cross-reactions appear to contain contributions from each. The partial development of the product charges 3+, 1− leading to increased solvent organization and the coordination of axial water to the copper complex would give rise to the observed negative ΔS^{*} values. It is interesting that the majority of the entropy change for each reaction is encountered in the activation steps prior to electron transfer.

Conclusions

The reactions of $Cu^{III}(H_{-2}Aib_3)$ with several $Cu^{II}(H_{-3}L)$ complexes show an excellent Marcus correlation and indicate an average self-exchange rate constant (corrected for electrostatic work terms) of $(2 \pm 1) \times 10^4$ M^{-1} s^{-1} for $Cu^{III,II}(H_{-3}L)$. The exchange rate constants can be used to predict accurately the rates of electron transfer between Cu(III)–peptide complexes and ruthenium(II) ammine complexes from the Marcus theory for outer-sphere reactions. The reactions of $Ru(NH_3)_5py^{2+}$ and $Ru(NH_3)_5pic^{2+}$ show no evidence of any special pyridyl-ring interaction by which facile electron conduction can occur.

The absence of bridging ligands on the Ru(II) complexes, the substitution rate constants of the complexes involved, and the adherence of the reactions to the Marcus theory suggest that Cu(III) peptides undergo electron transfer with Ru(II) complexes by an outer-sphere mechanism. This is in contrast to the inner-sphere reactions reported for $IrCl_6^{3-}$[4] and $Fe(CN)_6^{4-}$.[5] Thus, the reaction partner in cross-reactions with Cu(III, II)–peptide complexes determines whether the reactions proceed by an inner-sphere or an outer-sphere mechanism.

Acknowledgment. The investigation was supported by Public Health Service Grants No. GM-19775 and No. GM-12152 from the National Institute of General Medical Sciences.

Registry No. I, 69990-31-4; II, 82495-22-5; $Cu^{II}(H_{-3}Aib_3a)^-$, 85926-43-8; $Cu^{II}(H_{-3}G_2AibG)^{2-}$, 85926-41-6; $Cu^{III}(H_{-3}G_2AibG)^-$, 82495-23-6; $Cu^{II}(H_{-3}V_4)^{2-}$, 62959-94-8; $Cu^{III}(H_{-3}V_4)^-$, 62959-93-7; $Cu^{II}(H_{-3}A_3G)^{2-}$, 85926-42-7; $Cu^{III}(H_{-3}A_3G)^-$, 82495-25-8; $Cu^{II}(H_{-3}G_4)^{2-}$, 57603-18-6; $Cu^{III}(H_{-3}G_4)^-$, 57692-61-2; $Ru(NH_3)_6^{2+}$, 19052-44-9; $Ru(NH_3)_5py^{2+}$, 21360-09-8; $Ru(NH_3)_5pic^{2+}$, 19482-30-5.

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Contribution from the Institut de Chimie,
Université de Neuchâtel, CH-2000 Neuchâtel, Switzerland

Early Stages of the Hydrolysis of Chromium(III) in Aqueous Solution. 1. Characterization of a Tetrameric Species

HANS STÜNZI and WERNER MARTY*

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The first few members of the series of hydrolytic polymers of Cr(III), formed upon addition of hydroxide ion (<1 equiv) to the chromium(III) aqua ion, were separated on Sephadex SP C-25. Elution with sodium perchlorate (0.5–4 M) gave fractions containing $Cr^{3+}(aq)$, $Cr_2(OH)_2^{4+}(aq)$, $Cr_3(OH)_4^{5+}(aq)$, and $Cr_4(OH)_6^{6+}(aq)$, respectively. Two higher polymers, presumably pentamer and hexamer, were eluted with 4 M $LiClO_4$. The pK_a values of the first oligomers were determined (I = 1 M ($NaClO_4$) at 25 °C) from pH titrations: 4.29, 6.1 (monomer); 3.68, 6.04 (dimer); 4.35, 5.63, 6.0 (trimer); 2.55, 5.08 (tetramer). The visible spectra of the monomer, dimer, and trimer agree with those given in the literature, and $Cr_4(OH)_6^{6+}$ has λ_{max} = 426 nm (ϵ = 30.3) and 580 nm (ϵ = 15.6). The spectrum of the hexamer is very similar to that of the trimer. The tetramer is most conveniently synthesized by adding hydroxide ion to solutions of the pure dimer, but in acidic solution it cleaves rapidly and almost exclusively into monomer and trimer. The order of robustness (in acidic solution) and stability is dimer < trimer ≫ tetramer. The above observations agree best with a trimer consisting of a trigonal array of the three chromium ions sharing a common hydroxide bridge (**2**). The properties of the tetramer, $Cr_4(OH)_6^{6+}$, suggest that the fourth chromium center may be bound through OH bridges to two of the chromium ions of a trimer unit (**3a**). On deprotonation, intramolecular condensation is proposed to give $Cr_4O(OH)_5^{5+}$ (**3b**) with a central tetracoordinated oxo ligand. Reaction of ^{51}Cr-labeled monomer with excess deprotonated trimer afforded labeled tetramer, which was isolated and cleaved with acid to give equal amounts of label in the monomer and trimer. The tetramer thus contains two equivalent metal centers, consistent with the proposed structures of the tetramer and trimer.

