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Composition and Structure of Polynuclear Chromium(III) Hydroxo Complexes

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The structures of the polynuclear hydrolysis complexes of chromium(III) formed in acidic and alkaline aqueous solution have been determined by means of extended X-ray absorption fine structure and large angle X-ray scattering. Chromium(III) is present as mononuclear hydrated ions below pH 3−4, with the upper limit depending on concentration, ionic strength, and temperature. Chromium(III) hydrolyzes in aqueous solution above this pH in concentrated aged solutions to mainly cationic tetrameric complexes containing both single and double hydroxo bridges between the chromium(III) ions. Above pH 5, the solubility of chromium(III) decreases sharply to form solid hydrated chromium(III) hydroxide. The solubility of chromium(III) increases sharply at elevated pH, and fairly concentrated solutions can be prepared in concentrated aqueous solutions of sodium hydroxide. According to the literature, mononuclear tetrahydroxochromate(III) complexes, $Cr(OH)_4^-$, are formed in alkaline aqueous solution. However, this study shows polymeric chains of six-coordinated chromium(III) ions connected through double hydroxo bridges and with two terminal hydroxo groups giving an overall composition of $(Cr(OH)_4)_n^{n-}$. This polymer is stable for a long time in solution at pH=15. However, at pH < 15, this polymer precipitates slowly with time, over months, to an amorphous phase with a structure around chromium similar to that in α-chromium(III) oxide hydroxide.

Introduction

Chromium has a wide range of industrial applications, being a component in stainless steel as the most important one. An important area of application of chromium(III) salts is the tanning industry, unfortunately producing large quantities of chromium(III)-containing waste.[1] The main discharge of chromium(III) waste comes however from the metal industry. The two common oxidation states of chromium, +III and +VI, are toxic for both plants and animals, with chromium(VI) being 1000 times more toxic than chromium(III).[2] The mechanism of toxicity is pH-dependent.[3] Chromium(VI) is more mobile in soils than chromium(III), but it is usually reduced to chromium(III) compounds within a short period of time.[4] Chromium(III) is an essential trace element for humans. Together with insulin, it removes glucose from the blood and plays a vital role in fat metabolism.[5] However, long exposure to chromium(III) compounds may result in dermatitis and liver or kidney damage in humans and is thereby toxic in large doses.[6,7] It has been shown that chromium(III) oxide may cause lung and throat cancer.[8] The large interest in chromium(III) hydrolysis over the years has been caused by the uncertainties and complexity of hydrolytic polymerization processes together with the fact that chromium(III) is one of the contaminant metal ions hazardous for the environment; the removal of chromium(III) from industrial waste waters is a challenge.[9] The solubility of chromium(III) decreases sharply above pH 5, forming hydrated chromium(III) hydroxide, $Cr(OH)_3 \cdot 3H_2O$,[10] which is transferred to dehydrated oxyhydroxide, $CrO_{(3-x)/2}(OH)_x$, and finally to chromium(III) oxide, Cr_2O_3, upon heating and aging.[11] Chromium(III) is regarded as toxic, but due to the low solubility in water at neutral pH, it is not regarded as a hazardous material, in contradiction to chromium(VI) compounds, in neutral waters. However, the solubilities of chromium(III) compounds increase with

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increasing acidity and alkalinity due to the formation of charged hydrolysis complexes. The hydrated chromium(III) ion hydrolyzes fairly easily starting at pH 2−4, depending on the total concentration, temperature, and ionic strength and medium; pK_{a1} values of 4.1−4.3 are reported at 25 °C and infinite dilution.[10,12]

The hydrolysis of chromium(III) in slightly acidic aqueous solution results in the formation of monomeric, dimeric ($[Cr_2(OH)_2]^{4+}$), trimeric ($[Cr_3(OH)_4]^{5+}$), and tetrameric ($[Cr_4(OH)_6]^{6+}$) species.[13] The first acidic constants, pK_{a1}, of these complexes were determined to be 4.39, 3.68, 4.35, and 2.55, and the stability constants, log K, to be 5.1, 6.9, and 5.2 for the dimer, trimer, and tetramer, respectively.[13,14] This indicates that the tetramer, and in part the dimer, should form at the expense of the monomer and trimer at pH = 3.7. In another study, where 0.8 equiv of hydroxide was added to an acidic chromium(III) solution, the speciation was followed over four years. It was shown that the concentration of monomeric species decreased rapidly: the dimeric one reached a maximum after a few days, the trimeric one increased monotonously with time, and the tetrameric one became constant after some months.[14] Acidic cleavage of an alkaline chromium(III) solution, pH > 13, leads to the formation of mainly trimers.[15]

