

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF JYVÄSKYLÄ  
RESEARCH REPORT No. 45

**THERMAL BEHAVIOUR, INFRARED SPECTRA AND X-RAY  
STRUCTURES OF SOME NEW RARE EARTH CHROMATES(VI)**

**BY  
JAAKKO LEPPÄ-AHO**

Academic Dissertation  
for the Degree of  
Doctor of Philosophy



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*To Eija-Liisa, Janne and Katariina*

## PREFACE

This work was carried out at the Department of Chemistry, University of Jyväskylä, during the years 1987-1994 under the supervision of Professor Jussi Valkonen. I wish to express my sincere gratitude to Professor Valkonen, for his invaluable guidance, support and encouragement throughout these years.

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Jyväskylä, March 1994

Jaakko Leppä-aho

## ABSTRACT

Five kinds of rare earth chromates(VI) and one rare earth dichromate(VI), altogether sixteen compounds, were synthesized. The crystal structures were determined by single crystal X-ray diffraction for eleven of the compounds:  $[\text{Ln}_2(\text{CrO}_4)_3(\text{H}_2\text{O})_5]\cdot 2\text{H}_2\text{O}$  (Ln=Nd, Eu, Tb),  $[\text{Yb}_2(\text{OH})_2(\text{CrO}_4)_2(\text{H}_2\text{O})_{2.5}]\cdot 0.5\text{H}_2\text{O}$ ,  $\text{Ln}_2(\text{OH})_2(\text{CrO}_4)_2$  (Ln= Nd, Gd, Tb, Yb),  $\text{Ln}_3(\text{OH})(\text{CrO}_4)_4(\text{H}_2\text{O})_{3.5}$  (Ln= Pr, Nd), and  $\text{Pr}(\text{OH})\text{CrO}_4$ . The rare earth dichromate(VI),  $\text{Gd}_2(\text{Cr}_2\text{O}_7)_3\cdot 9\text{H}_2\text{O}$ , formed poor quality crystals and was studied only by thermal and infrared analysis. All the rare earth chromate(VI) compounds with the same chemical formula crystallized isostructurally. Different phases were not found for any of the compounds.

As the main object of the work was to synthesise new rare earth chromate(VI) crystals good enough for structural analyses, three different preparation methods were investigated: (1) crystallization by evaporation in air at standard temperature and pressure, (2) crystallization in gel and (3) crystallization in an autoclave. The last way proved to be the best. Exceptionally, gadolinium dichromate was prepared by evaporation.

Study of the thermal behaviour of the compounds revealed six decomposition mechanisms. Comparison of the thermal decomposition of the rare earth chromates(VI) from the crystal structure point of view showed the decomposition to depend on (1) how the  $\text{CrO}_4$  tetrahedra are coordinated to the structure (is there any bidentate coordination) and (2) the degree and nature of the distortion of the  $\text{CrO}_4$  tetrahedra.

Infrared spectra were recorded for eleven of the compounds, and powder diffraction data were obtained for  $[\text{Ln}_2(\text{CrO}_4)_3(\text{H}_2\text{O})_5]\cdot 2\text{H}_2\text{O}$  Ln=La, Pr, Nd, Sm, Eu. A short review of rare earth chromate chemistry is included as an introduction.

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## LIST OF ORIGINAL PAPERS

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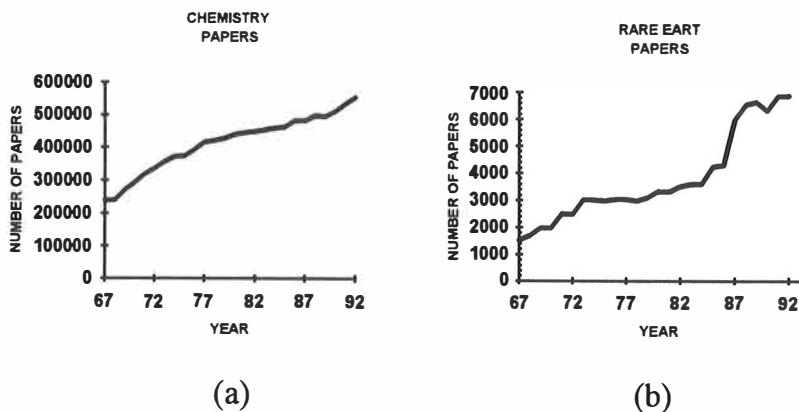
1. Leppä-aho, J. and Valkonen, J., The Crystal Structure of Neodymium and Europium Chromate Heptahydrate. Synthesis, Infrared Spectra, and Thermal Behavior of Rare Earth Chromate Heptahydrates,  $[\text{Ln}_2(\text{CrO}_4)_3(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$  (Ln=La, Pr, Nd, Sm, Eu, Gd). *J. Solid State Chem.* 92 (1991) 136.  
[https://doi.org/10.1016/0022-4596\(91\)90250-L](https://doi.org/10.1016/0022-4596(91)90250-L)
2. Leppä-aho, J. and Valkonen, J., Synthesis, Thermal Behavior, Infrared Spectra, and Crystal Structure of  $\text{Yb}_2(\text{OH})_2(\text{CrO}_4)_2$  and  $[\text{Yb}_2(\text{OH})_2(\text{CrO}_4)_2(\text{H}_2\text{O})_{2.5}] \cdot 0.5\text{H}_2\text{O}$ . *J. Solid State Chem.* 99 (1992) 364.  
[https://doi.org/10.1016/0022-4596\(92\)90325-P](https://doi.org/10.1016/0022-4596(92)90325-P)
3. Leppä-aho, J., Synthesis and Crystal Structure of  $\text{Ln}_3(\text{OH})(\text{CrO}_4)_4 \cdot 3.5\text{H}_2\text{O}$  (Ln = Pr, Nd) and  $\text{Ln}_2(\text{OH})_2(\text{CrO}_4)_2$  (Ln = Tb, Gd): Thermal Behavior and Infrared Spectra of  $\text{Pr}_3(\text{OH})(\text{CrO}_4)_4 \cdot 3.5\text{H}_2\text{O}$  and  $\text{Gd}_2(\text{OH})_2(\text{CrO}_4)_2$ . *J. Solid State Chem.* 106 (1993) 400.  
<https://doi.org/10.1006/jssc.1993.1300>
4. Leppä-aho, J., Structures of  $\text{Nd}_2(\text{OH})_2(\text{CrO}_4)_2$  and  $[\text{Tb}_2(\text{CrO}_4)_3(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$ . *Acta Crystallogr., Sect. C50* (1994). *In press.*  
<https://doi.org/10.1107/S0108270193010042>
5. Leppä-aho J. and Valkonen, J., X-Ray Powder Diffraction Pattern of  $[\text{Ln}_2(\text{CrO}_4)_3(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$  (Ln= La, Pr, Nd, Sm, Eu, Gd). *Powder Diffraction* 9(2) (1994). *In press.*  
<https://doi.org/10.1017/S0885715600014044>

## 1. INTRODUCTION

The development of catalyst and superconducting materials has triggered a surge of interest in compounds containing rare earth elements. While the number of chemistry publications per year doubled between 1967 and 1992, the number of papers dealing with rare earths quadrupled (Fig. 1). The presence of a rare earth element in a compound often gives that compound interesting properties – magnetic properties, luminescence – which opens the way to industrial applications.<sup>6</sup>

The aim of this work was to synthesize new rare earth chromates(VI) and determine their crystal structures and thermal behaviour. Compounds were preliminarily identified by infrared spectral method.

No crystal structure of the rare earth chromates(VI) was known before 1977, though various rare earth chromates(VI) had been prepared previous to that.<sup>7-26</sup> In 1977 the structure of  $\text{Ce}(\text{CrO}_4)_2(\text{H}_2\text{O})_2$  was reported.<sup>27</sup> A re-



*Fig. 1.* Growth in the publication of (a) chemistry papers and (b) chemistry papers dealing with rare earths between 1967 and 1992. Comparison was made from Chemical Abstracts using the keywords rare earths and lanthanoid in the case of (b).

view of rare earth chromate papers appearing before 1987 has been published by Leskelä and Niinistö.<sup>28</sup>

In this work I report the crystal structures of five rare earth chromates(VI) of different structure. The chemical formulas for these compounds, according to the crystal determinations, are  $\text{Ln}_2(\text{OH})_2(\text{CrO}_4)_2$ ,  $\text{Ln}_3(\text{OH})(\text{CrO}_4)_4(\text{H}_2\text{O})_{3.5}$ ,  $\text{Ln}(\text{OH})\text{CrO}_4$ ,  $[\text{Ln}_2(\text{OH})_2(\text{CrO}_4)_2(\text{H}_2\text{O})_{2.5}] \cdot 0.5\text{H}_2\text{O}$  and  $[\text{Ln}_2(\text{CrO}_4)_3(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$ . Examples of the IUPAC names are collected in Table 1. The chemical formulas quoted above are used in the following text, though the two last compounds are presented in tables in shorter form:  $\text{Ln}_2(\text{OH})_2(\text{CrO}_4)_2 \cdot 3\text{H}_2\text{O}$  and  $\text{Ln}_2(\text{CrO}_4)_3 \cdot 7\text{H}_2\text{O}$ .

*Table 1.* Nomenclature of the rare earth chromates(VI) discussed in this work (examples).

