tivation for decomposition of the dioxo dimer and the enhanced kinetic stability of the intermediate relative to that of the doubly bridged reactant. In any case, the vast difference between the UV–vis spectra of VII and the well-characterized [(tmpa)-(SCN)CrOCr(NCS)(tmpa)]$^{2+}$ ion[4] rules out the classification of the base hydrolysis intermediate as a linear, μ-oxo dimer. Mechanistic studies of the base hydrolysis reactions of [(tmpa)(SCN)CrOCr(NCS)(tmpa)]$^{2+}$ and related dimers are currently in progress.[14]

Registry No. I, 117603-54-0; II, 117773-50-9; III, 117709-84-9; IV, 117689-06-2; [H$_3$tmpa](ClO$_4$)$_3$, 117689-07-3; [(bpy)$_2$Cr(OH)$_2$Cr-(bpy)$_2$](ClO$_4$)$_4$·2H$_2$O, 31418-78-7; [(phen)$_2$Cr(OH)$_2$Cr(phen)$_2$]-(ClO$_4$)$_4$·3H$_2$O, 31282-13-0; [(tmpa)Cr(O)$_2$Cr(tmpa)]$^{2+}$, 117689-08-4; 2-picolyl chloride hydrochloride, 6959-47-3; bis(2-pyridylmethyl)amine, 1539-42-0.

Supplementary Material Available: Structure determination summary and listings of bond lengths and angles, anisotropic displacement parameters, and H atom coordinates and isotropic displacement parameters for [(tmpa)Cr(OH)$_2$Cr(tmpa)]Br$_4$·8H$_2$O (6 pages). Ordering information is given on any current masthead page.

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Early Stages of the Hydrolysis of Chromium(III) in Aqueous Solution. 4. Stability Constants of the Hydrolytic Dimer, Trimer, and Tetramer at 25 °C and I = 1.0 M[1]

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Received March 8, 1988

Addition of up to 0.8 equiv of base to aqueous Cr^{3+} results in the formation of Cr(III) hydrolytic oligomers in homogeneous solution. The evolution of these species was followed over a period of 4 years at 25 °C and I = 1.0 M (NaClO$_4$) by pH measurement, chromatographic separation, and determination of the Cr content of each oligomer fraction. After the addition of base, oligomerization caused a relatively rapid drop in monomer concentration and pH. The concentration of the dimer, Cr$_2$(OH)$_2$$^{4+}$, reached its maximum after a few days, while the trimer concentration increased monotonously throughout the reaction and Cr$_3$(OH)$_4$$^{5+}$ became the dominant oligomer. The concentration of the tetramer, Cr$_4$(OH)$_6$$^{6+}$, was rather constant after a few months. The higher oligomers were formed within a few days and subsequently decayed, contributing to the stabilization of pH after a few weeks. From the composition and the pH of Cr(III) solutions kept at 25 °C for 4 years, the cumulative stability constants β_{qp} = [Cr$_q$(OH)$_p$$^{(3q-p)+}$][H$^+$]^p/[Cr^{3+}]^q have been determined: For the fully protonated oligomers the values are log β_{22} = -5.25 ± 0.04, log β_{34} = -8.72 ± 0.06, and log β_{46} = -13.86 ± 0.15, and for the deprotonated species the values are log β_{23} = -8.93, log β_{35} = -13.07, and log β_{47} = -16.41. Combination with the pK_a values of Cr^{3+} and the oligomers gives the stepwise stability constants for the addition of Cr(OH)$_2$$^+$ to Cr^{3+} and Cr{Cr(OH)$_2$}$_{q-1}$: log K_{22} = 5.1, log K_{34} = 6.9, log K_{46} = 5.2, and log K_{58} < 6.4. For the addition of Cr(OH)$_2$$^+$ to either Cr(OH)$^{2+}$ or the monodeprotonated oligomers, one obtains log K_{23} = 5.8, log K_{35} = 6.3, log K_{47} = 7.0, and log K_{59} < 6.0.

Introduction

The determination of the stability of individual oligomeric intermediates, formed as a result of hydrolytic polymerization, is a classical theme in the coordination chemistry of metal ions in aqueous solution. Under the impact of Sillén and his group,[5] potentiometric titration methods have been used extensively to study the hydrolysis of metal ions.[6] Thus, potentiometric data are subjected to mathematical fitting procedures to determine the predominant solution species as well as their respective stability constants. In this process, the acid dissociation constants for each oligomer must also be taken into account. Due to the complicated nature of these systems, differences of opinion concerning the dominant oligomers for a particular metal ion are not uncommon.[7] Nevertheless, a considerable body of valuable and reliable information covering a variety of metal centers is available.[6] Of relevance to the work discussed here are recent pH-metric studies on the hydrolytic polymerization of Cr(III).[8-10]

For kinetically inert metal centers, protonation/deprotonation reactions are rapid while substitution processes, involved in the formation of oligomers, are slow. Thus, alkalinization deprotonates the aqua ions and promotes polymerization through the resulting conjugate bases, which are much more reactive in substitution processes than fully protonated aqua ions and oligomers.[1] Reacidification protonates the oligomers, thereby preventing further polymerization. At the same time, the acid cleavage of the protonated oligomers is slow,[11] and this inertness allows their isolation by chromatographic techniques and their further in-