The structure of the hydrated chromium(III) ion is well established in both the solid state and aqueous solution, with an octahedral configuration around chromium(III) with water molecules and Cr−O mean bond distance of 1.963 Å, Table S1 (Supporting Information), and ca. 12 water molecules in the second hydration sphere with a mean $Cr\cdots O_{II}$ distance of 4.05 Å.[16] The hydrated chromium(III) ion, $Cr(H_2O)_6^{3+}$, is known for its kinetic inertness of water exchange, $k = 2.36 \times 10^{-6}$ s^{-1}, while the water exchange rate of the $Cr(H_2O)_5OH^{2+}$ complex is ca. 75 times faster, $k = 1.78 \times 10^{-4}$ s^{-1} at 298.15 K.[17] The water exchange of the hydrolyzed dimeric complex, $[(H_2O)_4Cr(OH)_2Cr(H_2O)_4]^{4+}$, is, further, twice as fast, $k = 3.6 \times 10^{-4}$ s^{-1}.[18]

A limited number of structures of hydrolyzed chromium(III) complexes have been reported in the solid state. Salts containing hexahydroxochromate(III) complexes, $[Cr(OH)_6]^{3-}$, precipitate from very alkaline solutions.[19−21] The mean Cr−O bond distance in these complexes is 2.010 Å, significantly longer than in the hexaaquachromium(III) ions due to the larger atomic radius of oxygen in the hydroxide ion than in the water molecule.[22] Six types of hydrolyzed chromium(III) complexes are reported in the solid state, dimers with a single hydroxo bridge, $[L_5Cr{-}OH{-}CrL_5]^{5+}$;[23−26] a single oxo bridge, $[L_5Cr{-}O{-}CrL_5]^{4+}$;[27] a double hydroxo bridge, $[L_4Cr{-}(OH)_2{-}CrL_4]^{4+}$;[28−34] or a triple hydroxo bridge, $[L_3Cr{-}(OH)_3{-}CrL_3]^{3+}$;[35] trimers with a double hydroxo bridge and two single hydroxo bridges to the third chromium, $[Cr_3(OH)_4L_{10}]^{5+}$;[34,36] and a tetramer with a double hydroxo bridge and four single hydroxo bridges to the remaining two chromium atoms, $[Cr_4(OH)_6L_{12}]^{6+}$, L = H_2O or NH_3;[37−39] see the summary in Table S2 (Supporting Information). The structures of the Cr−OH−Cr, $Cr{-}(OH)_2{-}Cr$, $Cr_3(OH)_4$, and $Cr_4(OH)_6$ entities seem to be independent whether or not the solvent molecule is water or ammonia. The $Cr\cdots Cr$ distances in these type of structures are different from each other, 3.85−3.88, 2.97−3.05, ca. 3.00/3.6, and 2.92−2.93/3.6 Å for the Cr−OH−Cr, $Cr{-}(OH)_2{-}Cr$, $Cr_3(OH)_4$, and $Cr_4(OH)_6$ entities, respectively.

The different types of hydrolysis species were separated and characterized by ion-exchange chromatography on a Sephadex SP C-25.[13,40] The structures of these complexes in aqueous solution were characterized by means of extended X-ray absorption fine structure (EXAFS).[41] The monomeric complex, $CrOH(H_2O)_5^{2+}$, was found to have the same mean Cr−O bond distance as the hydrated chromium(III) ion.[41] The $Cr\cdots Cr$ distance in the dimeric species, 2.98−2.99 Å, shows that it has a double hydroxo bridge; thus, the composition is $[(H_2O)_4Cr(OH)_2Cr(H_2O)_4]^{4+}$. The trimeric species is reported to have a single $Cr\cdots Cr$ distance, 2.98 Å, with double hydroxo bridges between all of the chromium(III) ions with the composition $[Cr_3(OH)_4(H_2O)_9]^{5+}$. Any structure of this kind of proposed trimer has not yet been described in the solid state.

