

160. Morphological and Thermal Investigations of the 'Active' Dimer Hydroxide of Chromium(III)

by Leone Spiccia¹⁾* and Werner Marty²⁾

Institut de Chimie, Université de Neuchâtel, Av. de Bellevaux 51, CH-2000 Neuchâtel

and Rudolf Giovanoli

Laboratorium für Elektronenmikroskopie, Universität Bern, Freiestrasse 3, CH-3000 Bern 9

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The 'active' dimer hydroxide, $[\text{Cr}_2(\mu\text{-OH})_2(\text{OH})_4(\text{OH}_2)_4] \cdot 2 \text{H}_2\text{O}$, has been characterised by means of IR spectroscopy, thermal analysis, X-ray powder diffraction, and electron microscopy. Thermogravimetric measurements and the Cr content of the hydroxide are in agreement with this composition. The IR spectrum supports the notion that this hydroxide is composed of unaltered dimer fragments linked through hydrogen bonds of *ca.* 2.8 Å. The compound is microcrystalline in nature with an X-ray powder diffraction pattern distinctly different from that of the isomeric 'active' monomer hydroxide. Electron micrographs of the 'active' dimer hydroxide indicate that this material consists of platelets the size of which is dependent on the pH of precipitation.

Introduction. – In a recent publication [1], we have reported the preparation and synthetic utility of the 'active' dimer hydroxide of Cr(III), $[\text{Cr}_2(\mu\text{-OH})_2(\text{OH})_4(\text{OH}_2)_4] \cdot 2 \text{H}_2\text{O}$. This material can be precipitated from solution in a state of > 96% purity with slight contamination from what appear to be 'active' hydroxides derived from higher Cr(III) oligomers [2]. Dissolution in slightly more than stoichiometric amounts of either TsOH or mesitylene-2-sulfonic acid gives a concentrated solution of the hydrolytic dimer ($[\text{Cr}_2(\mu\text{-OH})_2(\text{OH}_2)_8]^{4+}$) from which the complexes $[\text{Cr}_2(\mu\text{-OH})_2(\text{OH}_2)_8](\text{tos})_4 \cdot 9 \text{H}_2\text{O}$ and $[\text{Cr}_2(\mu\text{-OH})_2(\text{OH}_2)_8](\text{dmtos})_4 \cdot 4 \text{H}_2\text{O}$ may be isolated. These complexes constitute the first crystalline salts of a transition-metal hydrolytic dimer derived from a simple aqua ion.

The work presented here extends our investigations of the 'active' dimer hydroxide to include IR, thermal, X-ray powder diffraction, and electron microscopic analyses. These results will be compared with those obtained for the 'active' monomer hydroxide [3–5]. This was the first 'active' hydroxide of Cr(III) to be structurally characterized.

Experimental. – *Materials.* Stock solns. of $[\text{Cr}(\text{OH}_2)_6](\text{ClO}_4)_3$ [2] [6] and $[\text{Cr}_2(\mu\text{-OH})_2(\text{OH}_2)_8](\text{ClO}_4)_4$ [2] [7] were prepared and standardized as described previously. The 'active' dimer hydroxide was prepared by precipitation with a pyridine buffer [1], while the 'active' monomer hydroxide was prepared by adding Cr^{3+} to a soln. of imidazole [8]. Pyridine (*Fluka, puriss.*) was used as received. Imidazole was purified as described in [8] prior to use. All buffer solns. were filtered through *Sartorius SM 11307* cellulose nitrate membrane filters (0.2- μm median pore size) prior to use.

Instruments and Methods. IR spectra were recorded on CsBr pellets (*Merck, Suprapur*) 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 Al foil. TG, DTG, and DSC measurements were carried out on a *Mettler TA 3000* system under a stream of either O_2 or N_2 (20 ml/min). The chromium [2] and perchlorate [9] content of the 'active' hydroxides were checked using literature methods.

¹⁾ Current address: Department of Chemistry, Monash University, Clayton, Victoria 3168, Australia.

²⁾ Deceased Sept. 20, 1986.

