funds.

Registry No. **2**, 37206-38-5; **5**, 37206-39-6; **6**, 114942-22-2; **7**, 114942-26-6; **8**, 114942-24-4; **9**, 114942-28-8; $Na[Mo(CO)_3(\eta^5\text{-}C_5H_5)]$, 12107-35-6; $InCl_3$, 10025-82-8; $Na[W(CO)_3(\eta^5\text{-}C_5H_5)]$, 12107-36-7.

Supplementary Material Available: Tables S1-S12, listing complete bond lengths and angles, anisotropic thermal parameters, and hydrogen atom parameters (11 pages); tables of observed and calculated structure factors and esd's (54 pages). Ordering information is given on any current masthead page.

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Hydrolytic Trimer of Chromium(III). Synthesis through Chromite Cleavage and Use in the Preparation of the "Active" Trimer Hydroxide

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Acidification of chromite solutions, prepared by addition of OH^- to Cr^{3+} (pH >13), generates a homogeneous mixture containing several oligomers, which in acid are slowly cleaved into monomer, dimer, and trimer. After 27 h of acid cleavage the hydrolytic trimer (65% of total Cr) predominates over the monomer (15%), dimer (16%), and higher oligomers (4%). The greater stability of the trimer compared with that of the other oligomers is interpreted in terms of a compact structure. Alkalinization of the trimer, $Cr_3(\mu\text{-}OH)_4(OH_2)_9^{5+}$, results in the formation of a finely dispersed light green precipitate of the "active" trimer hydroxide. Chromium and thermogravimetric analyses are consistent with the composition $[Cr_3(\mu\text{-}OH)_4(OH)_5(OH_2)_4]\cdot 4H_2O$. Dissolution in acid regenerates >90% of the original trimer, the difference being made up of hexamer and higher oligomers that, in acid, cleave back into trimer. This suggests that the hydroxide consists predominantly of unaltered trimer units. The IR spectrum indicates that these units are linked through H-bonds of ca. 2.9 Å. X-ray powder diffraction patterns and electron micrographs were also recorded. In aqueous suspension, "active" trimer hydroxide is readily transformed into higher oligomers. The aging profile exhibits minima at pH 5.5-5.7 and 11-11.8 and a distinct maximum at pH ≃8.2. For pH ≤8.2, the aging profile closely resembles that of the "active" dimer hydroxide although the "active" trimer hydroxide ages more rapidly. For pH >8.2, a reduction in aging rate, at present unique to this hydroxide, is observed. The aging process is proposed to occur predominantly through the release of trimer into solution and polymerization in solution, followed by adsorption of polynuclears onto the surface of the solid "active" hydroxide phase.

Introduction

The precipitation of metal hydroxides may be envisaged to result from a combination of the following processes (H_2O ligands are omitted for clarity):[4-7] (i) deprotonation of the aqua ions

$$M^{z+} \overset{K_a}{\rightleftharpoons} MOH^{(z-1)+} + H^+ \qquad (1)$$

(ii) intermolecular association of conjugate bases through H-bonding

$$2MOH^{(z-1)+} \rightleftharpoons \left[\begin{array}{c} H \quad H \\ O\cdots H\text{—}O \\ M \qquad\quad M \\ O\text{—}H\cdots O \\ H \quad H \end{array}\right]^{(2z-2)+} \qquad (2)$$

(iii) substitution of H_2O by OH^- to give polynuclears

$$2MOH^{(z-1)+} \rightarrow HOM(\mu\text{-}OH)M^{(2z-2)+} \rightarrow M(\mu\text{-}OH)_2M^{(2z-2)+} \qquad (3)$$

For labile metal centers, such as Fe(III), the H-bonded forms (eq 2) are expected to have only transient existence since deprotonation (eq 1) leads, initially, to the rapid formation of the hydrolytic dimer (eq 3)[5] followed by further substitution to give species of increasingly higher nuclearity and eventually to the precipitation of metal hydroxides. Since many different species coexist in solution at the same time, hydrolytic polymerization proceeds by a complicated mechanism and, as a consequence, these initial precipitates are usually amorphous. Such hydroxides, however, are often metastable, leading to the formation of microcrystalline phases when aged in contact with the mother liquor.[5,6]

For kinetically inert metal centers, such as Cr(III), substitution rates are many orders of magnitude slower than either deprotonation (eq 1) or association (eq 2) reactions. Furthermore, in dilute Cr^{3+} solutions, the concentration of H-bonding aggregates (eq 2) is likely to be small since this type of stabilization cannot compete with the more efficient H-bonding interactions between the solvent and the deprotonated metal ion.[7] While the $Cr(bpy)_2(OH)(OH_2)^{2+}$ complex is not a true aqua ion, three phase vapor tensiometry studies have demonstrated the concentration-dependent nature of different intermolecular H-bonding interactions. Thus, for [Cr(III)] < 5×10^{-4} M monomeric $Cr(bpy)_2(OH)(OH_2)^{2+}$ predominates while for [Cr(III)] > 0.1 M significant amounts of the dimer $(bpy)_2Cr(H_3O_2)_2Cr(bpy)_2^{4+}$, corresponding to eq 2 above, are present. A classical example of H-bonding aggregation in the solid state is the "active" monomer hydroxide,[8] which forms upon alkalinization of Cr^{3+} to pH >5 (eq 4). This hydroxide has a layer structure in which Cr(III)

$$Cr(OH_2)_6^{3+} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} Cr(OH)_3(OH_2)_3(s) \qquad (4)$$

octahedra are linked solely through H-bonding between OH^- and H_2O ligands of adjacent metal centers. As a foreseeable consequence of this structure, acidification of this hydroxide leads to

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(1) Monash University.
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(4) (a) Baes, C. F., Jr.; Mesmer, R. E. *Am. J. Sci.* **1981**, *281*, 935. (b) Baes, C. F., Jr.; Mesmer, R. E. *The Hydrolysis of Cations*; Wiley: New York, 1976.
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the rapid and quantitative regeneration of Cr^{3+}. This behavior is inconsistent with both the slow rupture of hydroxide bridges in classical Cr(III) hydroxides[8] and the slow rates of acid cleavage of Cr(III) oligomers.[9]

In contrast to the case of initial hydroxide precipitates formed by labile metal ions, e.g. Fe^{3+},[5,6] aging of the "active" monomer hydroxide in contact with the mother liquor results in the formation of an amorphous, and not microcrystalline, phase.[8a] Recent investigations[10] of the chemical changes associated with this transformation have established that all of the known Cr(III) oligomers (dimer–hexamer) and some yet to be characterized higher oligomers are formed. The significant dependence of the rate of polymerization of this "active" hydroxide on suspension pH was consistent with a solution mechanism in which monomeric units of the hydroxide first pass into solution (aided by either protonation or deprotonation at low and high pH, respectively), where they undergo polymerization followed at some stage by either precipitation or adsorption onto the surface of the "active" hydroxide.[10] An alternative solid-state mechanism was ruled out since it would be expected to occur in the interior of the solid and thus be independent of suspension pH.