The aim of this paper was to establish the structures of hydrolyzed chromium(III) species in a weakly acidic aqueous solution, pH = 2−4, sufficiently aged to have reached equilibrium, and in very alkaline aqueous solution, pH = 13−15, and to describe the stability of formed hydroxo complexes at high pH with time.

Experimental Section

Chemicals. Chromium(III) perchlorate hexahydrate, $[Cr(H_2O)_6](ClO_4)_3$ (Aldrich); concentrated perchloric acid (70%,

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Merck); and sodium hydroxide (Sigma) were used as purchased. Millipore filtered deionized water was used throughout the study.

Preparation of Solutions. Two series of aqueous solutions of chromium(III), total chromium(III) concentrations of ca. 0.1 and 1.0 mol dm^{-3}, were prepared by dissolving weighed amounts of perchlorate salt in water followed by the dropwise addition of sodium hydroxide solution, 1.0 and 0.1 mol dm^{-3}, under constant stirring to a predecided pH value, 2.2, 2.3, 2.4, 2.5, 2.6, 2.8, 3.0, 3.4, 3.5, 3.6, 3.7, and 3.8. The pH of the solutions was measured using an Orion Research 940 pH meter with a Ross glass electrode. The pH was adjusted over 45 days until a stable pH was reached. A pronounced color change from violet to dark green was observed from low to higher pH values, Figures S1 and S2 (Supporting Information). The LAXS measurements were performed in a chromium(III) perchlorate solution, with a pH of 3.7 and a total chromium(III) concentration of 0.98 mol dm^{-3}, stored for two years. Hydrolyzed chromium(III) solutions in 0.1, 0.5, 1.0, 5.0, and 10.0 mol dm^{-3} sodium hydroxide were prepared by dissolving weighted amounts of solid hexaaquachromium(III) perchlorate to a total chromium(III) concentration of 0.1 mol dm^{-3} directly in the sodium hydroxide solutions, giving transparent green solutions. The solution in 10.0 mol dm^{-3} sodium hydroxide was stable for at least half a year, while the other solutions were transparent for about one week, but thereafter, visible turbidity was observed. However, if undissolved crystals remain in the pH = 15 solution, a green amorphous gel-like phase precipitates out over time, ca. two months, until the chromium(III) concentration in the aqueous phase is negligible. The solid phase formed in weak alkaline medium (0.1 mol dm^{-3} NaOH) is soluble in 10 mol dm^{-3} NaOH.

Methods. The two-cell dialysis method was used to determine the chromium(III) distribution between its mononuclear and polynuclear hydroxo forms in aqueous solution. The studied chromium(III) solutions were stored for at least 40 days for polymerization, as the formation of polynuclear hydroxo complexes of chromium(III) is established within this time.[42] Cellophane (Millipore) with a pore diameter of 2−4 nm was used as the semipermeable membrane. The duration of the dialysis experiments was 4 days. It was shown that this time is required to reach the distribution equilibrium of the ions between the compartments of the dialyzer. The total concentration of chromium(III) in the solutions was determined by atomic absorption spectroscopy. The results of dialysis were expressed as dialysis coefficients (K_{dial}) and retention percent (α_r) by the following equations:

$$K_{dial} = \frac{C_{outer}}{C_{inner}} \qquad (1)$$

where C_{inner} is the concentration of chromium(III) or a complexing anion in the "inner" solution of the dialyzer (dialyzate) and C_{outer} is the concentration in the "outer" solution (diffusate);

$$\alpha_r = \frac{1 - K_{dial}}{1 + K_{dial}} \times 100\% \qquad (2)$$

The amount of chromium(III) present as large colloidal particles and sediment was determined by centrifugation. The experiments were carried out using a laboratory centrifuge (OPn-8UHL4.2) at 8000 rpm for 30 min; the results are given as a centrifugation sedimentation percentage. The determination of the OH$^-$/Cr ratio in the polynuclear complex was carried out using potentiometric titrations by adding a sodium hydroxide solution, 0.050, 0.50, or 5.0 mol dm^{-3}, to a 0.1 mol dm^{-3} chromium(III) perchlorate solution.[43]