Table I. Evolution of Species in Solutions of the Chromium Aqua Ion (Z = 0.3)[a]

time, h or days	pH	monomer %	dimer %	trimer %	tetramer %	higher %	sum,[b] mM	soln[c]
0.5[d]	3.93	98.7	0.5	0.1	0.1	0.6	39.6	D
1.0	3.92	97.2	1.4	0.2	0.1	1.1	40.2	D
2.0	3.89	95.8	2.3	0.7	0.2	1.1	39.4	A
4.0	3.78	94.5	3.1	0.6	0.2	1.6	39.3	A
6.0	3.68	91.6	3.9	0.6	0.5	3.4	39.0	B
8.0	3.57	89.4	4.5	0.7	0.3	5.2	39.3	C
12.0	3.35	86.7	4.7	1.1	0.7	6.8	40.4	E
18.0	3.10	83.4	5.2	2.1	1.2	8.2	40.2	E
1[e]	3.09	81.8	6.3	2.9	1.1	7.8	39.0	K
1	2.96	80.8	6.1	2.6	1.2	9.3	38.9	A
2	2.84	79.1	6.4	3.5	1.5	9.6	39.3	F
3	2.84	79.1	6.5	3.6	1.9	8.8	39.0	B
4	2.84	78.9	6.4	3.6	1.8	9.3	39.6	A
6	2.84	79.3	6.4	3.2	1.9	9.2	38.9	B
10	2.88	79.3	6.5	3.3	1.7	9.2	40.1	E
20	2.85	78.2	6.4	5.7	1.6	8.3	38.7	B
32	2.87	78.6	6.4	6.2	1.8	7.1	38.8	G
64	2.82	76.3	6.4	8.4	2.3	6.5	39.4	G
122	2.80	75.7	7.1	9.8	2.7	4.8	38.5	G
155	2.76	75.7	5.9	13.0	3.2	2.2	38.4	O
213	2.76	74.6	6.1	13.7	2.6	3.0	39.1	G
262	2.74	74.1	6.1	14.5	2.5	2.7	38.9	G
406	2.69	73.1	6.0	16.5	2.1	2.3	38.6	G
1613	2.70	72.9	5.6	17.4	2.2	1.9	37.9	G
1700	2.66	74.7	5.6	15.9	2.2	1.7	40.2	O

[a] I = 1.0 M (NaClO$_4$); 25 °C. [b] Total (eluted) chromium concentration. [c] Identifier for different solutions. [d] Hours. [e] Days.

vestigation. In the case of Cr(III), recent progress in the separation of hydrolytic oligomers[11] has led to the characterization of the

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dimer, $Cr_2(OH)_2^{4+}$ (**1**), trimer, $Cr_3(OH)_4^{5+}$ (**2**), and tetramer, $Cr_4(OH)_6^{6+}$ (**3a**), including their pK_a values (H_2O ligands are omitted for clarity). Pentamer and hexamer were observed during the chromatographic separation, but they were too dilute for the determination of the stoichiometric coefficients p in their general formula $Cr_q(OH)_p^{(3q-p)+}$.

The proposed structures **1–3** were derived from a multitude of data such as pK_a values, spectra, acid cleavage patterns, synthesis

1

2

3a

$-H^+, -H_2O$ ⇅ $+H^+, +H_2O$

3b
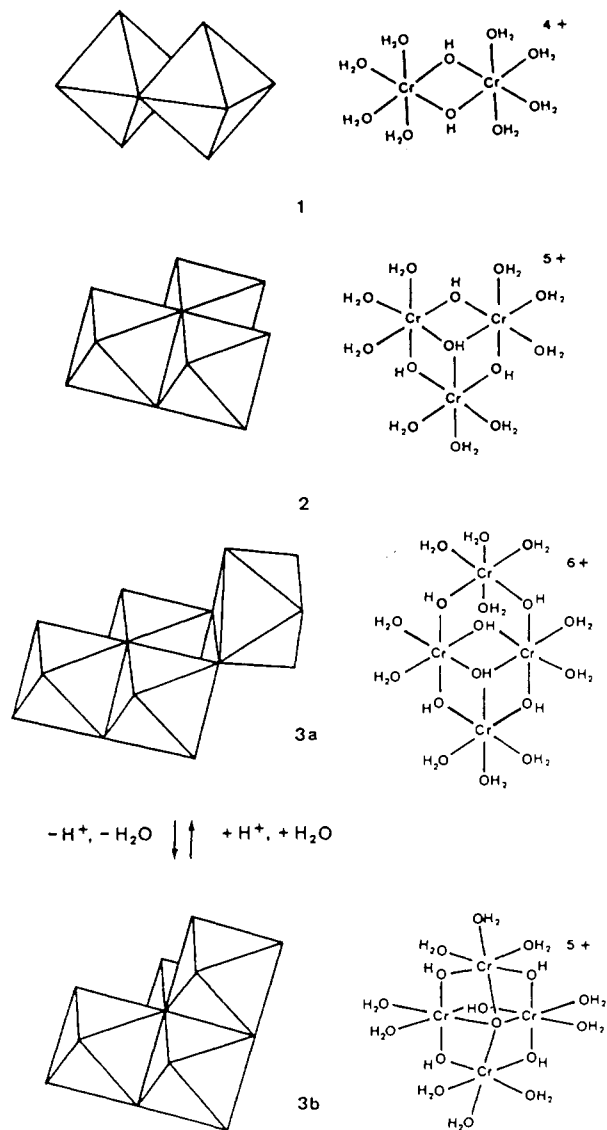
and cleavage of a ^{51}Cr-labeled tetramer, and preliminary values for the stability constants.[11] Only one isomer of the dimer and