Formula	IUPAC addition and ligand names
$\text{Gd}_2(\text{OH})_2(\text{CrO}_4)_2$ [ $\text{Gd}_2(\text{OH})_2(\text{CrO}_4)_2$ ]	Digadolinium bis(chromate(VI)) dihydroxide or bis(chromato)dihydroxidodigadolinium
$\text{Nd}_3(\text{OH})(\text{CrO}_4)_4 \cdot 3.5\text{H}_2\text{O}$ [ $\text{Nd}_3(\text{OH})(\text{CrO}_4)_4(\text{H}_2\text{O})_{3.5}$ ]	Trineodymium tetrakis(chromate(VI)) hydroxide - water (1/3.5) or (3.5)aquatetrakis(chromato)hydroxido-trineodymium
$\text{Pr}(\text{OH})\text{CrO}_4$ [ $\text{Pr}(\text{OH})\text{CrO}_4$ ]	Praseodymium chromate(VI) hydroxide or chromatohydroxidopraseodymium
$[\text{Yb}_2(\text{OH})_2(\text{CrO}_4)_2(\text{H}_2\text{O})_{2.5}] \cdot 0.5\text{H}_2\text{O}$	Diytterbium bis(chromate(VI)) dihydroxide-water (1/3) or (2.5)aquabis(chromato)-dihydroxidodiytterbium hemihydrate
$[\text{Tb}_2(\text{CrO}_4)_3(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$	Diterbium tris(chromate(VI)) heptahydrate or pentaquatrichromato diterbium dihydrate

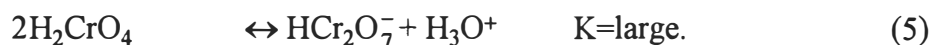
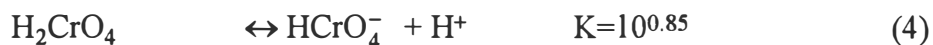
## 2. THE CHEMISTRY OF CHROMIUM AND RARE EARTH ELEMENTS

### 2.1. Chromium

Besides the familiar oxidation states +2, +3, and +6, chromium has been reported to exist in oxidation states -2, -1, 0, +4 and +5. The most important oxidation state is +6, with chromium occurring in the chromate group ( $\text{CrO}_4^{2-}$ ).<sup>29</sup> In the compounds of this work, chromium occurs in oxidation states +3, +5 and +6.

Most solid Cr(VI) compounds can be prepared from aqueous solution of chromium(VI) trioxide ( $\text{CrO}_3$ ). The structure of chromium(VI) trioxide consists of infinite chains of corner-sharing  $\text{CrO}_4$  tetrahedra. The bridging bond distance between Cr atoms is 1.748 Å, which is 0.149 Å greater than the mean bond distance of 1.599 Å. The compound crystallizes in the orthorhombic space group  $C2cm$ . When heated over 197°C, the orange-red crystals decompose through loss of oxygen to  $\text{Cr}_2\text{O}_3$ .<sup>29-32</sup>

In aqueous solutions of  $\text{CrO}_3$  a series of labile equilibria is established:



Above pH 8 only  $\text{CrO}_4^{2-}$  ions exist in appreciable concentration, but as the pH is lowered the equilibrium shifts, and at pH 2-6 the  $\text{HCrO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  ions are in equilibrium.<sup>33</sup>

Four different vibration modes are found for the free tetrahedral  $\text{CrO}_4^{2-}$  molecule (symmetry  $T_d$ ). All these are Raman active and two of them,  $\nu_3(F_2)$  and  $\nu_4(F_2)$ , are infrared active. On coordination, the symmetry of the tetrahedral  $\text{CrO}_4^{2-}$  ion may fall to  $C_{3v}$  or lower ( $C_{2v}$ ,  $C_s$ ). All four normal modes of vibration,  $\nu_1(A_1)$ ,  $\nu_2(E)$ ,  $\nu_3(F_2)$  and  $\nu_4(F_2)$ , are then infrared active, and this seems to be the situation in many rare earth chromates(VI).<sup>15</sup>

In the case of dichromates, the infrared spectra have been found consistent with the  $C_{2v}$  structure of an ion containing one bridging oxygen atom bound to two chromium atoms ( $\text{O}_3\text{Cr-O-CrO}_3$ ).<sup>34-36</sup> The infrared spectra of the  $\text{Cr}_2\text{O}_7^{2-}$  anion have been studied by Mestres *et al.* using the ab initio theoretical method. They report that their theoretical results are in fair agreement with existing experimental data.<sup>37</sup>

## 2.2. Rare earth elements

The rare earth elements comprise the elements from La to Lu (atomic numbers 57-71), also known as the lanthanoid (or lanthanide) series, plus yttrium and scandium.

The oxidation state +3 is characteristic for all rare earth elements, both in solid compounds and aqueous solutions. Besides  $\text{Ln}^{3+}$ , only  $\text{Eu}^{2+}$ ,  $\text{Yb}^{2+}$ ,  $\text{Sm}^{2+}$  and  $\text{Ce}^{4+}$  are sufficiently stable to exist in aqueous solution. The most important rare earth ion in our case is  $\text{Ln}^{3+}$ . In rare earth ions  $\text{Ln}^{3+}$  from lanthanum to lutetium, the two outer orbitals are almost the same: all ions have the configuration  $5s^25p^65d^16s^2$  and differences occur only in the 4f electron occupancy. The lanthanoid contraction – the decreasing ionic radius with increasing atomic number due to the imperfect shielding of one 4f electron by another – is clearly seen for the  $\text{Ln}^{3+}$  ion.<sup>38-40</sup>

Rare earths can exist in coordination numbers from three to twelve, but only rarely is the coordination number six or eleven. Coordination numbers ten and twelve are possible only for the largest rare earth ions, such as  $\text{La}^{3+}$ , but even for these the more characteristic coordination numbers (CN) are eight and nine. The known coordination geometries for CN eight are square anti-prismatic ( $D_{4h}$ ), triangular faced dodecahedral ( $D_{2h}$ ), cubic and bicapped trigonal prismatic ( $C_{2v}$ ). For CN 9 the confirmed coordination geometries are tricapped trigonal prism ( $D_{3h}$ ) and capped square anti-prism.<sup>37,41</sup>

Shannon<sup>42</sup> has published, the values of effective ionic radii for all stable  $\text{Ln}^{3+}$  and  $\text{Ln}^{2+}$  ions with CN six, eight, nine, ten and twelve. That work is based on structural data, empirical bond strength-bond length relationships, and plots of (1) radii vs volume, (2) radii vs coordination number, and (3) radii vs oxidation state.

### 2.3. Rare earth chromates

In 1987 when this work began, only a couple of papers dealing with rare earth chromates(VI) had been published.<sup>7-26</sup> The only known crystal structure was for  $\text{Ce}(\text{CrO}_4)_2(\text{H}_2\text{O})_2$ , which crystallizes in the space group  $P2_1/m$ . Ce atoms are eight-coordinated by oxygen atoms, the average Ce-O bond distance is 2.342 Å and the  $\text{CrO}_4$  tetrahedra are nearly regular.<sup>27</sup>

By the year 1987, the rare earth chromates(VI) could be divided into three groups: normal chromates(VI)<sup>□</sup>  $\text{Ln}_2(\text{CrO}_4)_3 \cdot n\text{H}_2\text{O}$  ( $n=0-4,6-10$ ); rare earth hydroxide chromates(VI),  $\text{Ln}(\text{OH})\text{CrO}_4 \cdot n\text{H}_2\text{O}$  ( $n=1,1.5,2$ ); and dichromates(VI),  $\text{Ln}_2(\text{Cr}_2\text{O}_7)_3 \cdot n\text{H}_2\text{O}$  ( $n=1,5,7,10$ ). In addition, a more complex compound of a mixed anion of chromate and dichromate of

<sup>□</sup> The word normal is widely used for rare earth chromates(VI) of formula  $\text{Ln}_2(\text{CrO}_4)_3 \cdot n\text{H}_2\text{O}$ .

formula  $Y(CrO_4)_2(Cr_2O_7) \cdot 8H_2O$  has been reported by Petrov *et al.*<sup>17</sup> Identification was made from the infrared spectrum, where the absorption bands characteristic of both  $CrO_4^{2-}$  and  $Cr_2O_7^{2-}$  were found. All the rare earth dichromates(VI) that have been crystallized are soluble in water.<sup>7-26</sup>

In the work before 1987 mainly the  $CrO_3-Ln_2O_3-H_2O$  system at 25°C was studied. As an exception, Doyle and Gibb<sup>43</sup> synthesized the anhydrous rare earth chromate(VI)  $Nd_2(CrO_4)_3$  in a high temperature reaction. The mixture of  $Nd_2O_3$  and  $Cr_2O_3$  was heated and the product formed in the temperature range of 350-600°C. As the temperature increased the thermal decomposition led in a first step to the formation of  $LnCrO_4$  and  $Cr_2O_3$  and in a second step to  $LnCrO_3$ .

The thermal behaviour was of interest in many papers and thermal decomposition processes are reported for a number of compounds.<sup>13,22,23,44-46</sup> As well, the infrared spectra have been determined for some rare earth chromates(VI). The main frequencies can be found fairly easily, but the additional splitting caused by the different coordinations of  $CrO_4^{2-}$  anion makes the spectra very complicated.<sup>15,17,46,47</sup>

Several papers dealing with the structures of rare earth chromates(VI) were published during the years of this study. The compounds structurally characterized included  $[Ln_2(CrO_4)_3(H_2O)_5] \cdot 2H_2O$  ( $Ln=La, Sm$ ),<sup>48,49</sup>  $Er_2(OH)_2(CrO_4)_2$ ,<sup>50</sup>  $La(OH)CrO_4$ ,<sup>51</sup>  $La_3(OH)(CrO_4)_4(H_2O)_3$ .<sup>5</sup> Applying factor group analysis in a study of the magnetic and vibrational properties of  $Ln(OH)CrO_4$  ( $Ln= La, Pr, Nd$ ), Bueno *et al.*<sup>47</sup> found 18 IR and 18 Raman active vibrations for the  $Ln(OH)CrO_4$  lattice. In both the IR and Raman spectra the number of bands observed was fewer than the number predicted.

Two very interesting and widely studied groups of rare earth compounds are the rare earth chromates(V) ( $LnCrO_4$ ) and the rare earth chromates(III) ( $LnCrO_3$ ).  $LnCrO_4$  compounds have attractive properties -

mainly magnetic - at low temperatures. Both groups can be prepared by the thermal decomposition of rare earth chromates(VI),<sup>52-61</sup> and in the present work they appear as decomposition products.



### 3. EXPERIMENTAL

#### 3.1. Synthesis of compounds

Three methods were studied for the preparation of rare earth chromates(VI):

1. Crystallization by evaporation at standard temperature and pressure (STP)
2. Crystallization in gelatinous  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$
3. Crystallization in an autoclave

All these methods produced some kind of crystals. Rare earth oxides of La, Pr, Nd, Sm-Er, Yb were used in the synthesis.