Results and Discussion. - *Thermal Analysis of the 'Active' Monomer and Dimer Hydroxides of Cr(III).* Thermogravimetry (= TG) and differential scanning calorimetry (= DSC) were used to study the thermal dehydration of the 'active' dimer hydroxide. Analogous measurements on the 'active' monomer hydroxide essentially confirmed the earlier results [5] and allowed close comparison with the results obtained for the dimer.

'Active' Monomer Hydroxide. Weight loss occurred in three distinct steps with differential thermogravimetry (= DTG) peak temperatures at $115(\pm 10)^\circ$, $250(\pm 10)^\circ$ (sh) and $470(\pm 10)^\circ$ (Fig. 1). The peak temperatures varied within the indicated limits for different samples. DSC peaks were found at $128(\pm 10)^\circ$ (endothermic) and at $510(\pm 10)^\circ$ exothermic. The last peak temperature is about 40° higher than the DTG peak temperature, and we tentatively attribute this to the differences in heat transfer in the two experiments. The first two steps are strongly overlapping, and the weight loss was, therefore, determined isothermally during 30 min and peak by peak in ascending order of temperatures. In the *Scheme*, the isothermal heating temperatures are given.

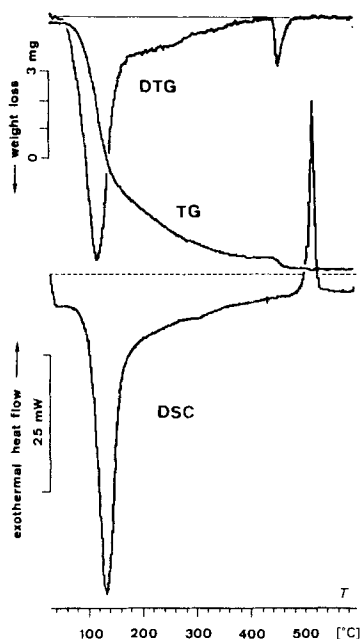


Fig. 1. DSC and TG/DTG curves for the thermal dehydration of the 'active' monomer hydroxide (streaming N_2 , 20 ml/min)

Careful choice of the isothermal heating temperatures and times gave good-to-acceptable agreement between the experimental weight loss and all the postulated steps (*Scheme*), and with previous work [5]. In particular, the exothermal transformation at 470° (TG) or 510° (DTG) has been attributed to the transformation of amorphous Cr_2O_3 into crystalline α - Cr_2O_3 [5]. This transformation is known to be accompanied by strong luminescence [10]. However, the weight loss accompanying this transformation has not been recognised so far. It is likely to result from desorption of chemisorbed H_2O or adventitious O_2 [11], while the great specific surface area diminishes during crystallisation

Scheme. Thermal Dehydration of the 'Active' Monomer and Dimer Hydroxides

'Active' Monomer Hydroxide			'Active' Dimer Hydroxide		
		Weight loss [%]			Weight loss [%]
$\text{Cr}(\text{OH})_3 \cdot 3 \text{H}_2\text{O}$			$\text{Cr}_2(\mu\text{-OH})_2(\text{OH})_4(\text{OH}_2)_4 \cdot 2 \text{H}_2\text{O}$		
120°C	– 3 H ₂ O	calc.: 34.41 found: (35.00 ± 0.24)	120°C	– 6 H ₂ O	calc.: 34.41 found: (31.62 ± 0.38)
	↓			↓	
	$\text{Cr}(\text{OH})_3$			$\text{Cr}_2(\text{OH})_6$	
220°C	– H ₂ O	calc.: 11.47 found: (9.82 ± 0.07)	220°C	– 2 H ₂ O	calc.: 11.47 found: (12.12 ± 0.09)
	↓			↓	
	$\text{CrO}(\text{OH})$			2 $\text{CrO}(\text{OH})$	
300°C	– ½ H ₂ O	calc.: 5.74 found: (5.32 ± 0.03)	300°C	– H ₂ O	calc.: 5.74 found: (6.03 ± 0.05)
	↓			↓	
	½ $\text{Cr}_2\text{O}_3(\text{amorphous})$			$\text{Cr}_2\text{O}_3(\text{amorphous})$	
470°C	– chemisorbed H ₂ O or O ₂	calc.: 0.00 found: (2.96 ± 0.09)	470°C	– chemisorbed H ₂ O or O ₂	calc.: 0.00 found: (2.56 ± 0.07)
	↓			↓	
	½ $\alpha\text{-Cr}_2\text{O}_3(\text{s})$	residue calc.: 48.38 found: (47.0 ± 0.20)		$\alpha\text{-Cr}_2\text{O}_3(\text{s})$	residue calc.: 48.38 found: (47.73 ± 0.45)

of $\alpha\text{-Cr}_2\text{O}_3$. Chemisorption of gases may, in part, explain why the losses at 220° and 300° are somewhat smaller than expected.