Table II. Evolution of Species in Solutions of the Chromium Aqua Ion $(Z = 0.8)^a$

time, h or days	pH	monomer %	dimer %	trimer %	tetramer %	higher %	sum,^{b} mM	soln^c
0.4^d	4.54	87.0	7.8	1.3	0.3	3.6	35.3	C
0.8	4.41	78.0	10.7	1.9	0.5	8.9	37.2	D
1.5	4.25	73.7	12.0	2.8	1.2	10.2	36.2	C
3.0	4.05	67.4	13.8	4.1	1.9	12.8	36.0	D
6.0	3.82	62.5	13.3	5.0	2.3	16.9	36.3	B
1^e	3.33	55.4	13.7	7.1	3.3	20.5	34.9	A
2	3.14	53.1	13.3	6.7	3.8	23.1	35.9	A
5	3.04	51.8	12.8	8.2	4.3	23.0	35.6	A
8	3.04	51.5	12.5	9.5	4.2	22.3	35.7	A
17	3.02	51.6	11.7	9.8	4.4	22.5	35.8	A
31	3.01	51.0	10.4	12.5	4.4	21.7	35.1	A
64	2.98	51.1	9.0	15.2	5.4	19.3	34.9	A
122	2.98	49.3	7.3	17.6	6.3	19.4	34.8	A
231	2.96	47.5	6.5	22.3	7.3	16.4	35.7	A
262	2.96	44.8	6.1	25.0	8.5	15.6	33.5	A
405	2.93	44.5	5.8	28.0	7.0	14.8	35.5	A
1613	2.94	44.7	6.1	30.5	7.6	11.1	35.9	A

$^a I = 1.0$ M ($NaClO_4$); 25 °C. ^{b}Total (eluted) chromium concentration. ^{c}Identifier for different solutions. ^{d}Hours. ^{e}Days.
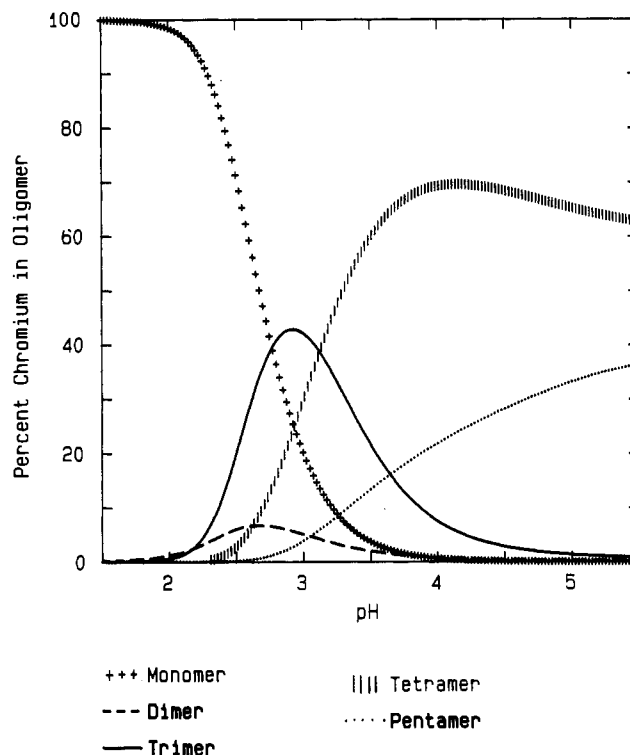

+++ Monomer   ‖‖‖ Tetramer
- - - Dimer   ·····Pentamer
—— Trimer

Figure 1. Distribution of chromium in the different oligomers as a function of pH for a solution with $[Cr]_{tot} = 0.1$ M.

trimer was formed, whereas two rapidly interchanging isomers of the tetramer were observed, for which the following structures were proposed:[11] $Cr_4(OH)_6^{6+}$ is more stable in the "open" form **3a**, but after deprotonation it isomerises into the "closed" form $Cr_4O(OH)_5^{5+}$ (**3b**) with $k = 0.24$ s^{-1}; the protonated "closed" form reconverts to **3a** with $k = 4.4$ s^{-1}.[12]

However, alternative "classical" structures, based on either linear or bent arrangements of Cr–amine fragments linked together via two μ-hydroxo bridges, have been proposed.[13] (No stability data for the formation of such Cr(III)–amine complexes are available.) These structures (derived from complexes containing amine instead of water ligands)[13] can account for some of the pK_a's of the oligomers, but they cannot accommodate the observed variability of their stability constants and cleavage rates: (i) the acid cleavage

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Table III. Composition of the Aged Solutions after 1–4 Years at 25 °C and Logarithms of the Stability Constants β_{qp} for the Chromium(III) Oligomers $Cr_q(OH)_p$

concn, M	Z	time, years	pH	monomer %	dimer %	trimer %	tetramer %	higher %	log β_{22}	log β_{34}	log β_{46}
0.01	0.1	0.7	2.93	83.9	4.9	9.0	1.7	1.4	−5.35	−8.97	−14.09
0.01	0.1	4	2.92	79.7	4.9	12.6	1.9	1.0	−5.28	−8.71	−13.89
0.01	0.8	0.7	3.18	49.1	4.9	19.5	7.5	18.9	−5.39	−8.87	−14.10
0.01	0.8	4	3.18	43.6	5.9	25.7	8.9	15.9	−5.22	−8.62	−13.87
0.04	−0.1	4	2.32	94.7	2.3	2.5			−5.15	−8.49	
0.04	0.3	0.7	2.74	74.1	6.1	14.5	2.5	2.7	−5.35	−9.04	−14.25
0.04	0.3	1.1	2.69	73.1	6.0	16.5	2.1	2.3	−5.24	−8.77	−13.98
0.04	0.3	4	2.70	73.1	5.7	17.4	2.2	1.6	−5.27	−8.76	−13.98
0.04	0.3	4	2.66	74.9	5.6	15.9	2.2	1.4	−5.24	−8.72	−13.85
0.04	0.3	4[a]	2.63	74.3	5.9	16.3	2.6	0.9	−5.19	−8.66	−13.69
0.04	0.8	0.7	2.96	44.8	6.1	25.0	8.5	15.6	−5.30	−8.88	−14.09
0.04	0.8	1.1	2.93	44.5	5.8	28.0	7.0	14.8	−5.28	−8.76	−14.04
0.04	0.8	4	2.94	44.7	6.1	30.5	7.6	11.1	−5.29	−8.77	−14.09
0.10	0.1	1	2.37	87.7	4.0	7.1	0.7	0.6	−5.33	−8.91	−13.90
0.10	0.1	4	2.34	87.0	4.2	7.6	0.8	0.4	−5.24	−8.76	−13.67

[a] This solution was heated to 90 °C and reached equilibrium from low pH.

