Inorg. Chem. **1987**, *26*, 474–482

Contribution from the Institut de chimie, Université de Neuchâtel, CH-2000 Neuchâtel, Switzerland,
and Laboratorium für Elektronenmikroskopie, Universität Bern, CH-3000 Bern 9, Switzerland

A New "Active" Chromium(III) Hydroxide: $Cr_2(\mu\text{-}OH)_2(OH)_4(OH_2)_4\cdot 2H_2O$. Characterization and Use in the Preparation of Salts of the $(H_2O)_4Cr(\mu\text{-}OH)_2Cr(OH_2)_4^{4+}$ Ion. Crystal Structure of $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(OH_2)_4][(H_3C)_3C_6H_2SO_3]_4\cdot 4H_2O$

Leone Spiccia,*[1] Helen Stoeckli-Evans,[1] Werner Marty,†[1] and Rudolf Giovanoli[2]

Received July 22, 1986

Rapid addition of a buffer (pH $\simeq$6.9, $T \simeq 0$ °C) to a solution of the hydrolytic dimer $(H_2O)_4Cr(\mu\text{-}OH)_2Cr(OH_2)_4^{4+}$ results in the formation of a light blue-green precipitate of "active dimer hydroxide" of chromium(III) with the empirical composition $Cr(OH)_3\cdot 3H_2O$. On rapid treatment with acid, this finely dispersed solid dissolves instantaneously to regenerate >95% of the original dimer. This observation, as well as powder X-ray diffraction, IR, and thermal analysis data, suggests that the "active dimer hydroxide" is composed of unaltered hydrolytic dimer fragments that are linked through Cr(H)O–H···O(H)Cr hydrogen bonds, consistent with the formula $[Cr_2(\mu\text{-}OH)_2(OH)_4(OH_2)_4]\cdot 2H_2O$. This microcrystalline compound resembles the previously known, isomeric "active" $Cr(OH)_3\cdot 3H_2O$, obtained from $Cr(OH_2)_6^{3+}$ in a similar manner. In aqueous buffers in the pH range 5.15–11.62, the "active dimer hydroxide" undergoes an aging process, whereby dimer is transformed into higher oligomers, probably through release of dimer into the solution, followed by hydrolytic polymerization in homogeneous solution. This aging process finally gives rise to an amorphous precipitate. The rate of aging goes through a minimum at pH $\simeq$5.5 and is distinctly faster for all pH values <5.5 and >5.7. Dissolution of "active dimer hydroxide" with slightly more than 4 equiv of concentrated aromatic sulfonic acids yields essentially pure solutions of the hydrolytic dimer with sufficiently high concentrations to achieve crystallization of sulfonate salts of the $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(OH_2)_4]^{4+}$ ion. The *p*-toluenesulfonate enneahydrate and mesitylene-2-sulfonate tetrahydrate salts have been isolated and characterized by thermal analysis. The compound $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(OH_2)_4][(H_3C)_3C_6H_2SO_3]_4\cdot 4H_2O$, forms monoclinic crystals (space group $P2_1/a$) with cell parameters $a = 8.720$ (1) Å, $b = 34.240$ (4) Å, $c = 8.921$ (1) Å, $\beta = 96.59$ (1)°, and $Z = 2$. The dimeric cation has a crystallographic center of symmetry. The nonbonded Cr–Cr distance is 3.006 (0) Å and the average bridging Cr–O distance, 1.936 (2) Å, is distinctly shorter than the terminal Cr–O distances (1.967 (2)–1.993 (2) Å). The O–Cr–O angle involving the two bridging oxygen atoms is 78.2 (1)°; the Cr–O–Cr angle at the bridge is 101.8 (1)°.

Introduction

The hydrolysis of metal ions is one of the most fundamental phenomena in the chemistry of aqueous solutions. Nonetheless, the inherent complexity of the sequence of hydrolysis steps has prevented their detailed, systematic study for the most relevant metal centers. This is due to the typical, high substitutional lability of the majority of the known aqua ions. For labile metal centers, individual hydrolytic steps cannot usually be singled out and studied in sufficient detail. This difficulty may, however, be resolved by the use of a substitutionally inert aqua ion, such as $Cr(OH_2)_6^{3+}$. Some of the early[3-9] and recent[10-14] studies on Cr(III) hydrolysis are very encouraging in this sense. Thus, the first and second pK_a values of $Cr(OH_2)_6^{3+}$[3,7] and of several hydrolytic oligomers[7,10] could be determined by conventional potentiometric titration[7,10] or by kinetic methods,[11] without perturbation by subsequent hydrolytic polymerization steps. As another consequence of the substitutional inertness, a complete series of pure hydrolytic oligomers (dimer,[4,5] trimer,[4,5] tetramer,[10,11] pentamer,[10] hexamer,[10] and even higher oligomers[15]) could be obtained by ion-exchange chromatography and characterized in solution, inter alia by cryoscopic determination of ionic weights[4,6] or by chemical correlation.[10] These oligomers are stable with half-lives of hours to days at room temperature in the pH range 1–2.[10]

The rates of individual polymerization steps, viz. the dimerization of monomer[12] (Scheme I) and the dimerization of dimer to form tetramer,[13] have been measured by a pH stat technique. These experiments show that pairs of conjugate bases of the starting material are very reactive, while the aqua ion alone or in combination with a conjugate base is not. There is a rather regular increase by about 2 orders of magnitude for each additional deprotonation in the formation of the conjugate bases (Scheme I).

Despite the labilization by the deprotonation of aqua ligands, the substitutional inertness of the Cr(III) aqua ion is sufficient to permit the isolation of pure "active" chromium hydroxide, $Cr(OH)_3(OH_2)_3$ (Scheme I), hereafter referred to as "active monomer hydroxide".[8,9] This microcrystalline compound precipitates upon rapid addition of base to $Cr(OH_2)_6^{3+}$ and dissolves instantaneously in acid, with >99% regeneration of $Cr(OH_2)_6^{3+}$. If hydrolytic polymerization was involved in the formation of this "active" hydroxide, then the complete regeneration of aqua ion would certainly take many hours. Indeed, according to the postulated structural model for the "active monomer hydroxide",[8,9] $Cr(OH)_3(OH_2)_3$ units are linked through Cr–(H)O–H···O(H)–Cr hydrogen bonds. This suggests that their formation and cleavage are much faster than any act of substitution at Cr(III). However, the "active monomer hydroxide" undergoes aging in aqueous suspension. This process is strongly pH-dependent and occurs through release of monomer units from the solid and subsequent hydrolytic polymerization in solution. As a consequence of this aging process, all of the known oligomers as well as higher polymers are formed.[14]

There remains one major challenge in this field: the isolation, in crystalline form, of the above members of the series of homologous oligomers would give access to detailed and straightforward structural information on these species. Furthermore, many investigations on these species would be greatly facilitated if concentrated, electrolyte-free solutions of individual oligomers

---

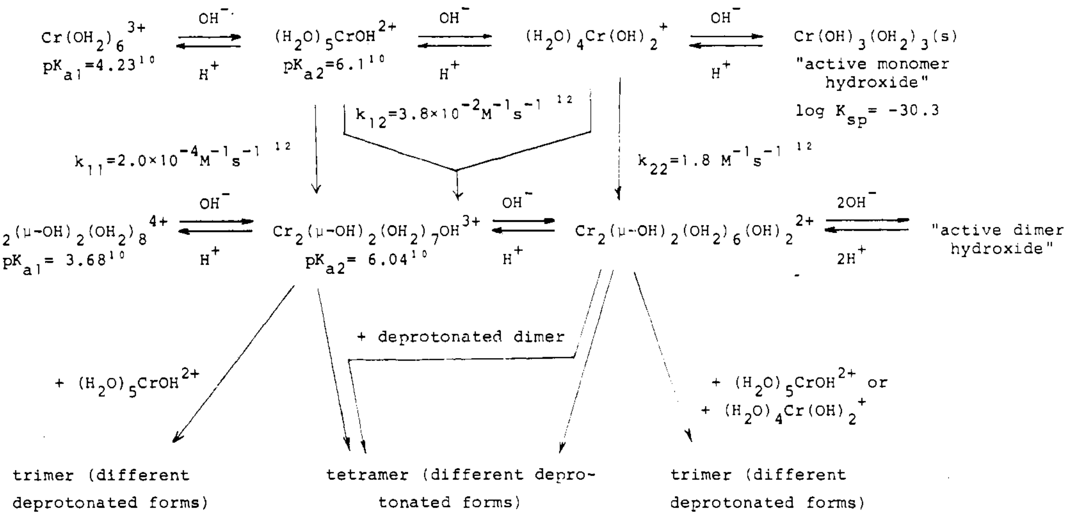
* To whom correspondence should be addressed at Research School of Chemistry, Australian National University, Canberra, ACT 2601, Australia.

† Deceased Sept 20, 1986.