Introduction

The hydrolysis of metal ions is a fundamental process occurring in natural waters and ore formation and also in biological systems. The knowledge even of the early stages of hydrolytic polymerization is still sketchy because formation of significant amounts of soluble oligomers is usually prevented by precipitation of insoluble hydroxo– and hydroxo–oxo–metal phases.[1] This does not hold for chromium(III) owing to its kinetic robustness. Furthermore, the hydrolytic polymerization of Cr(III) is not complicated by redox processes and structural assignments can be made by relying on the almost exclusive and constant octahedral coordination of Cr(III) centers.

Indeed, the study of the hydrolytic polymerization of chromium(III) started as early as 1908,[2] when Bjerrum postulated the presence of a dimeric species from pH titration experiments. Although no unambiguously characterized crystalline sample of this dimeric species has yet been obtained,[3] it has been studied extensively in solution[3-8] and its configuration ($(H_2O)_4Cr(OH)_2Cr(OH_2)_4^{4+}$ (**1**)) has been established.[9] A trimeric complex, $Cr_3(OH)_4^{5+}$, was obtained

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(3) Ardon, M.; Plane, R. A. *J. Am. Chem. Soc.* **1959**, *81*, 3197. The reported precipitation of a sulfate salt suffers from the uncertainty whether there was coordinated sulfate in the precipitate. Furthermore, in the strongly acidic solution the singly bridged dimer predominates so that it would seem possible that the crystals contained this species.

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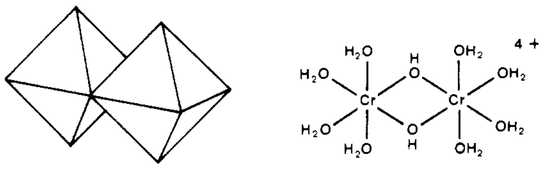

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by ion exchange[5,10] from mixtures of hydrolysis products, but the reported ESR and magnetic susceptibility data[10] did not allow a definitive deduction of the structure of this trimer.

The depolymerization reactions of various chromium(III) diols are described in the literature,[11] but little is known about the mechanism of their formation.[12,13] Thus, we have initiated a study of mechanistic and structural aspects of the hydrolytic polymerization of the chromium(III) aqua ion. In this first paper we describe the separation of oligomeric chromium(III) species among which several new polymeric complexes were discovered. For convenience, the species studied are referred to as the monomer, dimer, trimer, tetramer, pentamer, and hexamer, respectively. Kinetic investigations in progress required us to determine the physical and chemical properties of these oligomers. In particular, pK_a values are needed to characterize their degree of deprotonation at a given pH. Furthermore, these results enable us to discuss structures for the trimer and the tetramer.

Results and Discussion

Preparation, Separation, and Identification of Oligomers. Addition of up to 1 equiv of hydroxide ion to solutions of the chromium(III) aqua ion gave green solutions in which no precipitate or turbidity was apparent even after 1 year of aging at 25 °C. Such solutions contain numerous oligomeric hydrolysis products, many of which were readily and sufficiently completely separated by ion exchange on Sephadex SP C-25 gel. Solutions of sodium perchlorate of increasing concentration (0.5–4 M) first elute the blue-purple monomer $Cr^{3+}(aq)$ and then the greenish blue dimer $Cr(OH)_2Cr^{4+}(aq)$ and the green trimer $Cr_3(OH)_4{}^{5+}(aq)$. (Only the chromium ions and the hydroxide or oxide groups are given in the formulas. In each case, water molecules complete the presumed octahedral, six-coordinated first coordination sphere of each chromium center.) Separation of these three species proceeded similarly to the separation of Dowex[14] but much faster. In addition, an olive tetramer was easily eluted from Sephadex but not from Dowex, and with $LiClO_4$ (4 M), also a pentamer and a hexamer were obtained. The last two have not yet been extensively studied. In order to separate the oligomers in their fully protonated form, the eluents were made acidic (0.01–0.04 M $HClO_4$). Neither acid cleavage nor hydrolytic polymerization were noticeable under these conditions.

The monomer, dimer, and trimer were identified from their known absorption spectra.[7,10] The determination of the number of OH groups per chromium[10] confirmed the composition $Cr_3(OH)_4{}^{5+}$ for the trimer. Solutions of the tetramer were titrated with sodium hydroxide until the first equivalence point was reached (pH 3.8, see paragraph on pK_a determination). This monodeprotonated species had OH/Cr = 1.75 ± 0.03, consistent with e.g. $Cr_4(OH)_7{}^{5+}$. Thus, the complex obtained from the ion-exchange separation in 0.04 M $HClO_4$ was $Cr_4(OH)_6{}^{6+}$. The proposed 6+ charge is corroborated by the slower elution of the tetramer compared with that of the 5+ charged trimer.