Table 1. Mean Bond Distances, d/Å; Temperature Coefficients, b/Å^2 (LAXS), or the Debye−Waller Coefficient, σ^2/Å^2 (EXAFS); and Number of Distances, N, in the LAXS and EXAFS Studies of the Hydrolyzed Chromium(III) in Aqueous Solution at pH = 3.7 and 15.0 at Room Temperature

species	interaction	d	b/σ^2	N
	Chromium(III) Perchlorate in Water, 0.98 mol dm^{-3}, pH = 3.7, LAXS			
$[Cr_4(OH)_6(H_2O)_{12}]^{6+}$	Cr−O	1.977(4)	0.0019(2)	6.0
	Cr···O$_{II}$	4.080(7)	0.0132(10)	6.0
	Cr···Cr	2.970(5)	0.0068(6)	0.25
	Cr···Cr	3.597(5)	0.0096(6)	1.0
Na^+ (aq)	Na−O	2.43(2)	0.022(2)	6
ClO_4^- (aq)	Cl−O	1.463(4)	0.0018(1)	4
	(Cl−)O···O	3.056(6)	0.0235(10)	12
	Cl−(O)···O	3.700(7)	0.0379(7)	12
water bulk	O···O	2.888(3)	0.0201(5)	2.0
	Chromium(III) Perchlorate in Water, 0.98 mol dm^{-3}, pH = 3.7, EXAFS			
$[Cr_4(OH)_6(H_2O)_{12}]^{6+}$	Cr−O	1.970(2)	0.0044(2)	6.0
	Cr···Cr	2.982(3)	0.0029(2)	0.5
	Cr···Cr	3.591(4)	0.0080(4)	2.0
	MS(CrO$_6$)	3.892(8)	0.012(2)	3 × 6
	Chromium(III) Perchlorate in Water, 0.20 mol dm^{-3}, pH = 15.0, EXAFS			
$[Cr(OH)_4]_n^{n-}$	Cr−O	1.998(2)	0.0022(2)	6.0
	Cr···Cr	2.982(3)	0.0029(2)	2.0
	MS(CrO$_6$)	3.97(3)	0.025(2)	3 × 6

The OH$^-$/Cr ratio was calculated by the formula OH$^-$/Cr = $(n(OH^-)_{Cr} - n(OH^-)_{blank})/n(Cr^{III})$, where $n(OH^-)_{Cr}$ is moles of sodium hydroxide used for the titration of chromium(III) solution, $n(OH^-)_{blank}$ is moles of sodium hydroxide used for titration of the solution without chromium(III), and $n(Cr^{III})$ is moles of chromium(III) in solution.

EXAFS: Data Collection. Chromium K edge X-ray absorption spectra were recorded at the wiggler beamline I811 at the MAXLab, Lund University, Lund, Sweden. The EXAFS station was equipped with a Si[111] double-crystal monochromator. The data collection was performed in transmission mode. Higher-order harmonics were reduced by detuning the second monochromator to 30% of the maximum intensity at the end of the scans. The solutions were contained in liquid cells consisting of a 1.0-mm-thick Teflon spacer and 6 μm polypropylene X-ray film. The energy scales of the X-ray absorption spectra were calibrated by assigning the first inflection point of the K edge of a chromium foil to 5989.0 eV.[44] For each sample, two scans with a measuring time of 90 min each were averaged, giving satisfactory data (k^3-weighted) in the k range 2−13 Å^{-1}. The EXAFSPAK program package[45] was used for the data treatment.

The standard deviations given for the refined parameters in Table 1 are obtained from k^3-weighted least-squares refinements of the EXAFS function $\chi(k)$ and do not include systematic errors of the measurements. These statistical error estimates

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provide a measure of the precision of the results and allow reasonable comparisons, for example, of the significance of relative shifts in the distances. However, the variations in the refined parameters, including the shift in the E_o value (for which $k = 0$), using different models and data ranges, indicate that the absolute accuracy of the distances given for the separate complexes is within ±0.005−0.02 Å for well-defined interactions. The "standard deviations" given in the text have been increased accordingly to include estimated additional effects of systematic errors.

