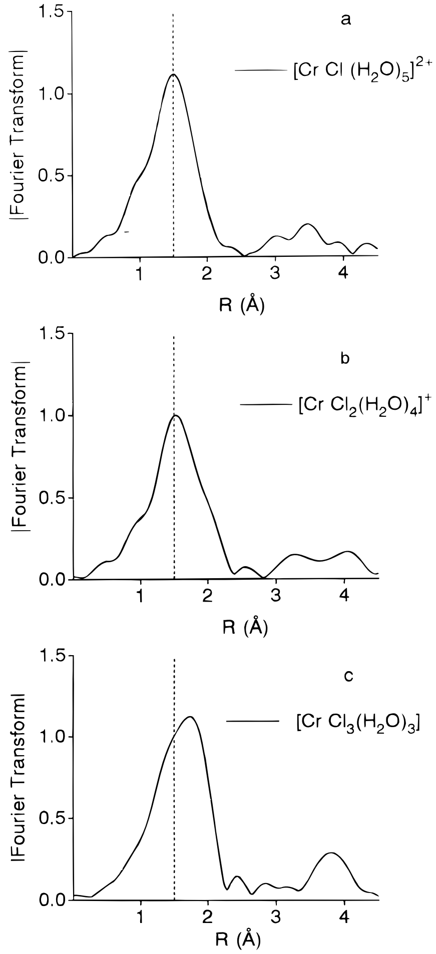

Figure 5. Modulus of the uncorrected Fourier transform of the EXAFS spectrum of the species indicated: (Δk = 2.9–11.0 Å^{-1}): (a) species [I], (b) species [II]; (c) species [III] (vertical dashed line at 1.5 Å is drawn for comparative purposes).

and [III] as well as that of species [0] measured in a wide range of concentrations taken from ref 10 are included in Table 2. There one can see that in species [I], $[CrCl(H_2O)_5]^{2+}$, the first coordination sphere is formed by two contributions, 5.1 Cr–O_1 at around 2.0 Å and 1.2 Cr–Cl_1 at 2.3 Å, while the second coordination sphere is formed by 13.9 Cr–O_2 contributions at 4.0 Å. This second coordination sphere is similar to that formed in aqueous solutions containing species [0], $[Cr(H_2O)_6]^{3+}$, in a wide range of concentrations.[10]

As explained in the experimental section, the EXAFS spectra of two solutions containing species [II] in different concentrations were analyzed. No significant differences in the fitting parameters of the first coordination sphere were obtained for both solutions. The second coordination sphere is formed by two shells in both cases, one similar to that formed in the hexaaquo and in the chloropentaaquo, but with a smaller coordination number and a new one formed by several chloride ions at around 4.4 Å. In the 1 *m* solution, the coordination number for Cr–Cl_2 is smaller than that of the 0.005 *m* solution, and for Cr–O_2 is higher. As explained in the Discussion, this change can be related to the variations in the ratio [free Cl^-]/[II] in both solutions.

Finally, the best fit for species [III] is obtained with a three-shell fit, two shells corresponding to the first coordination sphere, 3.2 Cr–O_1 at 2.0 Å and 3.0 Cr–Cl_1 at 2.3 Å, and the third, corresponding to the second coordination sphere around Cr^{3+} ions, formed by 7 Cr–Cl_2 bonds at 4.3 Å. This third shell resembles strongly, both in position and amplitude, the third shell of the EXAFS spectrum of anhydrous $CrCl_3$ in solid state, included in Figure 6, representing the absolute and imaginary parts of the uncorrected Fourier transform of the EXAFS spectrum. Previous X-ray diffraction studies[29] of this compound have shown that the first coordination sphere is formed by six chloride atoms at around 2.3 Å, the second by three chromium atoms at 3.4 Å and the third by six to eight chloride atoms at around 4.3 Å.

Additional information, such as Fourier filtering and fitting ranges, actual noise level and goodness of fit values are included in Table 3. Raw EXAFS data were fitted in 1 *m* solution containing species [I] and [II], while the Fourier filtered data were fitted in 0.005 *m* solutions. These $\chi(k)$ functions were multiplied by k^2 in all cases.

Comparative plots in *k* and *R* spaces of the experimental spectra, either raw or Fourier filtered, and the best fit for species [I], [II] (0.005 *m*) and [III] appear in Figures 7, 8, and 9, respectively, showing that good fits were obtained in all cases.

Table 3. Data Analysis Parameters[a]

species, concn	filtering range Δk/Å^{-1}	filtering range ΔR/Å	analysis range, Δk/Å^{-1}	noise amplitude	ϵ_v^2	v
[I], 1 *m*	raw data were fitted		3.0−11.0	0.0015	5.3	10.4
[II], 1 *m*	raw data were fitted		3.0−11.0	0.0015	14.4	10.5
[II], 0.005 *m*	3.1−11	0.14−4.4	3.1−11.0	0.0025	1.1	6.4
[II], 0.005 *m*	3.0−11.2	0.1−4.3	3.0−11.0	0.003	1.5	10.4

[a] Noise amplitude for $\chi(k)$; ϵ_v^2, goodness of fit; v, degrees of freedom.