##### 3.1.1. Crystallization by evaporation at STP

Three liquid systems were employed in the crystallization at STP:

1.  $\text{Ln}_2\text{O}_3\text{-CrO}_3\text{-H}_2\text{O}$
2.  $\text{Ln}_2\text{O}_3\text{-CrO}_3\text{-H}_2\text{O- HNO}_3$
3.  $\text{Ln}_2\text{O}_3\text{-CrO}_3\text{-H}_2\text{O-LiOH}$

In the  $\text{Ln}_2\text{O}_3\text{-CrO}_3\text{-H}_2\text{O}$  system,  $\text{CrO}_3$  was first dissolved in water to get  $\text{H}_2\text{CrO}_4$ . Then 150 mg of rare earth oxide was added to 2  $\text{cm}^3$  of 0.2-1.0  $\text{mol dm}^{-3}$   $\text{H}_2\text{CrO}_4$ . The mixture was put in an evaporation bowl and heated to boiling point, after which the bowl was covered with perforated plastic foil and left in air for the evaporation to occur. After a week small

crystals appeared in the mixture. Identification of products was carried out with the help of thermogravimetry and infrared spectrometry. The compounds crystallized by this method were:  $[\text{Ln}_2(\text{CrO}_4)_3(\text{H}_2\text{O})_5]\cdot 2\text{H}_2\text{O}$  ( $\text{Ln}=\text{La}, \text{Sm}, \text{Gd}$ ) from mixtures where the  $\text{H}_2\text{CrO}_4$  concentration was 0.2-0.6 mol  $\text{dm}^{-3}$ , and  $\text{Gd}_2(\text{Cr}_2\text{O}_7)_3\cdot 9\text{H}_2\text{O}$  from a mixture where  $\text{H}_2\text{CrO}_4$  concentration was 1.0 mol  $\text{dm}^{-3}$ .

In liquid systems 2 and 3,  $\text{HNO}_3$  and  $\text{LiOH}$  were used to adjust the pH.  $\text{HNO}_3$  was used in the system  $\text{Ln}_2\text{O}_3\text{-CrO}_3\text{-H}_2\text{O-HNO}_3$  to achieve low  $\text{H}_2\text{CrO}_4$  concentration and a highly acidic solution, and  $\text{LiOH}$  was used in  $\text{Ln}_2\text{O}_3\text{-CrO}_3\text{-H}_2\text{O-LiOH}$  to achieve high pH and high  $\text{H}_2\text{CrO}_4$  concentration. Only very fine powders were obtained in both systems and the compounds were not identified.

### 3.1.2. Crystallization in gelatinous $\text{Na}_2\text{SiO}_3\cdot 9\text{H}_2\text{O}$

This crystallization method is based on the gelation of a water solution of sodium silicate nonahydrate ( $\text{Na}_2\text{SiO}_3\cdot 9\text{H}_2\text{O}$ ) when the pH is adjusted under pH 8 with  $\text{H}_2\text{CrO}_4$  solution. Procedure: 6.5  $\text{cm}^3$  of 0.3 mol  $\text{dm}^{-3}$   $\text{H}_2\text{CrO}_4$  is mixed with 5.0  $\text{cm}^3$  of 0.35 mol  $\text{dm}^{-3}$  of  $\text{Na}_2\text{SiO}_3\cdot 9\text{H}_2\text{O}$  and to this is added a solution of 20 mg of  $\text{Ln}_2\text{O}_3$  dissolved in 5.0  $\text{cm}^3$  of 3.0 mol  $\text{dm}^{-3}$   $\text{HNO}_3$ . After a few days small crystals, combined into big clusters that looked like spruce branches, could be seen in the gel with the naked eye. Only one solid phase was obtained by this method:  $[\text{Ln}_2(\text{CrO}_4)_3\text{-(H}_2\text{O})_5]\cdot 2\text{H}_2\text{O}$ ,  $\text{Ln}=\text{La}, \text{Pr}$  and  $\text{Nd}$ . Crystals were identified with the help of thermogravimetry and infrared spectrometry. Although the single crystal X-ray diffraction method was applied to some crystals, all the crystals proved to be either twins or in some other way of poor quality.

### 3.1.3. Crystallization in an autoclave

All the compounds included in Table 2 were synthesized in a steel autoclave with a Teflon lining (Fig. 2). The reagents used in the synthesis are listed in Table 3. Rare earth oxides were mixed with  $\text{H}_2\text{CrO}_4$  and the mixtures were heated in the autoclave between 140 and 170°C. The molar ratios of the reagents and the temperatures to which the mixtures were heated are collected in Table 2. The whole procedure of the synthesis is explained in papers 1-5. If the temperature was lowered faster than 15 degrees/day, either a very fine powder was formed or lanthanoid oxides were present in the product. Quite often a mixture of crystals was obtained. In the case of  $[\text{Ln}_2(\text{CrO}_4)_3(\text{H}_2\text{O})_5]\cdot 2\text{H}_2\text{O}$  compounds, however, pure single crystalline products were easily obtained.

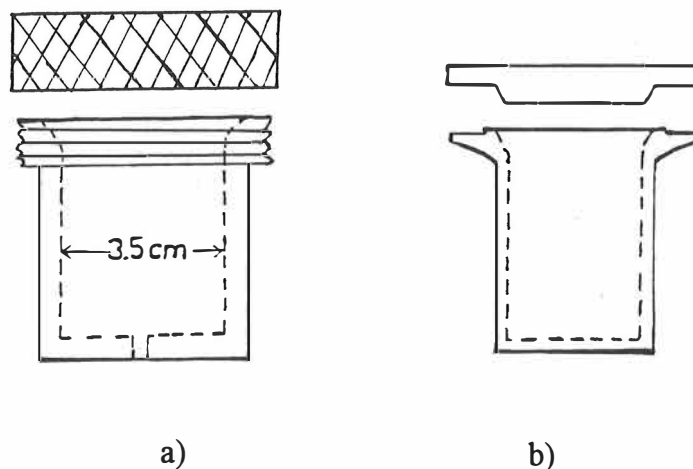


Fig. 2. Autoclave used in the synthesis. (a) Steel cell, (b) Inner cell made of Teflon.

*Table 2.* Experimental conditions for the compounds synthesized in an autoclave. The molar ratios of  $\text{Ln}_2\text{O}_3$  and  $\text{CrO}_3$  have been calculated from papers 1-5.

Compound	Ln	Molar ratio $\text{Ln}_2\text{O}_3^* : \text{CrO}_3$	Temperature °C	Ref.
$\text{Ln}_2(\text{CrO}_4)_3 \cdot 7\text{H}_2\text{O}$	La, Pr-Tb	1 : 5.2-6.3	150-170	1,4,5
$\text{Ln}_2(\text{OH})_2(\text{CrO}_4)_2$	Nd, Gd, Tb, Yb	1 : 2.5-3.5	140-160	2,3,4
$\text{Ln}_2(\text{OH})_2(\text{CrO}_4)_2 \cdot 3\text{H}_2\text{O}$	Yb	1 : 3.2	140	2
$\text{Ln}_3(\text{OH})(\text{CrO}_4)_4(\text{H}_2\text{O})_{3.5}$	Pr, Nd	1 : 5.5, 3.0	152	3
$\text{Ln}(\text{OH})\text{CrO}_4$	Pr	1 : 5.5	152	**

\*  $\text{Tb}_4\text{O}_7$ ,  $\text{Pr}_6\text{O}_{11}$  \*\* Not published before

*Table 3.* Reagents used in the synthesis of rare earth chromates(VI)

Reagents	Manuf.	Purity (%)
$\text{Ln}_2\text{O}_3$ (Ln=La, Nd-Gd, Dy-Yb)	Fluka AG	99.9
$\text{Pr}_6\text{O}_{11}$	Fluka AG	99.9
$\text{Tb}_4\text{O}_7$	Fluka AG	99.9
$\text{CrO}_3$	Merck	99
$\text{NaSiO}_3 \cdot 9\text{H}_2\text{O}$	Merck	99.9
$\text{HNO}_3$	Merck	98
LiOH	Merck	98

### 3.2. Infrared spectral studies

As reported in papers 1-3, the infrared spectra were recorded with a Perkin-Elmer 283 IR spectrometer, using the KBr method, a scan time of 12 min and a scan range of 4000 - 200  $\text{cm}^{-1}$ . The sample : KBr ratio was about 1:250-300. The same equipment and scanning parameters were used for the studies on  $\text{Pr}(\text{OH})\text{CrO}_4$  and  $\text{Gd}_2(\text{Cr}_2\text{O}_7)_3 \cdot 9\text{H}_2\text{O}$  reported in this summary.

### 3.3. Thermoanalytical studies

Thermal decomposition of the compounds was investigated first with a Perkin-Elmer TG-2 Thermobalance System (paper 1 and  $\text{Gd}_2(\text{Cr}_2\text{O}_7)_3 \cdot 9\text{H}_2\text{O}$ ) and later with a Perkin-Elmer Thermogravimetric Analyser TGA 7 (papers 2,3 and  $\text{Pr}(\text{OH})\text{CrO}_4$ ). The scanning rate varied from  $2^\circ\text{C min}^{-1}$  to  $10^\circ\text{C min}^{-1}$  and all the measurements were done in static atmosphere. Sample size varied from 2.5 to 11 mg.

### 3.4. Single crystal X-ray diffraction studies

All single crystal X-ray determinations were made with an Enraf-Nonius CAD4 automatic four-circle diffractometer. Except for  $\text{Pr}(\text{OH})\text{CrO}_4$  the Enraf-Nonius structure determination package SDP-plus,<sup>63</sup> incorporating the direct methods program MULTAN<sup>64</sup> and the plotting programs ORTEP<sup>65</sup> and PLUTO,<sup>66</sup> was used for data handling. For  $\text{Pr}(\text{OH})\text{CrO}_4$ , the Enraf-Nonius structure determination package MolEN<sup>67</sup> was employed.

### 3.5. X-ray powder diffraction studies

X-ray powder diffraction data were recorded with an Enraf-Nonius PDS 120 diffractometer equipped with an INEL CPS 120 curved position sensitive detector. DIFFRACTINEL software was used for measurement and data analysis of the diffraction pattern. For the refinement of the unit cell dimensions, measured  $2\theta$  values were entered into the least-squares program PIRUM.<sup>62</sup>

## 4. RESULTS AND DISCUSSION

### 4.1. Synthesis of compounds

#### 4.1.1. Evaporation method

No new normal or hydroxide rare earth chromates(VI) suitable for single crystal study were produced by the evaporation method, although some new  $[\text{Ln}_2(\text{CrO}_4)_3(\text{H}_2\text{O})_5]\cdot 2\text{H}_2\text{O}$  compounds (Ln= La, Sm, Gd) were obtained in the  $\text{Ln}_2\text{O}_3\text{-CrO}_3\text{-H}_2\text{O}$  system. The crystals were better formed when obtained from a concentrated  $\text{Ln}_2\text{O}_3$  mixture, but were always small and of poor quality. Since the evaporation method has been widely studied before this work, and almost never with the production of good quality crystals (good enough for single crystal X-ray determination), no more time was invested in this method.

