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Chromium(III) Hydrolysis Constants and Solubility of Chromium(III) Hydroxide

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The solubility of freshly precipitated $Cr(OH)_3$ was determined in 0.01 M perchlorate solutions over a pH range of 3.8–14 and under a nitrogen atmosphere. Chromium concentrations in 0.0018-μm filtrates at times between 6 and 134 days, when the solubility was approached from both the undersaturation and oversaturation directions, showed that equilibrium is attained in <6 days below pH 12 and in ~63 days above pH 12. X-ray diffraction analyses of the solids showed that freshly precipitated $Cr(OH)_3$ was amorphous and remained amorphous throughout the equilibration period. Chromium hydroxide exhibits amphoteric behavior, with a minimum solubility between pH 7 and 10. On the basis of the solubility of $Cr(OH)_3(s)$ as a function of pH, $CrOH^{2+}$, $Cr(OH)_3{}^0$, and $Cr(OH)_4{}^-$ were determined to be the dominant aqueous species in different pH regions. At zero ionic strength and room temperature (22 ± 2 °C), the logarithms of the thermodynamic equilibrium constants for solubility reactions involving these species [$Cr(OH)_3(s) + 2H^+ \rightleftharpoons CrOH^{2+} + 2H_2O$; $Cr(OH)_3(s) \rightleftharpoons Cr(OH)_3{}^0$; $Cr(OH)_3(s) + H_2O \rightleftharpoons Cr(OH)_4{}^- + H^+$] are 5.78 ± 0.08, ≤ -6.84, and -18.30 ± 0.12, respectively. No evidence for Cr^{3+}, $Cr(OH)_2{}^+$, or any polynuclear complexes was observed, even in solutions heated to 60 and 90 °C, where polynuclear species are expected to form more rapidly. Although it was not possible to determine from these experiments the absolute values of the hydrolysis constants for reactions involving $Cr(OH)_2{}^+$ and Cr(III) polymeric species, the results do set upper limits for log K_{sxy} [$xCr(OH)_3(s) + (3x - y)H^+ \rightleftharpoons Cr_x(OH)_y{}^{3x-y} + (3x - y)H_2O$] of <-0.49 for log K_{s12}, and <13.7, <17.3, and <20.8 for log K_{s22}, log K_{s34}, and log K_{s46}, respectively. The results provide no evidence for such reactions, but if they are assumed to occur, these upper limits (especially for polynuclear species) are many orders of magnitude lower than previously reported.

Introduction

Chromium can be present in the environment as Cr(III) or Cr(VI). To determine the chemical processes (precipitation/dissolution and adsorption/desorption) that affect the geochemical behavior of Cr, accurate thermochemical data for important solid phases and aqueous species of Cr(III), along with data for Cr(III) to Cr(VI) transformations are required. Although Cr is extensively used in industry, thermochemical data for important species either are lacking or are of uncertain quality. In this paper, thermochemical data for Cr(III) hydroxide solubility and the hydrolytic behavior of Cr(III) are discussed.

Rai et al.,[1] in reviewing the literature on precipitation/dissolution in soils, concluded that the Cr(III) solubility-controlling solids are thought to be either $Cr(OH)_3$ or Cr(III) coprecipitated with Fe oxides and hydroxides. However, the solubility product values for $Cr(OH)_3(s)$ reported in the literature are old (1895–1956) and are only approximately known,[2] and until our study[3] no thermochemical data for $(Cr,Fe)(OH)_3$ [coprecipitated Cr(III) and Fe(III)] were available.

Chromium(III) hydroxo complexes are expected to be the dominant species of Cr(III) in natural waters.[1] Thermochemical data for dominant aqueous species (in this case, Cr hydroxo complexes) are needed to predict aqueous concentrations in equilibrium with different solid phases. Baes and Mesmer,[2] reviewing the Cr(III) hydrolysis data, state that regardless of the large number of investigators who have studied Cr(III) hydrolysis, the value of $\beta_1{}^*$ [$\beta_n{}^*$, $Cr^{3+} + nH_2O \rightleftharpoons Cr(OH)_n{}^{3-n} + nH^+$] is not precisely known. Because the other Cr(III) hydrolysis constants are less well-known than $\beta_1{}^*$, the current understanding of the hydrolytic properties of Cr(III) is tenuous. Baes and Mesmer[2] recommend −4.0 for log $\beta_1{}^*$. Earley and Cannon,[4] on the basis of a literature review, report a range of −7.4 to −5.6 in log $K_2{}^*$ [$CrOH^{2+} + H_2O \rightleftharpoons Cr(OH)_2{}^+ + H^+$]. There are no experimental values for $\beta_3{}^*$. Fricke and Windhausen's[5] $Cr(OH)_3(s)$ solubility data can be used to calculate $\beta_4{}^*$ and thus demonstrate that Cr(III) shows amphoteric behavior, even though Rollinson[6] strongly questions whether chromic hydroxide is amphoteric. However, to calculate $\beta_4{}^*$ from Fricke and Windhausen's[5] data, an accurate value for the solubility product of $Cr(OH)_3(s)$, which is not currently available, is also needed. Using an estimated value of the $Cr(OH)_3(s)$ solubility product, Baes and Mesmer[2] calculated from Fricke and Windhausen's[5] data that log $\beta_4{}^*$ is −27.4. However, Fricke and Windhausen's[5] experiments were conducted in highly alkaline solutions (0.9–17.4 M NaOH) of high ionic strength, and the suspensions were not filtered before being analyzed. Because of these difficulties and the lack of an accurate solubility product for $Cr(OH)_3(s)$, the value of $\beta_4{}^*$ must be considered approximate.