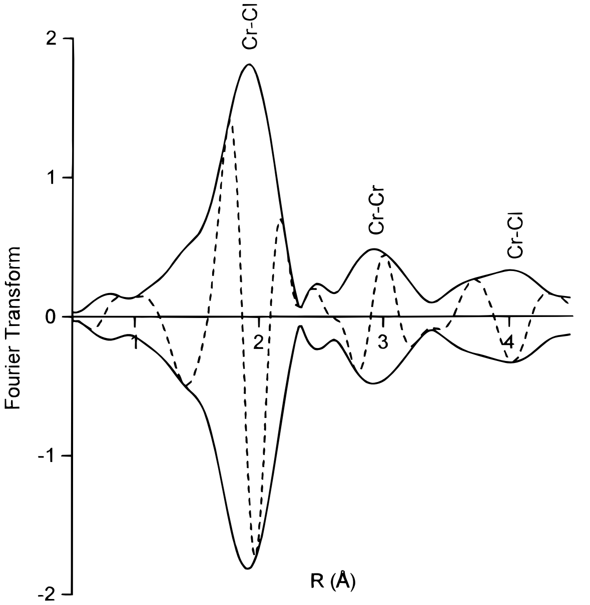

Figure 6. Modulus (solid line) and imaginary part (dashed line) of the uncorrected Fourier transform of the EXAFS spectrum of anhydrous $CrCl_3$ (Δk = 3.0−12.7 Å^{-1}).

Coordination distance for $Cr-O_1$ and $Cr-O_2$ contributions are the same within the limits of accuracy for species [0]−[III]. A slight tendency to decrease with the inclusion of chloride ligands in the first coordination sphere of Cr^{3+} ions can be observed for both contributions. Coordination distances for Cr−Cl contributions range between 2.26 and 2.31 Å for the first coordination sphere, and between 4.29 and 4.43 Å for the second. Both ranges are within the limits of accuracy. Debye−Waller factors for Cr−O contributions in the first and the second coordination spheres are similar to the values obtained in the aquo complexes,[9,10] $\Delta\sigma^2 = 0.0001-0.0015$ for $Cr-O_1$ and $\Delta\sigma^2 = 0.004-0.009$ for $Cr-O_2$. Debye−Waller factors for Cr−Cl shells are higher because phase and backscattering amplitude functions for these shells were derived from theoretical algorithms. Within each species these values are higher for the second sphere, $Cr-Cl_2$, than for the first, $Cr-Cl_1$. Inner potential corrections are close to 1 eV for the $Cr-O_1$ and $Cr-O_2$ in the aquo complexes, but with the inclusion of chloride ligands in the first coordination sphere, they increase in both spheres: to 4 eV in species [I], to 8 eV in species [II], and 10 eV for species [III]. For Cr−Cl contributions negative values are obtained in all cases, between −1.0 and −6 eV.

4. Discussion

4.1. First Coordination Sphere. The differences observed in the XANES region of the spectra, either in solid or liquid state, indicate substantial changes in the basic coordination polyhedron caused by the inclusion of chloride ligands in the inner-sphere complex. Likewise, the long-range order is reflected in the detailed structure of this region. Thus, in a detailed study of the Ti−K edge, where the effect of the cluster size around the absorbing atom in the features of the XANES region was analyzed, we observed that up to four shells were needed to reproduce all the features with the appropriate intensities.[31] Similarly, in the Cr−K edge, the long-range order existing in solid compounds determines the detailed features of the XANES region of the spectra shown in Figure 1, as compared to the smoothness observed in the spectra of solvated species (Figure 2), where only two coordination shells are identified.

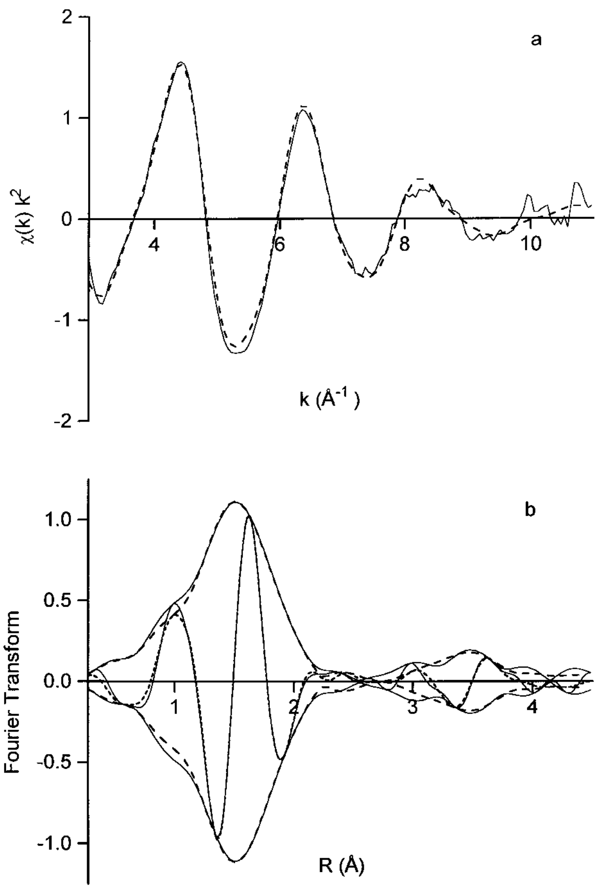

Figure 7. (a) k^2-weighted EXAFS raw data (solid line) and best fit with parameters included in Table 2 (dashed line) of $[CrCl(H_2O)_5]^{2+}$, 1 *m* aqueous solution, (b) Magnitude and imaginary part of the uncorrected Fourier transform of curves included in part a.

The study of the EXAFS spectrum for separate solutions containing species [I], [II], and [III] has provided a detailed picture of the Cr^{3+} inner-sphere chloroaquo complexes. This sphere is formed by Cr−O and Cr−Cl contributions, with bond distances differing in *ca.* 0.3 Å, which could have made difficult their resolution. But the differences in backscattering amplitude and phase shifts, they differ almost by π rad, has allowed the accurate determination of the structural parameters. Figure 10,

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[31] Bohr, F.; Ruíz-López, M. F.; Muñoz-Páez, A. *Catal. Lett.* **1993**, *20*, 59.