Large-Angle X-Ray Scattering (LAXS). The scattering of Mo K$_\alpha$ X-ray radiation ($\lambda = 0.7107$ Å) from the free surfaces of an aqueous solution of hydrolyzed chromium(III) perchlorate was measured by means of a large-angle $\theta-\theta$ diffractometer. The solutions were contained in a Teflon cup inside an airtight radiation shield with beryllium windows. The scattered radiation was monochromatized in a focusing LiF crystal monochromator, and the intensity was measured at discrete points in the range $1 < \theta < 65°$. The scattering angle is 2θ. The number of counts accumulated was 100 000 at each preset angle, and the entire angular range was scanned twice, which corresponds to a statistical error of about 0.3%. The divergence of the primary X-ray beam was limited by 1 or 1/4° slits for different θ regions, with overlapping data for scaling purposes. The experimental setup and the theory of the data treatment and modeling have been presented elsewhere.[46] All data treatment was carried out by means of the KURVLR program.[47] The experimental intensities were normalized to a stoichiometric unit of volume containing one chromium atom, using the scattering factors f for neutral atoms, including corrections for anomalous dispersion,[48] $\Delta f'$ and $\Delta f''$, and values for Compton scattering.[49] Least squares refinements of the model parameters were carried out by means of the STEPLR program,[50] where the expression $U = \sum w(s)[s \cdot i_{\text{exp}}(s) - s \cdot i_{\text{calc}}(s)]^2$ is minimized. The refinement of the model parameters was made for data in the high s region where the intensity contribution from the long-range distances can be neglected.[51] In order to obtain a better alignment of the intensity function before the refinements, a Fourier back-transformation procedure was used to correct the $i_{\text{exp}}(s)$ functions by removing spurious nonphysical peaks below 1.2 Å in the experimental radial distribution function (RDF).[52]

Results and Discussion

Chromium(III) Hydrolysis in Aqueous Solution. The speciation of chromium(III) in aqueous solution has been studied in the pH range 2.0−5.2 at chromium(III) concentrations in the range 2×10^{-4} to 1.5×10^{-1} mol dm^{-3} by dialysis, ultrafiltration, and centrifugation, Figure 1, and UV−vis spectrophotometry, Figure S1 (Supporting Information). Retention and spectrophotometry data show that the formation of polynuclear hydroxo complexes proceeds in solution with increasing pH, Figure S1 (Supporting Information). Under these conditions, the precipitation of chromium(III) compounds is negligible according to centrifugation data; that is, chromium(III) is present as dissolved species under these conditions. Potentiometric pH titration data show that the number of OH$^-$ groups binding to polynuclear hydroxo chromium(III) complexes increases up to pH 4.0, but thereafter no further hydrolysis seems to take place, Figure 2. At this point, the OH$^-$/Cr$^{\text{III}}$ ratio is ca. 2.3. If it is assumed that only tetramers are formed under these conditions, the mean composition will be $[\text{Cr}_4(\text{OH})_9]^{3+}$. The retention and UV−vis spectrophotometric data show further that the transfer from the hydrate to complete hydrolysis takes place within a very narrow pH range, less than one pH unit, Figure S3 (Supporting Information). This supports the fact that the number of hydroxo groups bound to the chromium(III) hydrolysis complex is on the order of the result of the pH titration.

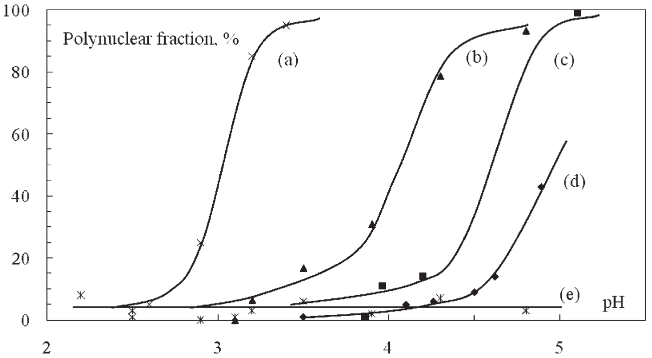

Figure 1. Dialysis, centrifugation, and calculations of chromium(III) solutions: (a) calculations, (b) dialysis $C_{\text{Cr}} = 1 \times 10^{-1}$ mol dm^{-3}, (c) dialysis $C_{\text{Cr}} = 9 \times 10^{-3}$ mol dm^{-3}, (d) dialysis $C_{\text{Cr}} = 2 \times 10^{-4}$ mol dm^{-3}, (e) centrifugation $C_{\text{Cr}} = 1 \times 10^{-1}$mol dm^{-3}.