The tetrameric nature of $Cr_4(OH)_6{}^{6+}$ was further confirmed from its efficient syntheses by two alternative routes. Thus, it was the main polymerization product obtained on addition of hydroxide ion to solutions of the pure dimer. Less than 7% of the trimer was formed in these experiments. Under similar conditions, mixtures of monomer and trimer afforded tetramer along with minor amounts of dimer. On the other hand, addition of hydroxide ion to the trimer alone gave no tetramer but a very slowly eluting larger polymer. Its acid cleavage is rapid and leads predominantly to trimer, suggesting it to be a hexamer.

The oligomer that elutes closely spaced behind the tetramer is believed to be a pentamer from its acid cleavage into a mixture of monomer, dimer, and trimer in which the quantity of chromium in the combined monomer and dimer fractions was $^2/_3$ of that in the trimer fraction. This pentamer slightly overlaps with the tetramer, and this complicates the isolation of pure tetramer from solutions obtained by adding base to monomer or to mixtures of monomer and trimer. Only small amounts of this pentamer were observed when the tetramer was prepared by dimerization of the dimer. In virtually all polymerization experiments, a further fraction containing even higher polymers was observed but not studied so far.

UV–Visible Spectra. The electronic spectra of the monomer, dimer, and trimer (Table I) agree with those given by Thompson and Connick[7] and Finholt et al.[10] (and references therein). The extinction coefficients increase monotonously from monomer to trimer, but the high-wavelength d–d band of the tetramer is significantly less intense than that of the trimer. The spectra of the larger polymers that elute after the tetramer resemble more closely the spectrum of the trimer. Only the monomer had a further weak absorption maximum at wavelengths below 300 nm, but the absorption of the polymers increased rapidly and steadily from 300 to 230 nm. The ratio between the extinction coefficients of the two d–d band maxima provides an easy identification and check on the purity of the oligomers. Thus, ϵ_{max} (ca. 420 nm)/ϵ_{max}(ca. 580 nm) is 1.17 ± 0.01 for the monomer, 1.18 ± 0.01 for the dimer, 1.60 ± 0.01 for the trimer, 1.95 ± 0.04 for the tetramer, and 1.5–1.56 for the pentamer and hexamer, respectively (the last two have not yet been studied in detail). A further check of the purity of the samples was a maximal ratio $\epsilon_{max}/\epsilon_{min}$ for each band (Table I).

pK_a Values. The pK_a values of the oligomers were determined from alkalimetric titrations and are listed in Table II. They are expressed in the concentration scale (M = mol dm^{-3}), thus

$$pH = -\log [H^+] \qquad pK_a = -\log ([H^+][X^{\nu+}]/[HX^{\nu+1}])$$

The fit between the experimental and computed titration data was good for all compounds (cf. "std dev in $\bar{n}$", $\bar{n}$ = average number of OH^- groups per complex, Table II). This indicates that the samples used were homogeneous and pure. The fitting procedure included the variation of the total concentration of the complex. The "best" total concentration was within 1% of the analytically determined chromium concentration divided by the nuclearity of the complex, except for one titration of the trimer (4%) and one of the tetramer (8%). This corroborated the assumed nuclearity of the oligomers. For the trimer, inclusion of a third pK_a value into the computations reduced the standard deviation by a factor of 10, but for the other complexes there was no evidence for a further deprotonation step within the accessible pH range. Readings were taken up to 0.2 pH unit below the point where continuing drifting of pH to lower values indicated that hydrolytic polymerization

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Table I. Visible Spectra of Chromium(III) Oligomers

	monomer	dimer	trimer	tetramer	hexamer
		Protonated Complexes			
λ_{max}, ϵ[a]	575, 13.2	582, 17.4	584, 19.2	580, 15.6	585, 18.6
$\lambda_{1/2}$[b]	109	147	121	115	129
λ_{min}, ϵ	481, 3.1	490, 5.2	499, 5.5	500, 5.6	503, 6.1
λ_{max}, ϵ	408, 15.5	417, 20.4	425, 30.5	426, 30.3	426, 29.0
$\lambda_{1/2}$	72	78	78	80	82
λ_{min}, ϵ	311, 0.4	345, 1.5	346, 2.1	347, 1.9	353, 2.4
		Monodeprotonated Complexes			
λ_{max}, ϵ	590, 16[c]	582, 19.7	586, ≃23.1	578, 21.8	
λ_{max}, ϵ	430, 28[c]	418, 21.8	426, ≃29.6	426, 27.8	
medium	1 M $NaClO_4$	2 M $NaClO_4$	3 M $NaClO_4$	4 M $NaClO_4$	4 M $LiClO_4$

[a] Wavelength in nm, ϵ (per chromium ion) in M^{-1} cm^{-1}. [b] Bandwidth at half-height in nm. [c] Emerson, K.; Graven, W. M. *J. Inorg. Nucl. Chem.* 1959, *11*, 309.