Polynuclear complexes of Cr(III) have been reported in the literature. However, the reported values of equilibrium constants for polynuclear species vary widely. For example, the values of log $\beta_{22}{}^*$ [$\beta_{nm}{}^*$ for $mCr^{3+} + nH_2O \rightleftharpoons Cr_m(OH)_n{}^{3m-n} + nH^+$] reported by several authors are as follows: −2.04 and −2.69 at 75 and 100 °C, respectively, in dilute solution (Bjerrum, 1908, as quoted by Earley and Cannon[4]); −3.82 at 50 °C in 1 M ionic strength solutions;[7] −4.25 and −4.58 at 50 and 27.5 °C, respectively, in 0.18 M ionic strength solutions.[8] Only one reference[8] reports the values of $\beta_{43}{}^*$ at different ionic strengths (0.2–2 M) and temperatures (38–68 °C). The log $\beta_{43}{}^*$ values at approximately 0.2 N and 38, 50, and 68 °C are −7.58, −6.05, and −6.23, respectively. Baes and Mesmer[2] reviewed the available data and report the thermodynamic equilibrium constants at 25 °C and zero ionic strength as −5.06 for log $\beta_{22}{}^*$ and −8.15 for log $\beta_{43}{}^*$.

The polymeric species of Cr(III) are generally absent in solutions at room temperature; this absence is generally attributed

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to the slow kinetics of the formation of polymeric species. Finholt[7] and Thompson[8] identified polymeric species of Cr in heated or boiled and refluxed acidic Cr(III) solutions through a combination of ion-exchange chromatography and spectrophotometric techniques. However, Postmus and King[9] found no evidence for the presence of polymeric species in solutions treated in a similar manner. On prolonged heating at temperatures near boiling, colloidal crystalline precipitates of Cr(III) solids (such as $HCrO_2$ and $Cr_2O_3 \cdot H_2O$) have been observed.[10,11]

The conflicting evidence for the presence of polymeric species casts doubt on their importance in aqueous solutions, especially in solutions of low total [Cr(III)]. The results of several authors who report the presence of polynuclear species[7,8,11] show that these species are present in small quantities compared with those of the mononuclear species. However, when hydrolysis constants[2] based on these studies (conducted in a limited pH range and at relatively high ionic strength) are used to calculate the solubility of $Cr(OH)_3(s)$ and the activities of different species, the results show (1) that the polynuclear species are dominant at pH values <7 and that, depending on the pH, the concentration of polynuclear species can be several orders of magnitude higher than the concentration of mononuclear species and (2) that the predicted Cr concentration (e.g., >10 g/L at pH 6) in equilibrium with $Cr(OH)_3(s)$ is unrealistically high and is completely at odds with the long-known descriptive solubility of $Cr(OH)_3(s)$.[12]

The foregoing discussion illustrates the need to determine accurate values for the solubility product of $Cr(OH)_3(s)$ and for Cr(III) hydrolysis constants. The results presented here clearly show that (1) polynuclear species do not become dominant, (2) $CrOH^{2+}$, possibly $Cr(OH)_3^0$, and $Cr(OH)_4^-$ are the dominant mononuclear species in a pH range of about 2.6–14, and (3) hydrolysis constants reported in the literature, especially for polynuclear species, are in error.

Materials and Methods

Reagents. Chromium(III) stock solutions (1.54 M Cr in 0.1 M $HClO_4$) were prepared by using $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ (green salt) or $Cr(NO_3)_3 \cdot 9H_2O$ and by treating the stocks with 30% H_2O_2 (1.6 mL/L of stock) to reduce trace amounts of hexavalent Cr that may have been present. The solution was heated at about 90 °C for about 30 min to remove excess H_2O_2.

In all cases, deionized water was deaerated by boiling and thorough sparging at room temperature with an inert gas (99.99% N_2 with a few parts per million of oxygen). Carbonate-free stock solutions of 0.67 M tetraethylammonium hydroxide [$(C_2H_5)_4NOH$] and 10 M NaOH were prepared under an inert atmosphere. The amount of dissolved carbonate in these bases was determined through treatment with $BaCl_2$ or $SrCl_2$ and gravimetric determination of the resulting carbonate precipitate; a 10% excess of Ba or Sr was added to the bases to ensure a low dissolved-carbonate concentration.