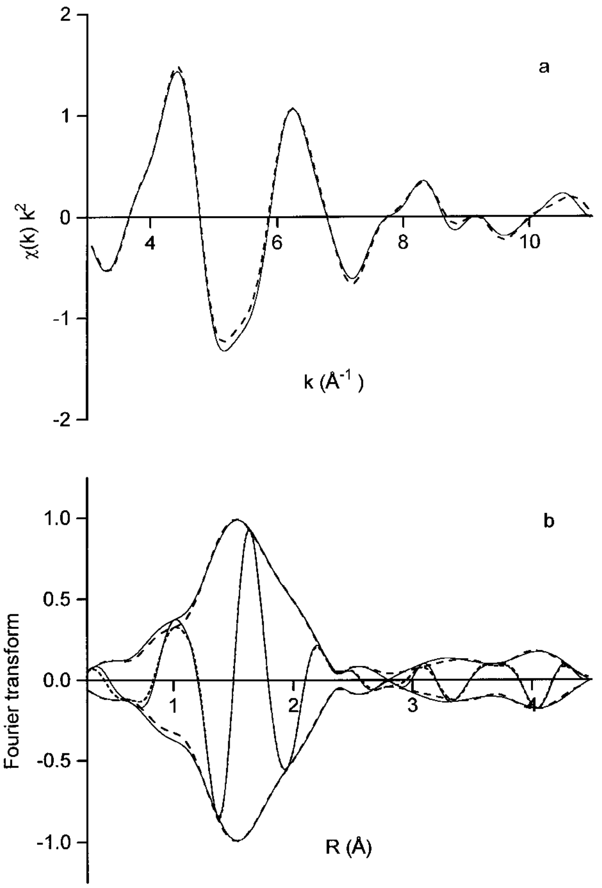

Figure 8. (a) k^2-weighted Fourier filtered EXAFS data (solid line) and best fit with parameters included in Table 2 (dashed line) of $[CrCl_2(H_2O)_4]^+$, 0.005 *m* aqueous solution. (b) Magnitude and imaginary part of the uncorrected Fourier transform of curves included in part a.

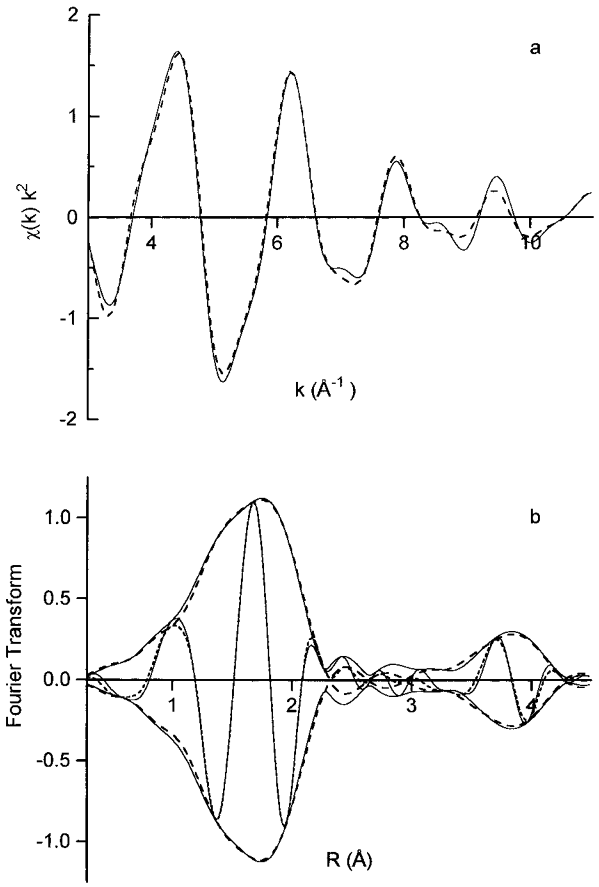

Figure 9. (a) k^2-weighted Fourier filtered EXAFS data (solid line) and best fit with parameters included in Table 2 (dashed line) of $[CrCl_3(H_2O)_3]$, 0.005 *m* aqueous solutions. (b) Magnitude and imaginary part of the uncorrected Fourier transform of curves included in part a.

parts a and b, including the comparative plots of the functions calculated for Cr−O$_1$ and Cr−Cl$_1$ EXAFS shells for species [I], [II], and [III] in *k* and *R* space respectively, show that although the distances are similar node positions in *k* space are very different due to the differences in phase shift. Likewise, the amplitude of Cr−Cl$_1$ contribution in species [I], where it is the minor component with coordination number 1 is not negligible versus Cr−O$_1$ contribution with coordination number 5.

In addition to the expected changes in coordination numbers for Cr−O$_1$ and Cr−Cl$_1$ (5 and 1, 4 and 2, and 3 and 3, for species [I], [II], and [III], respectively) the only fit parameter that changed systematically within the series was the inner potential correction, ΔE_o for Cr−O bonds, that increases with the number of chloride ions. Since ΔE_o can be related to the oxidation state of the absorbing atom, this increase can be explained as due to the partial electron charge transfer to Cr^{3+} ions induced by the inclusion of anionic ligands in the first coordination sphere.

In these complexes, coordination number was known, since the species present in each solution were identified through UV−vis spectroscopy, and partial information about coordination distances was available from the X-ray diffraction study of Magini.[12] In his pioneer work, this author obtains average values for the structural parameters of species [0], [I], [II], and [III] from a study of three solutions with different percentages of the four species. He gets average values of 1.97, 1.98, and 1.96 Å for Cr−O$_1$ coordination distance in each solution, showing respectively coordination numbers of (6−0.65), (6−1.1), and (6−1.5); similarly, he gets average values for coordination distances of 2.32, 2.32, and 2.30 Å and coordination numbers of 0.65, 1.1, and 1.5 for Cr−Cl contribution. This careful study provides one of the first insight into the structure of haloaquo complexes in aqueous solutions. The limitations imposed by the technique, both in concentrations and recording time, probably hampered the isolation and identification of each species separately. With a different technique, EXAFS, and taking as starting point Magini's results, we have overcome both problems.