'Active' Dimer Hydroxide. The appearance of TG and DTG diagrams (Fig. 2) for the 'active' dimer hydroxide is quite similar to those found for the 'active' monomer hydroxide except for a shoulder near 60° (which is attributed to the loss of adherent H₂O) and a well resolved peak at 260(±10)° on the DTG curve. The DTG peaks at 106(±10)° and 453(±10)° correspond to analogous monomer hydroxide peaks. The DSC curve shows endothermic peaks at 130(±10)°, 245(±10)°, 275(±10)°, and 320(±10)° and an exothermic peak at 435(±10)°. The peaks in the range 245–320° are much smaller in intensity than the one at 130° but are nevertheless reproducible. The discrepancy between the 435° DSC peak and the 453° DTG peak is smaller than for the 'active' monomer hydroxide.

Complete interpretation of TG results requires the formula weight of the starting material, but due to the ease of H₂O loss, this remains somewhat ill-defined. Thus, a starting estimate, 318.0(±4.7), was obtained from the chromium content (32.7%) of a 96.6% pure 'active' dimer hydroxide. The sample purity was determined by chromatographic analysis following acidification of the hydroxide [1]. The residue of thermal analysis was shown to be solely $\alpha\text{-Cr}_2\text{O}_3$ by X-ray powder diffraction and IR measurements (see below). On this basis, the same initial formula weight, *viz.* 318.4(±1.0), is

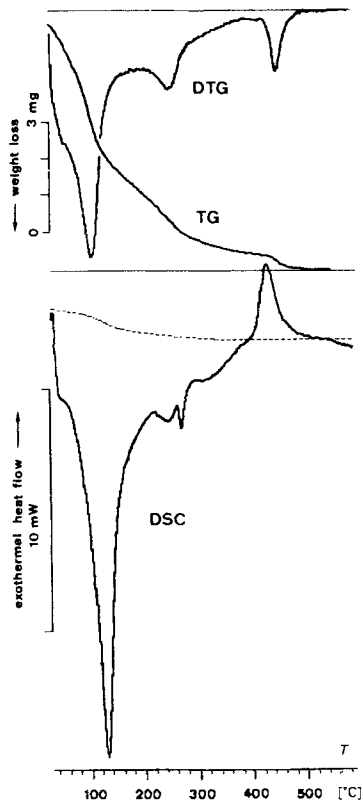


Fig. 2. DSC and TG/DTG curves for the thermal dehydration of the 'active' dimer hydroxide (streaming N_2 , 20 ml/min)

calculated from the total weight loss (*Scheme*). This is in good agreement with the formula weight of 314.1 for $[Cr_2(\mu-OH)_2(OH)_4(OH_2)_4] \cdot 2 H_2O$. The consistency of this proposed formula may be checked by calculating the weight loss in each individual TG step. The calculated and experimental results are summarized in the *Scheme*. The observed weight losses resulted from isothermal heating for 30 min at the indicated temperatures. The data were fitted to several possible formulae, and comparison shows that the most reliable parameter, *viz.* the amount of residue, matches the formula in the *Scheme* best and with the smallest deviation. The total loss of H_2O is subject to a greater uncertainty, owing to the possible interference from chemisorption and desorption from porous intermediates [11], but nevertheless gives satisfactory agreement. In conclusion, the composition of acetone-dried, fresh 'active' dimer hydroxide closely approximates the idealized formula $[Cr_2(\mu-OH)_2(OH)_4(OH_2)_4] \cdot 2 H_2O$. This formula is based on the assumption that the Cr(III) centre maintains a coordination number of six.