Table II. pK_a Values of Chromium(III) Oligomers and Experimental Conditions[a]

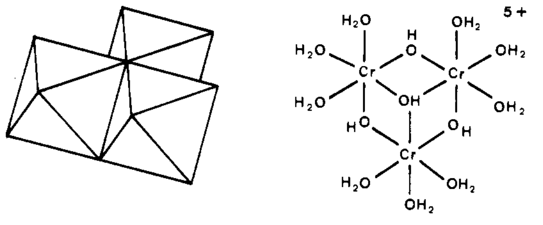
	monomer	dimer	trimer	tetramer
composition	Cr^{3+}	$Cr_2(OH)_2{}^{4+}$	$Cr_3(OH)_4{}^{5+}$	$Cr_4(OH)_6{}^{6+}$
pK_a values	4.29 6.1 ± 0.1	3.68 6.04	4.35 5.63 6.0 ± 0.1	2.55 ± 0.06[b] 5.08 ± 0.10
no. of titrations	3	3	3	4
total concn of complex, mM	10–52	3.7–13.0	1.6–3.1	1.8–6.9
no. of points	32	69	53	95
range of pH	3.3–4.8	2.8–5.0	3.1–5.3	2.3–5.1
std dev in $\bar{n}$	0.0003–14	0.0004–6	0.0004–8	0.0044–56

[a] I = 1.0 M $NaClO_4$ at 25 °C. There is no further pK_a between 1.3 and the first pK_a. The standard deviation in pK_a is smaller than 0.03 unless specified. [b] Best fits in the range pH 2.3–4.1 give pK_a = 2.54 ± 0.05 with standard deviations in $\bar{n}$ from 0.0016 to 0.0028 (76 points).

had become significant within the time scale of a titration (<20 s/reading).

The pK_a values of the monomer (Table II) agree well with those given by Beutler (4.30, 6.08)[15] for the same conditions (I = 1 M ($NaClO_4$) at 25 °C). The discrepancy between our pK_a values for the dimer and those from ref 15 (3.80, 5.75) might arise from the fact that the samples had not been purified by chromatography as in the present work.

The first pK_a of the dimer is smaller than that of the monomer, and this was expected from the higher charge of the dimer. It was thus surprising that the more highly charged trimer (5+) is less acidic than the dimer (4+). Hence, the dimer contains an "acidic type" of coordinated water that is no longer present in the trimer. In the dimer, there are two different kinds of coordinated water molecules, i.e. trans to a bridging hydroxide or trans to coordinated water, and they are expected to have different acidities. For Cr(III) complexes with nonbridging hydroxide ligands this phenomenon is well-known. For example, *trans*-aquahydroxobis(oxalato)chromium(III) is less acidic (pK_a = 10.5) than the cis isomer (pK_a 9.7 although the corresponding diaqua complexes have the same acidity (pK_a = 7.5).[16] Similarly, comparison of the pK_a values of *cis*- and *trans*-$(H_2O)_2(en)_2Cr^{3+}$ (4.8, 7.2 and 4.1, 7.5, respectively)[17] shows that an OH^- ligand in a cis position is less effective in reducing the acidity of the remaining water ligand. If a briding hydroxide ligand has a similar influence, the "acidic type" of coordinated water in the dimer is trans to another water ligand, and this structural fragment seems to be absent in the trimer. This supports structure **2** as suggested in ref 10.



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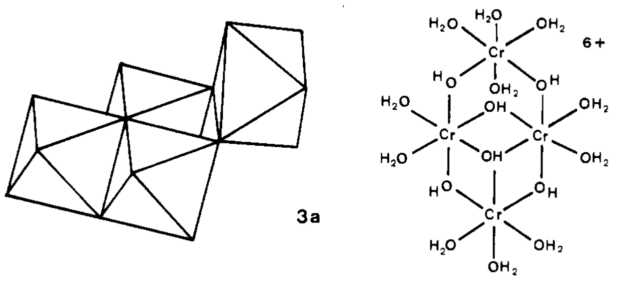
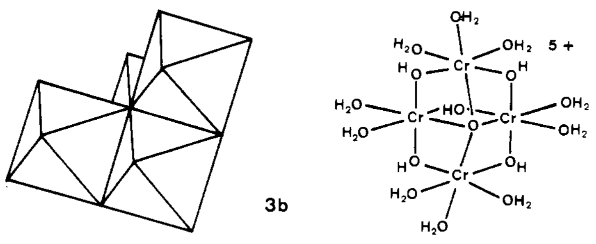


3a

$$-H^+, -H_2O \; \rightleftarrows \; +H^+, +H_2O$$



3b

The tetramer is considerably more acidic than the trimer, indicating that at least one of the chromium centers in $Cr_4(OH)_6{}^{6+}$ still has the "acidic type" of coordinated water. Such a structure is **3a**. Whereas the dimer has two *trans*-H_2O–Cr–OH_2 moieties, the tetramer **3a** contains only one such group and would thus be less acidic than the dimer (pK_a larger by the statistical term 0.3). On the other hand, the increase in acidity due to the higher charge of the tetramer would be modest because the charges in the vicinity of the acidic groups are quite similar: in the dimer, each chromium is attached to one "$Cr(OH)_{2/2}{}^{2+}$" unit whereas the extra chromium in the tetramer has two "$Cr(OH)_{3/2}(OH)_{1/3}{}^{7/6+}$" units as nearest neighbors. The observed pK_a value is thus smaller than expected and may be a composite quantity resulting from a deprotonation reaction and a concurrent further structural change. Indeed, the pH equilibration between pH 2.8 and 3.6 is too slow for a simple deprotonation of coordinated water.