(1) Université de Neuchâtel.
(2) Universität Bern.
(3) Bjerrum, N. *Z. Phys. Chem., Stoechiom. Verwandtschaftsl.* **1910**, *73*, 724.
(4) (a) Ardon, M.; Plane, R. A. *J. Am. Chem. Soc.* **1959**, *81*, 3197. (b) Kolaczkowski, R. W.; Plane, R. A. *Inorg. Chem.* **1964**, *3*, 322. (c) Ardon, M.; Linenberg, A. *J. Phys. Chem.* **1961**, *65*, 1443.
(5) Thompson, M.; Connick, R. E. *Inorg. Chem.*, **1981**, *20*, 2279.
(6) Finholt, J. E.; Thompson, M. E.; Connick, R. E. *Inorg. Chem.* **1981**, *20*, 4151.
(7) von Meyenburg, U.; Siroký, O.; Schwarzenbach, G. *Helv. Chim. Acta* **1973**, *56*, 1099.
(8) Giovanoli, R.; Stadelmann, W.; Feitknecht, W. *Helv. Chim. Acta* **1973**, *56*, 839.
(9) Giovanoli, R.; Stadelmann, W.; Gamsjäger, H. *Chimia* **1973**, *27*, 170.
(10) Stünzi, H.; Marty, W. *Inorg. Chem.* **1983**, *22*, 2145.
(11) Stünzi, H.; Rotzinger, F. P.; Marty, W. *Inorg. Chem.* **1984**, *23*, 2160.
(12) Rotzinger, F. P.; Stünzi, H.; Marty, W. *Inorg. Chem.* **1986**, *25*, 489.
(13) Rotzinger, F. P.; Besso, C.; Marty, W., unpublished results.
(14) Spiccia, L.; Marty, W. *Inorg. Chem.* **1986**, *25*, 266.
(15) Spiccia, L.; Grenacher, S.; Marty, W., work in progress.

0020-1669/87/1326-0474$01.50/0 © 1987 American Chemical Society

Scheme I[a]



[a] The rate constants k_{pq} refer to reactions between $(H_2O)_{6-p}Cr(OH)_p^{(3-p)+}$ and $(H_2O)_{6-q}Cr(OH)_q^{(3-q)+}$.[12]

could be prepared. So far, our chromatographic separations typically yield ca. 1–50 mM solutions of these species in the presence of 0.5–4 M $NaClO_4$ or $LiClO_4$ and 0.02–0.04 M $HClO_4$. Desalting of these rather dilute solutions by gel chromatography on a preparative scale has so far remained unsatisfactory. Concentrating such partially desalted solutions leads initially to copious precipitation of $NaClO_4$ or $LiClO_4$ contaminated by the Cr(III) oligomers. Also, upon evaporation of major amounts of solvent, the perchloric acid present in the eluents (to supress hydrolysis) is concentrated to levels where the acid-induced cleavage of at least some of the oligomers begins to interfere.[16]

The appreciable stability[14] of "*active monomer hydroxide*" suggested to us an alternative preparative strategy: if oligomers, such as the dimer, could also form insoluble, exclusively hydrogen-bonded aggregates (or, conversely, could form aggregates *without* the formation of additional hydroxo or oxo bridges between metal centers apart from those present in the parent oligomer), then they could be precipitated, recovered rapidly, and dissolved in a slightly more than stoichiometric amount of very concentrated acid to form a concentrated solution of the pure oligomer, which might then the crystallized. Indeed, a precipitate, similar in appearance to the "active monomer hydroxide", was observed in potentiometric titrations of the dimer.[7]

However, from our present knowledge of Cr(III) hydrolysis, two serious difficulties were foreseen: (i) In order to precipitate "active" hydroxides of Cr(III) oligomers, the parent aqua oligomer would have to undergo multiple deprotonation, to form an uncharged species. Multiple deprotonation leads to rapid, further polymerization (see above), and the "active" hydroxides would be contaminated by the resulting higher oligomers. (ii) The *aging* of the "active" hydroxide could interfere with its precipitation and workup. These two processes would need to be minimized in the synthetic procedure.

We report here on a study of a new "active" hydroxide derived from the Cr(III) hydrolytic dimer, hereafter referred to as "*active dimer hydroxide*". The synthetic utility of this species is exemplified by the isolation of the first fully characterized, crystalline salts of the hydrolytic dimer, $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(OH_2)_4](tos)_4\cdot 9H_2O$ and $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(OH_2)_4](dmtos)_4\cdot 4H_2O$ (tos = *p*-toluenesulfonate; dmtos = mesitylene-2-sulfonate).

Results and Discussion

Preparation and Composition of the "Active Dimer Hydroxide" of Cr(III). The addition of a solution containing the dimer $(H_2O)_4Cr(\mu\text{-}OH)_2Cr(OH_2)_4^{4+}$ (as the tetraperchlorate), as well as excess sodium perchlorate and perchloric acid, to a pyridine solution (pH ≃7) resulted in the formation of a light greenish blue precipitate (see Experimental Section). This "active dimer hydroxide" was recovered by ultrafiltration, washed twice with water and acetone, and briefly dried in a stream of air to remove the acetone. All these operations were carried out as rapidly as possible at −2 °C, to minimize degradation or contamination of the material by higher oligomers. These reactions conditions are optimized with respect to pH (described below), time, and temperature.

On the basis of the following analytical determination, the "active dimer hydroxide" forms according to

$$Cr_2(\mu\text{-}OH)_2(OH_2)_8^{4+} + 4OH^- \rightarrow Cr_2(\mu\text{-}OH)_2(OH)_4(OH_2)_4\cdot xH_2O \quad (1)$$

The stoichiometry with respect to OH^- was determined by the addition of a known excess of $HClO_4$ to a weighed sample of the "active dimer hydroxide". The resulting, homogeneous solution containing essentially the starting dimer (see below) was adsorbed onto Sephadex SP-C25 cation-exchange resin in the H^+ form. Adsorption of 1 equiv of dimer liberates 4 equiv of H^+. On the other hand, four protons are consumed in the reacidification of "active dimer hydroxide" if eq 1 is correct; i.e., there is no net gain or consumption of H^+ in this case. This was confirmed experimentally to within <1%. Thus, the "active dimer hydroxide" is an uncharged species.

Another representative sample of "active dimer hydroxide" was acidified with excess $HClO_4$. Ion-exchange chromatography[10] of the resulting solution afforded 96.6% of dimer, 2.5% of a combined fraction containing trimer to hexamer, and 0.9% of higher oligomers, based on dimer engaged in the precipitation of "active" hydroxide. Although this material contains detectable amounts of higher oligomers, it is sufficiently pure for most characterization procedures and for preparative applications. No contamination by monomer was found. The higher oligomers most probably result from polymerization in homogeneous solution during precipitation and from aging of the precipitate during workup.

Representative samples of "active dimer hydroxide" were analyzed for Na^+ and ClO_4^- impurities. The Na^+ content was 0.067 ± 0.002%. Determination of ClO_4^- gave 0.60 ± 0.01%. If all Na^+ was present as $NaClO_4$, this would account for 0.29% ClO_4^-. Thus, only 0.31% ClO_4^- is present in other forms, e.g. as counterions to cationic species. The presence of ClO_4^- was confirmed by very weak IR bands at 1100 and 625 cm^{-1}. In contrast, none of the strong IR bands of pyridine and acetone were detected. The low amounts of extraneous anions or cations support the stoichiometry given in eq 1.

Preliminary experiments showed that the "active dimer hydroxide" was dehydrated very readily in the atmosphere.

---

(16) The more volatile acids give rise to anation and would thus interfere with the isolation of unsubstituted aqua oligomers.

Table I. Effect of Drying over H_2SO_4 on the Aging in the Solid "Active" Dimer and Monomer Hydroxides

		product distribution[a]			
$[H_2SO_4]$, M	drying time, s	dimer or monomer	lower oligomers (trimer–hexamer)	higher oligomers	total Cr in aged sample, %
14.0	0	96.6	2.5	0.9	32.7
	8.4×10^2	92.1	6.0	1.9	34.5
	1.8×10^3	91.0	7.1	1.9	34.0
	4.5×10^3	85.0	12.1	2.9	34.6
11.0	0	96.6	2.5	0.9	32.7
	1.68×10^4	88.0	8.6	3.4	
	7.2×10^4	74.6	18.9	6.4	36.0
11.0[b]	0	98.7[b]	1.3		32.0
	8.6×10^4	98.0[b]	1.7		33.3

[a] Normalized to 100%. [b] "Active monomer hydroxide".

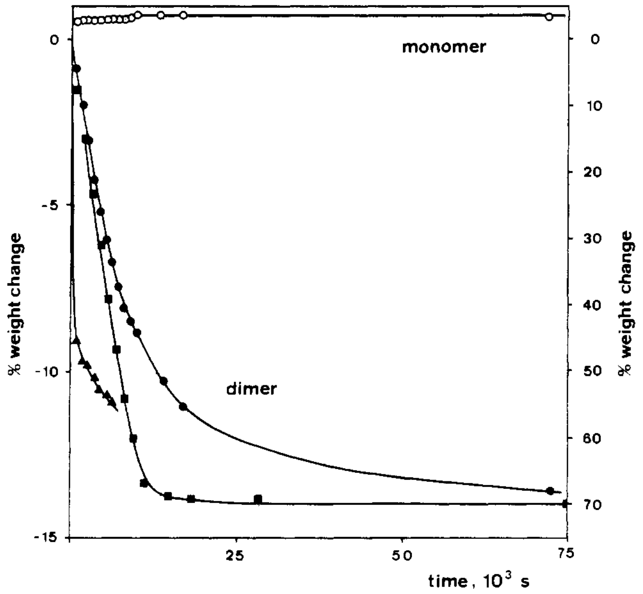


Figure 1. Weight changes as a function of time of samples of "active" hydroxides, upon storing over H_2SO_4 solutions: "active monomer hydroxide" over 11 M H_2SO_4 (○, left-hand scale); "active dimer hydroxide" over 11 M H_2SO_4 (●, left-hand scale) and over 14 M H_2SO_4 (■, left-hand scale); wet "active dimer hydroxide" sample over 14 M H_2SO_4 (▲, right-hand scale).