Recently, we reported the isolation and characterization of the "active" dimer hydroxide, $Cr_2(\mu\text{-}OH)_2(OH)_4(OH_2)_4\cdot 2H_2O$, formed on alkalinization of dilute solutions of the hydrolytic dimer.[11,12] Since the "active" dimer hydroxide is transformed into higher oligomers in a manner similar to that for the "active" monomer hydroxide, but at a considerably faster rate, the preparation was carried out under conditions that minimize aging ($T \simeq 0$ °C and pH $\simeq 5.7$).[11] Acidification led to the immediate and almost quantitative regeneration of the hydrolytic dimer, which suggested that this material may be considered as a moderately stable storage form (free of electrolyte or acid) of the hydrolytic dimer. The synthetic utility of this hydroxide was demonstrated by its use in the crystallization of the hydrolytic dimer, whose structure has been determined.[11]

We report here a convenient synthetic procedure for obtaining pure solutions of the hydrolytic trimer, $Cr_3(\mu\text{-}OH)_4(OH_2)_9^{5+}$, and in addition the preparation and characterization of the "active" trimer hydroxide.

Results and Discussion

1. Synthesis of the Hydrolytic Trimer through Chromite Cleavage. The addition of excess base to a solution of Cr^{3+}, at room temperature, affords a deep green solution presumably containing chromite anions. Immediate acidification of this solution does not regenerate Cr^{3+} (blue-purple) but instead yields a green solution (lighter than the chromite color) containing cationic forms of several oligomers. Although the nature of chromite solutions has not been studied in detail, this observation suggests that such solutions are composed of polynuclears linked through either hydroxo or oxo bridges. Thus, acidification leads to the protonation of all terminal OH^- groups followed by much slower cleavage processes.[9,10] Chromatographic analysis of chromite solutions immediately after acidification showed the presence of at least 10 different oligomers and a small amount of Cr^{3+}.[13]

A chromite solution was prepared by mixing rapidly and thoroughly a solution of Cr^{3+} ($[Cr(III)]_T = 0.5$ M, $[H^+] = 0.66$ M) with NaOH to give $[Cr(III)]_T = 0.167$ M and $[OH^-] \simeq 0.9$ M (calculated by assuming the formation of $Cr(OH)_4(OH_2)_2^-$ immediately after deprotonation). The solution was immediately acidified with $HClO_4$ to produce the protonated oligomers ($[Cr(III)]_T = 0.05$ M and $[H^+] \simeq 1.2$ M). This solution was equilibrated at 298.15 K, aliquots were taken periodically, and the oligomers present were determined by ion-exchange chromatography.[9,10] All of the known lower oligomers[9] and some yet to be characterized higher oligomers were observed. The results, summarized in Figure 1, show the eventual conversion of all these oligomers into monomer, dimer, and trimer.

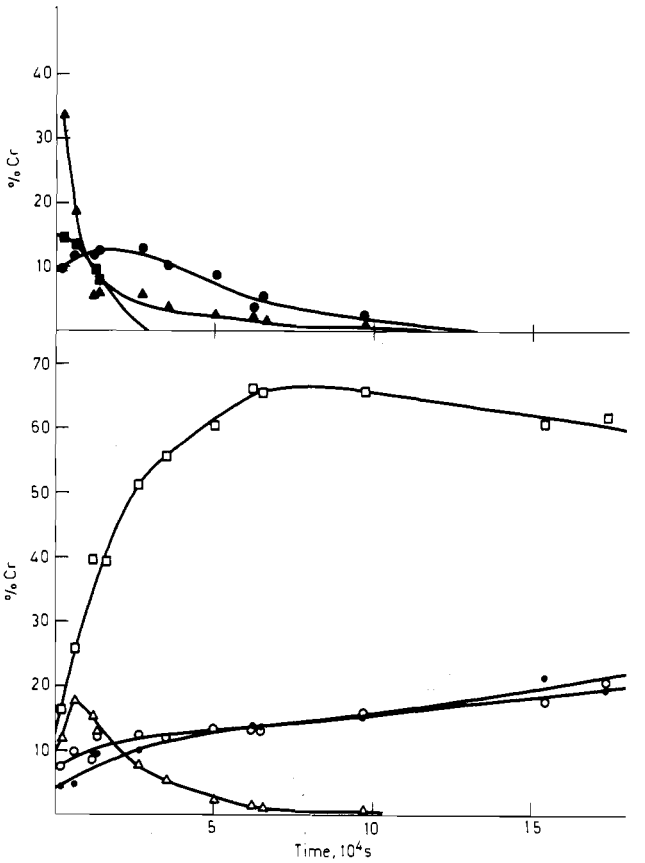

Figure 1. Time dependence of the oligomers formed by acid cleavage of chromite solutions ($[Cr(III)]_T = 0.05$ M) at 25 °C and $[H^+] \simeq 1.2$ M: (•) monomer; (○) dimer; (□) trimer; (△) tetramer; (●) pentamer; (■) hexamer; (▲) higher oligomers.