One new rare earth dichromate,  $\text{Gd}_2(\text{Cr}_2\text{O}_7)_3\cdot 9\text{H}_2\text{O}$ , was synthesized by evaporation in air, but again, crystal quality was poor. The crystals of  $\text{Gd}_2(\text{Cr}_2\text{O}_7)_3\cdot 9\text{H}_2\text{O}$  are dark brown, formed into large clusters and, as expected for a dichromate, are readily soluble in water. The surface of the crystals disintegrates rapidly in air.

#### 4.1.2. Gel method

The crystallization of rare earth chromates in gelatinous  $\text{Na}_2\text{SiO}_3\cdot 9\text{H}_2\text{O}$  is a promising but difficult method. Concentrations must be just right, and the gelation of the  $\text{Na}_2\text{SiO}_3\cdot 9\text{H}_2\text{O}\text{-H}_2\text{CrO}_4$  system must have reached exactly the right stage before the  $\text{Ln}_2\text{O}_3\text{-HNO}_3\text{-H}_2\text{O}$  mixture is added. If the rare earth mixture is added too early it may react too quickly with the

$\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O} - \text{H}_2\text{CrO}_4$  system (gel). If the gelation time is too long, on the other hand, the crystals will be formed very slowly or not at all. The more quickly the gel is formed the thicker it will be. Some of the mixtures were left to crystallize from two to four months before the crystals were large enough for single crystal X-ray study. Unfortunately, in most cases the crystals were twins or otherwise of poor quality, as noted above. The compounds crystallized (identified by thermogravimetry or infrared spectroscopy) were  $[\text{Ln}_2(\text{CrO}_4)_3(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$  Ln = La, Pr, Nd. The lanthanoids of higher atomic number formed very fine powders, which could not be separated from the gel.

#### 4.1.3. Autoclave method

The preparation of crystals in an autoclave at raised temperature and pressure proved to be a good method for the synthesis of rare earth (Ln= La, Pr, Nd, Sm-Er or Yb) chromates(VI). The major difficulty was the frequent formation of more than one kind of crystal. The compounds crystallized by this method were (1)  $[\text{Ln}_2(\text{CrO}_4)_3(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$ , Ln= La, Pr - Tb, (2)  $\text{Ln}_2(\text{OH})_2(\text{CrO}_4)_2$ , Ln= Pr - Er, Yb, (3)  $[\text{Yb}_2(\text{OH})_2(\text{CrO}_4)_2 \cdot (\text{H}_2\text{O})_{2.5}] \cdot 0.5\text{H}_2\text{O}$  (4)  $\text{Ln}_3(\text{OH})(\text{CrO}_4)_4(\text{H}_2\text{O})_{3.5}$  Ln= Pr, Nd and (5)  $\text{Pr}(\text{OH})\text{CrO}_4$ .

A good example of the synthesis of lanthanoid chromates(VI) in an autoclave was a mixture in which three different phases were found. Green-yellow crystals of  $\text{Pr}(\text{OH})\text{CrO}_4$  were first synthesized in the autoclave as an impurity in the synthesis of  $\text{Pr}_3(\text{OH})(\text{CrO}_4)_4(\text{H}_2\text{O})_{3.5}$ . Later yet another compound,  $\text{Pr}_2(\text{OH})_2(\text{CrO}_4)_2$ , was found in the mixture.

Synthesis of  $[\text{Yb}_2(\text{OH})_2(\text{CrO}_4)_2(\text{H}_2\text{O})_{2.5}] \cdot 0.5\text{H}_2\text{O}$  proved difficult, and my attempt to duplicate the first synthesis, was without success. Evidently

the formation of this compound is highly dependent on the cooling of the mixture.

The reason why so many compounds could be prepared by the autoclave is that at raised temperature and pressure it is easy to obtain a concentrated solution. This seems to be the requirement for the beginning of crystal growth of all the lanthanoid chromates(VI) and especially the hydroxide compounds.

## 4.2 Infrared spectra

The IR spectra of the rare earth chromates(VI) reproduced in papers 1, 2 and 3 are similar in appearance. Absorptions can be seen in roughly four different regions: at 3600-2900  $\text{cm}^{-1}$  OH (antisymmetric and symmetric) stretching and  $\text{H}_2\text{O}$  stretching bands, at about 1630-1600  $\text{cm}^{-1}$  HOH bending bands, at 990 to 300  $\text{cm}^{-1}$  all four possible  $\text{CrO}_4^{2-}$  stretching vibrations, and between 300 and 200  $\text{cm}^{-1}$  lattice vibrations.

The strongest peaks in the IR spectra of the compounds, collected from the papers 1-3, are compared in Table 4. The region from about 950 to 780  $\text{cm}^{-1}$  is very complex. Nakamoto<sup>34</sup> reports the vibrational frequencies of the tetrahedral  $\text{CrO}_4$ -type compound to be  $\nu_1$  (846  $\text{cm}^{-1}$ ),  $\nu_2$  (349  $\text{cm}^{-1}$ ),  $\nu_3$  (890  $\text{cm}^{-1}$ ) and  $\nu_4$  (378  $\text{cm}^{-1}$ ). As can be seen from the Table 4, the  $\nu_1$  and  $\nu_3$  bands have been split and some of the bands then overlap, making the assignment difficult. For example, for  $\text{Yb}_2(\text{OH})_2(\text{CrO}_4)_2$  the band at 797  $\text{cm}^{-1}$  (assigned as  $\nu_3$ ) may include the  $\nu_1$  band.



**Table 4.** A comparison of the assignment of the strongest peaks in the IR spectra ( $\text{cm}^{-1}$ ) of the compounds discussed in papers 1-3. Braces around the wavenumber indicate a weak peak.

La	Pr	[Ln <sub>2</sub> (CrO <sub>4</sub> ) <sub>3</sub> (H <sub>2</sub> O) <sub>5</sub> ] $\cdot$ 2H <sub>2</sub> O				Ln <sub>2</sub> (OH) <sub>2</sub> (CrO <sub>4</sub> ) <sub>2</sub> $\cdot$ nH <sub>2</sub> O			Pr <sub>3</sub> (OH)(CrO <sub>4</sub> ) <sub>4</sub> $\cdot$ 3.5H <sub>2</sub> O	Assign.
		Nd	Sm	Eu	Gd	Gd (n=0)	Yb (n=0)	Yb (n=3)		
3000- 3500 s , vb 1632 s 1600 sh	3100- 3500 s , vb 1636 s 1590 sh	3085- 3500 s , vb 1635 s 1600 sh	3150- 3500 s , vb 1632 s , b 1600 sh	3100- 3500 s , vb 1633 s , b 1600v w	3000- 3500 s , vb 1630 s , b 1600v w	3520 w 3486 w	3530 w 3490 w, sp	3480- 3100 vb 1627 s 1580 sh, m	3350- 3478 vb 1660 m, sp 1593 m	v OH  $\delta$ H <sub>2</sub> O
911 sh	909 sh	910 sh , sp	917 w , sh	910 m , sp	914 sh	915 m	925 s	932 s	938 s (915)	v <sub>1</sub> CrO <sub>4</sub> <sup>2-</sup> v <sub>3</sub> CrO <sub>4</sub> <sup>2-</sup>
855 w , sp	860 m , sh	860 m , sp	865 w	860 m , sp	867 w , sp	870 m (842)	853 m	(910) 857 m	883 sp 835 m	v <sub>3</sub> CrO <sub>4</sub> <sup>2-</sup> v <sub>1</sub> CrO <sub>4</sub> <sup>2-</sup>
817 w , sh	815 w , sh	820 w , sp	815 w	817 w	815 sh	(810)				v <sub>1</sub> CrO <sub>4</sub> <sup>2-</sup>
						791 b, sh 650 s, b	797 s, b 700 sp	780 w, b (732)	809 m 640 sh	v <sub>3</sub> CrO <sub>4</sub> <sup>2-</sup> $\delta$ LnOH
422 sh , w	425 w , sh	423 w , sh	430 w , sp	425 w	425 w , b	391 sh	400 s, sp	440 s, sp		v <sub>4</sub> CrO <sub>4</sub> <sup>2-</sup>

w =weak, m =medium, s =strong, v=very, b =broad, sp =sharp, sh =shoulder, v= stretching vibration,  $\delta$ = bending or rocking vibration

Shifts of the bands between the same phase of different lanthanoids are small. For example, for  $[\text{Ln}_2(\text{CrO}_4)_3(\text{H}_2\text{O})_5]\cdot 2\text{H}_2\text{O}$  compounds the frequencies are only slightly shifted to higher frequencies with increasing Ln atomic number.

The infrared spectral data for  $\text{Gd}_2(\text{Cr}_2\text{O}_7)_3\cdot 9\text{H}_2\text{O}$  are shown in Table 5. The assignments were made according to the literature.<sup>17,36,37</sup> However, the spectrum is highly complex in the region 350-700  $\text{cm}^{-1}$ , and the absorption bands at 600 and 650  $\text{cm}^{-1}$  could not be assigned according to Petrov *et al.*<sup>17</sup> Some of the nine water molecules must be coordinated to the lanthanoid and, following Nakamoto,<sup>34</sup> these two bands were assigned to the rocking and wagging modes of coordinated water molecules.