Determination of the formula weight (and thus of the coefficient x in eq 1) therefore required drying conditions under which ideally all adherent water, but no lattice water or coordinated water, could be removed. When acetone-washed samples were dried over 11 M or 14 M H_2SO_4, they underwent moderately rapid water loss (Figure 1). Over 14 M H_2SO_4, at least the initial water loss was much faster than over 11 M H_2SO_4. In one sample, adherent water was not previously removed with acetone. On drying over 11 M H_2SO_4, this sample lost water rapidly and extensively ($\simeq$69%), whereas acetone-washed samples lost only some 10–15% much more slowly. This suggests that washing with acetone removes essentially all of the adherent water.

The rapid weight loss of the "active dimer hydroxide" is in sharp contrast with the behavior of the "active *monomer* hydroxide", which remains essentially stable for at least 1 day under these conditions (Figure 1). Similarly, "active dimer hydroxide", is hygroscopic after drying while "active monomer hydroxide" is not.

Since in these experiments the water loss did not correspond to any of the expected values, it was checked whether the drying was accompanied by aging of the solid, i.e. whether any *coordinated* water molecules were removed and substituted by adjacent OH^- ligands with formation of hydroxide bridges. This was indeed the case. Samples of "active" dimer hydroxide were dissolved in excess acid after different drying times, and higher polymers were assayed after ion-exchange separation.

The results (Table I) show that the percentage of lower and higher oligomers increase with time, for samples of "active dimer hydroxide". The corresponding changes for "active monomer hydroxide" are much less extensive on the same time scale ($\simeq$2% vs. 10–20% for "active dimer hydroxide"). The weight loss and change in composition of Cr(III) species is paralleled by an increase in chromium content. In conclusion, drying of the "active dimer hydroxide" to constant weight appears impossible without concurrent, appreciable substitution at Cr(III) and change in composition beyond the loss of presumed water of crystallization. Thus, only acetone-washed and briefly air-dried samples of "active dimer hydroxide" were used throughout this work. The "active dimer hydroxide" is much less stable that the "active monomer hydroxide" under these conditions.

Table II. Infrared Adsorption Regions for the "Active" Monomer and Dimer Hydroxides

band position, cm^{-1}		
"active monomer hydroxide"	"active dimer hydroxide"	interpretation
308 strong (sharp)	330 weak	
500 strong (sharp)	490 strong (sharp)	Cr–O stretch
850 weak	860 weak	H_2O rocking
1560 moderate	1600 moderate	H_2O bending
3000 weak (broad)	3220 strong (sharp)	H-bonded O–H···O
3480 moderate		H-bonded O–H···O

Analyses of the "Active Dimer Hydroxide". The "active dimer hydroxide" has been characterized by means of thermogravimetry (TG), differential scanning calorimetry (DSC), X-ray powder diffraction, electron microscopy, and infrared spectroscopy. Only a brief summary of the TG and IR data is presented here, and a more detailed description of all these results will be published elsewhere.[17] It is worth pointing out, however, that the "active dimer hydroxide" is microcrystalline in nature with an X-ray powder pattern distinctly different from that of the "active monomer hydroxide".[8]

Thermal Analysis. Differential thermogravimetric analysis (DTG) of the "active dimer hydroxide" revealed the presence of four distinct regions of weight loss at 106 (±10), 220 (±10), 300 (±10), and 455 (±10) °C. The peak at 455 °C is attributed to the crystallization of α-Cr_2O_3,[18] which is accompanied by strong luminescence[19] and the loss of chemisorbed H_2O or adventitious O_2.[20] All the other weight losses are attributed to the dehydration of the "active dimer hydroxide". The observed losses were used to calculate a formula weight of 318.4 (±1.0) g, which is in good agreement with that calculated from the chromium content of the hydroxide of 318.0 (±4.7) g. These values support the formula $[Cr_2(\mu\text{-}OH)_2(OH)_4(OH_2)_4]\cdot 2H_2O$ (M_r 314.1), which is empirically

---

(17) Spiccia, L.; Giovanoli, R.; Marty, W., manuscript in preparation.

(18) Giovanoli, R.; Stadelmann, W. *Thermochim. Acta* **1973**, *7*, 41.

(19) (a) Berzelius, J. J. *Lehrbuch der Chemie*; 1834; Vol. III, p 33. (b) Böhm, J. *Z. Allg. Anorg. Chem.* **1925**, *149*, 217. (c) Wöhler, L. *Kolloid-Z.* **1926**, *38*, 97.

(20) Gregg, S. J.; Sing, K. S. W. *Adsorption, Surface Area and Porosity*, 2nd ed.; Academic: London, 1982, pp 263–281, 284.

(21) Nakamoto, K.; Margoshes, M.; Rundle, R. E. *J. Am. Chem. Soc.* **1955**, *77*, 6480.

Table III. pH and Time Dependence of the Aging of the "Active Dimer Hydroxide" at 25.0 °C and I = 1.0 M ($NaClO_4$)

		product distribution, %				
pH[a]	time, s	dimer	trimer–tetramer	pentamer–hexamer	higher oligomers	Cr recovery, %
5.15[b]	300	95.9	1.9	0.7	1.6	100.1
	1800	83.2	6.1	3.0	6.7	99.0
5.31[c]	60	96.7	2.9	0.3	0.3	100.2
	300	94.2	3.8	1.3	0.7	100.0
	1800	92.0	4.8	1.6	1.6	100.0
	7200	85.9	6.6	3.7	3.3	99.5
5.58[d]	60	97.4	1.7	0.5	0.6	100.2
	300	96.0	2.0	0.8	0.6	99.4
	1800	93.4	3.7	0.8	1.2	99.1
	7200	90.1	3.8	2.6	2.9	99.4
6.14[e]	60	95.3	2.3	0.6	0.7	98.9
	300	91.9	3.2	2.5	1.1	98.7
	1800	87.5	4.5	5.0	2.1	99.1
	1800	89.9[m]	5.3	2.8	3.2	100.2
	7200	83.3	5.8	4.1	5.9	99.1
7.23[f]	60	92.1	4.0	1.8	1.1	99.0
	300	86.8	5.6	4.3	2.0	98.7
	1800	83.3	5.8	4.3	5.6	99.0
	7200	78.9	6.3	6.9	6.8	98.9
7.52[g]	60	93.0	3.9	1.9	1.2	100.0
	300	87.6	6.4	3.8	1.8	99.6
	300	87.8	5.0	2.8	2.4	98.0
	1800	84.1	6.1	5.4	4.3	99.9
	1800	83.8	5.9	4.0	4.9	98.6
	7200	78.6	6.6	7.0	6.9	99.1
8.40[h]	60	89.8	5.8	2.7	1.9	100.2
	300	85.6	5.7	4.0	2.9	99.2
	1800	78.5	6.4	8.4	6.5	99.8
	7200	75.4	7.1	7.2	8.9	98.6
		73.3[m]	8.0	6.8	10.9	99.0
9.58[i]	60	85.0	7.8	4.2	3.0	100.0
	300	77.5	9.3	7.3	5.1	99.2
	1800	71.8	9.9	8.8	8.7	99.2
	7200	65.3	10.0	9.5	14.2	99.0
9.89[j]	60	82.8	8.6	4.5	3.7	99.6
	300	76.1	10.2	7.3	5.9	99.5
	1800	68.4	9.8	9.3	12.4	99.9
	7200	61.0	9.8	10.5	17.7	99.0
10.98[k]	60	82.3	8.1	5.2	4.7	100.3
	300	76.4	9.5	7.6	6.5	100.0
	1800	66.6	10.1	8.1	14.3	99.1
	7200	60.4	10.3	9.4	19.6	99.7
	7200	57.8[m]	8.8	8.7	22.7	99.0
11.62[l]	60	78.8	7.7	6.2	5.7	99.4
	300	75.5	9.3	7.2	8.1	100.1
	1800	63.4	11.2	9.1	15.7	99.4
	7200	58.0	12.0	11.0	18.1	99.1

[a] All pH values measured in the reaction mixtures. [b] pH maintained constant by using a pH stat; suspensions were stirred during aging. [c] Pyridine, 0.19 M. [d] Pyridine, 0.22 M. [e] Pyridine, 0.4 M. [f] Imidazole, 0.2 M. [g] Imidazole, 0.3 M. [h] Triethanolamine, 0.3 M. [i] Ethanolamine, 0.2 M. [j] Ethanolamine, 0.3 M. [k] *tert*-Butylamine, 0.3 M. [l] Piperidine, 0.4 M. [m] Suspension was stirred during aging.

identical with that of the "active monomer hydroxide", i.e. $Cr(OH)_3 \cdot 3H_2O$.

IR Spectra. The data for the "active dimer hydroxide" are presented in Table II, along with those for the "active monomer hydroxide".[9] Both spectra consist predominantly of broad absorption regions in similar frequency ranges. The 3000- and 3480-cm^{-1} bands in the "active monomer hydroxide" were previously attributed to stretching frequencies for Cr(H)O–H··· O(H)Cr hydrogen bonds of ca. 2.9 and 2.7 Å, respectively.[9,20] By the same token, the single 3220-cm^{-1} band of the "active dimer hydroxide" may be attributed to a similar hydrogen bond of 2.8 Å.