Although no restrictions were imposed during our fitting procedure, the fits yielded spontaneously the values expected for coordination numbers and coordination distances consistent with the results reported by Magini.[12] The consistency of both sets of results was a confirmation of the structure of these species, but overall was an internal test of the quality of our data and analysis procedure. Moreover, since we obtained the coordination parameters for each species independently, we would have been able of detecting trends in Cr−Cl and Cr−O bond distances within the series in case they have appeared. Thus, our results complement those of Magini[12] since we obtained, independently, the parameters for each species and examined the structure of the complexes in solutions 2 orders of magnitude less concentrated than those studied by Magini. Likewise, our structural parameters are very similar to those obtained from the analysis of XRD data of the *trans* isomer of species [II] in solid state obtained by Dance *et al.*,[17] who find distances of 2.004 Å for Cr−O bonds and 2.289 Å for Cr−Cl$_1$ bonds. Similar Cr−Cl$_1$ distances are obtained by Morosin *et al.*[29] in crystalline anhydrous $CrCl_3$, in solid state as well. In this compound, the first coordination polyhedron around chromium ions is formed by a slightly distorted octahedron of chloride ions at an average distance of 2.34 Å. This value is

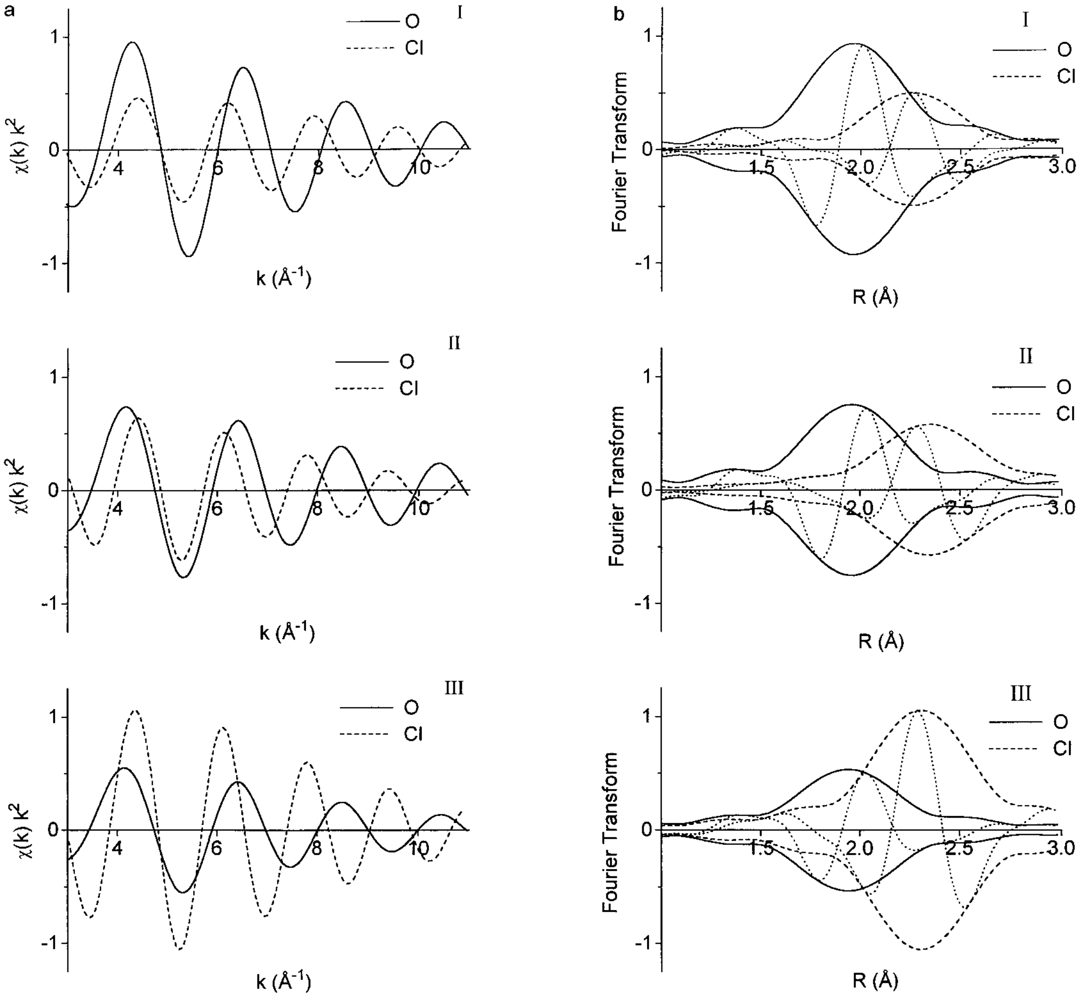

Figure 10. Contributions calculated for the first coordination sphere of chromochloroaquo complexes, species [I], [II], and [III]: (a) $\chi(k)\cdot k^2$ functions for Cr$-$O$_1$ (solid line); Cr$-$Cl$_1$ (dashed line); (b) Fourier transforms of curves included in part a. Cr$-$O$_1$ contributions: Cr$-$O phase corrected magnitude (solid line) and imaginary part (dotted line) of the FT's. Cr$-$Cl$_1$ contributions: Cr$-$Cl phase corrected magnitude (dashed line) and imaginary part (dotted line) of the FT's.

slightly longer than that detected in the dichlorotetrahydrate by Dance and by us in species [I]$-$[III]. This lengthening may be due to the fact that in the anhydrous salt, inner sphere chloride ligands are shared by several chromium ions, while in species [I]$-$[III] and in the chlorohydrate each chloride ion coordinates only one Cr^{3+} ion.