The observed extensive polymerization of chromite solutions, within the time required to mix Cr^{3+} with base, is perhaps to be expected. While kinetic data on the rate of substitution within these chromites are not available, estimates can be made by using existing data for H_2O exchange on Cr^{3+} and $CrOH^{2+}$[14] and intermolecular dimerization within deprotonated forms of Cr^{3+}.[15] Swaddle and co-workers[14] found that H_2O exchange of $CrOH^{2+}$ is 75 times faster than on Cr^{3+} ($k_{ex} = 2.4 \times 10^{-6}$ s^{-1} at 298.15 K). Furthermore, in the dimerization of Cr^{3+}, rate increases of 50–200-fold were observed for each additional deprotonation of the reactant.[15] Assuming a 75-fold increase in rate also applies to subsequent deprotonations of Cr^{3+}, the rate of substitution on $Cr(OH)_4(OH_2)_2^-$ (a chromite likely to form after four deprotonations of Cr^{3+}) would be ca. 75 s^{-1} (or $t_{1/2} \approx 0.015$ s). On this basis, Cr(III) is expected to polymerize rapidly in alkaline solutions in accord with experimental observations. What is remarkable here is that *deprotonation can readily transform a kinetically inert metal center like Cr(III) into a relatively labile one.*

Acid cleavage of the higher oligomers (nuclearity >6) into lower oligomers is rapid at first, with at least 85% cleaved after 200 min, but thereafter slows down considerably with some persisting even after 1600 min (Figure 1). Such variation in acid cleavage rates of greater than 10-fold (estimated from the drop in percentage of high oligomers with time) might be expected since differences of 100-fold are reported for cleavage of dimer, trimer, and tetramer.[9] At least for the lower oligomers, these variations in acid cleavage rates appear to be closely tied to the structure of the oligomer,[9,16] which may also be true for the higher oligomers.

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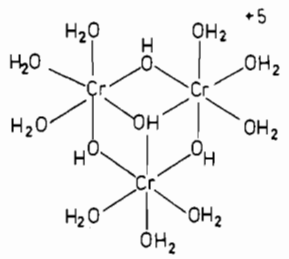
Cleavage of the higher oligomers results initially in increases in the amount of tetramer, pentamer, and hexamer, but these species then disappear as they are converted into monomer, dimer, and trimer. Peak concentrations are reached after ca. 200, 440, and 100 min for tetramer, pentamer, and hexamer, respectively (Figure 1). The fact that the pentamer reaches its concentration maximum more slowly than either tetramer or hexamer suggests that this oligomer results, at least in part, from cleavage of one or more relatively stable higher oligomers. The time for these oligomers to disappear from acidified chromite solutions provides an estimate of their respective cleavage rates. On this basis the rate of cleavage increases in the order pentamer $\leq$ tetramer $<$ hexamer. These rates ($t_{1/2} \simeq$ 30–300 min) are considerably faster than those measured for the cleavage of dimer and trimer.[9] Unfortunately, a more quantitative treatment of the present data is not possible because of the unknown rates of formation of oligomers in acidified chromite solutions. However, we note that an estimate of the cleavage half-life for tetramer of 240 min, determined as the time necessary for the tetramer to drop from its maximum concentration to half its value (Figure 1), is in good agreement with the value of 180 min measured in 1 M $HClO_4$ at 298.15 K.[9]

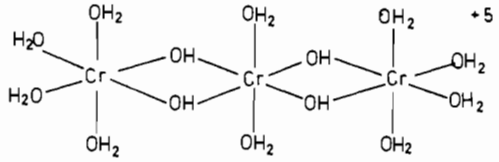
The most important feature of the present experiments is that cleavage of the acidified chromite solutions generates predominantly the hydrolytic trimer. The proportion of trimer increases rapidly below 1000 min, reaches a steady level (ca. 65%) for the period 1000–1600 min, and thereafter falls gradually. The observed trimer profile can be interpreted in the following way: (i) initially, the fast formation rate is due to the preponderance of higher oligomers that cleave relatively rapidly into predominantly trimer; (ii) after intermediate cleavage periods a steady-state situation is reached where the rates of formation and cleavage of trimer are approximately the same; (iii) after longer cleavage periods the formation of trimer has stopped (no higher oligomers left) and the drop in trimer content is due entirely to its cleavage. For synthesis purposes, cleavage periods of ca. 1600 min are ideal since conversion of the higher oligomers is almost complete, resulting in good yields (ca. 65%) of the hydrolytic trimer.

The formation of mainly trimer from chromite cleavage reflects the widespread occurrence of this structural unit in these solutions, suggesting that it plays an important role in the propagation of polymerization. Furthermore, since this unit is more stable to acid cleavage than other structural fragments (including dimer), it persists for longer periods in acidic solution. These observations can be rationalized by the proposed compact structure of this oligomer (**1**), in which a triangular arrangement of Cr atoms is



1

held together by three μ-hydroxo bridges per Cr atom.[9] Alternative "classical" structures, based on either linear or bent arrangements of Cr atoms linked together via two μ-hydroxo bridges (e.g. **2** and **3**), have been proposed.[17] While the last two structures can account for some of the pK_a's of the oligomers, they cannot accommodate the observed variability in stability and cleavage rates exhibited by these oligomers, for example (i) the dramatic differences in cleavage rates, i.e. the much faster rate of acid cleavage of tetramer, pentamer, and hexamer compared with that of trimer, (ii) the cleavage of higher oligomers into predominantly trimer, and (iii) the selective cleavage of tetramer into trimer and monomer,[9] consistent with cleavage at a terminal Cr group, and hexamer into exclusively trimer, consistent with cleavage at the



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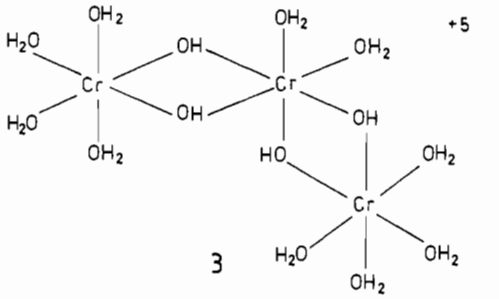

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central Cr atoms.[18] For the "classical" structures monotonic increases in cleavage rates and decreases in stability with increasing charge and nuclearity of the oligomers is to be expected since cleavage presumably occurs through breakage of two μ-hydroxo bridges. In addition, cleavage may occur at any position along the oligomer chain, thus giving rise to a variety of products rather than selected oligomers. Experimentally, however, cleavage is found to occur in clearly defined steps and at specific sites in the oligomer chain, leading to the formation of only some of the possible products (see (iii) above). Alternatively, the compact structure **1** should be more stable than the "classical" structure since in this case trimer cleavage requires the breaking of three μ-hydroxo bridges. Thus, cleavage of polynuclears containing trimer units would not destroy such units but rather cleavage would occur at less stable positions in the polynuclear structure. In example iii cited above, the hexamer probably consists of two trimer units joined together by a weak bridge(s) (possibly hydroxo), which cleave(s) easily; similarly, a weak link occurs in the tetramer, which, on cleavage, leads to the formation of trimer and monomer (and no dimer).