Aging Experiments on the "Active Dimer Hydroxide". These experiments established the optimal conditions of pH and time for the preparation of "active dimer hydroxide". In addition, they also yield qualitative information on the stability of this species and on the mechanism of the aging process. Our method of study is the same as in a previous study of the aging of "active monomer hydroxide".[14] Suspensions of "active dimer hydroxide" are prepared at different pH values and rapidly acidified after preset aging times. The resulting homogeneous solutions contain the fully protonated, unreacted dimer, and some aging products, viz. higher oligomers. Since their cleavage is very slow, they may be separated by ion-exchange chromatography and determined without alteration. In a similar manner to our previous study,[14] we have eluted the dimer (with 1–2 M $NaClO_4$), a combined fraction of trimer and tetramer (with 2–4 M $NaClO_4$), a fraction containing pentamer and hexamer (with 4 M $LiClO_4$) and a fraction containing the higher oligomers (by using saturated $K_2C_2O_4$ and 0.2 M NaOH). More than 98.5% of the initial chromium was recovered in all the experiments. Data were collected for buffer solutions in the range pH 5.15–11.62, for aging times between 60 and 7200 s (=2 h), and for stirred and unstirred suspensions (Table III; Figure 2).

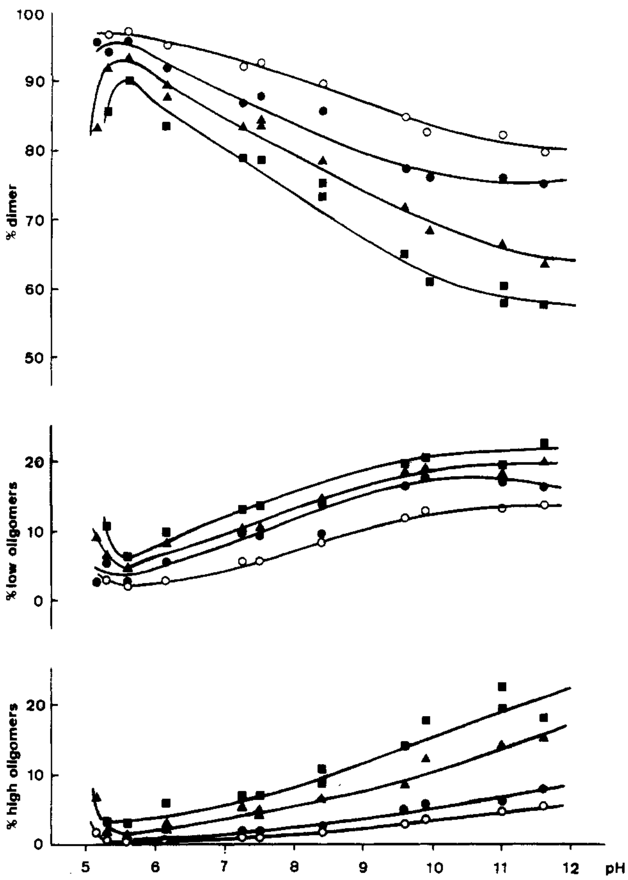


Figure 2. pH and time dependence of the aging of the "active dimer hydroxide". Aging time: (○) 60 s; (●) 300 s; (▲) 1800 s; (■) 7200 s.

The uncertainty in the determination of the dimer is of the order of ±1%, and this uncertainty is expected to propagate proportionally on the smaller oligomer fractions.[14] The error in defining the starting and end points in time is relatively large for the short aging times and leads to some scatter in the data points, irrespective of the good analytical precision and accuracy. Within the experimental accuracy, the following patterns emerge from these data. (1) Under all conditions of this study, the aging was generally more rapid for the "active dimer hydroxide" than for its monomer homologue.[14] Thus, at pH $\simeq$6.1, 91% of the monomer remains after aging of the "active monomer hydroxide" for 3 days, while about 90% of the dimer remains after aging of "active dimer hydroxide" for only 30 min. On the other hand, in a pH region where both hydroxides age rapidly, 93.7% of unreacted "active monomer hydroxide" remained after 10 min at pH 9.72, while 66.4% of unreacted "active dimer hydroxide" was found after 5-min aging at pH 9.89. (ii) the pH dependence of the aging for the two "active" hydroxides is distinctly different. For the "active dimer hydroxide", the minimal aging rate is confined to the narrow range pH $\simeq$5.5–5.7. In contrast, this range extends over more than two pH units (pH $\simeq$6 – 8.5) for the "active monomer hydroxide".[14] (iii) For the "active dimer hydroxide", there is a small, but significant increase in aging rate in the range pH $\simeq$5.5–5.15. A similar, but much larger increase was found for the "active monomer hydroxide". Likewise, the aging for both hydroxides becomes faster in going to more alkaline solutions. For the "active dimer hydroxide", this increase begins at pH >5.7. The rate increases nearly linearly up to pH $\simeq$10 and then becomes almost constant. For the "active monomer hydroxide", the rate of aging increases nearly exponentially above pH 8.5. (iv) The extent of aging progresses nonlinearly with time, for both hydroxides. (v) For the "active dimer hydroxide", stirring of the suspensions has little effect on polymerization, except at pH 10.98. This appears to correlate with the settling times of the suspensions. At pH 10.98, settling was achieved within the aging time, while at lower pH, the suspensions settled much more slowly.

A large-scale experiment at pH 7.24 and 10800 s (=3 h) aging time permitted the separation of most oligomers individually and in amounts sufficient for UV–vis spectral identification, while only small amounts of higher oligomers were present. The products were as follows: monomer, <1%; dimer, 73.8%; trimer, 2.3%; tetramer, 6.6%; pentamer and hexamer (eluted as one incompletely separated fraction), 8.0%; higher oligomers, 8.8%. The chromium recovery was 99.5%. A pure sample of hexamer was obtained from the tail fraction of the overlapping pentamer–hexamer bands. The UV–vis spectra of all the known oligomers (except for the pentamer for which no spectral data are presently available) were in good agreement with the literature values.[5,6,10] Thus, the complete series of oligomers, but very little monomer, is formed, and no new isomers of these oligomeric species appear to be formed. The odd oligomers, i.e. trimer and pentamer, are present in minor amounts among the aging products but were not detectable in the initial stage of hydrolytic dimerization in homogeneous solution (<5% conversion of dimer).[13] They might be formed by the incipient, relatively rapid cleavage of some of the members of the higher oligomer fraction during workup and separation. This hypothesis is supported by the observation that the acidification of chromite solutions ($Cr(OH)_4^-$; pH >12) initially leads to a large amount of relatively acid-labile, higher oligomers. Their cleavage was shown to product major amounts of trimer and pentamer.[22]

The generally faster aging and its efficient acceleration above pH 6.5 of "active dimer hydroxide" may be due to its higher solubility, when compared with the "active monomer hydroxide". Precipitation of (then uncharacterized) "active dimer hydroxide" in both continuous-flow[7] and conventional[23] titration led to the characteristic, abrupt leveling off of the titration curves, but the electrode potentials remained very unstable in this region, even in the continuous-flow titrations,[7] so that the solubility product could not be determined. Thus, there is no definitive proof for this rather plausible explanation.

The aging of "active dimer hydroxide" probably occurs through a *solution mechanism*, based on the general similarity of the aging pattern with that of the "active monomer hydroxide" whose mechanistic features have been discussed in detail.[14] After several days, the end product of aging is an essentially amorphous precipitate exhibiting one broad diffraction line at $d \simeq 4.81$ Å.

Preparation and Characterization of Salts of the $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(H_2O)_4]^{4+}$ Cation. The "active" hydroxides may be regarded as solid storage forms of the parent cationic species (monomer or oligomers). Addition of just a slight stoichiometric excess of acid regenerates the parent species, and the anion of the acid serves as a counterion to the Cr(III) species. When high concentrations of the acid are used, very concentrated solutions of nearly pure Cr(III) oligomers become available, and from these, the oligomers may crystallize if a suitable counterion has been chosen.

We have used *p*-toluenesulfonic acid (Htos) and mesitylene-2-sulfonic acid (Hdmtos) for dissolving "active dimer hydroxide", in order to introduce poorly coordinating anions:

$$[Cr_2(\mu\text{-}OH)_2(OH)_4(OH_2)_4]\cdot 2H_2O + 4Htos + 7H_2O = [Cr_2(\mu\text{-}OH)_2(OH_2)_8](tos)_4\cdot 9H_2O(s) \quad (2)$$

$$[Cr_2(\mu\text{-}OH)_2(OH)_4(OH_2)_4]\cdot 2H_2O + 4Hdmtos + 2H_2O = [Cr_2(\mu\text{-}OH)_2(OH_2)_8](dmtos)_4\cdot 4H_2O(s) \quad (3)$$

An excess of acid is necessary to suppress the polymerization of the dimer.[10] In very concentrated solution the dimer crystallizes as hydrated salts. Their UV–vis spectra were recorded in 0.01 M $HClO_4$/1 M $NaClO_4$ against the same medium containing equivalent concentrations of Htos and Hdmtos, respectively. The spectra are identical with the previously reported solution spectrum. ϵ_λ (M^{-1} cm^{-1}), with literature values in parentheses, are as follows. For the product of eq 2: ϵ_{580}, max = 17.5 (ϵ_{582}, max = 17.5); ϵ_{490},

---

(22) Toko, A. L. Travail de licence, Université de Neuchâtel, 1985.
(23) Beutler, P. Ph. D. Thesis, Universität Bern, 1973.