Table 5. IR spectral data ( $\text{cm}^{-1}$ ) of  $\text{Gd}_2(\text{Cr}_2\text{O}_7)_3\cdot 9\text{H}_2\text{O}$

Wave number	Assignment
3480 - 3240 s,vb	$\nu\text{OH}$ , $\nu\text{H}_2\text{O}$
1621 s	$\delta\text{H}_2\text{O}$
950 s, 935 sh	$\nu_{\text{asym}} \text{CrO}_3$
905 w, sp, 880 sp	$\nu_{\text{sym}} \text{CrO}_3$
770 sh, 740 s	$\nu_{\text{asym}} \text{CrOCr}$
650 sh	$\rho_{\text{r}} \text{H}_2\text{O}$
600 sh	$\rho_{\text{w}} \text{H}_2\text{O}$
570 w, 550 w, 520 w	$\nu_{\text{sym}} \text{CrOCr}$
332 m, sp	$\delta\text{CrO}_3$

s=strong, v=very, b=broad, sh=shoulder, w=weak, m=medium, sp=sharp,  $\delta$ =bending or rocking vibration,  $\nu$ = stretching vibration,  $\rho_{\text{r}}$ =rocking,  $\rho_{\text{w}}$ =wagging

The infrared spectrum of  $\text{Pr}(\text{OH})\text{CrO}_4$  resembles the spectrum reported by Bueno *et al.*<sup>47</sup>

### 4.3. Thermal behaviour

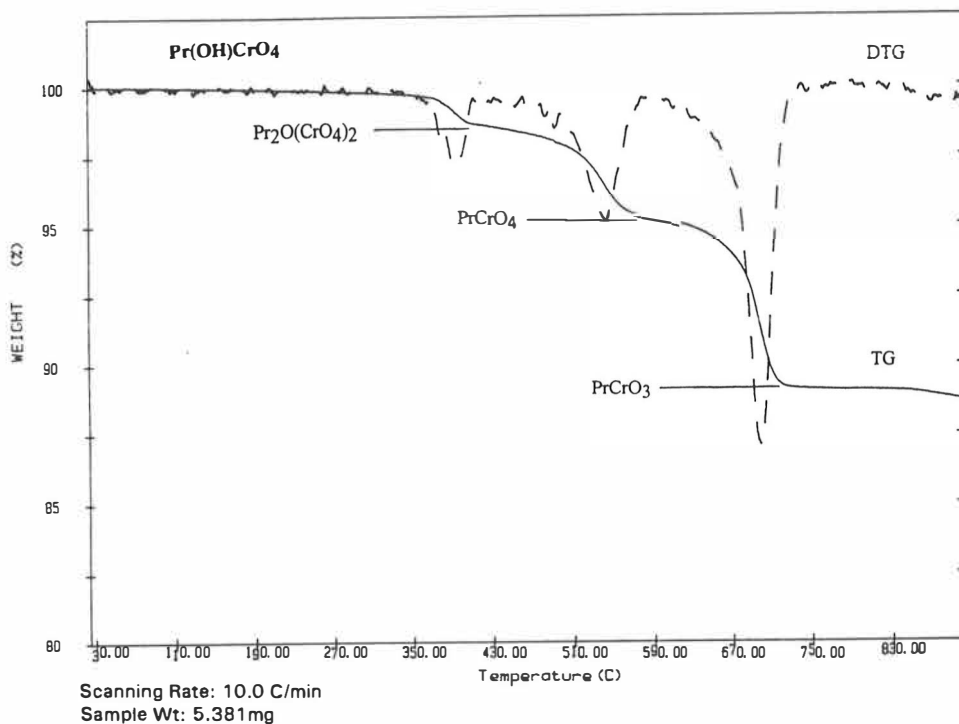
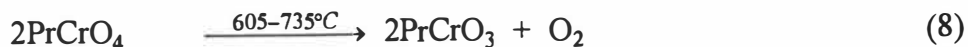
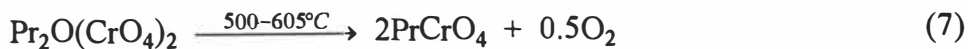
#### 4.3.1. Thermal behaviour of $\text{Pr}(\text{OH})\text{CrO}_4$

The thermal behaviour of  $\text{Pr}(\text{OH})\text{CrO}_4$  is shown in Fig. 3 and Table 6. To obtain the pure compound proved impossible, and small crystals for thermal analysis had to be hand picked out of a mixture of compounds. The worst impurity in the mixture was a very fine powder, which could not be totally separated from the  $\text{Pr}(\text{OH})\text{CrO}_4$  crystals. Through microscopic examination it was tentatively identified as praseodymium oxide. The sample used in the thermal experiment (Fig. 3) contained small amounts of this impurity, and also small amounts of  $\text{Pr}_2(\text{OH})_2(\text{CrO}_4)_2$ , identified by microscope from the shape of the crystals. The impurities may explain why the calculated total and observed total mass losses differed. In other mixtures where  $\text{Pr}(\text{OH})\text{CrO}_4$  was found, it was bound together with  $\text{Pr}_2(\text{OH})_2(\text{CrO}_4)_2$ . Despite the many samples investigated, the results were never very good.

Table 6. Thermal decomposition of  $\text{Pr}(\text{OH})\text{CrO}_4$

T (°C)	Weight loss (%)		Lost in Reaction	Eq. no.
	$\Delta$ Obs.	$\Delta$ Calc.		
340 - 500	2.14	3.29	$\text{H}_2\text{O}$	(6)
500 - 605	2.75	2.92	$0.5\text{O}_2$	(7)
605 - 735	6.04	5.84	$\text{O}_2$	(8)
340 - 735	10.94	12.05	*	

\* Total reaction.



*Fig. 3.* TG and DTG curves for  $\text{Pr}(\text{OH})\text{CrO}_4$

The decomposition mechanism for  $\text{Pr}(\text{OH})\text{CrO}_4$  is expressed in Eqs. (6)-(8). In the first stage, in the temperature range 340-500°C, the compound decomposed forming praseodymiumoxochromate(VI). Then  $\text{PrCrO}_4$  and  $\text{PrCrO}_3$  were formed in two successive processes. The decomposition temperatures for  $\text{Pr}(\text{OH})\text{CrO}_4$  were found to agree with

those for  $[\text{Yb}_2(\text{OH})_2(\text{CrO}_4)_2(\text{H}_2\text{O})_{2.5}] \cdot 0.5\text{H}_2\text{O}$ , from which it was assumed that the decomposition mechanisms were the same. In confirmation of this assumption, after  $[\text{Yb}_2(\text{OH})_2(\text{CrO}_4)_2(\text{H}_2\text{O})_{2.5}] \cdot 0.5\text{H}_2\text{O}$  had lost its three water molecules, both compounds - anhydrous  $\text{Yb}_2(\text{OH})_2(\text{CrO}_4)_2$  and  $\text{Pr}(\text{OH})\text{CrO}_4$  - decomposed first to  $\text{Ln}_2\text{O}(\text{CrO}_4)_2$  and subsequently to  $\text{LnCrO}_4$  and  $\text{LnCrO}_3$ .

In part, the thermal decomposition mechanism of  $\text{Pr}(\text{OH})\text{CrO}_4$  was also the same as that reported by Anoshina *et al.* for  $\text{Sc}(\text{OH})\text{CrO}_4 \cdot \text{H}_2\text{O}$ .<sup>22</sup> For both compounds the cleavage of the OH group occurs in the same temperature range and an intermediate product of formula  $\text{Ln}_2\text{O}(\text{CrO}_4)_2$  is formed. In the case of  $\text{Sc}(\text{OH})\text{CrO}_4 \cdot \text{H}_2\text{O}$ , however, the rest of the decomposition proceeds in a single step.

#### 4.3.2 Thermal behaviour of $\text{Gd}_2(\text{Cr}_2\text{O}_7)_3 \cdot 9\text{H}_2\text{O}$

The thermal decomposition of several rare earth dichromates(VI) has been reported in earlier papers. These dichromates contain 5, 7 or 10 molecules of crystal water, with dehydration occurring in three or four steps. The further decomposition of  $\text{Ln}_2(\text{Cr}_2\text{O}_7)_3 \cdot 10\text{H}_2\text{O}$  Ln= La, Nd includes the formation of the intermediate phase  $\text{Ln}_2(\text{CrO}_4)_3 \cdot \text{CrO}_3$ .<sup>12-14,17-21,24,25</sup>

As can be seen in Eqs. (9)-(12), Table 7 and Fig. 4, the thermal behaviour of  $\text{Gd}_2(\text{Cr}_2\text{O}_7)_3 \cdot 9\text{H}_2\text{O}$  is complicated, including three stages of dehydration of the water molecules. The last two water molecules leave the compound just before 470°C, and the rest of the compound then decomposes in three stages. The dehydration of  $\text{Gd}_2(\text{Cr}_2\text{O}_7)_3 \cdot 9\text{H}_2\text{O}$  differs from that of  $\text{Ln}_2(\text{Cr}_2\text{O}_7)_3 \cdot 10\text{H}_2\text{O}$  compounds.<sup>7</sup> At 240°C, where the  $\text{Ln}_2(\text{Cr}_2\text{O}_7)_3 \cdot 10\text{H}_2\text{O}$  compounds are totally dehydrated, one or more water

molecules are still bound to the  $\text{Gd}_2(\text{Cr}_2\text{O}_7)_3 \cdot 9\text{H}_2\text{O}$  structure. Evidently, differing from the decahydrate, two or more water molecules are coordinated to metal atoms in the structure of  $\text{Gd}_2(\text{Cr}_2\text{O}_7)_3 \cdot 9\text{H}_2\text{O}$ . A similar conclusion was drawn from the IR-spectral data.

The anhydrous  $\text{Gd}_2(\text{Cr}_2\text{O}_7)_3$  decomposes forming  $\text{Gd}_2(\text{CrO}_4)_3 \cdot 1.5\text{Cr}_2\text{O}_3$  and no intermediate phase  $\text{Gd}_2(\text{CrO}_4)_3 \cdot \text{CrO}_3$  exists (differing from  $\text{Ln}_2(\text{Cr}_2\text{O}_7)_3 \cdot 10\text{H}_2\text{O}$  Ln=La, Nd). The remaining part of the compound decomposes like the normal lanthanoid chromates(VI), forming first  $\text{GdCrO}_4$  (and  $\text{Cr}_2\text{O}_3$ ) and in the last step  $\text{GdCrO}_3$ .

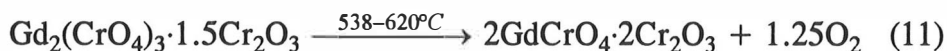


Table 7. Thermal decomposition of  $\text{Gd}_2(\text{Cr}_2\text{O}_7)_3 \cdot 9\text{H}_2\text{O}$

T (°C)	Weight loss (%)		Lost in Reaction	Eq. no.
	Δ Obs.	Δ Calc.		
30 - 95	4.8	5.2	3H <sub>2</sub> O	(9)
95 - 147	6.4	6.3	4H <sub>2</sub> O	(9)
147 - 470	3.2	2.9	2H <sub>2</sub> O	(9)
470 - 538	6.4	6.4	2.25O <sub>2</sub>	(10)
358 - 620	3.7	3.5	1.25O <sub>2</sub>	(11)
720 - 800	2.8	2.8	O <sub>2</sub>	(12)
30 - 800	27.2	27.6	*	

\*Total reaction.