2. "Active" Trimer Hydroxide. Preparation and Composition. Suspensions of the "active" trimer hydroxide were prepared by mixing a solution of chromatographically pure hydrolytic trimer with pyridine buffer (pH $\simeq$ 7.0) at −1 °C (see Experimental Section). The final pH of this suspension corresponded to a minimum in the rate of aging for this hydroxide (see Aging in Aqueous Solution). The light green precipitate was recovered by ultrafiltration and washed once with H_2O and twice with acetone (preparation time ca. 50 min). This procedure removed most of the $NaClO_4$ introduced during chromatographic purification of the trimer. Small amounts of ClO_4^- were detected in the IR spectrum, which showed characteristic bands at ca. 625 and 1100 cm^{-1}. These were also observed in the "active" dimer hydroxide but were of weaker intensity.[11] More thorough washing of the precipitate with H_2O was not possible because the "active" trimer hydroxide particles tended to disperse, causing a prolongation of the filtration time and, thus, increasing the likelihood of undesirable aging of the "active" hydroxide. The product was dried quickly in a stream of air prior to storage in a refrigerator at −18 °C.

The oligomeric content of the "active" trimer hydroxide was determined by using the procedures adopted for the "active" dimer hydroxide.[11] Thus, a sample of the "active" hydroxide was acidified with $HClO_4$ and analyzed by using ion-exchange chromatography. For the purest sample the oligomeric distribution was 93.6% trimer and 6.4% higher oligomers. This sample was used for most subsequent analyses. Reanalysis after 2 weeks, during which time the sample was periodically warmed to room temperature and various analyses were carried out, gave 91.4%

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(18) Stünzi, H.; Marty, W., unpublished results.

Table I. Changes in the Weight of the "Active" Trimer and Monomer Hydroxide as a Function of Desiccation Time over 11 M H_2SO_4

	wt change, %			wt change, %	
time, s	trimer	monomer	time, s	trimer	monomer
0	0	0	1.26×10^4	−7.8	0.1
9.0×10^2	−2.8	0.2	1.86×10^4	−8.2	0.1
2.7×10^3	−5.0	0.2	2.58×10^4	−8.6	0
4.2×10^3	−5.6	0.2	7.8×10^4	−9.2	0.1
5.7×10^3	−6.1	0.2	1.10×10^5	−9.3	0.1
7.8×10^3	−6.5	0.1	1.73×10^5	−9.4	0

Table II. Effect of Drying over 11 M H_2SO_4 on the Composition of the "Active" Trimer Hydroxide

	product distribn, %[a]			
time, s	trimer	hexamer	higher oligomers	% Cr[b]
0	89.7	8.3	2.0	33.7
9.0×10^2	85.5	9.4	5.1	34.0
1.8×10^3	82.9	10.2	6.9	34.3
4.8×10^3	80.4	11.7	7.9	34.6

[a] Normalized to 100%. [b] Cr content of sample after each drying period.

and 8.6% higher oligomers, suggesting that some aging occurs during handling. A number of "active" trimer hydroxide samples with preparation times between 30 and 150 min were, on average, found to contain 90.3 (±0.9)% trimer with only a slight correlation between purity and preparation time. This observation would suggest that the majority of the oligomers found in the "active" trimer hydroxide are formed in solution prior to precipitation. Experimentally some time elapsed (ca. 20 s) between the commencement of trimer addition and the first noticeable appearance of a precipitate. Attempts were made to reduce this time period by rapidly adding a small quantity of trimer (ca. 5 mL) to the pyridine buffer (10 mL). A precipitate was observed after 10 s, and the purity of the isolated "active" hydroxide was marginally higher (93.6%).

The "active" trimer hydroxide dehydrates readily in the atmosphere in a manner similar to that for the "active" dimer hydroxide.[11] Hence, accurate determination of the formula weight is not possible unless all adherent H_2O can be removed. Drying of the precipitate over 11 M H_2SO_4 led to considerable weight loss (Table I) and in addition to substantial changes in the oligomeric content of the hydroxide (Table II), indicating that the hydroxide could not be dried without changing its composition. Similar changes occurred with the "active" dimer hydroxide, although in this case the solid-state aging was much slower. In contrast, the "active" monomer hydroxide does not dehydrate or change its composition over similar time periods.[11]

The IR spectrum of the "active" trimer hydroxide shows bands at 490 cm^{-1} (strong Cr–O stretching), 840 cm^{-1} (weak, H_2O rocking), 1630 cm^{-1} (moderate, H_2O bending), and 3400 cm^{-1} (strong, H-bonded O–H···O). This spectrum is similar to that of the other active hydroxides[11] with the exception that the strong band found at 306 cm^{-1} for the monomer is not present in the trimer spectrum. The band at 3400 cm^{-1} corresponds to H-bonds of ca. 2.9 Å,[8b,11,12,19] weaker in strength than those found for the "active" dimer hydroxide (2.8 Å). The "active" monomer hydroxide exhibits two such H-bonds of 2.7 and 2.9 Å, the latter of which probably connects the different layers together ("active" monomer hydroxide has a layer structure complementary to that of bayerite[8]). Assuming a layer structure is generally adopted by the "active" hydroxides, the presence of only one H-bond in the dimer and trimer indicates either a lack of H-bonding between Cr(III) octahedra of adjacent planes or, alternatively, interactions of similar strength both within and between planes. The importance of H-bond interactions in the solid state appear to diminish with increasing nuclearity of the hydroxide; viz., H-bonding strength follows in the order monomer > dimer > trimer.