Table IV. Crystal Data for $[Cr_2(\mu\text{-}OH)_2(OH_2)_8][(H_3C)_3C_6H_2SO_3]_4\cdot 4H_2O$[a]

formula	$C_{36}H_{70}O_{26}S_4Cr_2$
fw	1151.2
space group	$P2_1/a$
a, Å	8.720 (1)
b, Å	34.240 (4)
c, Å	8.921 (1)
β, deg	96.59 (1)
V, Å^3	2646.0
Z	2
d_{calcd}, g cm^{-3}	1.444
cryst color and habit	blue-green prisms
cryst dimens, mm	0.19 × 0.23 × 0.72
radiation	Mo K$\bar{\alpha}$, λ = 0.71073 Å (graphite monochromated)
data collcn	ω–θ scans
θ limits, deg	$2 < \theta < 27.5$
index limits	h, −11 to 11; *k*, 0 to 44; l, 0 to 11
no. of unique reflcns	5895
no. of reflcns used	4272 ($I > 3\sigma(I)$)[b]
abs coeff (μ_λ), cm^{-1}	5.8
refinement method	full-matrix least squares
no. of reflcns/no. of params	10.1
final *R* value	0.038
weighted final *R* value	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)/\sum w\lvert F_o\rvert = 0.041$
w	$[\sigma\lvert F_o\rvert + 0.00036\lvert F_o\rvert^2]^{-1}$
param shift/esd in last cycle of refinement	0.65; <0.2 (av)
residual density in final difference map, e Å^{-3}	+0.31 (max); −0.31 (min)

[a] Standard deviations of last significant figure in parentheses. [b] Six reflections (probably suffering from extinction) removed.

Table V. Final Positional and Equivalent Isotropic Thermal Parameters[a] for Non-Hydrogen Atoms in $[Cr_2(\mu\text{-}OH)_2(OH_2)_8](dmtos)_4\cdot 4H_2O$

atom	*x/a*	*y/b*	*z/c*	U_{eq},[b] Å^2
Cr	0.6406 (0)	0.5102 (0)	0.6063 (0)	0.0293 (1)
S(1)	0.6405 (1)	0.6018 (0)	1.1166 (1)	0.0401 (2)
S(2)	0.8995 (1)	0.4188 (0)	0.3301 (1)	0.0371 (2)
O(1)	0.5611 (3)	0.4861 (1)	0.7820 (2)	0.0435 (6)
O(2)	0.7426 (3)	0.5368 (1)	0.4457 (2)	0.0393 (5)
O(3)	0.8479 (2)	0.4853 (1)	0.6549 (3)	0.0425 (5)
O(4)	0.5575 (2)	0.4685 (1)	0.4748 (2)	0.0330 (5)
O(5)	0.7025 (3)	0.5546 (1)	0.7450 (3)	0.0452 (6)
O(11)	0.5714 (3)	0.5849 (1)	0.9768 (2)	0.0586 (7)
O(12)	0.5809 (3)	0.5826 (1)	1.2432 (2)	0.0527 (6)
O(13)	0.8066 (3)	0.6024 (1)	1.1325 (4)	0.0830 (9)
O(21)	0.9716 (2)	0.4331 (1)	0.4764 (2)	0.0454 (5)
O(22)	1.0033 (2)	0.4233 (1)	0.2148 (2)	0.0485 (6)
O(23)	0.7508 (2)	0.4375 (1)	0.2872 (2)	0.0465 (6)
O(W1)	0.9903 (3)	0.5416 (1)	1.0989 (3)	0.0603 (7)
O(W2)	1.2602 (4)	0.5114 (1)	0.9630 (3)	0.0726 (9)
C(11)	0.5837 (3)	0.6517 (1)	1.1237 (3)	0.0387 (7)
C(12)	0.5612 (4)	0.6732 (1)	0.9901 (3)	0.0492 (8)
C(13)	0.5174 (4)	0.7121 (1)	0.9999 (4)	0.0600 (10)
C(14)	0.4940 (4)	0.7298 (1)	1.1320 (5)	0.0597 (10)
C(15)	0.5213 (5)	0.7082 (1)	1.2615 (5)	0.0648 (11)
C(16)	0.5680 (4)	0.6693 (1)	1.2626 (4)	0.0556 (9)
C(17)	0.4432 (5)	0.7724 (1)	1.1381 (6)	0.0895 (15)
C(18)	0.5791 (8)	0.6572 (2)	0.8350 (5)	0.0825 (15)
C(19)	0.6092 (8)	0.6495 (1)	1.4153 (4)	0.1025 (17)
C(21)	0.8605 (3)	0.3681 (1)	0.3478 (3)	0.0406 (7)
C(22)	0.8323 (4)	0.3522 (1)	0.4880 (4)	0.0545 (9)
C(23)	0.7958 (5)	0.3129 (1)	0.4915 (5)	0.0682 (11)
C(24)	0.7850 (5)	0.2891 (1)	0.3668 (5)	0.0659 (11)
C(25)	0.8098 (4)	0.3059 (1)	0.2312 (5)	0.0635 (11)
C(26)	0.8443 (4)	0.3450 (1)	0.2169 (4)	0.0505 (8)
C(27)	0.7377 (7)	0.2469 (1)	0.3778 (6)	0.0968 (17)
C(28)	0.8307 (8)	0.3757 (2)	0.6328 (5)	0.0904 (16)
C(29)	0.8519 (6)	0.3609 (1)	0.0579 (4)	0.0737 (13)

[a] Esd in parentheses. [b] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\bar{a}_i\cdot\bar{a}_j$.

Table VI. Selected Bond Distances (Å) and Angles (deg)

Cr–O(1)	1.967 (2)	S(1)–O(12)	1.454 (2)
Cr–O(2)	1.991 (2)	S(1)–O(13)	1.440 (2)
Cr–O(3)	2.000 (2)	S(1)–C(11)	1.782 (3)
Cr–O(4)	1.936 (2)	S(2)–O(21)	1.466 (2)
Cr–O(4′)	1.937 (2)	S(2)–O(22)	1.454 (2)
Cr–O(5)	1.993 (2)	S(2)–O(23)	1.457 (2)
S(1)–O(11)	1.443 (2)	S(2)–C(21)	1.780 (3)
O(1)–Cr–O(2)	173.1 (1)	O(11)–S(1)–O(12)	109.8 (1)
O(1)–Cr–O(3)	92.3 (1)	O(11)–S(1)–O(13)	114.0 (2)
O(2)–Cr–O(3)	83.3 (1)	O(12)–S(1)–O(13)	112.0 (2)
O(1)–Cr–O(4)	91.8 (1)	O(11)–S(1)–C(11)	109.0 (1)
O(2)–Cr–O(4)	93.9 (1)	O(12)–S(1)–C(11)	106.3 (1)
O(3)–Cr–O(4)	94.9 (1)	O(13)–S(1)–C(11)	105.3 (1)
O(1)–Cr–O(4′)	94.3 (1)	O(21)–S(2)–O(21)	110.9 (1)
O(2)–Cr–O(4′)	90.7 (1)	O(21)–S(2)–O(23)	111.4 (1)
O(3)–Cr–O(4′)	170.5 (1)	O(22)–S(2)–O(23)	112.1 (1)
O(4)–Cr–O(4′)	78.2 (1)	O(21)–S(2)–C(21)	108.2 (1)
O(1)–Cr–O(5)	85.4 (1)	O(22)–S(2)–C(21)	107.9 (1)
O(2)–Cr–O(5)	89.3 (1)	O(23)–S(2)–C(21)	106.1 (1)
O(3)–Cr–O(5)	91.0 (1)	S(1)–C(11)–C(12)	119.2 (2)
O(4)–Cr–O(5)	173.7 (1)	S(1)–C(11)–C(16)	120.0 (2)
O(4′)–Cr–O(5)	96.4 (1)	S(2)–C(21)–C(22)	120.6 (2)
Cr–O(4)–Cr′	101.8 (1)	S(2)–C(21)–C(26)	118.6 (2)

min = 5.1 (ϵ_{490}, min = 5.2); ϵ_{416}, max = 20.6 (ϵ_{417}, max = 20.4); ϵ_{345}, min = 1.3 (ϵ_{345}, min = 1.5); intensity ratio $\epsilon_{416}/\epsilon_{580}$ = 1.17 (1.17). For the product of eq 3: ϵ_{580}, max = 17.5; ϵ_{489}, min = 5.4; ϵ_{415}, max = 20.5; ϵ_{345}, min = 2.1; $\epsilon_{415}/\epsilon_{580}$ = 1.17. These results suggest that the compounds contain the unaltered dimer, without coordinated anions, as the enneahydrate (eq 2) and tetrahydrate (eq 3), respectively. This was further substantiated by elemental and thermal analysis (see below) and by elution of the species from Sephadex SP-C25 as one band with >99% recovery as the dimer. Our first preparation of the tosylate salt, however, contained 11.5 H_2O of hydration. Seeding of solutions with these crystals invariably gave the enneahydrate.

Crystals of the dimer tetratosylate readily weathered in the atmosphere, with loss of water. A sample dried isothermally at 50 °C at atmospheric pressure analyzed as the dihydrate. In contrast, the tetramesitylene-2-sulfonate tetrahydrate compound is stable in the atmosphere.

Thermal analysis data on the two sulfonate salts are summarized in Scheme II and Figure 3, where the temperatures given are those of isothermal heating. The runs were performed under a dioxygen atmosphere, which caused oxidation of the sulfonate anions without residue. In contrast, no clear TG steps for tosylate and mesitylene-2-sulfonate degradation and no interpretable residual weight were found for runs under dinitrogen.