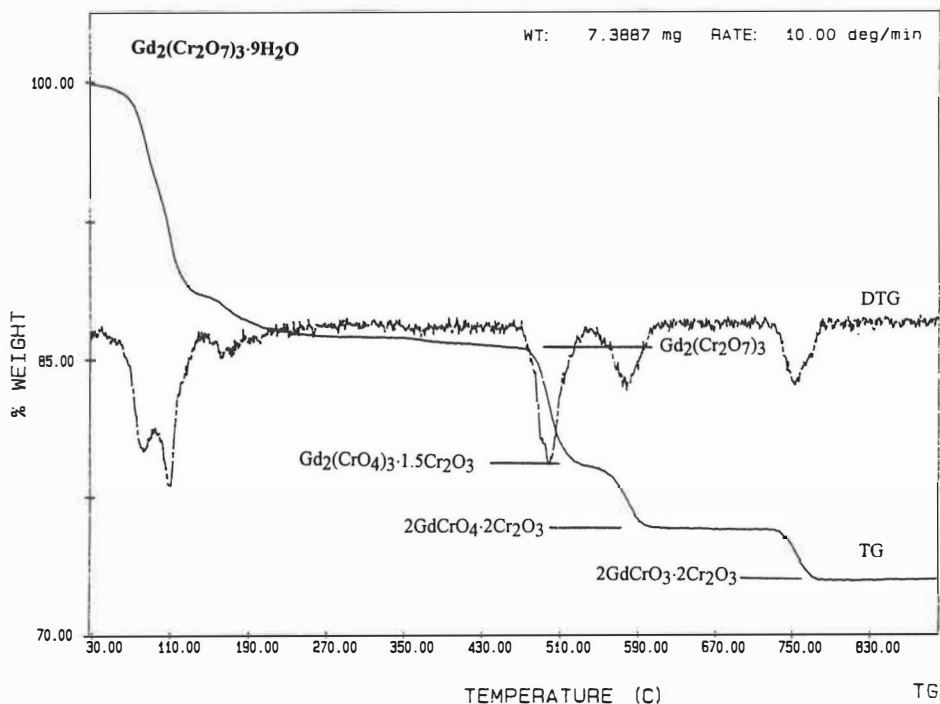


Fig. 4. TG and DTG curves for  $\text{Gd}_2(\text{Cr}_2\text{O}_7)_3 \cdot 9\text{H}_2\text{O}$ .

#### 4.3.3. Similarities and dissimilarities in thermal behaviour

##### *Dehydration*

The thermal decomposition of rare earth chromates(VI) of formula  $\text{Ln}_2(\text{CrO}_4)_3 \cdot 7\text{H}_2\text{O}$  has been widely studied, but not as here, from the point of view of the crystal structure.

In the thermal decomposition of  $[\text{Ln}_2(\text{CrO}_4)_3(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$  compounds the two non-coordinated water molecules are not released in a separate process. This means that the structure breaks up when the two non-coordinated water molecules leave the compound, and at the same time

one coordinated water molecule is lost (except for the La compound from which three are lost). In the thermal dehydration of compounds containing Pr, Nd, Sm, Eu and Gd, the temperature at which the fourth water molecule begins to leave increases with the atomic number, as would be expected from the average Ln-O(H<sub>2</sub>O) distances (Table 11). The situation is the reverse at the beginning of the dehydration, as discussed in paper 1 where it was shown that the greater the ionic radii the tighter the non-coordinated water molecules are bound to the structure. The temperature differences are nevertheless small.

An exception was found in the thermal dehydration of [La<sub>2</sub>(CrO<sub>4</sub>)<sub>3</sub>·(H<sub>2</sub>O)<sub>5</sub>]·2H<sub>2</sub>O, which loses five rather than three water molecules in the first stage. From the data of Habekost *et al.*<sup>48</sup> and Shannon,<sup>42</sup> I calculated a difference of 1.240 Å for [La<sub>2</sub>(CrO<sub>4</sub>)<sub>3</sub>(H<sub>2</sub>O)<sub>5</sub>]·2H<sub>2</sub>O between the average La-O(H<sub>2</sub>O) distance and the ionic radius of the La<sup>3+</sup> atom (CN 9), whereas the values for the corresponding Nd, Eu and Tb compounds according to my Ln-O(H<sub>2</sub>O) data are 1.222 Å, 1.22 Å and 1.221 Å, respectively. This shows that, on average, the coordinated water molecules are more weakly bound in [La<sub>2</sub>(CrO<sub>4</sub>)<sub>3</sub>(H<sub>2</sub>O)<sub>5</sub>]·2H<sub>2</sub>O than in the other normal lanthanoid chromates(VI) studied in this work. This may explain the difference in the thermal dehydration.

In the thermal decomposition of [Yb<sub>2</sub>(OH)<sub>2</sub>(CrO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2.5</sub>]·0.5H<sub>2</sub>O (paper 2) the non-coordinated half water molecule splits off first, in a separate process. Evidently oxygens O11 (population parameter 0.5) and O13 leave the compound in the second step. After that cleavage, both Yb atoms have 7 oxygen atoms left around them. When the last water of crystallization has left the compound, decomposition continues immediately to Yb<sub>2</sub>(OH)<sub>2</sub>(CrO<sub>4</sub>)<sub>2</sub>. Judging from the TG curve (paper 2) of the [Yb<sub>2</sub>(OH)<sub>2</sub>(CrO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2.5</sub>]·0.5H<sub>2</sub>O compound, the phase Yb<sub>2</sub>(OH)<sub>2</sub>(CrO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O is more stable than the phase Yb<sub>2</sub>(OH)<sub>2</sub>(CrO<sub>4</sub>)<sub>2</sub>.

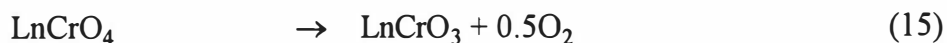
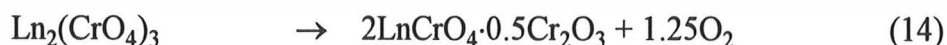
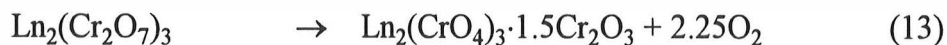


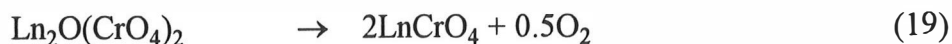
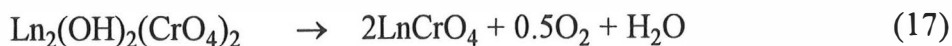
The thermal dehydration of  $\text{Pr}_3(\text{OH})(\text{CrO}_4)_4(\text{H}_2\text{O})_{3.5}$  begins at a very high temperature compared with the other compounds in this work (see Fig. 5). As one would expect, the coordinated water molecules are more tightly bound to the structure than non-coordinated water molecules, those in  $[\text{Ln}_2(\text{CrO}_4)_3(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$ , for example.

### *Decomposition of anhydrous compounds*

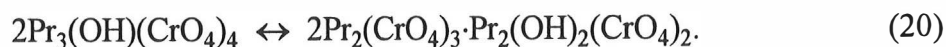
Only one significant exception was found in the thermal decomposition of normal rare earth chromates(VI).  $[\text{Pr}_2(\text{CrO}_4)_3(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$  decomposes from dehydrated form to  $\text{PrCrO}_3$  in one step instead of the two steps seen for the other  $[\text{Ln}_2(\text{CrO}_4)_3(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$  ( $\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}$ ) compounds. The unique behaviour of the Pr compound is a consequence of the dimorphic<sup>58</sup> structure of  $\text{PrCrO}_4$ . The decomposition process from  $\text{Ln}_2(\text{CrO}_4)_3$  to  $\text{LnCrO}_4$  (for  $[\text{Ln}_2(\text{CrO}_4)_3(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$   $\text{Ln} = \text{La}, \text{Nd}, \text{Eu}, \text{Sm}, \text{Gd}$ ) cannot be studied from the point of view of structure because the dehydrated  $\text{Ln}_2(\text{CrO}_4)_3$  compound crystallizes near  $470^\circ\text{C}$ , as found by Bashilova *et al.*<sup>13</sup>

Equations (13)-(19) describe the thermal decomposition processes after dehydration (where this occurs) for the compounds of this work.





Depending on the original compound,  $\text{Ln}_2(\text{OH})_2(\text{CrO}_4)_2$  may decompose through the intermediate product  $\text{Ln}_2\text{O}(\text{CrO}_4)_2$  or directly to  $\text{LnCrO}_4$ . In the thermal decomposition of  $\text{Pr}_3(\text{OH})(\text{CrO}_4)_4(\text{H}_2\text{O})_{3.5}$ , the dehydrated formula can be written as follows:



This means that in the next step in the temperature range 450-540°C the hydroxo part of this compound (i.e.  $\text{Pr}_2(\text{OH})_2(\text{CrO}_4)_2$ ) decomposes directly to  $\text{PrCrO}_4$ . The decomposition is similar to that reported for  $\text{Ln}_2(\text{OH})_2(\text{CrO}_4)_2$  ( $\text{Ln}=\text{Gd}, \text{Yb}$ ).<sup>1,3</sup> The decomposition temperature ranges for the two parts distinguished in Eq. (20) agree with those for known compounds (see Table 8).