The presence of two 'extra' H_2O molecules in this 'active' hydroxide might explain its ready dehydration and instability relative to the 'active' monomer hydroxide. In an extension of the structural proposal for the 'active' monomer hydroxide [3–5] (*Fig. 3a*), one could envisage a similar layer structure for the 'active' dimer hydroxide (*Fig. 3b*). However, it is not obvious how this structure could accommodate the two additional H_2O molecules.

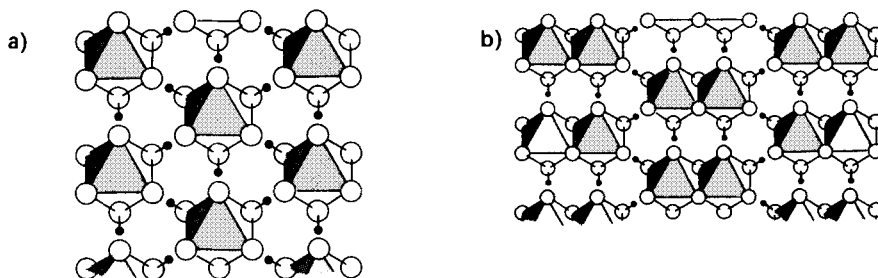


Fig. 3. a) Proposed layer structure of the 'active' monomer hydroxide [3–5]; b) Hypothetical layer structure of the 'active' dimer hydroxide. This proposal is at variance with the observed composition of this material.

IR Spectra. The data for the 'active' dimer hydroxide are presented in *Table 1*, along with those of the 'active' monomer hydroxide. *Table 1a* is reproduced from our previous publication [1]. The spectra of the 'active' hydroxides consist predominantly of broad absorptions in similar frequency ranges. For the monomer, two bands are found at 3000 cm^{-1} and 3480 cm^{-1} , which were previously attributed to H-bonds of *ca.* 2.9 and 2.7 Å, respectively [3] [12]. Similarly, the single band at 3220 cm^{-1} of the 'active' dimer hydroxide may be attributed to an H-bond of 2.8 Å. For the 'active' dimer hydroxide, bands are observed at 500, 850, and 1560 cm^{-1} corresponding to Cr-O stretching, H₂O rocking, and H₂O bending modes, respectively. Analogous bands are observed for the 'active' monomer hydroxide.

Table 1. IR Adsorption Regions for the 'Active' Monomer and Dimer Hydroxides and of Hydroxide Samples Heated to Different Temperatures

a) 'Active' Hydroxides

'Active' monomer hydroxide		'Active' dimer hydroxide		Interpretation
Band position [cm^{-1}]		Band position [cm^{-1}]		
308	<i>s</i> (sharp)	330	<i>w</i>	
500	<i>s</i> (sharp)	490	<i>s</i> (sharp)	Cr-O stretch
850	<i>w</i>	860	<i>w</i>	H ₂ O rocking
1560	<i>m</i>	1600	<i>m</i>	H ₂ O bending
3000	<i>w</i> (br.)	3220	<i>s</i> (sharp)	H-bonded O–H···O
3480	<i>m</i>			H-bonded O–H···O

b) Dehydrated 'Active' Hydroxides

Dried at 120°			Dried at 600°		
Monomer Band position [cm^{-1}]	Dimer Band position [cm^{-1}]		Monomer Band position [cm^{-1}]	Dimer Band position [cm^{-1}]	
520	510	<i>s</i>	298	295	<i>m</i>
800–900	840	<i>v. br.</i>	407	405	<i>s</i> (sharp)
1620	1615	<i>m</i> (br.)	438	436	<i>m</i>
1950	1980	<i>w</i> (br.)	550	555	<i>s</i>
3340	3360	<i>s</i>	620	620	<i>s</i>
			3300	3280	<i>v. w</i>

IR spectra were also recorded of the thermal dehydration products of the 'active' monomer and dimer hydroxides. After heating to 120°, the spectra of both hydroxides show a single, very broad band at 3360 or 3340 cm⁻¹, respectively, and a decrease in the intensity of the 3000–2500 cm⁻¹ shoulder of the H-bond absorptions. A very broad weak band develops at 1980 or 1950 cm⁻¹, respectively. The bands at 510, 840 and 1615 cm⁻¹ found in the dehydrated samples were also observed in the 'active' hydroxide spectrum. These observations suggest that H-bonding still persists despite some structural changes. After heating to 600°, the two substances show identical spectra, *viz.* that of α -Cr₂O₃.