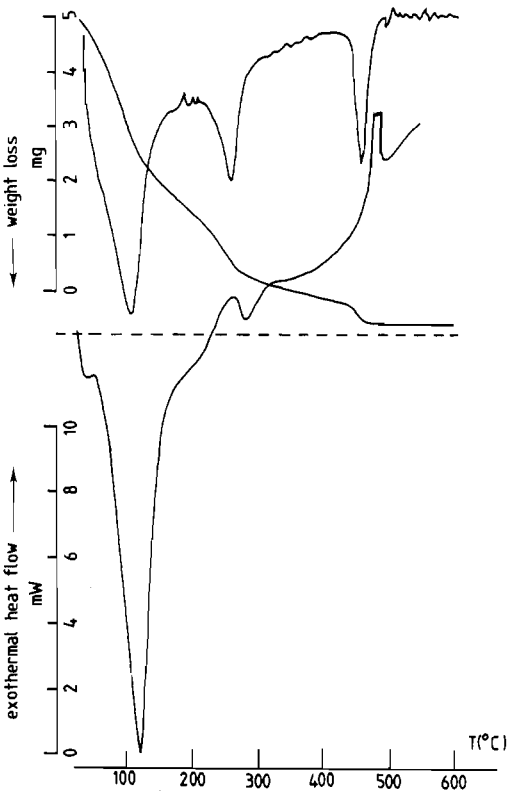

Figure 2. DSC and TG/DTG curves for the thermal dehydration of the "active" trimer hydroxide (streaming N_2, 20 mL/min).

Thermal Analysis. The "active" trimer hydroxide was analyzed by using thermogravimetry (TG) under a stream of nitrogen. The differential thermogravimetric (DTG) curves (Figure 2) show three distinct regions of weight loss with peak temperatures at 100, 250, and 450 °C (reproducible to within ±10 °C). Analogous regions of weight loss were observed for the "active" monomer and dimer hydroxides.[12] The peak at 250 °C becomes more pronounced as the nuclearity of the hydroxide increases; viz., trimer > dimer > monomer. The dehydration of the "active" dimer hydroxide was followed by measuring weight losses for the same sample during isothermal heating at each peak position, in ascending order of temperature. After heating at 110 and 250 °C, another weight loss was found at 330 °C, which was not apparent in the dynamic DTG curve (Figure 2). The differential scanning calorimetry (DSC) curve of the "active" trimer hydroxide (Figure 2) shows three endothermal peaks at 120, 220 (shoulder), and 290 °C (reproducibility ±10 °C), consistent with the dehydration of the hydroxide. In addition, an exothermal peak, due to the crystallization of α-Cr_2O_3, occurs at 490 °C. Thus, every peak in the DSC curve has a corresponding one in the DTG curve although, due to differences in heat transfer between the two experiments, some variation in peak position is found.

The interpretation of the TG results requires the formula weight of the starting material, which is not accurately defined due to the ease of dehydration of this "active" hydroxide. However, from the chromium content of 33.7% and correction for the presence of $NaClO_4$ in the sample (2.5%, calculated from the ClO_4^- content of 2.0%) we arrive at a Cr content of 34.6%, which corresponds to a formula weight of 451 (±1) g and a molecular formula of $[Cr_3(\mu\text{-}OH)_4(OH)_5(OH_2)_4]\cdot 4H_2O$ (M_r = 453.2). The observed weight losses, determined by isothermal heating (see above), were consistent with the dehydration steps given in Scheme I. Good agreement is found between the observed and postulated weight losses for the first two dehydration steps. The poor agreement between calculated (6.0%) and observed (4.3%) weight losses at 330 °C is due to the chemisorption of O_2 and/or H_2O within microporous, amorphous Cr_2O_3.[12] These are desorbed on crystallization of α-Cr_2O_3, and consequently, a weight loss is observed

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Scheme I. Thermal Dehydration of the "Active" Trimer Hydroxide

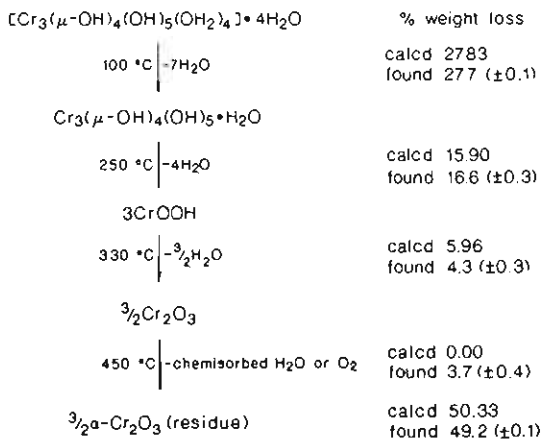

Table III. X-ray Powder Diffraction Pattern of the "Active" Trimer Hydroxide

4θ,[a] deg	d, Å	intens	comments
18.1	9.76	1	br
24.5–25.5	7.22–6.94	4	vbr
36.7	4.83	10	s
44.5–45.0	3.99–3.95	4	br

[a] Cu $K\alpha_1$ radiation was used.

at 450 °C (the decomposition of $NaClO_4$ may also make a small contribution here). In contrast to the case of the other "active" hydroxides, the "active" trimer hydroxide does not lose all its coordinated H_2O at the first peak temperature to give $Cr_3(OH)_9$. Instead, one coordinated H_2O is retained. It is difficult to pinpoint the reason for this in the absence of detailed structural information.

An intriguing feature of the "active" Cr(III) hydroxides is that after dehydration in the temperature range 100–350 °C they gain weight on cooling to room temperature, even under an N_2 atmosphere. This feature becomes more pronounced with increasing nuclearity of the "active" hydroxide. Despite being qualitative, these observations suggest the need for further study with respect to catalytic applications. The classical chromia catalysts[20] are usually generated by heating a chromium(III) hydroxide that consists of several polynuclear species. The use of well-characterized "active" hydroxides to generate these catalysts has, to our knowledge, not been investigated in any detail.

X-ray Powder Diffraction and Electron Microscopy. The X-ray powder diffraction pattern of the "active" trimer hydroxide consists of a number of lines with d values as listed in Table III. All of the lines are broad with the exception of the most intense line at d = 4.83 Å. While there are insufficient lines for structural assignment, this pattern is nevertheless distinctly different from those of the other "active" chromium(III) hydroxides[8a,12] and thus may be used to detect the presence of the "active" trimer hydroxide. Electron micrographs show that the "active" trimer hydroxide consists of small, elongated spindle shaped particles (Figure 3), a morphology that contrasts with the platelets with broken edges observed for the "active" dimer hydroxide.[12]

Aging in Aqueous Solution. As for the aging studies on the "active" monomer and dimer hydroxides,[10,11] suspensions of the "active" trimer hydroxide were prepared at various pH values (5.15 < pH < 11.76) and aged for periods between 1 and 30 min. The aging process was quenched by acidification with $HClO_4$ and the resulting solution analyzed by using ion-exchange chromatography. Three major bands consisting of trimer, hexamer, and higher oligomers were eluted, and the Cr content was determined.[9,10] The results are summarized in Figure 4. These experiments served to establish the reactivity of the "active" hydroxide in aqueous suspension and hence the optimum conditions for its preparation.