General Procedures. All experiments for the determination of Cr(III) hydrolysis constants were performed under an inert atmosphere (99.99% N_2 with a few parts per million of oxygen). Small aliquots of 1.54 M Cr(III) stock in 0.1 M $HClO_4$ containing between 20 and 250 mg of Cr were added to different polyethylene centrifuge tubes containing about 10 mL of 0.01 M sodium or ammonium perchlorate. In the majority of experiments, the stock solution prepared from $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ was used, and the stock solution prepared from $Cr(NO_3)_3 \cdot 9H_2O$ was used for comparative purposes only. The pH of these solutions was adjusted to about 9.5 with carbonate-free $(C_2H_5)_4NOH$ or NaOH to precipitate $Cr(OH)_3(s)$. The suspensions were aged for at least 3 h and then washed with 0.01 M NH_4ClO_4 or $NaClO_4$ (depending on the base used for precipitation). To approach the solubility limit from undersaturation, the $Cr(OH)_3$ precipitates were washed to remove chloride and suspended in about 30 mL of 0.01 M NH_4ClO_4 or $NaClO_4$ to maintain constant ionic strength, and the suspensions were adjusted to pH values ranging from about 4 to 14 with $HClO_4$ or the bases discussed above. To approach the solubility limit from the oversaturation direction, washed $Cr(OH)_3(s)$ precipitates were first dissolved in solutions with a pH of about 3 maintained with $HClO_4$. These solutions were then adjusted to pH values ranging from about 4 to 14, where $Cr(OH)_3(s)$ reprecipitated. The $Cr(OH)_3(s)$ suspensions were continuously agitated on a shaker and equilibrated for long periods. At different times, the pH values of the suspensions were measured and aliquots were withdrawn for Cr analyses.

Table I. Effectiveness of Amicon Membrane Cones (~0.0018-μm Pore Size) in Separating Solution from $Cr(OH)_3(s)$ Suspensions

		log (mol of Cr/L)[a]		
pH	aliquot no.	filtrate (filter 1)	filtrate filtration (filter 2)	unfiltered
3.99	1	−2.50	−2.66	−2.03
	2	−2.44	−2.67	
5.36	1	−5.15	−5.30	−2.16
	2	−5.15	−5.26	
5.98	1	−6.24	−6.46	−2.36
	2	−5.96	−6.20	
6.80	1	−7.18		
	2	−7.49		
	3	−7.30		
11.24	1	−5.57	−5.57	−2.12
	2	−5.54	−5.53	

[a] Filters were washed in deionized water adjusted to the sample pH. Filter 1 was then preequilibrated with sample suspension by filtering a portion of the suspension and discarding the resultant filtrate before filtering additional aliquots (1 and 2) for analyses. A portion of the filtrate from filter 1 was passed through filter 2 and discarded before the rest was filtered for analysis. Unfiltered suspensions were centrifuged at about 1800 g for about 10 min.

Measurements. The pH (<12) was measured to within 0.01 unit with a combination glass reference electrode calibrated against pH buffers covering the range of pH values in the experiments. The pH values of solutions containing high concentrations of NaOH were calculated from the molarity of the base and the ionic medium and from the mean ionic activity coefficients from Hamer and Wu.[13]

The suspensions were filtered through fine filters because centrifugation alone is not adequate to separate solids from solutions.[14] Because of their ease of use and effectiveness of filtration, we have used Amicon Type F-25 Centriflo membrane cones (Amicon Corp., Lexington, MA) with effective molecular weight 25 000 cutoffs and approximately 0.0018-μm pore sizes. The results of tests to determine the effectiveness of these filters are given in Table I. The filters were pretreated as suggested by Rai;[15] the pretreatment steps consisted of (1) washing and equilibrating the filters with deionized water adjusted to the pH values of the given samples to avoid precipitation or dissolution of the solid phase caused by a pH change during filtration and (2) passing a small aliquot of the sample through the filters (this filtrate was discarded) to saturate any possible adsorption sites on the filters and filtration containers. Observation of the filters after filtration showed the presence of green $Cr(OH)_3(s)$ in several samples. This observation, along with (1) the similarities of Cr concentrations in different aliquots passed through a filter and (2) concentrations in solutions obtained from passing a filtrate through a new filter (Table I), showed that Amicon membrane cones were effective in separating solid from solution and that the absorption of soluble Cr by the filters was not significant.