Table IV. Summary of the Stability Constants for Chromium(III) Hydrolytic Oligomers (25 °C; I = 1.0 M ($NaClO_4$))

	monomer	dimer	trimer	tetramer	pentamer
q, p	1, 0	2, 2	3, 4	4, 6	5, 8
$pK_{aq1}{}^a$	4.29	3.68	4.35	2.55	
$pK_{aq2}{}^a$	6.1	6.04	5.63	5.08	
log β_{qp}		−5.25 ± 0.04	−8.72 ± 0.06	−13.86 ± 0.15	<−17.9
		−5.0[b]	−8.2[c]		
		−4.7[d]	−9.0[d]	−13.4[d]	
log $\beta_{qp+1}{}^e$		−8.93	−13.07	−16.41	<−20.8
log K_{qp}		5.14 ± 0.04	6.92 ± 0.04	5.24 ± 0.14	<6.4
log $K_{qp+1}{}^e$		5.75 ± 0.04	6.25 ± 0.04	7.04 ± 0.14	<6.0

[a] Reference 11. [b] Extrapolated from ref 20. [c] Extrapolated from ref 21. [d] Extrapolated from ref 10. [e] The deprotonated species.

++ + Monomer ||||| Tetramer

— — — Dimer   ······ Pentamer
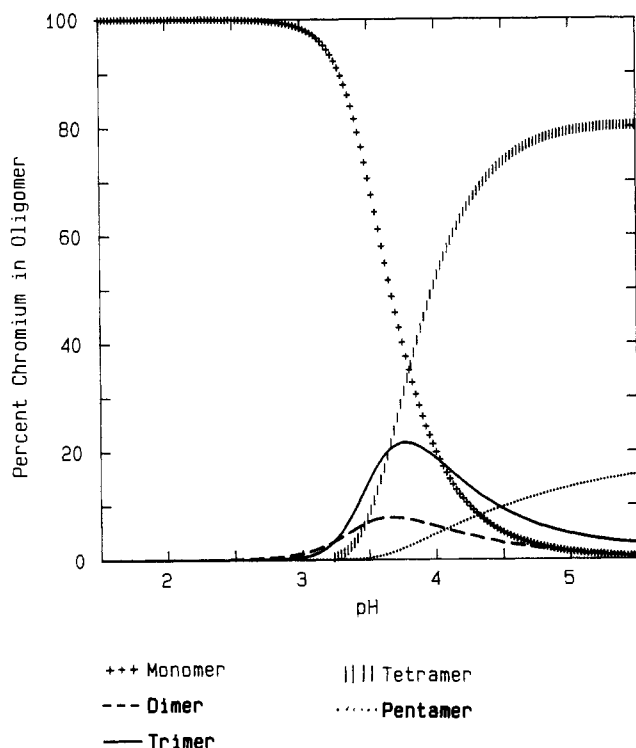
——— Trimer

Figure 2. Distribution of chromium in the different oligomers as a function of pH for a solution with $[Cr]_{tot}$ = 0.001 M.

in 1 M $HClO_4$ at 25 °C of the tetramer, pentamer, and hexamer ($t_{1/2}$ = 30–300 min)[11,14] is dramatically more rapid than that of the trimer ($t_{1/2}$ = 21 days);[11] (ii) the cleavage of the higher oligomers produces predominantly the trimer; (iii) on acid cleavage

of the tetramer only the trimer and monomer are formed, consistent with cleavage of the "dangling" Cr group in **3a**,[11] and furthermore the hexamer cleaves exclusively into the trimer.[14] For the structures proposed in ref 13 cleavage is expected to occur at different positions along the polymer chain, thus giving rise to a variety of products rather than selected oligomers as observed experimentally. Concerning the two isomers of the tetramer, the "bridge shift" mechanism proposed in ref 13 is an interesting new idea, but experimental support for it is presently completely lacking.

This paper reports the evolution of individual oligomers after addition of base to solutions of the Cr^{3+} aqua ion and the stability constants for the hydrolytic dimer, trimer and, tetramer determined after equilibrium was reached.

Definitions

[X] = molar concentration of X

pH = −log[H$^+$]

$Cr_q(OH)_p{}^{(3q-p)+}$ = general formula of oligomer with nuclearity q

$[Cr]_{tot}$ = total chromium concentration of a solution

Z = average number of OH$^-$ ions per chromium ion

$[Cr_q]_{tot}$ = concentration of all oligomers of same nuclearity = $[Cr_q(OH)_{2q}]$ + $[Cr_q(OH)_{2q+1}]$ + $[Cr_q(OH)_{2q+2}]$ + ...

% = $100q[Cr_q]_{tot}/[Cr]_{tot}$ = % Cr in oligomer fraction with nuclearity q

β_{qp} = $[Cr_q(OH)_p{}^{(3q-p)+}][H^+]^p/[Cr^{3+}]^q$

K_{qp} = $[Cr_q(OH)_p{}^{(3q-p)+}]/([Cr_{q-1}(OH)_{p-2}{}^{(3q-p-1)+}][Cr(OH)_2{}^+])$

K_{aq1} = $[Cr_q(OH)_{p+1}{}^{(3q-p-1)+}][H^+]/[Cr_q(OH)_p{}^{(3q-p)}]$, $p = 2(q-1)$

K_{aq2} = $[Cr_q(OH)_{p+2}{}^{(3q-p-2)+}][H^+]/[Cr_q(OH)_{p+1}{}^{(3q-p-1)+}]$, $p = 2(q-1)$

pK_a = −log K_a

Results and Discussion

Evolution of the Oligomers. Solutions for these studies were prepared by adding up to 0.8 equiv of hydroxide to Cr^{3+} (0.01–0.1 M). They were kept at 25 °C, and the progress of polymerization