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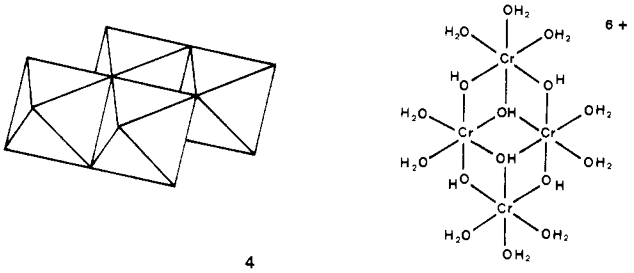
After each addition of base in alkalimetric titrations the pH values drifted to more acidic values by a few thousandths of a pH unit before stabilizing after 0.5–1 min. Back-titration showed this to be reversible, as after each addition of acid the pH values increased by up to $^1/_{100}$ of a pH unit before stabilizing after 1–2 min. No such slow equilibration was observed with any other species studied. A slow reaction ($t_{1/2} \simeq 0.3$ s) was also observed spectrophotometrically (λ_{max} = 426 and 580 nm) when the deprotonated tetramer was acidified to pH 1. The slow reaction thus accompanying the deprotonation of $Cr_4(OH)_6{}^{6+}$ (**3a**) is likely to be intramolecular condensation to give $Cr_4O(OH)_5{}^{5+}$ (**3b**). Note that the alternative way of ring closure (**4**) would not require a deprotonation.



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In view of the multitude of possible structures for the tetramer, it was necessary to assure that our fractions contained but one isomer. The presence of other isomers would be detected from an inferior goodness of the fit for the individual titration curves, because such isomers are expected to have sufficiently different pK_a values. Furthermore, the samples for the titrations were prepared individually and separated by slightly different procedures (their ratio $\epsilon_{426}/\epsilon_{580}$ varied from 1.91 to 1.99). If there was a mixture, the proportions of the isomers would vary and this would be detected from variations in the measured pK_a values from different titrations. However, no such effects were observed.

Robustness and Stability of the Oligomers. The acid cleavage of the dimer has been reported[14] to proceed in two different reaction phases. A fast reaction ($t_{1/2}$ = 23 min in 1 M $HClO_4$ at 25 °C) gives the singly bridged dimer Cr–OH–Cr^{5+}, which slowly cleaves into monomeric units ($t_{1/2}$ = 6 days in 2–6 M $HClO_4$ at 25 °C).[14] Our experiments confirmed this reported time scale: in 1 M $HClO_4$ (I = 4 M ($NaClO_4$) at 25 °C) the half-life of disappearance of the dimer (doubly and singly bridged)[18] was 7.0 days. Under the same conditions, the trimer was more robust ($t_{1/2}$ = 21 days), but the tetramer was considerably more labile. Product analysis showed that after 16 h less than 6% of the tetramer was not cleaved. There was no dimer (<2%) in the reaction mixture, and the quantities of monomer and trimer were equal within the experimental accuracy. In preliminary experiments, the reaction was also followed by visible spectrophotometry, which showed that the acid cleavage of the tetramer was biphasic with approximate half-lives of 0.5 and 3 h (1 M $HClO_4$, I = 4 M ($NaClO_4$) at 25 °C).

Product analysis of equilibrated chromium(III) solutions containing up to 1 equiv of base can be employed to determine the stability constants:

$$\beta_{qp} = [Cr_q(OH)_p][H]^p/[Cr]^q$$

Preliminary results on not yet completely equilibrated solutions (1 year at 25 °C) give log β_{22} = −5.34 (dimer), log $\beta_{34} \geq -8.9$ (trimer), and log $\beta_{46} \geq -14.1$ (tetramer) at I = 1 M $NaClO_4$ and 25 °C. For comparison, the constants reported[7,10] for the temperature range 37.5–67.5 °C were extrapolated to 25 °C (log β_{qp} vs. T^{-1}) and gave somewhat larger values: log β_{22} = −5.1 and log β_{34} = −8.3. Further values of log β_{22} are compiled in ref 1. Combination of these β_{qp} values with the pK_a values of the oligomers gives the stability constants of the individual polymerizations

$$CrOH^{2+} + CrOH^{2+} = Cr_2(OH)_2{}^{4+} \quad \text{(dimer)}$$

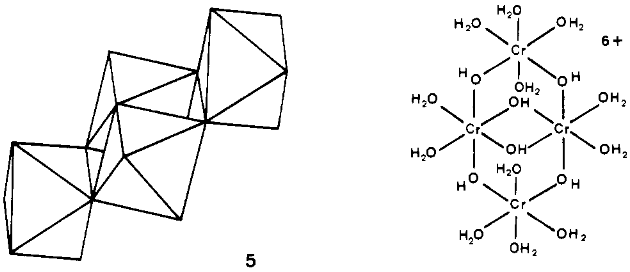
$$CrOH^{2+} + Cr_2(OH)_3{}^{3+} = Cr_3(OH)_4{}^{5+} \quad \text{(trimer)}$$

$$CrOH^{2+} + Cr_3(OH)_5{}^{4+} = Cr_4(OH)_6{}^{6+} \quad \text{(tetramer)}$$

Thus, log K_{dimer} = log ($[Cr_2(OH)_2]/[CrOH]^2$) $\simeq$ 3.3 and the analogous constants for the formation of the trimer and tetramer are log $K_{trimer} \simeq 4.5$ and log $K_{tetramer} \simeq 3.5$. (With the β_{qp} values extrapolated from ref 7 and 10 one obtains log $K_{dimer} \simeq 3.5$ and log $K_{trimer} \simeq 4.9$.)