The 0.0018-μm filtrates were analyzed for Cr(VI) spectrophotometrically[16] and for total Cr by inductively coupled plasma spectroscopy (Jarrell-Ash 975 Atomcomp) and by atomic absorption spectrophotometry (AAS; Perkin-Elmer 5000 with graphite furnace). The most sensitive measurements were made by AAS using a method of known additions; the working detection limit was 2 μg of Cr/L. The solids were examined by X-ray diffraction with a Gandolfi camera using Cu Kα radiation.[17]

Results and Discussion

The solubility of $Cr(OH)_3(s)$, precipitated from $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$, in the noncomplexing perchlorate medium is shown in Figure 1. Except for the intermediate-pH range (~6–11), the measured Cr concentrations are well above the instrumental detection limit (2 μg/L). The Cr concentrations in the intermediate-pH range are close to the detection limit; values below

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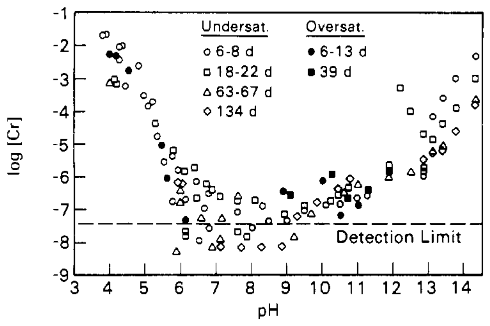

Figure 1. Chromium concentrations in 90 0.0018-μm filtrates from N_2-equilibrated $Cr(OH)_3(s)$ suspensions in pH-adjusted 0.01 M NH_4ClO_4 or $NaClO_4$. High-pH solutions were adjusted by NaOH only. The Cr concentrations at pH values >12 were corrected to 0.01 M ionic strength by assuming that mean activity coefficients for $NaClO_4$[13] apply to $NaCr(OH)_4$. [$Cr(OH)_4^-$ is the dominant Cr species at these pH values; see Figure 2.]

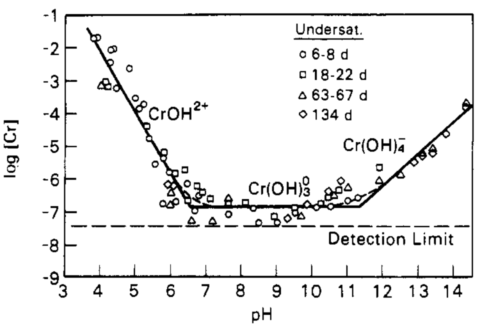

Figure 2. Experimental data (77 points) used for nonlinear least-squares regression analysis. The data were taken from Figure 1 except for samples with Cr concentrations below the detection limit and samples above pH 12 that were equilibrated in solutions for less than 63 days. Lines represent the three-parameter model that best fits the data. (Concentrations of Cr species are indicated by the solid lines, and total Cr concentrations are given by the dashed line.)

the detection limit represent instrument readings that cannot be considered accurate. The Cr concentrations display a parabolic trend over a pH range of about 4–12, which is similar for different time periods and directions of approach to equilibrium. This similarity shows that the kinetics of precipitation/dissolution are very rapid and that equilibrium is reached in 6 days or less below pH 12. Steady-state Cr concentrations in suspensions with pH values >12 were reached slowly (in approximately 63 days), especially when solubility was approached from the undersaturation direction. The results of experiments in which $Cr(OH)_3(s)$ was precipitated from $Cr(NO_3)_3 \cdot 9H_2O$ are similar to those in which $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ was used. This similarity indicates that the solubilities of the precipitates do not critically depend on the initial composition of the chromium solution.

The total aqueous Cr concentrations in 0.0018-μm filtrates in equilibrium with $Cr(OH)_3(s)$ plotted against pH (Figure 1) show that $Cr(OH)_3(s)$ exhibits amphoteric behavior; the Cr concentrations first decrease and then, at pH values >10, increase with increasing pH. The changes in Cr concentrations with the changes in pH can be attributed to the formation of Cr(III) hydroxo complexes because other complexing ligands, including carbonates, were absent from these experiments. In general, the Cr concentrations in filtered solutions are more variable at pH values >6. The variability at intermediate-pH values appears to be due to the close proximity of measured Cr to the Cr detection limit. At pH values >12, the variability appears to be due to the effects of aging in alkaline media, as the Cr concentrations at later times are less erratic and generally have lower values. Therefore, the Cr data that are above the detection limit and those data at pH >12, where Cr concentrations had reached steady state (>63 days equilibration), were selected for further interpretation of $Cr(OH)_3$ solubility (Figure 2).

Chromium(III) is reported to form several hydroxo species, including $CrOH^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_3^0$, $Cr(OH)_4^-$, $Cr_2(OH)_2^{4+}$, and $Cr_3(OH)_4^{5+}$.[2] In addition, Stünzi and Marty[18] have identified a tetrameric species, $Cr_4(OH)_6^{6+}$. The $Cr(OH)_3(s)$ reactions involving these species are given in eq 1–8

$$Cr(OH)_3(s) + 3H^+ \rightleftharpoons Cr^{3+} + 3H_2O \quad K_{s10} \tag{1}$$

$$Cr(OH)_3(s) + 2H^+ \rightleftharpoons CrOH^{2+} + 2H_2O \quad K_{s11} \tag{2}$$