A color change from blue-green to violet is observed upon heating these salts to 120 (tosylate) or 170 °C (mesitylene-2-sulfonate), respectively. Concurrently, the IR spectrum of the tosylate shows changes characteristic of the coordination of the $-SO_3^-$ groups. The intense bands at 1165 (broad) and 1125 cm^{-1} (sharp) observed at <50 °C change into a pattern of three broad absorptions at 1260, 1140, and 1115 cm^{-1}.

The separate TG step in the tosylate salt at 170 °C, attributed to the reaction $Cr_2(\mu\text{-}OH)_2(tos)_4 = Cr_2(\mu\text{-}O)(tos)_4 + H_2O$, has no counterpart in the mesitylene-2-sulfonate case; careful search for it has remained negative. Sulfonate coordination is strongly suggested for the fully dehydrated compounds, but the species tentatively formulated as $Cr_2(\mu\text{-}OH)_2(RSO_3)_4$ (RSO_3 = tos, dmtos) and $Cr_2(\mu\text{-}O)(tos)_4$ require further study. The oxidation of the mesitylene-2-sulfonate anions occurs at somewhat lower temperature (320 °C) than tosylate oxidation (380 °C). The end product, $\alpha\text{-}Cr_2O_3$, was confirmed by X-ray powder diffraction and IR spectroscopy. No sulfur-containing species remains from the oxidative degradation of these two sulfonates.

Crystal and Molecular Structure of $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(OH_2)_4](dmtos)_4\cdot 4H_2O$. To our knowledge, this is the first crystal structure of an unsubstituted hydrolytic aqua hydroxo dimer of a transition-metal center. Single-crystal X-ray analysis (Tables IV–VII; Figures 4 and 5) fully confirms the earlier assertions of Kolaczkowski and Plane[4b] regarding the number of water molecules and the number and ligacy of the hydroxide bridges in the

Scheme II

$[(H_2O)_4Cr(\mu-OH)_2Cr(OH_2)_4](tos)_4\cdot 9H_2O$
m.w. = 1054.2
% weight loss

$[Cr_2(\mu-OH)_2(OH_2)_8](tos)_4\cdot 9H_2O$
< 50°C $\downarrow$ $-7H_2O$ calcd: 11.17 found: (11.26±0.15)
$[Cr_2(\mu-OH)_2(OH_2)_8](tos)_4\cdot 2H_2O$
120°C $\downarrow$ $-10H_2O$ calcd: 15.96 found: (16.34±0.07)
$Cr_2(\mu-OH)_2(tos)_4$
170°C $\downarrow$ $-H_2O$ calcd: 1.60 found: (2.41±0.06)
$Cr_2(\mu-O)(tos)_4$
370°C $\downarrow$ tos oxidation calcd: 57.81 found: (56.94±0.06)
$\alpha-Cr_2O_3$ residue: calcd: 13.46 found: (13.37±0.04)

$[(H_2O)_4Cr(\mu-OH)_2Cr(OH_2)_4](dmtos)_4\cdot 4H_2O$
m.w. = 1151.2
% weight loss

$[Cr_2(\mu-OH)_2(OH_2)_8](dmtos)_4\cdot 4H_2O$
90°C $\downarrow$ $-4H_2O$ calcd: 6.23 found: (6.60±0.03)
$[Cr_2(\mu-OH)_2(OH_2)_8](dmtos)_4$
170°C $\downarrow$ $-8H_2O$ calcd: 12.52 found: (12.13±0.03)
$Cr_2(\mu-OH)_2(dmtos)_4$
320°C $\downarrow$ $-H_2O$, dmtos oxidation calcd: 68.02 found: (67.77±0.06)
$\alpha-Cr_2O_3$ residue: calcd: 13.20 found: (13.50±0.07)

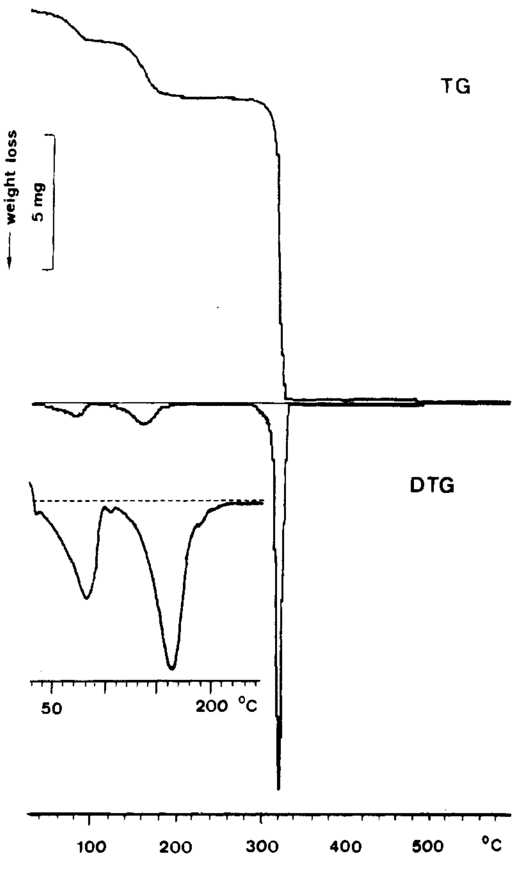


Figure 3. TG/DTG curves for the thermal dehydration and oxidation of $[(H_2O)_4Cr(\mu-OH)_2Cr(OH_2)_4](dmtos)_4\cdot 4H_2O$ under streaming O_2 (20 mL/min). Inset: amplified portion of DTG curve.

dimeric cation. These conclusions[4b] were reached, inter alia on the basis of an ^{18}O-labeling experiment to determine the number of "exchangeable" oxygens.

The $(H_2O)_4Cr(\mu-OH)_2Cr(OH_2)_4^{4+}$ cation has a crystallographic center of symmetry, C_i ($=\bar{1}$), with oxygen O(4) as the bridging atom. The Cr atom has a distorted octahedral environment, primarily as a consequence of the geometry of the bridging moiety. Thus, the angles within the cyclic Cr_2O_2 unit are O(4)–Cr–O(4′) = 78.2 (1) and Cr–O(4)–Cr′ = 101.8 (1)°, and the nonbonded atom distances are Cr⋯Cr′ = 3.006 (0) and O(4)–O(4′) = 2.441 (1) Å. The average Cr–O(4) distance within the bridge is 1.936 (2) Å and thus 0.052 Å shorter than the average $Cr-OH_2$ bond length of 1.988 Å.

The two $Cr-OH_2$ bond lengths trans to the OH bridges, viz. Cr–O(3) = 2.000 (2) and Cr–O(5) = 1.993 (2) Å, are very similar to the axial Cr–O(2) bond length of 1.991 (2) Å, but ca. 0.03 Å longer than the second axial bond, Cr–O(1) = 1.967 (2) Å. Thus, there is presently no clear indication whether the OH^- bridges exert a significant trans influence. In tandem with the small O(4)–Cr–O(4′) angle at the bridge, adjacent angles >90° are found in that same plane: O(3)–Cr–O(4) = 94.4 (1) and O(4)–Cr–O(5) = 96.4 (1)°. However, the angle O(3)–Cr–O(5) = 91.0 (1)° opposite the bridging angle in the same plane of coordination is not appreciably widened beyond an ideal octahedral angle. The axial water ligands are bent away from the bridging oxygens by 0.7–4.3° only. (Table VI) Thus, the nonbonded distances between the axial oxygen atoms are >3 Å.

Two water molecules of crystallization, O(W1) and O(W2), are involved in five hydrogen bonds via which the cations form chains extending in the direction [101] (Figure 4). Parallel chains are linked in the *c* direction by two hydrogen bonds and in the *a* direction by three hydrogen bonds while the bridging OH group (atom O(4)) hydrogen bonds to atom O(23) of a sulfonate anion only.

The anions are arranged in double layers where the sulfonate groups are all oriented toward the Cr(III) cations (Figure 5). The hydrocarbon moieties point toward each other. However, there are no short intermolecular contacts between non-hydrogen atoms of the anions related by the 2-fold screw axes or glide planes.

The geometry of the $(H_2O)_4Cr(\mu-OH)_2Cr(OH_2)_4^{4+}$ cation may be compared with that of the only known *aqua*ammine diol of Cr(III), *trans*-$[(H_2O)(NH_3)_3Cr(\mu-OH)_2Cr(NH_3)_3OH]^{3+}$[24] and with that of the only known main-group aqua dimer, $(H_2O)_4Al(\mu-OH)_2Al(OH_2)_4^{4+}$.[25] The angles within the four-membered, cyclic bridging moiety are the same within <2°, despite some differences in the M–O bond lengths within the bridge (1.950–1.975 Å for the Cr–ammine species and 1.88–1.95 Å for the Al dimer). The $Al-OH_2$ bonds are generally somewhat shorter than the $Cr-OH_2$ bonds, as expected. The two nonbridging Cr–O distances (1.975 and 1.983 Å) in the Cr–ammine dimer cannot be assigned unequivocally to Cr–OH or $Cr-OH_2$ bonds, respectively, because the two oxygens are involved in strong hydrogen bonding. However, they are intermediate between those in the pure aqua dimer (1.967–2.000 Å).