The reactivity and stability of the oligomers are in accord with the proposed structures. Thus, the compact trimer structure **2**, where each chromium is bound to the two others by a total of three hydroxide bridges, is more robust and more stable than the doubly bridged dimer. The tetramer $Cr_4(OH)_6{}^{6+}$ is less stable and much less robust than the trimer, and it cleaves almost exclusively into monomer and trimer. This is consistent with structure **3a**, where a fourth chromium center is bound to a trimer unit through only two OH bridges.

The above results clearly exclude a number of structures that would fit the stoichiometry $Cr_4(OH)_6{}^{6+}$. Thus, linear tetrameric structures such as Cr–$(OH)_2$–Cr–$(OH)_2$–Cr–$(OH)_2$–Cr^{6+} (six isomers) and the "hexol" type (Cr-$(OH)_2)_3Cr^{6+}$ would not be compatible with the special robustness and stability of the trimer. Furthermore, in such a series all oligomers would contain the group *trans*-H_2O–Cr–OH_2 and would have pK_a values decreasing regularly with increasing nuclearity and charge of the complexes. This is contradicted by the experimental pK_a values. The clean formation of the tetramer by dimerization of the dimer further contradicts the "hexol" type structure. By the same reasoning, the tetramer cannot be one of the five isomers obtained by adding a fourth chromium to a $\overline{\text{Cr–OH–Cr–(OH)}_2\text{–Cr–OH}}$ moiety. One of the isomers, **5**,would be the structural analogue to Pfeiffer's cation ($Cr_4(OH)_6(en)_6{}^{6+}$)[19] or the rhodoso complex ($Cr_4(OH)_6(NH_3)_{12}{}^{6+}$).[20] This structure **5**, as well as **4**, differs from the proposed tetramer **3a** by only one Cr–OH bond. However, these two structures cannot explain the difference by orders of magnitude in robustness and stability between trimer and tetramer.



5

Synthesis and Cleavage of a ^{51}Cr-Labeled Tetramer. The fully protonated tetramer, **3a**, contains one labile chromium center, viz., the one that is linked to the others by only two OH bridges, and this will cleave off selectively in acid. This same Cr(III) center most likely originates from a monomeric unit when the tetramer is synthesized from monomer and trimer. However, under the conditions of this synthesis, the tetramer is deprotonated and gives **3b**, in which the original

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(18) The reaction was quenched by dilution, thereby increasing pH. Under these conditions, the singly bridged dimer present in the reaction mixture converts into the doubly bridged dimer.[7]

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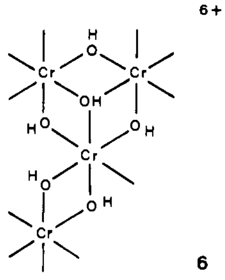
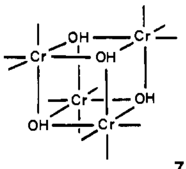
monomer becomes indistinguishable from the second, chemically equivalent Cr(III) center (C_{2v} symmetry). If ^{51}Cr-labeled monomer is used in this tetramer synthesis, the label is equally distributed over the above two centers. On subsequent protonation to **3a**, there is equal probability of having the label in the labile position or in the trimer unit. Acid cleavage of this labeled tetramer should then produce equal amounts of label in monomer and trimer.

This was indeed confirmed by experiments such as the following: tetramer was synthesized by adding sodium hydroxide to a solution of ^{51}Cr-labeled monomer and a fivefold excess of unlabeled trimer. The large excess of trimer is necessary to suppress the concurrent, stepwise tetramerization of labeled monomer. The tetramer was isolated by ion exchange and cleaved with perchloric acid (1 M, 25 °C, 16 h) to give back monomer and trimer. In two samples, the activity was 102 and 110 μCi/mmol of monomer compared with 116 and 125 μCi/mmol of trimer; i.e., the distribution of label between monomer and trimer was 1:1.14, which is close to the expected 1:1 distribution.

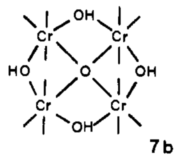
On the basis of these experiments, we can exclude structure **6**, where no exchange of label would occur. A few further structures, **7a–d**, can be disregarded because they cannot account for the high pK_a, the robustness, and the great stability of the trimer compared with the small pK_a, the lability, and the low stability of the tetramer. Two additional possible structural fragments are (i) linear bridging by O^{2-} (Cr–O–Cr) and (ii) formation of triols between adjacent chromium ions (Cr–$(OH)_3$–Cr). As neither (i) nor (ii) is observed in the dimer and trimer,[7,10] they are not expected to be present in the tetramer.