$$Cr(OH)_3(s) + H^+ \rightleftharpoons Cr(OH)_2^+ + H_2O \quad K_{s12} \tag{3}$$

$$Cr(OH)_3(s) \rightleftharpoons Cr(OH)_3^0 \quad K_{s13} \tag{4}$$

$$Cr(OH)_3(s) + H_2O \rightleftharpoons Cr(OH)_4^- + H^+ \quad K_{s14} \tag{5}$$

$$2Cr(OH)_3(s) + 4H^+ \rightleftharpoons Cr_2(OH)_2^{4+} + 4H_2O \quad K_{s22} \tag{6}$$

$$3Cr(OH)_3(s) + 5H^+ \rightleftharpoons Cr_3(OH)_4^{5+} + 5H_2O \quad K_{s34} \tag{7}$$

$$4Cr(OH)_3(s) + 6H^+ \rightleftharpoons Cr_4(OH)_6^{6+} + 6H_2O \quad K_{s46} \tag{8}$$

where K_{s10}–K_{s14} and K_{s22}, K_{s34}, and K_{s46} represent the equilibrium constants for the equations. These reactions indicate that, for the Cr solution species in eq 1–8, lines representing log [Cr] vs. pH will have slopes of −3, −2, −1, 0, +1, −4, −5, and −6, respectively, in the regions of dominance for each hydrolyzed species. The data in Figure 2 show that log [Cr] vs. pH is most negative below pH 6. A least-squares linear regression of the data in this region (24 points) gives a slope of −1.98 ± 0.15, which is significantly less than −4; thus, the species $Cr_2(OH)_2^{4+}$, $Cr_3(OH)_4^{5+}$, and $Cr_4(OH)_6^{6+}$ do not have a region of dominance, and the reactions indicated in eq 6–8 can be ignored. Thermodynamic data reported in the literature[2] indicate that Cr^{3+} should be the dominant mononuclear species below pH 4. Evidence for the dominance of Cr^{3+} and its hydrolysis derivatives was tested statistically at pH values above approximately 3.80.

Assuming that the Cr species represented by eq 1–5 are the only species present in significant amounts in solution, the total concentration of Cr in equilibrium with $Cr(OH)_3(s)$ can be expressed as

$$\log [Cr(total)] = \log [Cr^{3+} + CrOH^{2+} + Cr(OH)_2^+ + Cr(OH)_3^0 + Cr(OH)_4^-] \tag{9}$$

Substituting concentrations of Cr^{3+}, $CrOH^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_3^0$, and $Cr(OH)_4^-$ from the equilibrium expressions (eq 1–5), we obtain

$$\log [Cr(total)] = \log (10^{\log K_{s10} - 3pH} + 10^{\log K_{s11} - 2pH} + 10^{\log K_{s12} - pH} + 10^{\log K_{s13}} + 10^{\log K_{s14} + pH}) \tag{10}$$

A nonlinear least-squares curve-fitting program (RS/1 "FIT FUNCTION"; Bolt, Beranek, and Newman, Inc.) with a no-weighting option was used to evaluate the K_{sxy} parameters from the data in Figure 2. Models with different numbers of parameters were tested to select the model, and hence the values of K_{sxy}, that best describes the [Cr] vs. pH relationship shown in Figure 2. In addition to the full five-parameter model, which includes all possible mononuclear Cr species (eq 10), two four-parameter truncated models (excluding either Cr^{3+} or $Cr(OH)_2^+$) and one three-parameter (excluding both Cr^{3+} and $Cr(OH)_2^+$) truncated model were tested. Two statistical calculations were used to select the most appropriate model: (1) the multiple coefficient of determination (R^2) and (2) the residual mean square (SS). Higher R^2 and lower residual mean square values (Table II) for the three-parameter model compared with those of the four- and five-parameter models show that the three-parameter model representing $CrOH^{2+}$, $Cr(OH)_3^0$, and $Cr(OH)_4^-$ (eq 2, 4, and 5) best describes $Cr(OH)_3(s)$ solubility. The calculated log K_{s11}, log K_{s13}, and log K_{s14} values at 0.01 M ionic strength are 5.96 ± 0.08, −6.84 ± 0.08, and −18.25 ± 0.12, respectively (Table II). The concentrations of different species calculated by using these three log K_{sxy} values are plotted in Figure 2, along with the total Cr concentration.

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Table II. Nonlinear Least-Squares Fitting Parameters (log K_{sxy})[a]

	no. of params[b]			
	5	4	4	3
log K_{s10}	9.64 ± 0.23	9.93 ± 0.17		
log K_{s11}	6.09 ± 0.20	6.01 ± 0.13	6.02 ± 0.11	5.96 ± 0.08
log K_{s12}	−0.95 ± 0.37		−0.73 ± 0.21	
log K_{s13}	−6.82 ± 0.10	−6.84 ± 0.09	−6.83 ± 0.10	−6.84 ± 0.08
log K_{s14}	−18.26 ± 0.13	−18.25 ± 0.13	−18.25 ± 0.12	−18.25 ± 0.12
SS[c]	14.4590	14.2013	13.5676	13.1246
R^2[d]	0.9944	0.9945	0.9947	0.9949

[a] The relationship between log K_{sxy} and total aqueous Cr is given in eq 10. Error terms are standard errors of determination. [b] Number of data points is 77. [c] Sum of squares. [d] Multiple coefficient of determination.