No similar studies of chromiumchloro octahedral complexes have been carried out using the EXAFS technique, but Beagley *et al.*[32] have used it to study the structure of MnBr$_2$ and MnCl$_2$ aqueous solutions. These authors do not analyze the structure of the isolated species, but rather they analyze solutions of different salt concentrations that present variable proportions of each chloroaquo complexes [MnCl$_n$(H$_2$O)$_{6-n}$]$^{(2-n)+}$, as Magini does. During the fitting procedure they determine the coordination number for the major contribution Mn$-$O, N_1, being used this value to calculate the coordination number for the Mn$-$Cl contributions, N$_2$ = 6 $-$ N_1, thus imposing the usual restriction in XRD studies of fixing the total coordination number for the first sphere. In the study of MnCl$_2$ salt solutions they obtain values for $N_2 \leq 1$ and observe, as in the present work, that the most reliable calculations are from solutions with the largest value of N_2 (3 in our case and 1 for their study). The main conclusions of their study are similar to ours. In contrast, in an EXAFS study of NiCl$_2$ aqueous solutions,[33] D. R. Sandström does not find evidence of first sphere halogen coordination to the cation, but finds three chloride ions coordinating the Ni^{2+} cations at 3.11 Å. This singular behavior of the Ni^{2+} ions in chloride environment is surprising taking into account that the crystalline hydrate [NiCl$_2$(H$_2$O)$_4$]·2H$_2$O(s) is isomorphous with the corresponding Cr^{3+} chlorohydrate,[17] in spite of the stoichiometric difference due to the different metal charges.

When studying the geometric structure of a series of octahedral complexes with two types of ligands, one tries to discriminate between the *cis*- and *trans*-isomers in the disubstituted complexes (species [II]), or the *fac*- and *mer*-isomers in the trisubstituted complexes (species [III]). Although the isomers of [II] can be separated and characterized spectroscopically in solution, they have an exchange rate high enough[34] to preclude the isolation of one of the isomers during the recording time needed by a conventional EXAFS spectrum. A similar situation appears for the isomers of species [III]. Therefore, for each species we have obtained average values of the structural parameters of the different isomers. Concerning species [I], the effect caused by the unique Cr$-$Cl bond on the *trans* Cr$-$O bond should lead to a distortion in the coordination polyhedron, where two different Cr$-$O distances would appear

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[32] Beagley, B.; McAuliffe, C. A.; Smith, S. P. B.; White, E. W. *J. Phys. Condens. Matter* **1991**, *3*, 7919.

[33] Sandström, D. R. *J. Chem. Phys.* **1979**, *71*, 2381.

[34] King, E. L.; Woods, M. J. M.; Gates, H. S. *J. Am. Chem. Soc.* **1958** *80*, 5015.

with relative intensity 4:1. In the case investigated this splitting of the Cr−O shell is beyond the limits of accuracy of the EXAFS technique and was not detected. An increase in the average $Cr-O_1$ distance would be detected if a lengthening in some of the $Cr-O_1$ distances happened due to the *trans* effect; but as observed in Table 2, this is not the case.

4.2. Second Coordination Sphere. Several authors have proposed the existence of outer-sphere complexes involving chloride anions.[35] The existence of such complexes, formed by an anion and the metal cation with its first coordination sphere intact, was postulated by Elving and Zemel[13] for $[Cr(H_2O)_4Cl_2]^+$ and by Gates and King[14] for $[Cr(H_2O)_6]^{3+}$ in the 1950s. The former authors explain the requirements of high concentrations of both H_3O^+ and Cl^- to obtain $[Cr(H_2O)_3Cl_3]$ from $[Cr(H_2O)_4Cl_2]^+$ as due to the formation of the outer-sphere complex $[Cr(H_2O)_4Cl_2]^+Cl^-$, while the latter explain the changes in the equilibrium quotient Q_1 of the formation reaction of $[Cr(H_2O)_5Cl]^{2+}$ as due to the formation of the outer-sphere complex $[Cr(H_2O)_6]^{3+}Cl^-$. On the other hand, according to other authors[35] the outer-sphere complexes formed between the anion and the metal cation with its first coordination sphere, are responsible for the spectral changes at wavelengths shorter than 250 μm induced by high concentrations of the anion in the solutions containing the inner-sphere aquo, amino, or chloroaquo complexes. Some of these authors explicitly discard the term "ion pair" to describe these species because it is not defined with respect to the constitution of the complex ion and offers no distinction between inner-sphere and outer-sphere forms of the associated species. Although the existence of these outer-sphere complexes was postulated more than 40 years ago, there had not been direct structural evidence of them until very recently when Grigoriew and Siekierski[15] and Yamaguchi *et al.*[16] detected them by XRD in concentrated solutions of $LaCl_3$ and LiCl, respectively.

On the contrary, there is abundant information about the structure of the second hydration spheres of aquo complexes, most part of it coming from X-ray and neutron diffraction.[5−7,36] As we have shown previously,[9−11] the EXAFS technique is capable of supplying information on this second hydration sphere and the examination of the changes for these complexes should reinforce our previous arguments

Therefore, our aim in this field was to determine how the second hydration sphere of Cr^{3+} hexahydrate was modified when some of the water molecules in the inner sphere were replaced by chloride ligands, and if outer-sphere complexes involving chloride anions were formed in solutions containing species [II] and [III]. These complexes cannot be formed in solutions containing species [0] and [I] because they were obtained from nitrate and sulfate salts, respectively, and no HCl was added during the synthesis process, thus, no free chloride ions were available in solutions containing both species.

In Table 2, the second hydration sphere detected in the solution containing species [I] is very similar both in structure (coordination number and distance) and kinetic stability (Debye−Waller factor) to the second hydration sphere of the hexaaquocomplex, species [0]. This similarity is an additional proof to those presented in ref 10 that the second peak in the radial distribution function (RDF) of the EXAFS spectra of aquo complexes is essentially due to a second hydration sphere and not to MS effects inside the first coordination sphere. In fact, the inclusion of a chloride ligand, a substantial change in the structure of this sphere that should cause changes in the MS paths, does not alter the second peak in the RDF, that is fitted with the same structural parameters.