---

(24) Andersen, P.; Nielsen, K. M.; Petersen, A. *Acta Chem. Scand., Ser. A* **1984**, *A38*, 593.
(25) Johansson, G. *Acta Chem. Scand.* **1962**, *16*, 403.

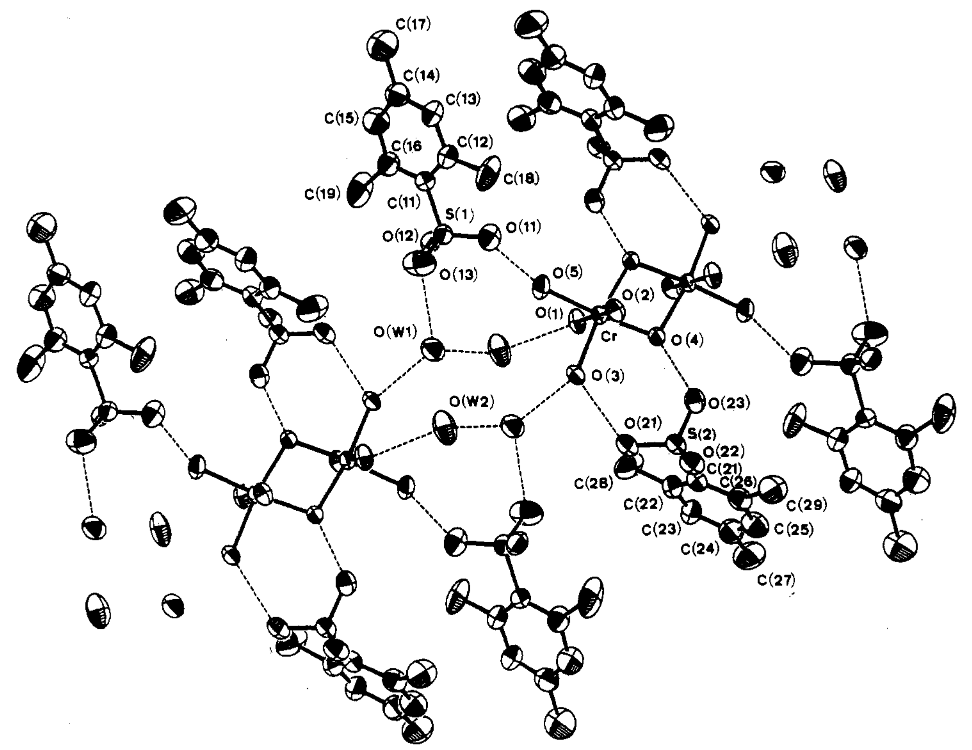


Figure 4. ORTEP[31] diagram of the structure of $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(OH_2)_4](dmtos)_4{\cdot}4H_2O$ with the atom-numbering scheme and the hydrogen-bonding network.

Table VII. Hydrogen Bond Lengths (Å) and Angles (deg)[a]

A–H	A···B	H···B	A–H···B
O(1)–HA(01) 1.028	O(1)···O(12$^{\text{i}}$) 2.655	HA(01)···O(12$^{\text{i}}$) 1.641	O(1)–HA(01)···O(12$^{\text{i}}$) 168.1
O(1)–HB(01) 0.636	O(1)···O(W2$^{\text{ii}}$) 2.607	HB(01)···O(W2$^{\text{ii}}$) 1.981	O(1)–HB(01)···O(W2$^{\text{ii}}$) 169.0
O(2)–HA(02) 0.722	O(2)···O(21$^{\text{iii}}$) 2.713	HA(02)···O(21$^{\text{iii}}$) 2.075	O(2)–HA(02)···O(21$^{\text{iii}}$) 170.6
O(2)–HB(02) 0.921	O(2)···O(12$^{\text{iv}}$) 2.668	HB(02)···O(12$^{\text{iv}}$) 1.777	O(2)–HB(02)···O(12$^{\text{iv}}$) 162.1
O(3)–HA(03) 0.807	O(3)···O(W1$^{\text{ii}}$) 2.637	HA(03)···O(W1$^{\text{ii}}$) 1.846	O(3)–HA(03)···O(W1$^{\text{ii}}$) 166.4
O(3)–HB(03) 0.835	O(3)···O(21) 2.700	HB(03)···O(21) 1.875	O(3)–HB(03)···O(21) 169.8
O(4)–H(04) 0.612	O(4)···O(23) 2.723	H(04)···O(23) 2.127	O(4)–H(04)···O(23) 165.4
O(5)–HA(05) 1.045	O(5)···O(11) 2.684	HA(05)···O(11) 1.649	O(5)–HA(05)···O(11) 169.8
O(5)–HB(05) 0.615	O(5)···O(22$^{\text{iii}}$) 2.659	HB(05)···O(22$^{\text{iii}}$) 2.047	O(5)–HB(05)···O(22$^{\text{iii}}$) 173.7
O(W1)–HA(W1) 0.873	O(W1)···O(13) 2.665	HA(W1) ···O(13) 1.841	O(W1)–HA(W1)···O(13) 156.5
O(W2)–HA(W2) 0.808	O(W2)···O(23$^{\text{iii}}$) 2.829	HA(W2)···O(23$^{\text{iii}}$) 2.045	O(W2)–HA(W2)···O(23$^{\text{iii}}$) 163.6
O(W2)–HB(W2) 0.833	O(W2)···O(W1$^{\text{ii}}$) 2.844	HB(W2)···O(W1$^{\text{ii}}$) 2.016	O(W2)–HB(W2)···O(W1$^{\text{ii}}$) 172.4

[a] Symmetry operations: (i) $1 - x, 1 - y, 2 - z$; (ii) $2 - x, 1 - y, 2 - z$; (iii) $2 - x, 1 - y, 1 - z$; (iv) $x, y, z - 1$.

Conclusions. Charge neutralization by deprotonation of the hydrolytic Cr(III) dimer leads to a rather unstable but reproducible microcrystalline material that is only slightly (<4%) contaminated by the products of further hydrolytic polymerization (trimer, tetramer, etc.), if precipitated under carefully selected and controlled conditions. Its precipitation results in efficient concentration of this species from rather dilute solution. The "active dimer hydroxide" may thus be considered as a moderately stable, solid storage form of the hydrolytic dimer. Its synthetic utility has been shown by the crystallization, for the first time, of a pure salt of the fully protonated dimer. The procedure involves protonation of the "active dimer hydroxide" to form a very concentrated solution of the nearly pure (>96%) dimer, in the absence of inert electrolyte. This rational approach to this synthetic problem has some promise for other hydrolytic oligomers of Cr(III) as well as for oligomers of other metal centers.

Experimental Section

Materials. Stock solutions of $[Cr(OH_2)_6](ClO_4)_3$ were prepared and standardized as described.[10,12] Solutions of dimer perchlorate, $[Cr_2(\mu\text{-}OH)_2(OH_2)_8](ClO_4)_4$, were prepared by O_2 oxidation of Cr^{2+} (prepared by Zn amalgam reduction of $Cr(OH_2)_6{}^{3+}$),[4] followed by ion-exchange chromatography to remove some monomer and higher oligomers.[10] Sodium perchlorate (Merck, p.a.), 70% perchloric acid (Fluka, puriss.), and *p*-toluenesulfonic acid monohydrate (Fluka, puriss.) were used as received. Water was deionized and distilled before use. The buffer bases used (Table III) were all puriss. grade and used as received, except for imidazole, which was purified as described.[11,14] The buffers were prepared by mixing each buffer base with appropriate volumes of 0.01 M $HClO_4$, and $NaClO_4$ was added to maintain an ionic strength of $I = 1.0$ M in the aging experiments.

All buffer and $NaClO_4$ solutions used were filtered through Sartorius SM 11307 cellulose nitrate membrane filters (0.2 μm median pore size) prior to use. "Active monomer hydroxide" was available from previous work.[14]

Instruments and Methods. UV–vis spectra were recorded on a Uvikon 810 spectrophotometer. The pH values of aging suspensions were measured as described,[14] except that the electrode was allowed to equilibrate for 15 min instead of 20 min prior to recording. Stable pH readings were obtained after this time. IR spectra were recorded on CsBr pellets (Merck Suprapur) by using a Perkin-Elmer 521 instrument. X-ray powder patterns were taken on a Guinier-de Wolff camera using Cu radiation, in most cases with screening of Cr fluorescence radiation with an aluminum foil. TG and DTG measurements were carried out on a Mettler TA 3000 system under a stream of either O_2 or N_2 (20 mL/min). In the "active" chromium hydroxide preparations, the temperature was maintained constant by using a Haake Q cryostat, and in the aging experiments a Haake N3 thermostat was used. Chromium[10,26] and perchlorate[27] were determined by literature methods.

Preparation of "Active Dimer Hydroxide". All operations were carried out at −2 ± 0.5 °C by using jacketed glassware (reaction vessel, dropping funnel, and filter) and a circulating methanol cooling bath set to −5 °C.

---

[26] Haupt, G. W. *J. Res. Natl. Bur. Stand. (U.S.)* **1952**, *48*, 414.
[27] Tsubouchi, M.; Yamamoto, Y. *Bunseki Kagaku* **1970**, *19*, 966.