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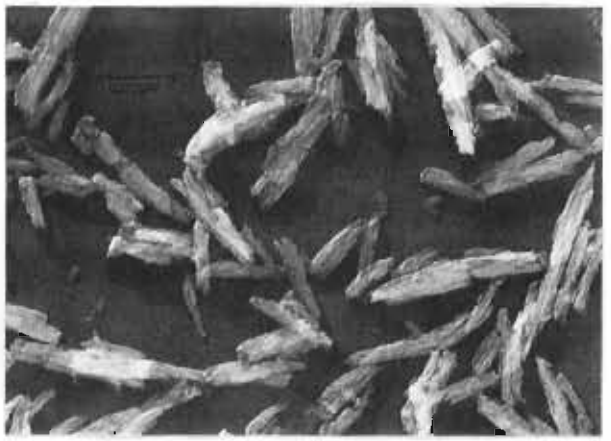

Figure 3. Transmission electron micrograph (Cr shadowed) of a sample of the "active" trimer hydroxide dispersed in doubly distilled H_2O.

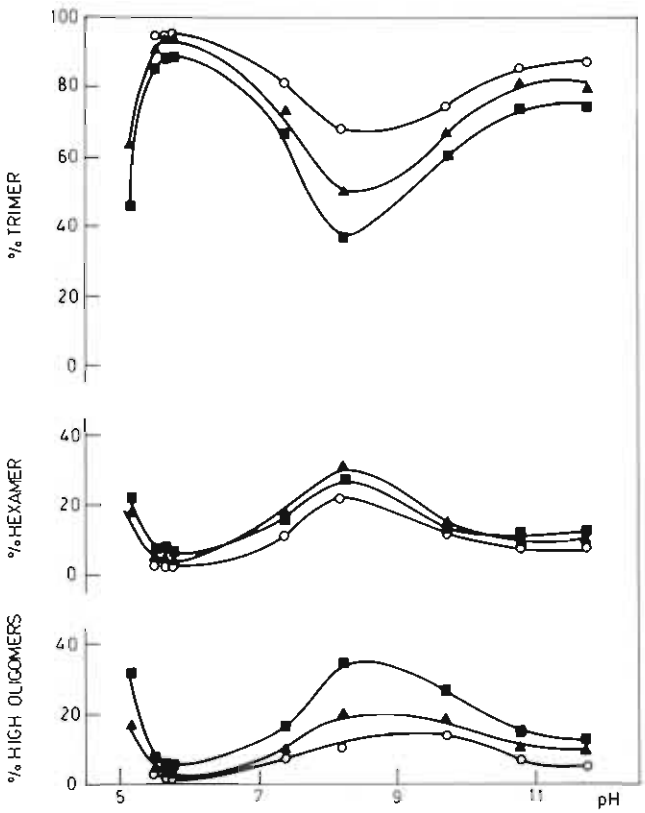

Figure 4. pH and time dependence of the aging of the "active" trimer hydroxide at 25 °C and I = 1.0 M. Aging times: (○) 60 s; (▲) 300 s; (■) 1800 s.

Compared with the case for the other "active" hydroxides,[10,11] the "active" trimer hydroxide generally ages more rapidly. The only exception is that the "active" dimer hydroxide ages more rapidly at pH >10. Thus, the order of reactivity monomer < dimer < trimer is satisfied over most of the pH range. A large (up to 100-fold) increase in the rate of transformation is observed on going from monomer to dimer, followed by a smaller but significant increase on going from dimer to trimer. Thus, the overall polymerization of the "active" monomer hydroxide[10] is governed by its initial conversion into dimer since subsequent aging processes are faster. Given that these processes occur principally via a solution mechanism,[10,11] the faster polymerization of the "active" dimer and trimer hydroxide is due either to the greater solubility of these hydroxides compared with that of the monomeric hydroxide or alternatively to the greater reactivity of their soluble forms in polymerization processes.

The aging profile for the "active" trimer hydroxide (Figure 4) is similar to that for the "active" dimer hydroxide for pH ≤8.2.[10,11]

Both hydroxides show increases in the rate of transformation with decreasing pH for pH <5.5 and with increasing pH for pH >5.7. As pointed out previously,[10,11] this behavior is consistent with a solution mechanism and the variation in aging rate with pH is due to changes in the solubility of the "active" hydroxides. Thus, below the aging minimum protonation leads to soluble cationic forms that are very reactive in polymerization processes, while above the minimum further deprotonation to give soluble anionic forms occurs, followed by rapid aging.

When compared to the "active" monomer and dimer hydroxides,[10,11] the "active" trimer hydroxide showed an unexpected decrease in its rate of aging for pH >9, although this rate is still much faster than for the "active" monomer hydroxide. A plausible explanation for this behavior can be based on the possibility that some of the oligomers formed during aging cleave into the trimer during analysis.[21] The analysis procedure involves acidification with $HClO_4$ (pH ~0.5–1.0) to solubilize the suspension, followed by dilution (pH ~1.5–2.0), adsorption onto ion-exchange columns, and elution of each oligomer band. During the time required to carry out this analysis (ca. 1–2 h) some of the less robust oligomers may cleave back into the trimer. We point out that, in the cleavage of chromite solutions (Figure 1), initial formation of trimer and hexamer is fast, with 30% of total Cr in either of these forms after 30 min. Of relevance here is the detection of small amounts of trimer and pentamer in the aging of the "active" dimer hydroxide.[11] Since polymerization of this dimeric hydroxide might be expected to produce even oligomers (tetramer, hexamer, etc.), these odd oligomers probably result from cleavage of higher oligomers during experimental workup and analysis.