X-Ray Powder Diffraction and Electron Microscopy. Precipitates of the 'active' dimer hydroxide yield an X-ray diffraction pattern (Fig. 4) with *d* values as listed in Table 2. The most intense reflection is sharp, while the weaker ones are all more or less broadened. This pattern does not correspond to any lattice type known to us and is clearly different from the patterns of the 'active' monomer hydroxide [3] and of the 'active' trimer hydroxide, [Cr₃(μ -OH)₄(OH₂)₃] · ~ 8.5 H₂O [13]. The number of observed lines (= 10) is much smaller than the smallest possible number of independent structural parameters. Accordingly, we have not attempted to solve the structure on the basis of the present powder data.

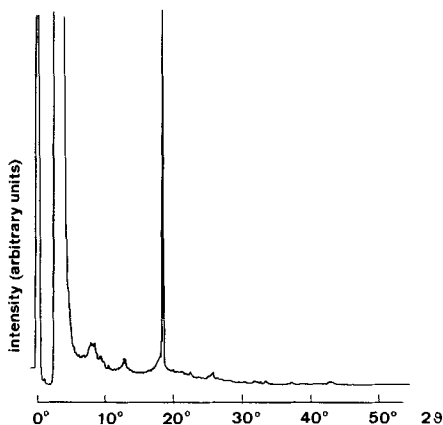


Fig. 4. Densitometer curve for the X-ray diffraction pattern of 'active' dimer hydroxide

Table 2. X-Ray Powder Diffraction Pattern of the 'Active' Dimer Hydroxide

$4\theta^\circ$ (CuK α_1)	d [Å]	Estimated intensity	Comments
18.1	9.76	1	
24.9	7.10	2	
37.0	4.79	10	
44.0	4.04	1	
50.3	3.54	3	br.
62.0	2.88	2	
65.5	2.73	2	
73.0	2.46	2	
84.0–85.0	2.15–2.13	2	v. br.
107.5	1.70	2	br.

Samples of the 'active' dimer hydroxide heated isothermally at either 50° or 120° for 30 min showed only one diffraction line which coincides with the most intense line observed for the 'active' dimer hydroxide. Samples of the 'active' monomer hydroxide were totally amorphous to X-ray after heating to 120° for 30 min, and so were samples of the 'active' dimer hydroxide but only after heating to > 220°. Samples of both 'active' hydroxides were no longer readily soluble in acid after heating to 120°. The diffraction pattern after total dehydration of either hydroxide ($T > 500^\circ$) corresponded to that of $\alpha\text{-Cr}_2\text{O}_3$ and, thus, the IR result is confirmed.

Electron micrographs of the 'active' dimer hydroxide, prepared in either pyridine buffer (pH \approx 6.1) or in imidazole buffer (pH \approx 7.5) indicate a particle thickness of ca. 10^4 Å (pyridine buffer) or 100 Å (imidazole buffer) (Fig. 5). These platelets appear to grow out of a nucleus as rosettes. Their morphology remains unchanged even after drying over 1M H_2SO_4 (30 min). However, the platelets' size appears to be significantly affected by either the buffer or the pH of precipitation. Hydroxide samples from these two preparations exhibit identical diffraction patterns.



Fig. 5. Electron micrograph of 'active' dimer hydroxide suspended in H_2O , after ultrasound treatment and drying on carbon grid. Cr-shadowed, 40°; magnification 50000 \times .

Conclusions. – The hydrolytic dimer is the second member of the Cr(III) oligomeric series to form an 'active' hydroxide. The parent member of the group, the 'active' monomer hydroxide, has been studied in detail [3–5], and an 'active' hydroxide derived from the hydrolytic trimer has also been prepared [13]. Although these hydroxides differ in terms of their IR spectra, diffraction patterns, electron micrographs, and thermal decomposition, they do have one property in common: dissolution in acid regenerates the starting oligomer almost quantitatively. Hence, the terminology 'active' is used to describe them. In addition to forming a class of their own, these materials are extremely useful starting materials in attempts to crystallize the Cr(III) hydrolytic oligomers. The

catalytic properties of these materials also require investigation with a view to comparing their performance with the well-known Cr catalysts [14].

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