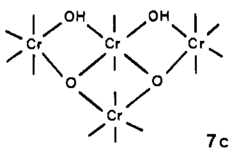
6



7a



7b



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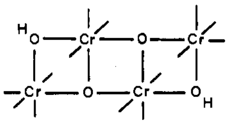


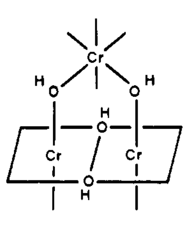
7d

Conclusion

In the foregoing discussion we have argued that the proposed structures for the trimer and tetramer (**2** and **3**, respectively) account most readily for all observations in the series monomer, dimer, trimer, tetramer.

These two structures can be interpreted to provide two clues as to their building-up principle.

(1) The proposed structural fragment **8** occurs not only in the tetramer **3a** but most likely also as an intermediate in the process dimer + monomer = trimer. This intermediate would undergo one further intramolecular condensation step to give the trimer **2**. The condensation process proposed for the transformation $Cr_4(OH)_6^{6+} \rightarrow Cr_4O(OH)_5^{5+}$ (**3a** → **3b**) proceeds analogously except that a tetracoordinate O^{2-} bridge is generated and not a tricoordinate OH^- as in the formation of the trimer. Also the dimerization of the dimer can be envisaged to go through an intermediate that contains the same structural fragment **8**. Two fragments of this kind are found in the tetrameric amine complexes $(en)_6Cr_4(OH)_6^{6+}$ (Pfeiffer's cation)[19] and $(NH_3)_{12}Cr_4(OH)_6^{6+}$ (rhodosochromium cation),[20] which have the $Cr_4(OH)_6$ connectivity as in **5**. Thus, the structural unit **8** is suggested to occur rather generally. With the tetrameric amine complexes, however, there is no further condensation to structures such as **3a** or **3b** because this would require the loss of a stable amine or ammonia ligand.



8

(2) In the series monomer, dimer, trimer, tetramer the charge of the fully protonated species $Cr[(OH)_2Cr]_q^{3+q}$ increases regularly by one unit. Clearly, this increase must discontinue at some stage and oxo bridge formation is one effective mechanism of achieving the necessary reduction of the charge of these cations. We propose formation of a tetracoordinate O^{2-} ligand to occur subsequent to deprotonation of the tetramer. This particular type of condensation process deserves attention and is currently being investigated by us. The important question remains open whether the proposed structure for the tetramer retains its connectivity in higher polymers. The known CrO(OH)[21] has a layer structure, and if its formation were to occur from the proposed tetramer, then rearrangement is implied. On the other hand, the basic array of chromium ions in $Cr_4O(OH)_5^{5+}$ (**3b**) fits nicely into the lepidocrocite (FeO(OH))[22] structure.

Experimental Part

Materials. Stock solutions of the chromium(III) aqua ion (monomer) were prepared by reducing CrO_3 in perchloric acid with 30% hydrogen peroxide[7] so that the excess of acid was approximately 0.3 M. Reduction of such a solution with zinc amalgam in a serum-capped flask gave a solution of Cr^{2+}, which was oxidized with dioxygen to give a solution of bis(μ-hydroxo)octaaquadichromium(III) perchlorate (dimer).[23] This dimer was separated from small impurities of monomer and other polymers by ion-exchange chromatography on Sephadex SP C-25. ^{51}Cr-labeled monomer was obtained as above from a solution of ^{51}Cr-labeled sodium chromate (Amersham). All other reagents were analytical grade and were used without further purification.

Instrumentation. UV–visible spectra were recorded on Kontron Uvikon 810 and 820 spectrophotometers. Measurements of pH were performed in a jacketed vessel kept at 25.0 °C, with a Ross electrode (Orion) that had 1 M NaCl as the intermediate electrolyte.[24] The pH scale was calibrated by titration of 0.01 M $HClO_4$ with NaOH (0.2 M), and the pH was measured on a Metrohm pH meter. The pH values were corrected for the liquid junction potential originating from the higher mobility of the hydrogen ion by using the Henderson equation.[25] All pH measurements were done at an ionic strength of 1 M, which was adjusted with $NaClO_4$. The pK_a values were

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computed with an updated version of the program SCOGS[26] (SCOGS2)[27]. The "standard deviation in milliliters of added base" from the program SCOGS was converted into the more descriptive "standard deviation in $\bar{n}$" ($\bar{n}$ = mean number of hydroxide groups per complex) by multiplication with the concentration of the titrant NaOH and division by the quantity in millimoles of the complex.