(14) Spiccia, L.; Marty, W.; Giovanoli, R. *Inorg. Chem.* **1988**, *27*, 2660.

was followed over a period of 4 years by pH measurement, chromatographic separation of the oligomers, and chromium determination using established methods.[11] The sum of Cr recovered from chromatographic separation accounted for 98.5–100.5% of the amount used. Tables I and II summarize the relevant data for two of these solutions. Similar patterns were also observed in other solutions although they were studied in less detail. In general, measurable concentrations of oligomers were present a few minutes after the addition of base. Polymerization is accompanied by a decrease in pH, as expected from the stoichiometry and the pK_a values of the oligomers. At pH 4.3, for example, 0.9 equiv of H^+ is liberated for each monomer that undergoes dimerization: $2Cr(OH)_{0.5} = Cr_2(OH)_{2.8} + 1.8H^+$ (charges of the species and the H_2O ligands are omitted for clarity).

The monomer concentration decreased significantly during the first day as it was converted into the hydrolytic oligomers. As expected, the trimer and tetramer evolved more slowly than the dimer, but it was somewhat surprising that the concentration of the higher oligomers appeared to increase at a faster rate than any of the lower oligomers (Tables I and II). Closer inspection of the results in Table I shows that there was some formation of higher oligomers very early after the addition of base and that further significant increases were delayed by a few hours. The intial formation of the higher oligomers may be due, at least in part, to the mixing procedure, where addition of strong base to a Cr^{3+} solution can give rise to localized regions of higher alkalinity promoting rapid polymerization (no higher oligomers were formed on mixing, when weak bases such as dilute solutions of imidazole or ethanolamine were used).[1]

For the time period between 4 and 12 h, substantial increases in the amount of higher oligomers were observed coupled with little change in trimer and tetramer and a decreased rate of dimer formation. These observations suggest that once critical concentrations of the lower oligomers are reached, rapid and efficient conversion into higher oligomers occurs. This agrees with the results of aging studies on the "active" hydroxides of Cr(III),[14-16] where polymerization was faster for the dimer and trimer than for the monomer, and as a consequence, in the latter case initial conversion of the monomer into the dimer was rate determining.

One day after the addition of base, pH had dropped by ca. 1 unit and the rate of the reaction had decreased markedly. This is consistent with previously published rates for the dimerization of Cr(III),[1] where the rate constants increased by a factor of ca. 100 for each additional deprotonation of Cr^{3+}. Thus, the increasing acidity lowers the concentrations of the more reactive deprotonated species, thereby reducing the reaction rate. There was no further increase in the concentration of the dimer, because its formation from the monomer and its continuing condensation to the trimer and tetramer were of comparable rates and/or because cleavage of the higher oligomers led to the formation of some dimer. Indeed, the concentration of the higher oligomers decreased due to their cleavage back into the lower oligomers in the more acidic media. Without product analysis, constancy of pH might have suggested attainment of equilibrium after a few weeks, but a constant pH is no proof for equilibrium because decay of higher oligomers and continuing condensation of monomer produce opposite pH effects.

After approximately 1 year, pH and the concentrations of the monomer, dimer, and tetramer had stabilized. However, the trimer concentration continued to increase while that of the higher oligomers decreased, indicating that the main product of the decay of the higher polymers is the trimer. This preferential decay is corroborated by a convenient synthesis of the trimer; viz., addition of excess base to solutions of Cr^{3+} produces chromites that, after acidification, slowly cleave to give solutions containing predominantly the trimer.[14] Thus, the trimer clearly marks the maximum in stability and inertness within the series of Cr(III) hydrolytic

oligomers, and that can easily be rationalized with the proposed compact structure (**2**).

Only minor changes in composition and pH were observed for equilibration periods between 1 and 4 years (Table III), suggesting that equilibrium had been attained. In all these cases, however, equilibrium was approached from the high pH, low degree of polymerization, side. To approach equlibrium from the opposite side, a solution with $[Cr]_{tot} = 0.04$ M and $Z = 0.3$ was heated to 90 °C for 1 h to promote polymerization and then allowed to equilibrate at 25 °C for 4 years. After 10 days the pH value had increased from 2.0 to 2.12 and the Cr distribution was 62% monomer, 10.4% dimer, 18.8% trimer, 2.7% tetramer, and 6.1% higher oligomers, indicating a higher degree of polymerization and lower pH than for any of the equilibrated solutions with $Z = 0.3$ (Table III). The pH value slowly increased, reaching 2.63 after 4 years, a value similar to those of the unheated solutions after the same equilibration period. The final composition was also close to that of the unheated solutions (Table III), demonstrating that true equilibrium was attained after 4 years at 25 °C.

Determination of the Cumulative Stability Constants β_{qp}. The calculation of the cumulative stability constants requires the concentrations of the fully protonated oligomers present in the equilibrated solutions. For the chromatographic separation procedure,[11] however, the solutions were acidified, whereupon all oligomers were fully protonated. Thus, the concentrations $[Cr_q]_{tot}$ determined from the separation procedure include all forms of the species of same nuclearity q—whether protonated or deprotonated—present in the equilibrated solution. The sought concentrations $[Cr_q(OH)_p]$ (with $p = 2(q - 1)$ and $q = 1$–4) are evaluated from the experimentally determined total concentrations, the pH value of the equilibrated solutions, and the pK_a values of Cr^{3+} and the protonated oligomers by using the expression

$$[Cr_q(OH)_p^{(3q-p)+}] =$$
$$[Cr_q]_{tot}/\{1 + K_{aq1}/[H^+] + K_{aq1}K_{aq2}/[H^+]^2\}$$