In the second hydration sphere of species [II] there are decreases in coordination number, coordination distance, and Debye−Waller factor. But the most relevant change in the second coordination sphere is the appearance of a new $Cr-Cl_2$ shell at ∼4.4 Å. Since there were no clear precedents of this shell, we checked carefully the detection of this new $Cr-Cl_2$ contribution, repeating the analysis to discard alternative ascriptions. First of all, as can be seen in Figure 11a,b, including comparative plots in k and R spaces of $Cr-O_2$ and $Cr-Cl_2$ contributions calculated for solutions containing species [I], [II], and [III], the $Cr-Cl_2$ shell is considerably more intense than the $Cr-O_2$ shell of complexes [I] and [II]. Secondly, it can not be fitted as a Cr−O EXAFS contribution due to the differences in phase shift (nearly π rad) and backscattering amplitude for Cr−Cl and Cr−O contributions. As in the analysis of the first sphere, their fitting parameters were obtained spontaneously; what's more, for this sphere we had no preconceived idea of the possible values of coordination distances or coordination numbers of the $Cr-Cl_2$ shell. Only *a posteriori* we found that our structural parameters were similar to the values obtained by Dance and Freeman[17] in related solid compounds using XRD. Also a similar structure in which the inner-sphere complex is further coordinated by water molecules and chloride ligands has been described by Grigoriew *et al.*[15] in concentrated $LaCl_3$ solutions using XRD. The absolute values of the structural parameters obtained by them cannot be compared with our results because of the singular coordination of lanthanum—nine water molecules in the inner-sphere complex forming a tricapped trigonal prism—and its high radius—minimum distance La−O = 2.55 Å. But the model they propose for the bond structure of outer-sphere chloride ligands is compatible with our results. They have more information than we have because their best model pair function includes seven contributions, four of them including lanthanum, similar to our EXAFS shells, and three additional between water molecules and chloride ligands. In particular, the distance for one of these contributions $Cl\cdots H_2O$, at 3.2 Å corresponds to hydrogen bond formation. From this and other data, they deduce that outer-sphere chloride ligands must be hydrogen bonded to inner-sphere water molecules. Yamaguchi and colleagues[16] obtain a small shoulder in their XDR diffractogram corresponding to a concentrated LiCl aqueous solution, which is resolved as a $Li\cdots(OH_2)\cdots Cl$ contribution with a Li···Cl distance of 4.75 Å. Similarly, Dance and Freeman[17] in an XRD study of the crystalline solid $[CrCl_2(H_2O)_4]Cl\cdot 2H_2O$ detect external Cl^- ions hydrogen bonded to inner-sphere water molecules, the Cl···(H)O distance being 3.1 Å. These bond distances are within the range expected for chlorine atoms hydrogen bonded to water molecule.[37] The Cr^{3+} dichlorotetrahydrate studied by Dance presents a layer structure in which $[CrCl_2(H_2O)_4]^+$ units are linked by free chloride ions and water molecules. Every unit is surrounded by four others and each chloride anion is almost equidistant from the four octahedra containing the basic unit, the average $Cr-Cl_2$ distance being 4.5 Å.[17] Moreover, these authors give some hints about the structure of solutions containing the dichlorotetraaquo species, since they observe that the whole solid presents an open structure with cubic empty cages formed by the free chloride anions and water molecules

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[35] (a) Posey, F. A.; Taube, H. *J. Am. Chem. Soc.* **1956**, *78*, 15. (b) Taube, H.; Posey, F. A. *J. Am. Chem. Soc.* **1953**, *75*, 1463. (c) Adamson, A. W.; Wilkins, R. G. *J. Am. Chem. Soc.* **1954**, *76*, 3379. (d) Phipps, A. L.; Plane, R. A. *J. Am. Chem. Soc.* **1957**, *79*, 2458.

[36] Magini, M.; Licheri, G.; Paschina, G.; Piccaluga, G. *X-Ray Diffraction of Ions in Aqueous Solutions: Hydration and Complex Formation*; CRC Press: Boca Raton, FL, 1988.

[37] Pimentel, G. C.; Mcllan, A. L. *The Hydrogen Bond*; Freeman: San Francisco, CA, 1960; Chapter 9.