Separation and Analysis of Oligomeric Chromium(III) Species. The hydrolytic oligomers of chromium(III) were separated by ion-exchange chromatography on Sephadex SP C-25. Typically, a sample of 5 mL of a solution with a total chromium concentration of ca. 0.04 M in 1 M $NaClO_4$ was diluted to 50 mL. To this solution was added $HClO_4$ to give a H^+ concentration of ca. 0.05 M. This solution was adsorbed on the resin (8 × 1 cm), and elution was started by adding 1 mL of 0.5 M $NaClO_4$ + 0.01 M $HClO_4$. When the level of supernatant eluent was down to 2 mm, another 1 mL of this 0.5 M $NaClO_4$ was added, then 1 mL of 1 M $NaClO_4$ + 0.01 M $HClO_4$, and again a further 6-mL portion of this last solution. By this time, the band of the blue-purple monomer had moved down significantly and also the blue-green dimer had separated from the green polymers at the top of the resin. Elution was continued with 1 and then 6 mL of 2 M $NaClO_4$ + 0.02 M $HClO_4$ and then 1 mL of 4 M $NaClO_4$ + 0.04 M $HClO_4$. In the meantime, monomer and dimer had been completely eluted and the green band of the trimer had reached the bottom of the column. Further elution with this 4 M $NaClO_4$ solution gave the trimer and the olive tetramer. Further bands were sometimes clearly observable, but they eluted too slowly.[28]

In order to remove the polymers still remaining on the resin, 3 mL of water was added, followed by 3 mL of a nearly saturated potassium oxalate solution (which elutes a narrow green band) and then by 6 mL of 0.2 M NaOH (giving a diffuse and irregular green band). The Sephadex was brought back to the H^+ form with 0.4 M HCl (8 mL). If the resin was not yet completely white, the cleaning with oxalate and sodium hydroxide was repeated after 1 day. On larger columns, treatment with potassium oxalate was preceded by addition of a nearly saturated KCl solution followed by rinsing with water. Note that the use of larger concentrations (>4 M) does not increase the efficiency of the elution, but 4 M $LiClO_4$ can be employed to elute some of the larger polymers (pentamer and hexamer).

For quantitative chromium analysis, the eluted solutions of monomer, dimer, etc. were made alkaline with 2 mL of NaOH (1 M), oxidized with 30% H_2O_2 (0.5 mL), and boiled twice for ca. 10 s. The samples were allowed to stand for 20 min and were appropriately diluted in volumetric flasks. The total chromium concentrations were determined spectrophotometrically with $\epsilon_{374} = 4830\ M^{-1}\ cm^{-1}$ for CrO_4^{2-}.[29]

Larger quantities of the oligomers were obtained similarly using columns of up to 7 cm diameter. After separation, the concentration of a desired oligomer was usually too small for further experiments. Hence, such solutions were diluted to an ionic strength of <0.1 M, adsorbed on the minimum amount of Sephadex, and eluted directly with 2 M $NaClO_4$ (dimer), 4 M $NaClO_4$ (trimer and tetramer), or 4 M $LiClO_4$ (pentamer and hexamer). The ionic strength of the resulting solutions was determined by passing a known volume through an ion-exchange column in the H^+ form and titrating the eluted acid. For the pK_a determinations, the samples were diluted to give 1 M ionic strength.

Syntheses of the Tetramer. The most convenient synthesis of the tetramer is by adding NaOH to a solution of the dimer. For example, to the dimer (15 mmol) was added NaOH (1 M) to give pH 3.8 ($\bar{n}$ = 0.6). After 3 days at 25 °C, the distribution of the chromium in the different oligomers was determined as above on 1% of the solution: monomer, <1%; dimer, 69%; trimer, <2%; tetramer, 21%; larger polymers, 7%. From the remaining solution, tetramer (0.8 mmol, 50%, $\epsilon_{426}/\epsilon_{580} = 1.98$) was recovered by ion exchange on a 20 × 7 cm column. The tetramer was followed by less pure fractions ($\simeq$0.5 mmol, $\epsilon_{426}/\epsilon_{580} \geq 1.84$). The dilute solution of the tetramer (0.002 M) was concentrated by adsorption on a 4.5 × 4.5 cm column and elution with 4 M $NaClO_4$ + 0.04 M $HClO_4$ to give a 0.007 M solution of the tetramer (0.45 mmol, $\epsilon_{426}/\epsilon_{580} = 1.99$).

Similarly, by the addition of NaOH to a 1:1 mixture of monomer and trimer, large quantities of tetramer were formed. When 0.8 equiv of hydroxide ion was added and the solution was kept at 25 °C for 5 days, it contained the following mixture: monomer, 4%; dimer, 6%; trimer, 33%; tetramer, 25%; higher polymers, 32%. When monomer but no trimer was present in the initial solution, less tetramer was obtained under the same conditions: monomer, 63%; dimer, 13%; trimer, 5%; tetramer, 2%; higher polymers, 17%. In all cases, tetramer fractions with $\epsilon_{426}/\epsilon_{580} > 1.9$ were obtained. An impurity in the later fractions may be pentamer because acid cleavage gave more monomer than trimer, whereas acid cleavage of the tetramer gave trimer: monomer = 1:<1.1.

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Registry No. 1, 23852-05-3; **2**, 78939-63-6; **3a**, 85864-57-9; **3b**, 85864-58-0; $Cr(aq)^{3+}$, 14873-01-9.

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