With these concentrations, the evaluation of the stability constants $\beta_{qp} = [Cr_q(OH)_p^{(3q-p)+}][H^+]^p/[Cr^{3+}]^q$ is straightforward: e.g., for the final solution in Table II, $[Cr]_{tot} = 0.0359$ M, $[Cr_1]_{tot} = 0.0161$ M, $[Cr^{3+}] = 0.0154$ M, $[Cr_2]_{tot} = 0.001\,09$ M, $[Cr_2(OH)_2^{4+}] = 0.000\,92$ M, and $[H^+] = 10^{-2.94}$, giving $\beta_{22} = 5.11 \times 10^{-6}$ M. All the stability constants given in Table III were calculated accordingly. Slight increases in these constants were observed as the equilibration period increased from 1 to 4 years: viz., for the five solutions that have been measured after 0.7 to 1.1 years and again after 4 years, the average increase is 0.06 for log β_{22} and 0.2 for log β_{34} and log β_{46}. The log β_{qp} values in Table IV are the average for seven solutions investigated after 4 years. The solution with $Z = -0.1$ was not included in the average because only small amounts of dimer and trimer were present, limiting the accuracy of their determination. The stability constants for the deprotonated oligomers were obtained from the expression log $\beta_{qp+1} = $ log $\beta_{qp} - pK_{aq1}$ and are also given in Table IV.

Repetition of the separation procedure gave relative standard deviations of up to 4, 7, and 13% for the concentrations of dimer, trimer, and tetramer, respectively. This contributes ≤ 0.05 to the standard deviation of log β_{46} and less for log β_{22} and log β_{34}. More important is the influence of the uncertainty in pH, where an error of 0.01 gives errors of 0.02, 0.04, and 0.06 for log β_{22}, log β_{34}, and log β_{46}, respectively. Thus, the standard deviation of log β_{46} is larger than for the others because of the difficulty in determining accurately the comparatively small percentages of the tetramer coupled with the error propagation in the pH term. The 95% confidence interval of the average values of log β is close to the experimental standard deviation S (i.e. 0.92 S, whereby the factor 0.92 derives from $t_{0.95} = 2.45$ for 6 degrees of freedom, divided by $7^{0.5} = 2.65$). A systematic error not included in the calculation is the standard deviation of the pK_a values of the tetramer, which adds an uncertainty of ≤ 0.05 to log β_{46}.

Similar values for log β_{22} and log β_{34} were obtained from analogous studies in the temperature range 37.5–67.5 °C at $I = 1.0$ M,[20,21] where the separation was performed with Dowex

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cation-exchange resin instead of Sephadex as in the present work. Extrapolation to 25 °C (log β vs $1/T$) gives log β_{22} = -5.0 and log β_{34} = -8.2, i.e. values larger by 0.3 and 0.5 log unit. This may be due to differences in the pH scale: in ref 20 and 21, the H^+ activity scale (pH_a) was used and calibration with a buffer of pH_a = 4.0 was extrapolated to the measurements in the pH range 1.6–2.2. In the present work, pH was calibrated in the concentration scale (pH 2–3) by titration of strong acid with base, using a constant ionic strength liquid junction, and correcting for the liquid-junction potential arising from the higher mobility of H^+.[11,17,18] Furthermore, the deprotonated forms of the dimer and trimer were not taken into account in ref 20 and 21; i.e., $[Cr_q]_{tot}$ was used instead of $[Cr_q(OH)_p]$.

Other studies have used the traditional pH method, where the pH, the total concentration of Cr(III), and the amount of added base are the variables from which composition and constants are derived.[5–10,19] The corresponding data were fitted with the following sets of complexes: $Cr_2(OH)_2^{4+}$, $Cr_6(OH)_{12}^{6+}$, Cr_{12}-$(OH)_{30}^{6+}$;[5,19] $Cr_2(OH)^{5+}$, $Cr_2(OH)_2^{4+}$, $Cr_3(OH)_2^{7+}$, $Cr_3(OH)_3^{6+}$, $Cr_3(OH)_4^{5+}$, $Cr_3(OH)_5^{4+}$, $Cr_4(OH)_6^{6+}$, ...[8–10] (Note that in ref 8 the solutions were considered at equilibrium when the pH changed less than 0.005 unit in 4 days, but this is open to question in view of our data, which show that changes in composition can occur without significant pH drift.) The model postulated in ref 8–10 suggests that the species $Cr_2(OH)^{5+}$, $Cr_3(OH)_2^{7+}$, and $Cr_3(OH)_3^{6+}$ are stable at pH > 1.6. This proposal, however, is at variance with titrations of pure samples of dimer and trimer[11] and with measurements of the equilibrium between $Cr_2(OH)^{5+}$ and $Cr_2(OH)_2^{4+}$.[20] Nevertheless, the results from ref 10 (log β_{22} = -4.19, log β_{34} = -8.23, and log β_{46} = -12.28 at 40 °C and I = 0.5 M) are in reasonable agreement with our values when extrapolated to 25 °C by using ΔH_{pq} = 12.7 kcal/mol for the dimer,[20] 23 kcal/mol for the trimer,[21] and 33 kcal/mol for the tetramer (estimated). This gives log β_{22} = -4.7, log β_{34} = -9.0, and log β_{46} = -13.4; cf. our respective values of -5.26, -8.72, and -13.86.

The higher oligomers were not further investigated in this study due to difficulties encountered in the quantitative separation of pentamer and hexamer and the lack of information on the even higher oligomers. Qualitatively, the pentamer fraction was always much smaller than the rest of the higher oligomers. Upper limits for log β_{58} and log β_{59} were estimated (Table IV) by assuming that not more than 50% of the higher oligomers are present as the pentamer, either $Cr_5(OH)_8^{7+}$ or $Cr_5(OH)_9^{6+}$. However, the pronounced pH dependence of the concentration of the higher oligomers suggests that more highly deprotonated species might become important with increased nuclearity of the complexes. This is reasonable in view of the increasing charge of the oligomers which favors further deprotonation and possibly formation of oxo bridges.