Table III. Thermodynamic Equilibrium Constants (log *K*) for Cr(III) Hydrolysis Reactions

	log *K*		
	this study		lit.[b]
reacn[a]	0.01 M	0.00 M	0.00 M
$Cr(OH)_3(s) + 3H^+ \rightleftharpoons Cr^{3+} + 3H_2O$	<9.76	<9.35	12.0
$Cr(OH)_3(s) + 2H^+ \rightleftharpoons CrOH^{2+} + 2H_2O$	5.96 ± 0.08	5.78 ± 0.08	8.0
$Cr(OH)_3(s) + H^+ \rightleftharpoons Cr(OH)_2^+ + H_2O$	<−0.44	<−0.49	2.3
$Cr(OH)_3(s) \rightleftharpoons Cr(OH)_3^0$	<−6.84	<−6.84	−6.0
$Cr(OH)_3(s) + H_2O \rightleftharpoons Cr(OH)_4^- + H^+$	−18.25 ± 0.12[c]	−18.30 ± 0.12[c]	−15.4
$2Cr(OH)_3(s) + 4H^+ \rightleftharpoons Cr_2(OH_2)^{4+} + 4H_2O$	<14.4	<13.7	18.9
$3Cr(OH)_3(s) + 5H^+ \rightleftharpoons Cr_3(OH)_4^{5+} + 5H_2O$	<18.5	<17.3	27.9
$4Cr(OH)_3(s) + 6H^+ \rightleftharpoons Cr_4(OH)_6^{6+} + 6H_2O$	<22.4	<20.8	<39.2

[a] No evidence was found for the presence of polynuclear species [$Cr_2(OH)_2^{4+}$, $Cr_3(OH)_4^{5+}$, and $Cr_4(OH)_6^{6+}$]. Values given for reactions with these species are upper limits, if these species are assumed to be dominant at pH <3.80. Experiments were conducted in NH_4ClO_4 or $NaClO_4$. Values for zero ionic strength (0.00 M) were calculated by means of the Davies[19] equation. [b] Values for all reactions except the last are for zero ionic strength and are from Baes and Mesmer;[2] the value for the last reaction was obtained by combining the 1.0 M ionic strength value for log $\beta_{46}^* \geqslant -14.1$ from Stünzi and Marty[18] with the calculated log *K* value of the first reaction (13.33) at 1.0 M ionic strength from Baes and Mesmer.[2] [c] The error associated with log K_{s14} is believed to be greater than the standard error shown; see text for discussion.

The dominance of $Cr(OH)_3^0$ (eq 4) at pH values between about 6.5 and 10.5 is consistent with the data in Figure 2. However, Cr concentrations at these pH values are at or near the detection limit. Therefore, the value of −6.84 ± 0.08 represents the upper limit for log K_{s13}.

Although Rollinson[6] questions whether $Cr(OH)_3(s)$ is amphoteric, our experimental data clearly show amphoteric behavior, which we attribute to the dominance of $Cr(OH)_4^-$ above pH 11.4 (eq 5). However, the determination of log K_{s14} is complicated by (1) greater variability in Cr concentrations above pH 12, (2) an apparent inflection in the solubility data between pH 10 and 11.5, and (3) a general decrease in solubility with time above pH 12. Thus, the real error for log K_{s14} may be considerably larger than the calculated error (Tables II and III).

Because Cr^{3+} and $Cr(OH)_2^+$ are not statistically needed to describe the data over any pH range, eq 1 and 3 contribute only marginally, if at all, to the total Cr concentration. The maximum possible contribution of eq 1 would necessitate that Cr^{3+} achieve dominance below the lowest measured pH (about 3.80). Assuming that Cr^{3+} does become dominant at pH 3.80, log K_{s10} has a maximum value of 9.76 at 0.01 M ionic strength. The maximum possible contribution of eq 3 would dictate that eq 2 and 4 intersect at one point (at pH 6.40 and log [Cr] = −6.84). On the basis of this requirement, the upper limit of the log K_{s12} value of eq 3 was calculated to be −0.44 at 0.01 M ionic strength.