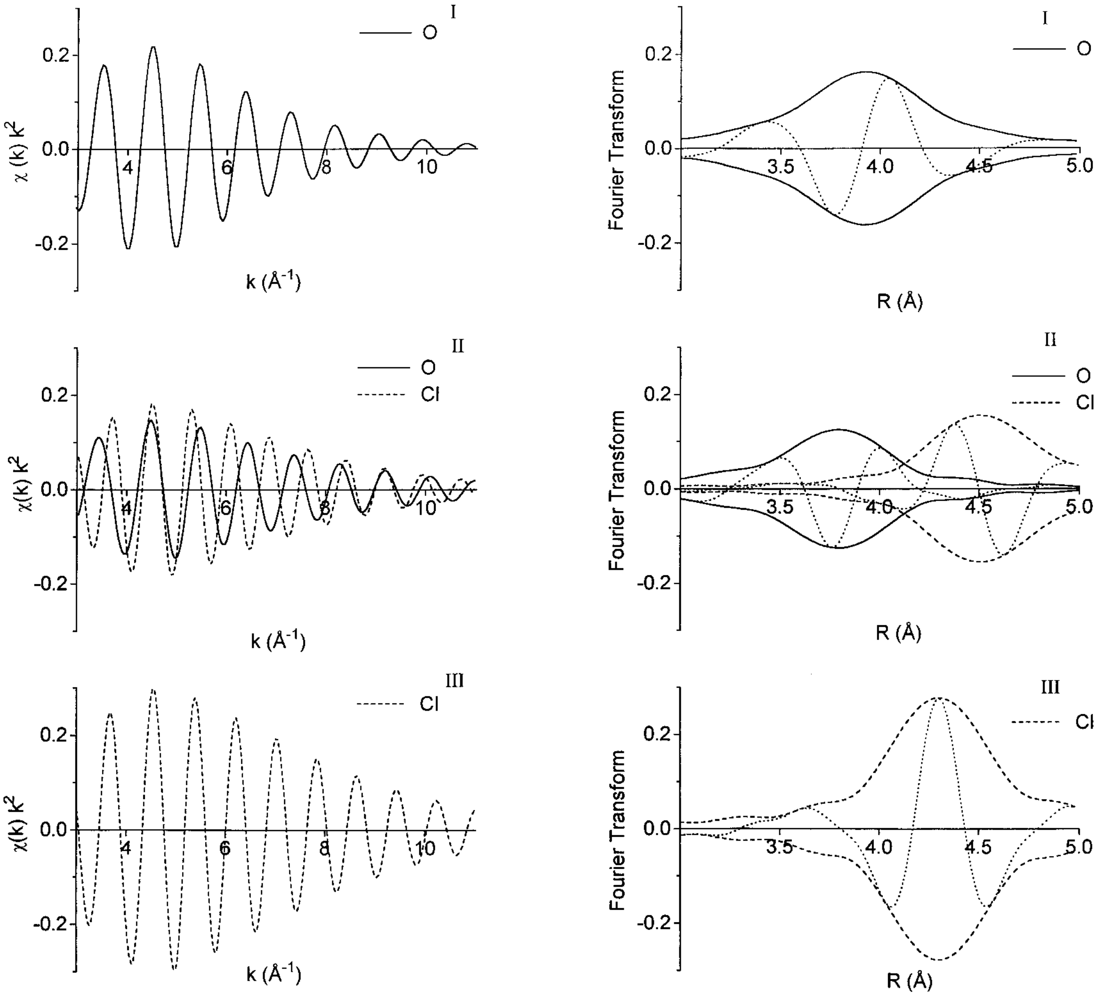

Figure 11. Contributions calculated for the second coordination sphere of chromochloroaquo complexes, species [I], [II], and [III]: (a) $\chi(k)\cdot k^2$ functions for $Cr-O_2$ (solid line); $Cr-Cl_2$ (dashed line); (b) Fourier transforms of curves included in part a. $Cr-O_2$ contributions: Cr−O phase corrected magnitude (solid line) and imaginary part (dotted line) of the FT's. $Cr-Cl_2$ contributions: Cr−Cl phase corrected magnitude (dashed line) and imaginary part (dotted line) of the FT's.

that, according to them, is maintained in small domains when the salt is dissolved in water. In a similar way, our outer-sphere chloride ligands can be hydrogen-bonded to the water molecules in the first coordination sphere. In a related compound, but without hydrogen bonds, anhydrous $CrCl_3$ chromium cations are coordinated in the third shell by eight Cl^- at distances within the range 4.2−4.5 Å.[29]

The effect of the complex concentration on the coordination number of this shell deserves some comments. In both solutions pH, and therefore hydrogen chloride concentration, were similar. But the concentration of the complex was quite different, and consequently, the ratio [free Cl^-]/$[CrCl_2(H_2O)_4]^+$ was considerably greater for the most dilute solution. Thus, in this case more chloride ions were available to coordinate species [II], and consequently, a higher coordination number was obtained for this shell in the solution in which the concentration of the complex was smaller, $[CrCl_2(H_2O)_4{}^+] = 0.005\ m$.

In solution containing species [III], the second hydration sphere is not detected but appears a well-defined (see Figure 5c) coordination sphere formed by seven chloride ions at 4.29 Å. This $Cr-Cl_2$ contribution is similar to that detected in solutions containing species [II], although the coordination number is higher and the distance is slightly shorter. The bond structure can be similar to that described for solutions containing species [II], with outer chloride anions hydrogen bonded to the inner-sphere water molecules. Nevertheless, given the high concentration of HCl (12 M) in this solution, hydrogen bonding could involve as well hydrogen ions.

Some authors have attributed the peak appearing at about 4 Å in the Fourier transform of the EXAFS spectra of aquo complexes to multiple scattering (MS) effects.[38] We have discussed elsewhere[10] the weak points of this ascription, that although plausible, requires a careful and detailed study. In chromium chloroaquo complexes the ascription of peaks at high *R* to MS effects is even more unlikely. In fact, existing two different distances in the first coordination polyhedron, Cr−Cl at 2.3 Å and Cr−O at 2.0 Å, the pathlengths for the possible double scattering phenomena, the most relevant contribution to MS in aquo complexes, would be 4.0, 4.3, and 4.6 Å if one includes $2Cr-O_1$, $1Cr-O_1 + 1Cr-Cl_1$, and $2\ Cr-Cl_1$, respectively. Thus, in a complex having three chloride ions and three water molecules in the first coordination sphere, the contributions from double scattering would be an average of these distances, and then the signal would be smeared out, even if these contributions were significant.

The quality of the fit of species [II] and [III], the amplitude of $Cr-Cl_2$ contribution, the standard deviations of the fitting parameters and the similarities of these parameters with the values in the crystalline solids allow us to confirm the formation

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(38) (a) Benfatto, M.; Natoli, C. R.; Bianconi, A.; García, J.; Marcelli, A.; Fanfoni, M.; Davoli, I. *Phys. Rev. B* **1986**, *34*, 5774. (b) Filiponi, A.; D'Angelo, P.; Viorel Pavel, N.; Di Cicco, A. *Chem. Phys. Lett.* **1994**, *225*, 150.

of outer-sphere complexes involving chloride ligands in solutions containing $[CrCl_n(H_2O)_{6-n}]^{(3-n)+}$ species.