The Stepwise Stability Constants K_{qp}. While the cumulative stability constants β_{qp} characterize the stability of a species in an unambigous and mathematically straightforward manner, the stepwise constants are more appropriate for comparative purposes. They were calculated from combinations of the cumulative stability constants with pK_a values. As an example, the expression for K_{34} is

$$K_{34} = [Cr_3(OH)_4^{5+}]/\{[Cr_2(OH)_2^{4+}][Cr(OH)_2^+]\} =$$
$$\beta_{34}/\{\beta_{22}K_{a11}K_{a12}\}$$

The other constants in Table IV were calculated in a similar manner.

The series K_{22}, K_{34}, and K_{46} corresponds to the addition of $Cr(OH)_2^+$ to the monomer, dimer, and trimer to form Cr{Cr-

$(OH)_2\}_{q-1}$, whereas K_{23}, K_{35}, and K_{47} represent the formation of $CrOH\{Cr(OH)_2\}_{q-1}$ by addition of $Cr(OH)_2^+$ to the deprotonated monomer, dimer, and trimer, respectively. If each step corresponded to a structurally similar condensation, comparable K_{qp} values would be expected within either series, i.e. $K_{22} \sim K_{34} \sim K_{46}$ and $K_{23} \sim K_{35} \sim K_{47}$.

In the series of protonated oligomers, log K_{22} (5.14) is comparable with log K_{46} (5.24), but log K_{34} is much larger (6.92). Our proposed structures 1–3 agree with these data because *two* new Cr–(OH)–Cr bridges are established when $Cr(OH)_2^+$ reacts with either the monomer or trimer to give the dimer (**1**) or tetramer (**3a**), respectively. In the condensation of $Cr(OH)_2^+$ with the dimer, however, the more stable trimer with *three* new OH– bridges is formed.

Among the constants for the deprotonated oligomers, log K_{47} (7.04) is larger than log K_{23} (5.75) and log K_{35} (6.25). This, too, fits our proposed structures because the last monomeric unit involved in the formation of $Cr_4(OH)_5O^{5+}$ (**3b**) attaches to the trimer via two OH bridges and one O bridge. Again, extra stability is found for a compact structure. There is, however, a 9 times less stable form of the deprotonated tetramer, $Cr_4(OH)_7^{5+}$,[12] and allowing for this difference in stability, log K'_{46} (6.1) for the formation of this proposed "open" form is comparable with K_{23} and K_{35}.

These stepwise constants do not, however, imply that the reaction mechanisms follow the above reaction sequences (cf. ref 1). The differences between the K_{qp} values suggest that curve fitting with the core and links procedure[9,10] (i.e., all K_{qp} and all K_{qp+1} assumed identical except for statistical factors) is of limited value. As mentioned above, the pH dependence of the higher oligomers indicates that they contain more OH$^-$ than given by the core and links type formulas $Cr\{Cr(OH)_2\}_{q-1}$ and $CrOH$-$\{Cr(OH)_2\}_{q-1}$.

Thus, the stabilities of the individual oligomers are in complete agreement with the structures proposed in earlier work,[11,12] but they are difficult to rationalize for the "classical" structures proposed in ref 13. Such a "classical" isomer of the trimer (or tetramer) may have been observed after the synthesis of the dimer by oxidation of Cr(II). On purification of the dimer by chromatography, a blue oligomer of charge 5+ to 6+ is eluted after the dimer. Its color is unlike that of the trimer (dark green) and the tetramer (olive) formed under nonredox hydrolytic conditions, but it is similar to that of the pale blue dimer. This oligomer may therefore be a "classical" isomer of the trimer (or tetramer), resembling the dimer by having two μ-OH bridges between each chromium center, and it is formed only in a kinetically controlled reaction under redox conditions but not after alkalinization of Cr(III).

Hydrolysis as a Function of pH. Figures 1 and 2 show the distribution of chromium in the different oligomers as a function of pH. To obtain some information about the polymerization beyond tetramer, estimated stability constants for the pentamer were included: it was assumed that the reaction between the trimer and dimer to form the pentamer, $Cr_5(OH)_8^{7+}$, has the same formation constant as was found for the reaction $Cr_3(OH)_4^{5+}$ + Cr^{3+} + $2H_2O$ = $Cr_4(OH)_6^{6+}$ + $2H^+$, i.e. $10^{-5.15}$. Thus, log β_{58} = -19.12 was estimated and analogously: log β_{59} = -21.67 and log β_{510} = -26.75.

Figure 1 shows the distribution for a solution with $[Cr]_{tot}$ = 0.1 M. Here significant polymerization sets in at about pH 2 and the dimer, trimer, and tetramer evolve successively toward higher pH. The protonated trimer dominates at pH < 3, and then the deprotonated tetramer (and pentamer) are formed. At pH > 4.5 there are no significant further changes within this model, but in this range more extensively deprotonated higher polymers are likely to become important. At the lower $[Cr]_{tot}$ = 0.001 M (Figure 2) there is little polymerization below pH 3, but then the dimer, trimer, and tetramer appear over a narrow range of pH. This is reminiscent of titrations of metal ions, where at a given pH the addition of one drop of base promotes sudden precipitation of large amounts of hydroxide. With these constants, the pentamer never dominates, and this is in accord with our observations.

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However, it is expected that at pH > 4 a large series of higher oligomers are evolving.

Conclusions

The present work substantiates a number of important observations:

(1) Monitoring the evolution of Cr(III) hydrolytic oligomers after the addition of base to Cr^{3+} has shown that an apparently constant pH does not necessarily indicate that equilibrium has been reached.