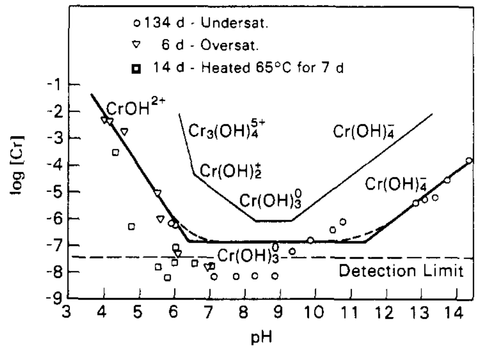

Figure 3. Comparison of experimental and predicted Cr concentrations in 0.0018-μm filtrates from N_2-equilibrated $Cr(OH)_3(s)$ suspensions in pH-adjusted 0.01 M NH_4ClO_4 or $NaClO_4$. Heavy solid lines represent concentrations of Cr hydrolysis species given in Figure 2, and thin solid lines represent the concentrations of hydrolysis species in 0.01 M solutions predicted from the thermodynamic data reported by Baes and Mesmer.[2] The dashed line represents total Cr concentrations. (When the thermodynamic data at 1.0 M ionic strength calculated from Baes and Mesmer[2] and those given by Stünzi and Marty[18] are combined, as shown in footnote *b* of Table III, the dominant polynuclear species at pH <7 is predicted to be $Cr_4(OH)_6^{6+}$.)

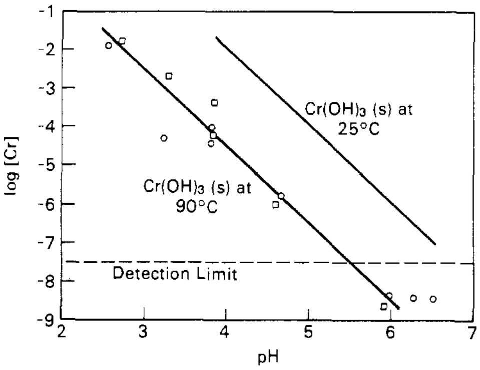

Figure 4. Chromium concentrations in 0.0018-μm filtrates from N_2-equilibrated $Cr(OH)_3(s)$ suspensions in pH-adjusted 0.01 M $NaClO_4$. The suspensions were heated to 90 °C for 4 days and sampled after 11 days (○) and 103 days (□) of equilibration at room temperature.

Although no evidence was found for the presence of polynuclear species (Figure 1), the use of the available thermodynamic data[2] at 0.01 M ionic strength indicates that $Cr_3(OH)_4^{5+}$ should be the dominant species in low-pH regions. When the experimental $Cr(OH)_3(s)$ solubility (with dominant hydrolysis species identified) is plotted along with the solubility predicted from the thermodynamic data quoted by Baes and Mesmer[2] (Figure 3), unreasonably high solubilities are predicted, casting doubt about the presence of polynuclear species. Data in the literature suggest that polynuclear species have slow kinetics of formation at 25 °C and that a long equilibrium period (~100 days) or elevated temperatures (35–50 °C) are required for their formation.[4] Therefore, as an additional means to determine whether polynuclear species are dominant in low-pH regions, several $Cr(OH)_3(s)$ solubility experiments were conducted in which (1) solubility was approached from oversaturation, where polynuclear species should form readily, (2) long-term solubility measurements were made (over a 134-day equilibration period), and (3) solubility experiments at relatively high temperatures (65 °C) were carried out. However, the results from all these experiments were similar to the results obtained at 22 ± 2 °C and shorter equilibration periods (Figure 3). Additional $Cr(OH)_3(s)$ solubilities measured at 22 ± 2 °C in suspensions that were previously maintained at 90 °C for 4 days (Figure 4) also provide no evidence of the existence of polynuclear species. Therefore, we conclude that polynuclear species do not become dominant and that $Cr(OH)_3(s)$ solubility and the nature of dominant aqueous species in low-pH regions, as predicted from the thermochemical data reported in the literature, are inaccurate.

The solubility of $Cr(OH)_3(s)$ (Figures 2 and 3) indicates that $CrOH^{2+}$ is the dominant Cr species between pH 3.8 and 6.4. Heating the $Cr(OH)_3(s)$ suspensions to 90 °C shows that the Cr concentrations in the suspensions are approximately 2.5 orders of magnitude lower than the Cr concentrations in unheated $Cr(OH)_3(s)$ (Figure 4), indicating the formation of a more ordered solid phase with lower solubility. X-ray diffraction patterns show that the heated solids are amorphous, as were the unheated solids. Heating the $Cr(OH)_3(s)$ suspensions to near boiling is reported to produce crystalline $HCrO_2$ and $Cr_2O_3{\cdot}H_2O$.[10,11] Even if $HCrO_2$ and/or $Cr_2O_3{\cdot}H_2O$ forms in the suspensions, the aqueous Cr concentrations in equilibrium with the solids would show the same pH dependence as in the case of $Cr(OH)_3(s)$ (eq 1–8). A best-fit straight line through 12 data points between pH 2.6 and 6.0 in Figure 4 has slope -2.00 ± 0.15, indicating (1) that the solubility reaction is similar to that of eq 2 and (2) that Cr^{3+} has no region of dominance above pH 2.6. These findings suggest that the value of the first hydrolysis constant ($\beta_1{}^*$) reported in the literature may be in error and that $CrOH^{2+}$ or some other Cr(III) species that has the same pH dependence as $CrOH^{2+}$ is dominant in the low-pH region.