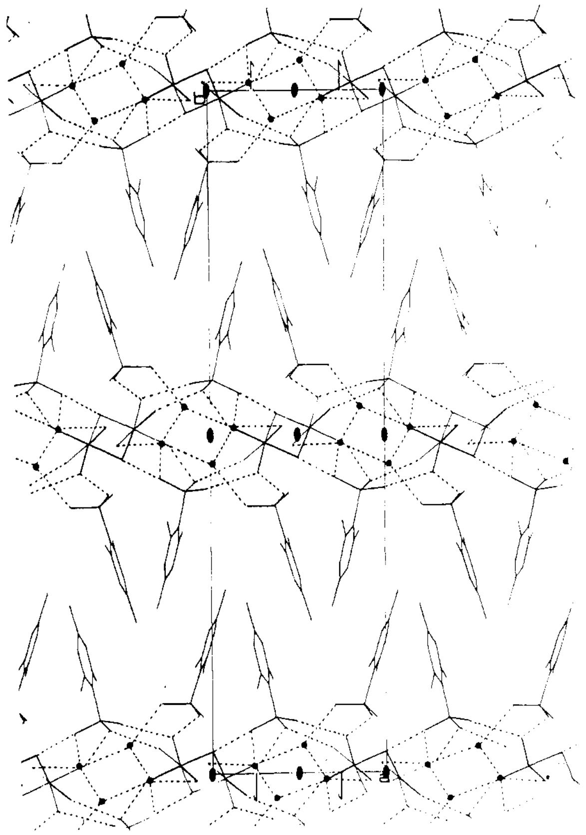


Figure 5. Packing diagram of $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(OH_2)_4](dmtos)_4\cdot 4H_2O$ showing one cation layer as surrounded by two anion double layers. Key: broken lines, hydrogen bonds; solid circle, water molecules of crystallization; solid ellipse, center of symmetry; arrow, two-fold screw axis. The contents of the unit cell were projected onto the *ab* plane. (Those parts of the molecule marked in heavy lines are in front of those parts marked in thin lines.)

Thus, in a typical preparation, an aqueous solution of dimer perchlorate (125 mL, $[Cr]_{tot}$ = 0.042 M, $[H^+]$ = 0.01–0.02 M, $[NaClO_4]$ = 0.5–1 M) was added with stirring to pyridine buffer (125 mL, 0.2 M, $[H^+]_{tot}$ = 0.01 M, pH ≃6.9).[28] The first few milliliters of dimer solution were added *rapidly* until a precipitate appeared. This reduced the time in which hydrolytic polymerization could occur in solution. The addition was then continued dropwise and was complete in ca. 30 min. The final pH of the suspension was ca. 5.7. It was filtered through a Sartorius SM 11607 regenerated cellulose membrane filter (0.2 μm median pore size). The residue was washed with water (2 times, ca. 30 mL, 0 °C) and with acetone (2 times, ca. 30 mL) and dried in a stream of air until the acetone was evaporated. The dried product was stored in a freezer (−18 °C). The preparation was usually complete within ca. 60 min. It is important to maintain the lowest possible temperature and to minimize handling time, while the precipitate is in contact with the mother liquor, in order to avoid contamination by higher oligomers. The addition of dimer to the buffer must be done slowly (≃30 min.), except for the first few mL, otherwise the precipitate is too finely dispersed to be effectively filtered, even by a membrane filter. Yield: 0.650 g, 79%. Anal. Calcd for $Cr(OH)_3\cdot 3H_2O$: Cr, 33.10; Na, 0.00; ClO_4^-, 0.00. Found: Cr, 32.6; Na, 0.067; ClO_4^-, 0.60.

Aging Experiments. Suspensions of the "active dimer hydroxide" were prepared by adding at once, and with continuous stirring, 4 mL of dimer ($[Cr]_{tot}$ = 0.0402 M, $[H^+]$ = 0.0201 M) to 4 mL of each buffer (Table III), such that the final pH was in the range 5.3–11.6. The suspensions were then stoppered to exclude atmospheric CO_2 (despite the observation that it had no measurable effect on the aging of the "active monomer hydroxide"[14]) and immersed in a thermostat bath at 25.0 ± 0.1 °C. The suspensions were then quenched after aging periods of 5–120 min. by adding 1–2 mL of 5 M $HClO_4$. The resulting, homogeneous solutions were diluted to 50 mL, adsorbed onto Sephadex SP-C25 and eluted as described previously.[10,14] A small amount of chromium (<1%) ran through during adsorption and was determined separately but included as part of the dimer fraction.

A large-scale aging experiment for the identification of the individual oligomers at pH 7.24 was carried out by adding 125 mL of dimer ($[Cr]_{tot}$ = 0.0402 M, $[H^+]$ = 0.020 M, $[NaClO_4]$ ≃ 1 M) to a 125-mL sample of 0.2 M imidazole. The resulting suspension was thermostated for 180 min aging time and then dissolved with $HClO_4$ (10 mL, 5 M) and diluted to 1 L. This solution was then adsorbed onto Sephadex SP-C25. Oligomers up to the hexamer were eluted in turn by varying concentrations of $NaClO_4$ (0.5–4 M) to remove dimer, trimer, and tetramer and $LiClO_4$ (4 M) to elute pentamer and hexamer as two overlapping bands. Unlike in the analogous experiment on "active monomer hydroxide", the amount of higher oligomers was smaller, and thus no floating of the resin occurred during adsorption and elution. Floating complicated, however, some of the small-scale aging experiments.

Preparation of $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(OH_2)_4](tos)_4\cdot 9H_2O$. "Active dimer hydroxide" (ca. 0.3 g, 0.95 mmol) was added portionwise to a solution of *p*-toluenesulfonic acid monohydrate (0.8 g, 4.2 mmol; puriss. Fluka) in 20 mL of water, at ambient temperature, until an insoluble residue persisted. It is important to perform the addition at ambient temperature as heating enhances the polymerization of the dimer. The resulting solution was sufficiently acidic to supress further hydrolytic polymerization of the dimer. It was filtered, evaporated (Rotavap) to ca. 6 mL, and stored in a refrigerator (2 °C). Large, dark blue-green crystalline aggregates formed within 2 weeks. They were filtered and stored in a tightly sealed sample bottle to avoid dehydration in the atmosphere. In subsequent preparations, seeding reduced the crystallization time to ca. 1 day. Yield: 0.52 g, 46%. Anal. Calcd for $C_{28}H_{64}O_{31}S_4Cr_2$: C, 29.78; H, 5.71; S, 11.34; Cr, 9.21. Found: C, 29.70; H, 4.96; S, 10.89; Cr, 9.10. Drying at 50 °C and atmospheric pressure gave the corresponding, hygroscopic dihydrate. Anal. Calcd for $C_{28}H_{50}O_{24}S_4Cr_2$: C, 33.53; H, 5.03; S, 12.79; Cr, 10.37. Found: C, 32.80; H, 5.23; S, 12.49; Cr, 10.38 ± 0.03.

Preparation of $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(OH_2)_4](dmtos)_4\cdot 4H_2O$. "Active dimer hydroxide" (0.8 g, 2.5 mmol) was added to a solution of mesitylene-2-sulfonic acid dihydrate (2.55 g, 10.8 mol; purum Fluka) in 20 mL of water. The resulting solution was filtered and evaporated to ca. 10 mL and stored in a refrigerator at 2 °C. Large crystals formed within ca. 3 days. These were filtered and washed with ice-cold water. Yield: 1.88 g, 63%. Anal. Calcd for $C_{36}H_{70}O_{26}S_4Cr_4$: 37.56; H, 6.13; S, 11.14; Cr, 9.03. Found: C, 37.61; H, 6.04; S, 11.04; Cr, 9.07 ± 0.03.

Crystal Structure Determination. Preliminary Weissenberg and precession photographs served to determine the space group. Intensity data were measured on a Stoe-Siemens AED diffractometer at room temperature. Accurate cell parameters were obtained from 2θ values of 13 reflections and their equivalents (30° < 2θ < 40°). No absorption or extinction corrections were applied, and there was no significant intensity variation for four standard reflections. The SHELX-76 program system[29] was used for solving the structure by Patterson and Fourier methods and in further calculations. Complex neutral-atom scattering factors were taken from the literature.[30] Hydrogen atoms were located in difference maps except for those for $-CH_3$ groups C(17), C(19), and C(27), which were included as rigid methyl groups with freely refined rotation: C–H = 1.08 Å; H–C–H = 109.5°; U_{iso} refined to the value 0.207 Å^2.

Acknowledgment. This work was supported by the Swiss National Science Foundation (Grant 2.838–0.83).

Note Added in Proof. Prof. W. Marty passed away suddenly during the final stages of the review of this paper. He was, therefore, unable to see the final form of this publication which reflects his work and dedication to science.

Supplementary Material Available: Tables of weight change of "active" hydroxides as a function of time upon drying over H_2SO_4 (Table S1), individual numerical results for thermal analyses from Figure 3 (Tables S2 and S3), and hydrogen atom positions with isotropic thermal parameters and anisotropic thermal parameters (Tables S5 and S6) (5 pages); a table of observed and calculated structure factors (Table S4) (26 pages). Ordering information is given on any current masthead page.

---

(28) This choice of buffer is deliberate. If a pH closer to the pK_a of pyridine had been chosen, a much larger volume of buffer would have been necessary to maintain a similar buffer capacity (within the rather wide limits of pH variation involved). This would, however, unduly lengthen the time required for filtration, which would give rise to more extensive aging of the suspension. For this reason, the dimer has to be added to the buffer and not vice versa.

(29) Sheldrick, G. M. "SHELX-76", Program for Crystal Structure Determination, University of Cambridge, Cambridge, G.B.

(30) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1976; Vol. IV, pp 99, 149.

(31) Johnson, C. K. *ORTEP-II*, Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.