(2) The trimer was the predominant oligomer in all solutions studied (pH 2.3–3.2). This stable and inert[11] oligomer may be the prototype for Cr(III) polymerization. In contrast, the compact deprotonated tetramer (**3b**) is the most stable among the deprotonated oligomers.

(3) The stability constants support the structures proposed for these oligomers in our earier work.[11,12]

(4) Core and links calculations, with one polymerization constant, cannot appropriately describe the hydrolysis of chromium-(III) aqua ion.

Work aimed at the isolation and characterization of further members of the Cr(III) hydrolytic oligomer series is continuing (L.S.[3]).

Experimental Procedures

All experimental methods including the preparation and analysis of Cr^{3+} stock solutions, the procedure for chromatographic analysis of solutions of Cr(III), and the procedure for pH measurement have been described previously.[11] Where necessary, details of conditions used in the equilibration studies are given in Tables I–III.

Registry No. Cr, 7440-47-3.

Use of Thermal Lensing Spectrophotometry (TLS) for the Study of Mononuclear Hydrolysis of Uranium(IV)

Ingmar Grenthe,*,[†] Giovanni Bidoglio,[‡] and Nicolo Omenetto[‡]

The possibility of using thermal lensing spectrophotometry (TLS) for the quantitative determination of chemical equilibria in very dilute ($\sim 10^{-5}$ M) aqueous solution has been explored. The hydrolysis of uranium(IV) has been used as a test case. TLS turned out to be a convenient, precise, and rapid method to obtain information about the mononuclear hydrolysis, information that is difficult to obtain with more traditional solution chemical methods. The TLS data were obtained at 25 °C in the concentration range of $0 \leq -\log [H^+] \leq 2.8$ by using a 3 M $(Na,H)ClO_4$ ionic medium. The data were described with the following chemical model: $U^{4+} + H_2O \rightleftharpoons UOH^{3+} + H^+$, $\log *\beta_1 = -1.65 \pm 0.05$; $U^{4+} + 2H_2O \rightleftharpoons U(OH)_2^{2+} + 2H^+$, $\log *\beta_2 < -4.5$. Apart from its higher sensitivity, the TLS method has the same characteristics as ordinary spectrophotometric methods. The experimental results of this study and previous literature information were interpreted by using the specific ion interaction theory to give $\log *\beta^\circ_1 = -0.51 \pm 0.03$ ($\log *\beta^\circ_1$ is the equilibrium constant at zero ionic strength) and $\Delta\epsilon = -0.14 \pm 0.02$, where $\Delta\epsilon$ is the ion interaction term $\Delta\epsilon = \epsilon(UOH^{3+}, ClO_4^-) + \epsilon(H^+, ClO_4^-) - \epsilon(U^{4+}, ClO_4^-)$.

Introduction

Aquometal ions are acids, and the stoichiometry and equilibrium constants of metal hydroxide complexes

$$pM^{n+} + qH_2O \rightleftharpoons M_p(OH)_q^{np-q} + qH^+ \qquad (1)$$
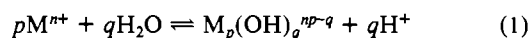
is a "traditional" field of solution chemistry. A recent review is given by Baes and Mesmer in ref 1. Polynuclear complexes are the predominant hydroxide complexes formed for most metal ions, particularly for those with a high oxidation state. The stoichiometry of these complexes is many times identical with the stoichiometry of polynuclear units that are found in solid "basic salts" of the metal ions; e.g. basic bismuth perchlorate $BiO\text{-}ClO_4 \cdot nH_2O(s)$ contains discrete hexanuclear complexes $Bi_6O_4\text{-}(OH)_4^{6+}$,[2] and this complex has also been identified in solution.[3]
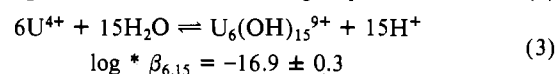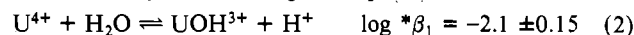
The polynuclear complexes are presumably formed by condensation reactions involving species of lower nuclearity, e.g. the mononuclear hydroxide species $M(OH)_p^{n-p}$. In order to explore the fundamental chemistry of these reactions, it is important to have access to thermodynamic data for the mononuclear hydrolysis reactions.

It is obvious that the formation of polynuclear complexes is strongly dependent on the total concentration of the metal ion; cf. eq 1. Hence, the relative importance of mononuclear species over the polynuclear ones increases with decreasing total concentration of M. This fact may be of importance for the speciation of metal ions, e.g. in natural water systems where the total metal concentrations are often very low. Such trace metals may, for example, be uranium or transuranium elements released from radioactive waste repositories of various kinds.

Potentiometry is the most precise experimental method for the study of chemical equilibria in solution. However, it requires fairly large total concentrations of the reacting species. Hence, it may be difficult to study mononuclear complex formation in systems where polynuclearity is predominant. In the following we will explore the utility of thermal lensing spectrophotometry (TLS)[4] as a quantitative tool for the study of such a system. No previous quantitative studies of the use of TLS in equilibrium analysis have been published as far as we are aware. We have selected the uranium(IV)–H_2O system because of its interest from both the fundamental and the applied points of view.

Chemistry of the U(IV)–H_2O System. The hydrolysis of uranium(IV) has previously been studied by Kraus and Nelson,[5,6] Sullivan and Hindman,[7] and Hietanen and Sillen.[8] The data can be described by the following two equilibria:

$$U^{4+} + H_2O \rightleftharpoons UOH^{3+} + H^+ \qquad \log *\beta_1 = -2.1 \pm 0.15 \qquad (2)$$

$$6U^{4+} + 15H_2O \rightleftharpoons U_6(OH)_{15}^{9+} + 15H^+$$
$$\log *\beta_{6,15} = -16.9 \pm 0.3 \qquad (3)$$

Both values refer to a 3 M perchlorate medium.

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