The only known oligomer identified as a product of the aging of the "active" trimer hydroxide is hexamer (no dimer, tetramer, and pentamer was observed). As pointed out earlier, this is in marked contrast to the aging of the "active" dimer hydroxide, where in addition to the expected even oligomers, trimer and pentamer were observed. The presence of these oligomers suggests that some of the polynuclear species formed during aging on the dimeric hydroxide rearrange to structures that are more stable at the pH values of aging. In acidic media, these rearranged polynuclears appear to be susceptible to acid cleavage, leading to the formation of some trimer and other more acid resistant products. The formation of trimer suggests that this structural unit comprises an important part of the structure of the rearranged oligomers. In contrast, the results of the trimer aging indicate that the trimer unit retains its structure during aging and subsequent analysis. All of these observations are entirely consistent with the compact trimer structure (**1**) and mitigate against the proposed "classical" structures.[17]

Conclusion

Solutions of the hydrolytic trimer of Cr(III) can be obtained in good yields by acid cleavage of chromite solutions. The predominance of trimer over other oligomers suggests that it consists of a stable, structural unit that is frequently repeated in these chromites. The observed robustness of this oligomer supports the proposed compact structure. With suitable modification, the outlined synthetic method may be adapted for the preparation of solutions of other Cr(III) hydrolytic oligomers.

The "active" trimer hydroxide is the third in the series of "active" chromium(III) hydroxides to be isolated and characterized. This microcrystalline material is more unstable with respect to dehydration and polymerization than both the "active" monomer and dimer hydroxides. Consequently, a greater percentage of polynuclear impurities are found in this hydroxide. By analogy with the case for the hydrolytic dimer, it may, nevertheless, provide a convenient route to the crystallization of the hydrolytic trimer. Work in this area is continuing.

(21) Alternatively, this drop in reactivity could be interpreted in terms of either an increase in crystallinity of the "Active" trimer hydroxide or the adsorption of higher polynuclear species onto the surface of the "active" hydroxide, as aging progresses, leading to an overall decrease in solubility. At present, however, there is no experimental evidence supporting these possibilities.

Experimental Section

Materials. Stock solutions of $[Cr(OH_2)_6](ClO_4)_3$ were prepared and analyzed as described elsewhere.[9] Sodium perchlorate (Merck, p.A.), sodium hydroxide, 70% perchloric acid, lithium perchlorate, and the buffer bases (Fluka, puriss.) were all used as received with the exception of imidazole, which was recrystallized from benzene.[15] Water was deionized and doubly distilled before use. Buffer solutions were prepared by mixing the buffer bases with 0.01 M $HClO_4$. Where necessary, constant ionic strength was maintained at 1.0 M by adding $NaClO_4$. All solutions were filtered through Sartorius SM11307 cellulose nitrate membrane filters (0.2-μm median pore size) to remove any suspended material.

Instruments and Methods. A Uvikon 810 spectrophotometer was used to record all UV–vis spectra. The cell compartment was maintained at 25.0 (±0.1) °C by using a Haake N3 thermostat. A Haake Q cryostat was used to maintain constant temperature during the preparation of the "active" trimer hydroxide. Suspension pH values were determined as described previously,[10,11] and where necessary constant pH was maintained with a pH stat. TG and DSC measurements were carried out with a Mettler TA 3000 system under a constant stream of N_2 (20 mL/min). X-ray powder diffraction patterns were recorded on a Guinier de Wolff camera with Cu radiation and generally with screening of Cr fluorescence using Al foil. IR spectra were recorded on CsBr pellets (Merck, Suprapur) with a Perkin-Elmer 521 instrument. For electron microscopy, samples of the "active" trimer hydroxide were first dispersed in doubly distilled H_2O by using ultrasonic treatment and collected on carbon film coated bronze grids, and after air-drying, Cr was shadowed at an angle of 30° in a Balzers BA 350E metal evaporation unit. Photographs were taken on a Hitachi H-600-2 electron microscope. Chromium[22] and perchlorate[23] were determined by established methods.

Preparation of the Hydrolytic Trimer. A solution of Cr^{3+} (5 mL, 0.5 M) in acid (ca. 0.66 M $HClO_4$) was transferred into a volumetric flask (50 mL) by using a pipet and NaOH (10 mL, 2 M) added while stirring vigorously and continuously. The resultant green solution was immediately acidified by adding $HClO_4$ (35 mL, 2 M) to the mark. This solution was placed in a thermostat at 25 °C. Aliquots (3 mL) were then taken at different times and stored in a refrigerator at −18 °C until required. These samples were thawed to room temperature, diluted to ca. 100 mL, and adsorbed onto Sephadex SP C25 cation-exchange columns (1 × 30 cm) and the columns washed thoroughly with H_2O. The elution of the oligomers has been described in detail previously.[9] Briefly, Cr^{3+}, dimer, trimer, and tetramer were eluted with increasing concentrations of $NaClO_4$ (0.5–4.0 M), pentamer and hexamer with $LiClO_4$ (4 M), and the higher oligomers with $K_2C_2O_4$ (saturated) and NaOH (0.2 M). As in previous studies, the eluants contained acid to suppress the polymerization of the oligomers. Each band was analyzed for Cr spectrophotometrically following conversion to CrO_4^{2-}.[9]

Large-scale preparations of the hydrolytic trimer solutions involved scaling up of the above procedure. Thus, NaOH (400 mL, 2 M) was added to a solution of Cr^{3+} (200 mL, 0.5 M) in a 2-L volumetric flask with continuous stirring. This chromite solution was immediately acidified by adding $HClO_4$ (1400 mL, 2 M) up to the mark. The solution was placed in a thermostat at 25 °C for a cleavage period of 1800 min; it was then diluted to 25 L ($[Cr(III)]_T \simeq 4 \times 10^{-3}$ M, $[H^+] \simeq 0.1$ M) and sorbed onto a Sephadex SP C25 cation-exchange column. The resin was saturated with trimer by continuing adsorption of the solution until the characteristic bands of monomer and dimer had passed through the column and only the green band of trimer (and some higher oligomers) remained. The trimer was then eluted with acidified 2 M $NaClO_4$ (pH 1.7). Purity checks were carried out by comparison of the UV–vis spectra of the eluted fractions with that reported in the literature for the hydrolytic trimer[9] (in particular, the ratio of the maxima $\epsilon_{425}/\epsilon_{584}$ is a good indicator of purity) and by chromatographic analysis of the eluted fractions. In the event that the trimer was contaminated with other oligomers, chromatography was used to further purify these solutions.