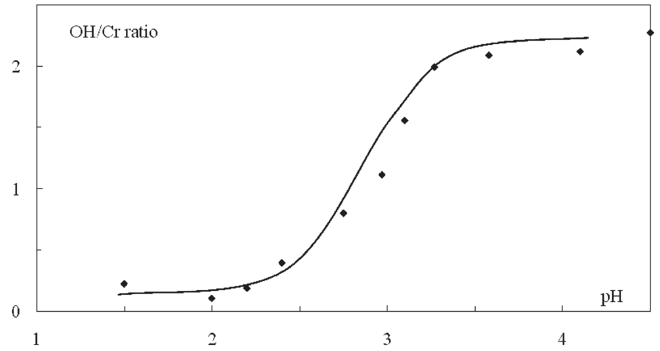

Figure 2. Potentiometric titration of a 0.1 mol dm^3 chromium(III) nitrate solution.

Structural Studies of Hydrolyzed Chromium(III) Complexes in Aqueous Solution. The EXAFS functions of the 0.1 mol dm^{-3} aqueous solutions of chromium(III) at low pH, 0−2, were fitted with six water molecules in the first coordination sphere, $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, and a mean Cr−O bond distance of 1.95 Å, in full agreement with several previous studies.[16] Due to its high charge density, the hydrated chromium(III) ion exists only in acidic solutions; the higher concentration of chromium(III) ions is, the lower a pH that is required to maintain a hydrated state.

The Fourier transform of a chromium(III) solution at pH 3.7, and stored for two years, showed two distinct peaks at 2.98(1) and 3.59(1) Å, corresponding to Cr···Cr

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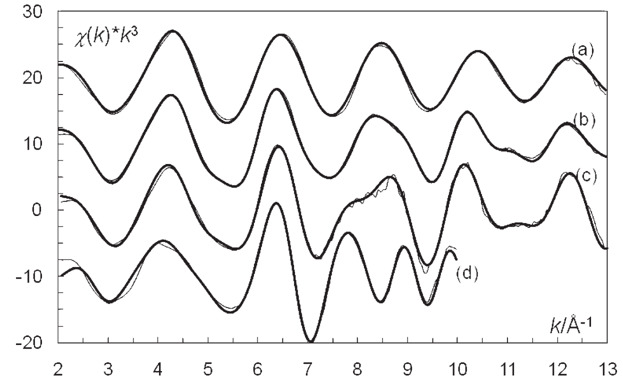

Figure 3. k^3-weighted EXAFS data of experimental (thin line) and theoretical (thick line) data of aqueous chromium(III) perchlorate at (a) pH = 1.0, dominating species $[Cr(H_2O)_6]^{3+}$; (b) pH = 3.7, dominating species $[Cr_4(\mu_2\text{-}OH)_2(\mu\text{-}OH)_4(OH)_n(H_2O)_{12-n}]^{(6-n)+}$, $n \approx 3$; and (c) pH = 15.0, dominating species $[Cr(\mu_2\text{-}OH)_2(OH)_2]_m{}^{m-}$; and of (d) amorphous precipitation from alkaline solution.