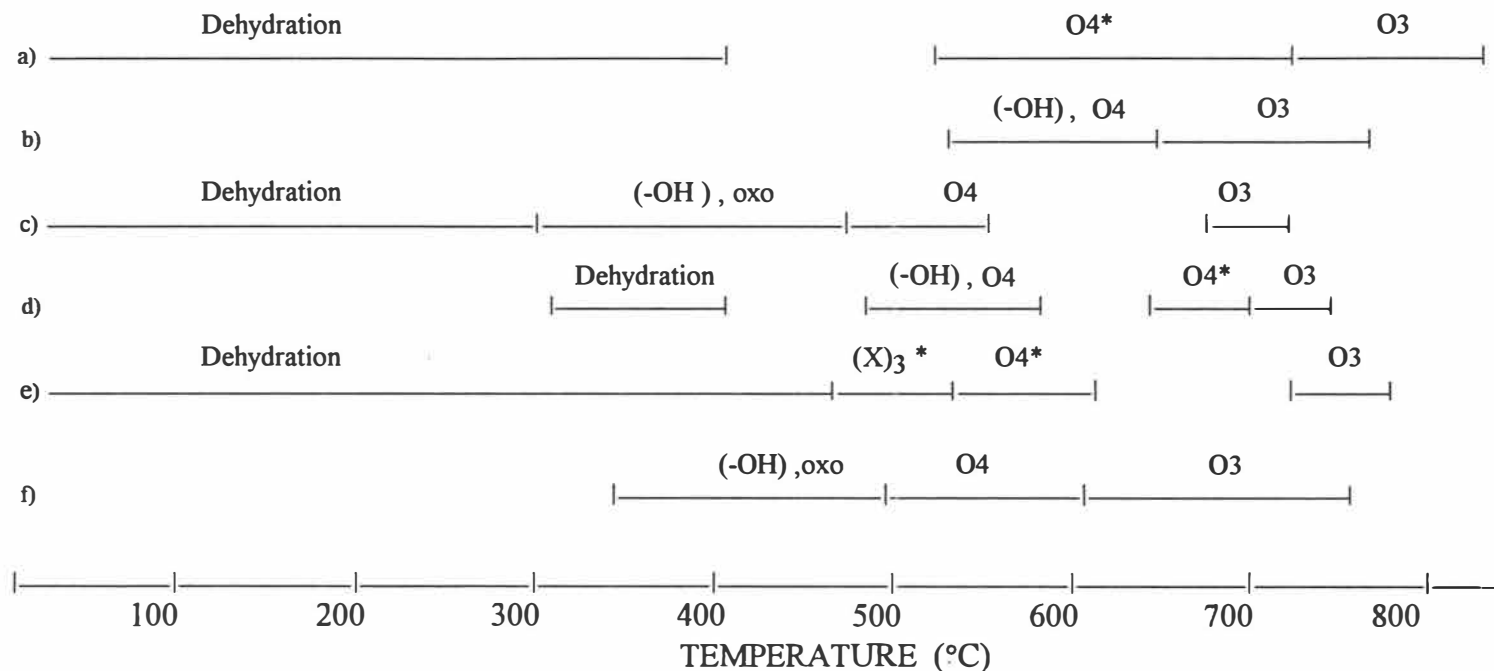
*Table 8.* Comparison of DTG temperatures of two processes for three compounds.

Compound	Heating rate (°C/min)	Eq. number for decomp. process	
		(17)	(15)
$\text{Pr}_3(\text{OH})(\text{CrO}_4)_4(\text{H}_2\text{O})_{3.5}$	2	520°C	630°C
$\text{Gd}_2(\text{OH})_2(\text{CrO}_4)_2$	2	575°C	-
$[\text{Gd}_2(\text{CrO}_4)_3(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$	10	-	650°C

Variation in the heating rate did not significantly influence the shape of the TG curves of rare earth chromates(VI), but the thermal decomposition temperatures drifted to slightly higher temperatures when heating rates were faster.

From the temperature ranges for decomposition of the compounds, shown in Fig. 5, it can be seen that the normal chromates are thermally more stable than the hydroxide chromates or dichromate, decomposing for example at a higher temperature in the last step.

The maximum temperature difference for the last decomposition step (counted from DTG temperatures) for  $[\text{Ln}_2(\text{CrO}_4)_3(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$  is  $60^\circ\text{C}$ , between the La and Gd compounds.  $[\text{Eu}_2(\text{CrO}_4)_3(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$  and  $[\text{Gd}_2(\text{CrO}_4)_3(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$  have a stable  $\text{LnCrO}_4$  phase, which cannot be seen from this figure. Both  $[\text{Yb}_2(\text{OH})_2(\text{CrO}_4)_2(\text{H}_2\text{O})_{2.5}] \cdot 0.5\text{H}_2\text{O}$  and  $\text{Gd}_2(\text{Cr}_2\text{O}_7)_3 \cdot 9\text{H}_2\text{O}$  have a fairly stable  $\text{LnCrO}_4$  phase, too, but the temperature area is at lower temperature than for the corresponding phase of  $[\text{Ln}_2(\text{CrO}_4)_3(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$  compounds.



*Fig. 5.* Schematic illustration of thermal decomposition of a)  $[\text{Ln}_2(\text{CrO}_4)_3(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$   $\text{Ln}=\text{La, Pr, Nd, Sm, Eu, Gd}$ , b)  $\text{Ln}_2(\text{OH})(\text{CrO}_4)_2$   $\text{Ln}=\text{Gd, Yb}$ , c)  $[\text{Yb}_2(\text{OH})(\text{CrO}_4)_2(\text{H}_2\text{O})_{2.5}] \cdot 0.5\text{H}_2\text{O}$ , d)  $\text{Pr}_3(\text{OH})(\text{CrO}_4)_4 \cdot 3.5\text{H}_2\text{O}$ , e)  $\text{Gd}_2(\text{Cr}_2\text{O}_7)_3 \cdot 9\text{H}_2\text{O}$ , f)  $\text{Pr}(\text{OH})\text{CrO}_4$ . Explanations: Dehydration = the cleavage of  $\text{H}_2\text{O}$ -group(s); (-OH)= the cleavage of OH-group(s); O4= formation of  $\text{LnCrO}_4$ ; O3= formation of  $\text{LnCrO}_3$ ; \* = formation of  $\text{Cr}_2\text{O}_3$ ; oxo= formation of  $\text{Ln}_2\text{O}(\text{CrO}_4)_2$ ; (X)<sub>3</sub>= formation of  $\text{Ln}_2(\text{CrO}_4)_3$ . See also Eqs. (13)-(19).

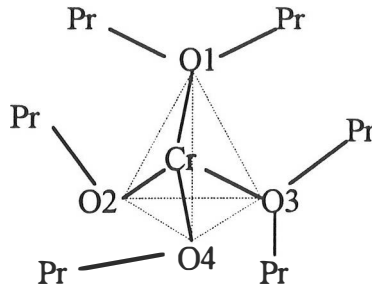
#### 4.4. Single crystal studies

Papers 1-4 present the crystal structures of four rare earth chromates(VI), describe the data collection and report the experimental parameters together with the crystallographic details. The crystallographic data for  $\text{Pr}(\text{OH})\text{CrO}_4$ , which is isostructural with  $\text{La}(\text{OH})\text{CrO}_4$ ,<sup>51</sup> are as yet unpublished and are reported below. This is followed by a summary discussion of the structural data for all five compound groups, the  $(-\text{Ln}-\overset{\text{H}}{\underset{\text{H}}{\text{O}}}-)$  structures of hydroxide compounds and the shape of the  $\text{CrO}_4$  tetrahedra.

##### 4.4.1. Crystal structure of $\text{Pr}(\text{OH})\text{CrO}_4$

The crystals of  $\text{Pr}(\text{OH})\text{CrO}_4$  are monoclinic, space group  $P2_1/c$  (No. 14) with lattice parameters  $a= 4.6877(7) \text{ \AA}$ ,  $b= 13.066(2) \text{ \AA}$ ,  $c= 7.0965(8) \text{ \AA}$  and  $\beta= 111.59(1)$ ,  $Z= 4$ ,  $D_x= 4.50 \text{ Mgm}^{-3}$ . Conditions for unit cell determination and data collection are summarized in Appendix I. Fractional coordinates and B-values are listed in Appendix II, while bond distances and O-Cr-O angles are presented in Appendix III and O-Pr-O angles in Appendix IV. A stereoscopic view of the  $\text{Pr}(\text{OH})\text{CrO}_4$  unit cell is shown in Fig. 6.

The coordination polyhedron of nine oxygen atoms around Pr atoms is a tricapped trigonal prism. The structure forms a three-dimensional network. The  $\text{CrO}_4$  tetrahedron is nearly regular and bound to six different Pr atoms (see scheme).



O-Cr-O angles are in the range  $107.5^\circ$ -  $112.0^\circ$ , and the mean Cr-O, Pr-O(Cr) and Pr-O(OH) distances are 1.645(4), 2.540(4) and 2.529(4) Å, respectively. The two mean Pr-O distances are 0.026 and 0.050 Å longer than the corresponding distances of  $\text{Pr}_3(\text{OH})(\text{CrO}_4)_4(\text{H}_2\text{O})_{3.5}$ .

Bueno *et al.*<sup>47</sup> have earlier measured the X-ray powder diffraction data for  $\text{Pr}(\text{OH})\text{CrO}_4$ . They chose the crystal system  $P2_1/n$ , however, while I prefer  $P2_1/c$ . Direct comparison of the crystal data is possible only for the unit cell volume and b-axis, which are 404.2(1) Å<sup>3</sup> and 13.066(2) Å in this work and 406.0(3) Å<sup>3</sup> and 13.071(6) Å in that of Bueno *et al.*

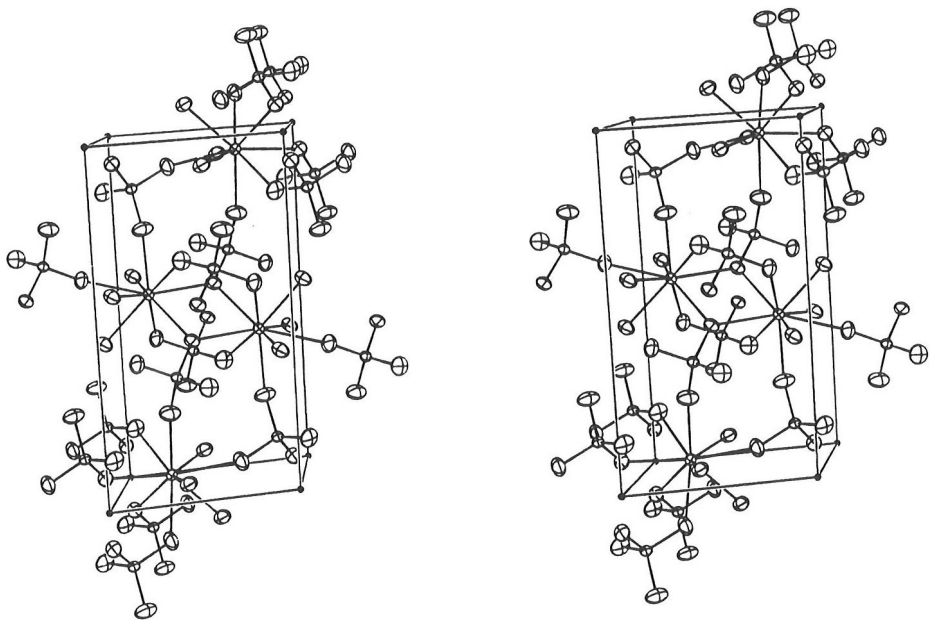


Fig. 6. A stereo view of the  $\text{Pr}(\text{OH})\text{CrO}_4$  unit cell.