Preparation of the "Active" Trimer Hydroxide. Two solutions, one of chromatographically pure trimer (50 mL, $[Cr(III)]_T = 0.07$ M) and the other of pyridine (60 mL, 0.25 M), were placed in dropping funnels fitted with cooling jackets. The temperature was maintained at −1 °C by circulating methanol from a Haake Q cryostat. A small amount of the pyridine solution (ca. 10 mL) was drained into a jacketed vessel at −1 °C and stirred continuously. Some of the hydrolytic trimer (5 mL) was added rapidly until precipitation of the "active" hydroxide commenced (10–20 s). At this point the remaining portions of the two solutions were added dropwise, at approximately equal rates. Addition was complete within 20 min, and the final pH of the suspension was ca. 5.7. The

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suspension was filtered through Sartorius SM 11607 regenerated cellulose membrane filters (0.45-μm mean pore size) and the residue washed once with H_2O (15 mL) and twice with acetone (2 × 15 mL). The total preparation time was typically 50 min. Anal. Calcd for $Cr_3(\mu\text{-}OH)_4(OH)_5(OH_2)_4\cdot 4H_2O$: Cr, 34.42; ClO_4^-, 0. Found: Cr, 33.69 (±0.03); ClO_4^-, 2.0 (±0.1). Washing of the sample prior to analysis reduced the ClO_4^- content to 1.2%, a value closer to that found for the "active" dimer hydroxide.[11] As for the "active" dimer hydroxide,[11] the purity of "active" trimer hydroxide samples was determined by using ion-exchange chromatography.

A number of experiments were designed to study how the solid-state aging of the "active" trimer hydroxide might be affected by drying. Dehydration of the "active" trimer hydroxide was followed by measuring losses in weight of a sample (ca. 100 mg) after progressively longer dessication periods over 11 M H_2SO_4 (Table I). From time to time samples of the "active" hydroxide were analyzed, with use of using established methods,[11] to determine any changes in composition that accompanied the dehydration process (Table II).

Aging Experiments. Suspensions of the "active" trimer hydroxide were prepared by adding rapidly, with stirring, the hydrolytic trimer (5 mL, $[Cr(III)]_T$ = 0.0328 M, $[H^+]$ = 0.032 M, and $[Na^+]$ = 1.85 M) to 5 mL of each buffer solution. The final pH values of these suspensions were in the range 5.50–11.76. A different procedure was followed for aging experiments at pH 5.15; viz., 10 mL of trimer was diluted to 20 mL (I = 1.0 M) and then brought to the correct pH by adding 0.1 M NaOH (0.9 M $NaClO_4$ added to maintain I = 1.0 M). During the aging period a pH stat was used to maintain constant pH. In all cases, suspensions were aged for periods of 1, 5, or 30 min at 25.0 (±0.1) °C, followed by quenching with 5 M $HClO_4$ (1–2 mL) and analysis by ion-exchange chromatography.[9,10] Three distinct fractions were eluted: trimer (2 M $NaClO_4$, 0.02 M H^+), hexamer (4 M $LiClO_4$, 0.04 M H^+), and higher oligomers (saturated $K_2C_2O_4$ and 0.2 M NaOH). The Cr content of each band was determined as before.[9]

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Registry No. 1, 78939-63-6; $[Cr(OH_2)_6](ClO_4)_3$, 27535-70-2; $Cr_3(\mu\text{-}OH)_4(OH)_5(OH_2)_4\cdot 4H_2O$, 114978-36-8.

Supplementary Material Available: The distribution of oligomeric products generated by acid cleavage of chromite solutions (Table S1) and the pH and time dependence of the oligomers formed on aging of the "active" trimer hydroxide (Table S2) (3 pages). Ordering information is given on any current masthead page.

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Characteristic Vibrational Frequencies and Normal Modes of the CCO Ligand in Trinuclear Ketenylidene Clusters

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The two stretching vibrations associated with the CCO ligand in $[PPN]_2[Ru_3(CO)_6(\mu\text{-}CO)_3(\mu_3\text{-}CCO)]$ (**1**) have been identified by isotopic substitution and fit to an approximate normal-coordinate analysis. The high-frequency CCO stretching component occurs in the carbonyl stretching region (1977 cm^{-1}), and significant mixing occurs between this CCO stretch and a terminal carbonyl stretch of the same symmetry. The low-frequency CCO stretching vibration has been identified in the Raman spectrum of **1** and in the IR or Raman spectra of the ketenylidene clusters $H_2Ru_3(CO)_9(\mu_3\text{-}CCO)$, $[PPN]_2[Fe_3(CO)_9(\mu_3\text{-}CCO)]$, and $[Co_3(CO)_9(\mu_3\text{-}CCO)][PF_6]$. This mode was found in the 1200–1350-cm^{-1} range, with the more positively charged clusters having lower frequencies. The position of the high-frequency CCO stretch of $[PPN]_2[Ru_3(CO)_6(\mu\text{-}CO)_3(\mu_3\text{-}CCO)]$ is sensitive to isotopic substitution at the central carbon atom of the CCO but relatively unaffected by ^{13}C substitution at the basal carbon. The converse is true for the low-frequency CCO stretch. This pattern of isotope shifts has a simple explanation in the form of the normal modes, and it should prove useful in the search for CCO on metal surfaces. Several of the framework vibrations associated with the M_3C core of the above ketenylidene clusters are reported. Assignments were made with the aid of Raman depolarization ratio measurements on samples in CH_2Cl_2 solution and in some cases on polycrystalline solids.

Introduction

Ligands attached to metal clusters are useful structural models for similar species on metal surfaces,[1] and the spectroscopic fingerprints of these ligands in structurally characterized metal clusters are useful for the identification of surface species. For example, alkyl and vinyl fragments have been detected on metal surfaces by the correspondence of vibrational spectra of surfaces to spectra of the metal cluster analogues.[1b,2]

The ready conversion of carbide (C) and methylene (CH_2) to the CCO moiety in molecular clusters[3-5] suggests that a similar process may occur on metal surfaces that contain low-coordinate surface-bound carbide or methylene functionalities.[6] Although the μ_3-CCO ligand is stable on a variety of trimetallic group VIII transition-metal clusters with a range of electronic charges from −2 to +1,[3,4,7-14] the μ_3-CCO moiety has not been identified on metal surfaces. In order to extend the vibrational spectroscopic data on possible surface species, we have undertaken the characterization by infrared and Raman spectroscopy of the μ_3-CCO ligand in several metal clusters. A preliminary report of this work has appeared.[15]

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