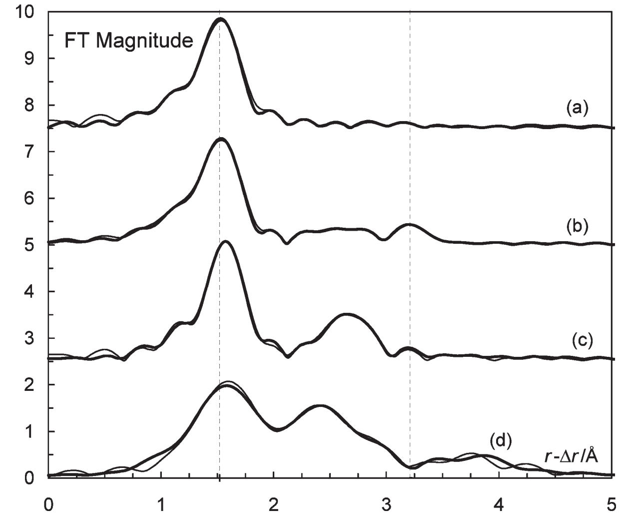

Figure 4. Fourier transforms of k^3-weighted EXAFS data of experimental (thin line) and theoretical (thick line) data of aqueous chromium(III) perchlorate at (a) pH = 1.0, dominating species $[Cr(H_2O)_6]^{3+}$; (b) pH = 3.7, dominating species $[Cr_4(\mu_2\text{-}OH)_2(\mu\text{-}OH)_4(OH)_n(H_2O)_{12-n}]^{(6-n)+}$, $n \approx 3$; (c) pH = 15.0, dominating species $[Cr(\mu_2\text{-}OH)_2(OH)_2]_m{}^{m-}$; and of (d) amorphous precipitation from alkaline solution. The dashed bars represent 1.95 and 3.60 Å after phase correction.

distances, in addition to the Cr−O peak at 1.97(1) Å. Stünzi and Marty proposed a trimeric structure where three chromium atoms share a common hydroxide, or more likely an oxide group.[13] This type of structure assumes three equal Cr···Cr distances at about 3 Å. Our data show a strong contribution at 3.59 Å supporting tetra- or trimeric hydroxo complexes with a double hydroxo bridge between two chromiums and additional single hydroxo bridges from these chromiums to the remaining one(s). Considering the reported pK_{a1} values for the hydrolyzed chromium(III) monomer (4.29), dimer (3.68), trimer (4.35), and tetramer (2.55),[13] it is to be expected that, given a relatively low pH and sufficient time for the system to equilibrate, the tetramer, and in part the dimer, should form at the expense of the monomer and trimer. The formation of the dimer should suppress the existence of the monomer to undetectable amounts at concentrations used in this study. It is therefore expected that the predominating hydrolyzed chromium(III) species at a pH of 3.7 and a long equilibration time of two years is the tetramer. Our EXAFS data support a structure in solution identical to the tetrameric hydrolysis complex reported in the solid state;[24,37-39] the refined structure parameters are summarized in Table 1.

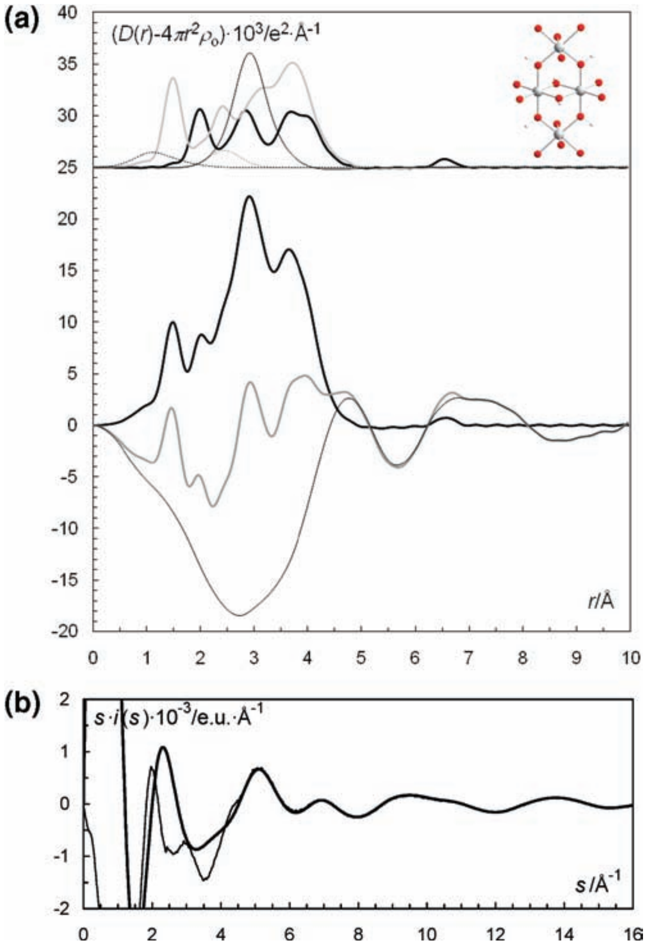

Figure 5. LAXS. (Top, a) The individual peak shapes for all contributing species in the 0.98 mol dm^{-3} aqueous chromium(III) perchlorate solution at pH = 3.7: distances in the $[Cr_4(\mu_2\text{-}OH)_2(\mu\text{-}OH)_4(OH)_n\text{-}(H_2O)_{12-n}]^{(6-n)+}$ complex (thick black line), the hydrated perchlorate ion (thick gray line), O···O distances in aqueous bulk (thin black line), the hydrated sodium ion (dotted gray line), and O−H distances in water (dotted black line). (Middle, a) Experimental $D(r) - 4\pi r^2\rho_o$ (thick gray line); model (thick black line); difference (thin black line). (Bottom) Reduced LAXS intensity functions, $s\cdot i(s)$ (thin line); model $s\cdot i_{calc}(s)$ (thick line).