Concluding Remarks

The structure of inner-sphere Cr^{3+} chloroaquo complexes $[CrCl_n(H_2O)_{6-n}]^{(3-n)+}$, $n = 1-3$, the further ordering of water molecules around them and the existence of outer-sphere chloride ligands have been investigated with the aid of EXAFS. The accurate determination of coordination parameters for each species was allowed since they were obtained from solutions containing only one of them. It was shown that the sensitivity of the technique allows the structural resolution of the local environment of ions whose concentration is 2 orders of magnitude smaller than that needed for the diffraction studies.

The inner-sphere complexes can be described as formed by $5H_2O + 1Cl^-$ (species [I]), $4H_2O + 2Cl^-$ (species [II]), and $3H_2O + 3Cl^-$ (species [III]) at average Cr−O and Cr−Cl distances of 2.00 and 2.30 Å, respectively. These results obtained spontaneously during the fitting procedure without imposing restrictions to coordination numbers nor to coordination distances are consistent with previous XRD studies of related compounds in aqueous solutions[12] and in solid state.[17,29] No significant change is observed in these distances either within the series, nor with the concentration (0.005 *m* and 1 *m*) in the case of species [II].

In all solutions, ordering beyond the first coordination sphere has been detected between 3.9 and 4.5 Å. For solution containing species [I], this sphere is formed only by water molecules, is quite similar to the second hydration shell previously detected by us in the $Cr(NO_3)_3$ aqueous solutions,[9,10] and is also quite similar to the second hydration shell observed in perchlorate and nitrate aqueous solutions of many divalent and trivalent cations.[6,7,36] For the two solutions (0.005 and 1 *m*) containing species [II], there is a contraction in $Cr-O_2$ distance ($R = 3.88-3.89$ Å) and a decrease in coordination number of this second hydration shell. Outer-sphere chloride ligands appear in the second coordination sphere of species [II] at 4.4 Å. The number of chloride anions (five in the 0.005 *m* solution and three in the 1 *m*) is a function of the ratio $[\text{free } Cl^-]/[CrCl_2(H_2O)_4{}^+]$. For solution containing species [III], the second coordination sphere is formed only by seven chloride anions at 4.3 Å. Similar outer-sphere complexes involving chloride ligands have been detected in $LaCl_3$ and LiCl aqueous solutions by XRD.[15,16] A $Cr-Cl_2$ contribution at 4.5 Å has been detected as well in the crystalline compound $[CrCl_2(H_2O)_4]Cl\cdot 2H_2O$ and in anhydrous $CrCl_3$ by XRD.[17,29]

These results report structural evidences of the existence of the outer-sphere complexes involving chloride ligands postulated by several authors more than 40 years ago. Moreover they provide additional information—coordination numbers and distances—on these outer-sphere complexes, which are said to have an important role in the reactivity of solutions. Even more, they represent a further step in the knowledge of the structure of solutions and show the capabilities of the EXAFS technique, a powerful tool in this field.

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Appendix

References for Cr−Cl Contributions Used in the EXAFS Data Analysis. In a first stage, phase and backscattering amplitude functions for Cr−Cl contribution was obtained from the EXAFS spectrum of anhydrous $CrCl_3$ included in Figure 6, in which the first coordination polyhedron is formed by six chloride anions. But meaningless fits of the EXAFS spectra of chloroaqoucomplexes were obtained with these reference functions. On the other hand, the coordination number obtained in the fit of the first shell of anhydrous $CrCl_3$ using the functions obtained theoretically, either using the algorithm of Rehr[39] of that of McKale,[28] was smaller than 6.

A detailed study of the X-ray pattern of this compound revealed some inconsistencies. The X-ray diffractogram we recorded had more peaks than that included in the corresponding ASTM Tables (6−0535), and some of the peaks were shifted in position. An early X-ray diffraction study of this compound described the first coordination sphere as a symmetric octahedron formed by six chloride ions at 2.371 Å.[40] Nevertheless, a more recent study[29] proposed two crystalline structures, each showing slightly distorted octahedra, the first formed by 3Cr−Cl at 2.329 Å ⊕ 3Cr−Cl at 2.365 Å, and the second formed by 2Cr−Cl at 2.340 Å ⊕ 2Cr−Cl at 2.342 Å ⊕ 2Cr−Cl at 2.348 Å. Taking into account these diffraction data and given the difficulties in isolating one of the crystalline phases, we carried out the fit of the first coordination sphere of the anhydrous $CrCl_3(s)$ by introducing two EXAFS shells. Distances were averaged from the crystallographic data ($\Delta R \simeq 0.02$ Å), and the phase and backscattering amplitude functions were calculated theoretically by means of McKale's algorithm.[28] A good fit was obtained with the first shell formed by 3.13 Cr−Cl at 2.335 Å ($\Delta\sigma^2 = 0.0035$ Å^2) and the second one by 2.80 Cr−Cl at 2.356 Å ($\Delta\sigma^2 = 0.0055$ Å^2).

From these results we confirmed that the structure of the $CrCl_3$ phase, for which we recorded the EXAFS spectrum, presented a nonsymmetric coordination polyhedron of chloride ions around chromium atoms, as already observed in Morosin's XRD study.[29] But, overall we checked the validity of the McKale reference functions to fit Cr−Cl contributions. The functions derived from Rehr's algorithm[39] do not work for the Cr−O nor for the Cr−Cl contribution, although the efficiency of this algorithm has been satisfactorily verified by the authors for many other reference functions obtained to fit contributions such as Lu−Lu,[41] Lu−Si,[42] Zn−O, Ga−O, Rh−O,[11] and Pt-N.[23]

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