Although it is not possible to determine the absolute values of equilibrium constants for eq 1, 6, 7, and 8 from these experiments, our results can be used to set upper limits for the constants. Assuming that $Cr_2(OH)_2{}^{4+}$, $Cr_3(OH)_4{}^{5+}$, or $Cr_4(OH)_6{}^{6+}$ becomes dominant at pH 3.8 (the approximate limit of our $Cr(OH)_3(s)$ solubility measurements), the calculated values of log K_{s22}, log K_{s34}, and log K_{s46} in 0.01 M perchlorate are <14.4, <18.5, and <22.4, respectively.

The values of equilibrium constants determined in this study (at 0.01 M ionic strength, and at zero ionic strength as calculated from the Davies[19] equation) are tabulated in Table III, along with the values proposed by Baes and Mesmer,[2] based on a literature review, and Stünzi and Marty.[18] The data given in Table III show that the values obtained in this study for $Cr(OH)_3(s)$ solubility reactions involving different hydrolysis species, especially polynuclear species, are several orders of magnitude less than the values reported in the literature. Because the observed $Cr(OH)_3$ solubility qualitatively confirms the well-known low solubility of $Cr(OH)_3$,[12] the large discrepancy between the observed and the predicted solubility (Figure 3) must be the result of inaccuracies in the values of polynuclear species and/or inaccuracies in extrapolating the values of polynuclear species to low ionic strengths and temperatures.

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Synthesis, Crystal Structure, and EHMO Calculations for the Nickel(II) Complexes of Imines Derived from Salicylaldehyde, 2-Hydroxy-1-naphthaldehyde, and 3-Hydroxy-2-naphthaldehyde

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The Ni(II) complexes of the imine ligands derived from 2-(aminomethyl)-1,3-dioxolane with salicylaldehyde (**1**), 2-hydroxy-1-naphthaldehyde (**2**), and 3-hydroxy-2-naphthaldehyde (**3**) were synthesized and characterized by elemental analysis, magnetic moments, and infrared and absorption spectra. The structures of the three complexes were determined by single-crystal X-ray diffraction. Crystallographic details for the $C_{22}H_{24}N_2O_6Ni$; are as follows. For **1**: formula $C_{22}H_{24}N_2O_6Ni$; $M_r = 470.7$; space group $P\bar{1}$, with $a = 10.215$ (2) Å, $b = 10.305$ (3) Å, $c = 11.019$ (2) Å, $\alpha = 86.97$ (2)°, $\beta = 69.19$ (2)°, $\gamma = 74.74$ (2)°, and $Z = 2$; $d_{calcd} = 1.497$ g cm^{-3}; μ(Mo Kα) = 9.71 cm^{-1}; $R = 0.044$ for 2119 reflections. For **2**: formula $C_{30}H_{28}N_2O_6Ni$; $M_r = 570.7$; space group $P2_1/c$, with $a = 4.563$ (1) Å, $b = 11.159$ (3) Å, $c = 24.834$ (5) Å, $\beta = 93.21$ (13)°, and $Z = 2$; $d_{calcd} = 1.496$ g cm^{-3}; μ(Mo Kα) = 7.86 cm^{-1}; $R = 0.042$ for 1684 reflections. For **3**: formula $C_{30}H_{28}N_2O_6Ni$; $M_r = 570.7$; space group $P2_1/n$, with $a = 13.677$ (5) Å, $b = 5.585$ (2) Å, $c = 17.267$ (5) Å, $\beta = 93.06$ (3)°, and $Z = 2$; $d_{calcd} = 1.439$ g cm^{-3}; μ(Mo Kα) = 7.84 cm^{-1}; $R = 0.048$ for 1388 reflections. The metal is placed in a center of symmetry in all three cases with square-planar coordination. Compounds **1** and **3** deviate from planarity in a stepped fashion. The height of the step and the magnitude of some interatomic distances in the chelate rings, particularly Ni–N, are analyzed in terms of steric and electronic effects. EHMO calculations were carried out in order to evaluate some of these effects.

Introduction

Metal derivatives of Schiff-base ligands have been extensively studied for a long time[1] and the chemistry of bis(bidentate Schiff-base)copper(II) and -nickel(II) complexes has been particularly enriched by many contributions in both synthetic and structural areas.[2-4] These studies have shown that while in the solid state the structure of these complexes may lie anywhere between square planar and tetrahedral with other intermediate structures also being found (mainly stepped and umbrella-shaped square-planar conformations), in solution several of these conformations can exist in equilibrium.[4,5] This variety of structures has been interpreted in terms of both steric[4] and electronic[6] factors.

The differences in structure (planar or tetrahedral) of copper and nickel bis(substituted salicylaldimines) have been observed to affect the expression for the rate of ligand substitution process.[7] Furthermore, a relationship can be drawn between the steric bulk of the N substituents and the relative importance of the solvent-

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