The LAXS data for the same solution, pH 3.7, fully support the tetrameric structure, with distances in close agreement with those from the EXAFS data, Table 1 and Figure 3. The trimeric and tetrameric structures have the same Cr···Cr distances, and only the numbers of distances differ. However, in the tetramer, there is an additional long diagonal Cr···Cr distance at ca. 6.85 Å. A small peak at this distance is indeed found in the RDF of the LAXS data, Figure 5, further supporting the predominance of the tetramer over the trimer.

At a pH of 5.5, an insoluble amorphous precipitate of $Cr(OH)_3$ is formed. However, at a high pH, ~15, a soluble stable hydrolysis species is formed, solubility = ca. 0.2 mol dm^{-3}; the UV−vis spectrum of this solution is given in Figure S4 (Supporting Information). EXAFS data on such alkaline aqueous solutions show the presence of a mean Cr–O bond distance of 2.00(1) Å, slightly longer than in the hydrate[16] and the hydrolyzed tetramer and similar to what is observed in the $[Cr(OH)_6]^{3-}$ complexes,[19–21] and only one Cr···Cr distance, at 2.98(1) Å, Figure 4. The number of Cr···Cr distances at 2.98 Å is larger than in the solution with a pH = 3.7, Figure 4. This strongly indicates a polymeric chain structure with double hydroxo bridges separating the chromium(III) ions, $[Cr(\mu_2\text{-}OH)_2(OH)_2]_n^{n-}$. It is however not possible from the present data to determine the mean length of these chains. This complex is stable over time at a pH = 15, while precipitation of a gray-green gel or amorphous solid takes place at lower pH values. EXAFS data on the amorphous solid indicate that this compound has a structure around chromium similar to that of α-chromium(III) oxide hydroxide.[51] It is reasonable that aquation of the terminal hydroxo groups in the $[Cr(\mu_2\text{-}OH)_2(OH)_2]_n^{n-}$ complex causes reduction in the charge and thereby lower solubility. Crystalline α-CrOOH is formed in an alkaline solution under high pressures,[53] and the formation of a similar structure under the conditions used in this study is therefore likely.

Conclusions

A tetramer with the composition $[Cr_4(\mu_2\text{-}OH)_2(\mu\text{-}OH)_4(OH)_n(H_2O)_{12-n}]^{(6-n)+}$ is the predominating hydrolysis species at pH = 3.7 after two years of aging. Data from dialysis, ultrafiltration, and centrifugation studies indicates that *n* reaches a value of 3 at a pH = 3.7. The transition between different species took place in a narrow pH range, less than one pH unit, as determined by retention and UV–vis spectrophotometry; this supports the fact that several bound hydroxide ions are in the terminal positions, giving a relatively low charge for the complex, Figure S3 (Supporting Information). The tetramer has one double and four single hydroxo bridges with Cr···Cr distances of 2.98(1) and 3.59(1) Å. The configuration around the chromium(III) ions is octahedral, with a mean Cr–O bond distance of 1.97(1) Å.

The hydrolyzed chromium(III) complex at a pH = 15 is most probably a polymeric chain with double hydroxo bridges $[Cr(\mu_2\text{-}OH)_2(OH)_2]_n^{n-}$, with mean Cr–O and Cr···Cr distances of 2.00(1) and 2.98(1) Å, respectively. The lengthening of the Cr–O bond distance in this complex in comparison to the hydrated chromium(III) ion[16] supports a large number of bound hydroxide ions. A gel or an amorphous solid with a structure similar to that of α-CrOOH precipitates from the alkaline chromium(III) solution with a pH < 15 over a period of weeks.

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Supporting Information Available: Additional figures and tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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