#### 4.4.2. Overview of the crystal structures

##### *Summary of the crystal data*

The single crystal data for compounds investigated in this work are presented in Tables 9 and 10. Four of the five compound types crystallize in the monoclinic crystal system, while  $[\text{Ln}_2(\text{OH})_2(\text{CrO}_4)_2(\text{H}_2\text{O})_{2.5}] \cdot 0.5\text{H}_2\text{O}$  crystallizes in the orthorhombic system. For all five structures the number of oxygen atoms coordinated to the Ln atoms is eight or nine, which are typical coordination numbers for  $\text{Ln}^{3+}$  atoms. Ln coordination polyhedra of the compounds are more or less distorted.

The picture (a stereo view) presenting the three dimensional structures of  $[\text{Ln}_2(\text{CrO}_4)_3(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$  in paper 1 showed the Ln coordination polyhedron to be tricapped trigonal prism for the Ln1 atom and capped square anti-prism for the Ln 2 atom. Habekost *et al.*<sup>48</sup> describe the coordination polyhedron of both atoms as tricapped trigonal prism.

Table 10 shows that, almost without exception, within a compound group the final R-value decreases with increasing Ln atomic number. This is of course an indication of better crystal quality for compounds with higher Ln atomic number. But why is this so? One answer is suggested below in the section describing the  $\text{CrO}_4$  tetrahedra of the compounds.

Table 9. Crystallographic data for rare earth chromates(VI).

Compound formula	Crystal system	Space group	Ln coord. number	Ln coord. polyhedra*	CrO <sub>4</sub> coord.**
$\text{Ln}_2(\text{CrO}_4)_3 \cdot 7\text{H}_2\text{O}$	monocl.	$P2_1/c$ , No.14	9	TPRS-9, CSAPR-9	[1],[6]
$\text{Ln}_2(\text{OH})_2(\text{CrO}_4)_2$	monocl.	$P2_1/c$ , No.14	8	SAPR-8	[4]
$\text{Ln}_2(\text{OH})_2(\text{CrO}_4)_2 \cdot 3\text{H}_2\text{O}$	ortho.	$Pccn$ , No.56	8	SAPR-8	[1],[2]
$\text{Ln}_3(\text{OH})(\text{CrO}_4)_4(\text{H}_2\text{O})_{3.5}$	monocl.	$C2/c$ , No.15	9	TPRS-9	[3],[7],[8]
$\text{Ln}(\text{OH})\text{CrO}_4$	monocl.	$P2_1/c$ , No.14	9	TPRS-9	[5]

\* TPRS-9= tricapped trigonal prism, CSAPR-9= capped square anti-prism, SAPR-8= square anti-prism. \*\* Numbering for Fig. 7 and Table 12.



Table 10. Crystal data for compounds discussed in this work

Compound	<i>F.W.</i>	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\beta$ (°)	<i>V</i> (Å <sup>3</sup> )	Final <i>R</i> (%)	<i>R<sub>w</sub></i> (%)	<i>D<sub>calc</sub></i> (Mg m <sup>-3</sup> )	Ref.
La <sub>2</sub> (CrO <sub>4</sub> ) <sub>3</sub> ·7H <sub>2</sub> O	751.91	8.181(6)	19.294(6)	13.436(8)	128.09(6)	1669(2)	-	-	-	1*
Nd <sub>2</sub> (CrO <sub>4</sub> ) <sub>3</sub> ·7H <sub>2</sub> O	762.57	8.052(4)	19.143(4)	13.326(6)	128.15(4)	1615(1)	6.5	7.1	3.14	1
Sm <sub>2</sub> (CrO <sub>4</sub> ) <sub>3</sub> ·7H <sub>2</sub> O	774.82	7.975(9)	19.00(1)	13.18(1)	127.5(2)	1583(6)	-	-	-	1*
Eu <sub>2</sub> (CrO <sub>4</sub> ) <sub>3</sub> ·7H <sub>2</sub> O	778.01	7.965(3)	18.985(4)	13.185(4)	128.00(2)	1571(1)	5.2	4.8	3.29	1
Tb <sub>2</sub> (CrO <sub>4</sub> ) <sub>3</sub> ·7H <sub>2</sub> O	791.94	7.922(1)	18.954(4)	13.142(2)	128.02(1)	1554.3(5)	4.3	5.3	3.38	4
Nd <sub>2</sub> (OH) <sub>2</sub> (CrO <sub>4</sub> ) <sub>2</sub>	554.48	8.416(2)	11.424(3)	12.362(2)	136.62(1)	816.4(4)	4.1	4.8	4.51	4
Gd <sub>2</sub> (OH) <sub>2</sub> (CrO <sub>4</sub> ) <sub>2</sub>	580.50	8.2454(4)	11.3834(5)	12.1420(8)	136.590(5)	783.2(1)	2.3	2.8	4.92	3
Tb <sub>2</sub> (OH) <sub>2</sub> (CrO <sub>4</sub> ) <sub>2</sub>	583.85	8.214(1)	11.348(1)	12.094(2)	136.59(1)	774.7(2)	2.7	3.1	5.01	3
Yb <sub>2</sub> (OH) <sub>2</sub> (CrO <sub>4</sub> ) <sub>2</sub>	612.08	8.057(2)	11.297(1)	11.915(1)	136.67(3)	744.2(1)	2.1	2.1	5.46	2
Yb <sub>2</sub> (OH) <sub>2</sub> (CrO <sub>4</sub> ) <sub>2</sub> ·3H <sub>2</sub> O	666.13	10.884(2)	12.023(1)	16.033(8)	90	2098.2(2)	2.5	3.1	4.22	2
Pr <sub>3</sub> (OH)(CrO <sub>4</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>3.5</sub>	966.76	32.779(3)	7.137(1)	14.183(4)	97.41(1)	3290(1)	3.9	4.8	3.90	3
Nd <sub>3</sub> (OH)(CrO <sub>4</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>3.5</sub>	976.76	32.643(3)	7.1093(7)	14.122(1)	97.421(8)	3249.9(6)	2.3	2.6	3.99	3
Pr(OH)CrO <sub>4</sub>	273.91	4.6877(7)	13.066(2)	7.0965(8)	111.59(1)	404.2(1)	2.7	3.4	4.50	**

\* Only unit cell dimensions.

\*\* Single crystal data published here for the first time.

*Table 11.* Interatomic mean bond distances (Å) with their standard deviations\* for rare earth chromates(VI) discussed in this work

Compound	Cr-O	Ln-O(Cr)	Ln-O(H <sub>2</sub> O)	Ln-O(OH)
Nd <sub>2</sub> (CrO <sub>4</sub> ) <sub>3</sub> ·7H <sub>2</sub> O	1.65(2)	2.48(2)	2.52(2)	-
Eu <sub>2</sub> (CrO <sub>4</sub> ) <sub>3</sub> ·7H <sub>2</sub> O	1.641(8)	2.451(8)	2.482(8)	-
Tb <sub>2</sub> (CrO <sub>4</sub> ) <sub>3</sub> ·7H <sub>2</sub> O	1.650(7)	2.433(7)	2.456(8)	-
Nd <sub>2</sub> (OH) <sub>2</sub> (CrO <sub>4</sub> ) <sub>2</sub>	1.651(7)	2.468(9)	-	2.463(8)
Gd <sub>2</sub> (OH) <sub>2</sub> (CrO <sub>4</sub> ) <sub>2</sub>	1.647(4)	2.414(4)	-	2.407(4)
Tb <sub>2</sub> (OH) <sub>2</sub> (CrO <sub>4</sub> ) <sub>2</sub>	1.650(5)	2.400(5)	-	2.393(5)
Yb <sub>2</sub> (OH) <sub>2</sub> (CrO <sub>4</sub> ) <sub>2</sub>	1.653(3)	2.349(3)	-	2.336(3)
Yb <sub>2</sub> (OH) <sub>2</sub> (CrO <sub>4</sub> ) <sub>2</sub> ·3H <sub>2</sub> O	1.650(6)	2.355(6)	2.450(6)	2.295(5)
Pr <sub>3</sub> (OH)(CrO <sub>4</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>3.5</sub>	1.648(7)	2.514(7)	2.596(8)	2.479(6)
Nd <sub>3</sub> (OH)(CrO <sub>4</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>3.5</sub>	1.646(3)	2.499(3)	2.574(4)	2.464(3)
Pr(OH)CrO <sub>4</sub>	1.645(4)	2.540(4)	-	2.529(4)

$$\text{*Standard deviation} = \sqrt{\frac{\sum_{i=1}^n (\Delta)^2}{n}} \quad (\text{calculated from papers 1-4}),$$

where  $\Delta$  = deviation of each bond distance.

Table 11 shows the mean bond distances for those compounds whose structures were fully resolved. The lanthanoid contraction can very clearly be seen for the [Ln<sub>2</sub>(CrO<sub>4</sub>)<sub>3</sub>(H<sub>2</sub>O)<sub>5</sub>]·2H<sub>2</sub>O and Ln<sub>2</sub>(OH)<sub>2</sub>(CrO<sub>4</sub>)<sub>2</sub> compounds; all three Ln-O mean bond distances decrease with the increasing atomic number.

The mean Ln-O(H<sub>2</sub>O) distance in Nd<sub>3</sub>(OH)(CrO<sub>4</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>3.5</sub> is 2.574(4) Å, which is longer than the value of 2.52(2) Å for Nd<sub>2</sub>(CrO<sub>4</sub>)<sub>3</sub>·7H<sub>2</sub>O. The mean Ln-O(Cr) distances for these two compounds are 2.499(3) Å and 2.48(2) Å, respectively. Both compounds have CN of 9 for Nd atoms. The mean Ln-O(Cr) distances in Pr<sub>3</sub>(OH)(CrO<sub>4</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>3.5</sub> and Pr(OH)CrO<sub>4</sub> are 2.514(7) Å and 2.540(4) Å, respectively, while the mean Ln-O(OH)

distances are 2.479(6) Å and 2.529(4). In compounds with the same CN, variation of the mean Ln-O bond distances is smaller for Ln-O(Cr) than for Ln-O(H<sub>2</sub>O) or Ln-O(OH) bonds.

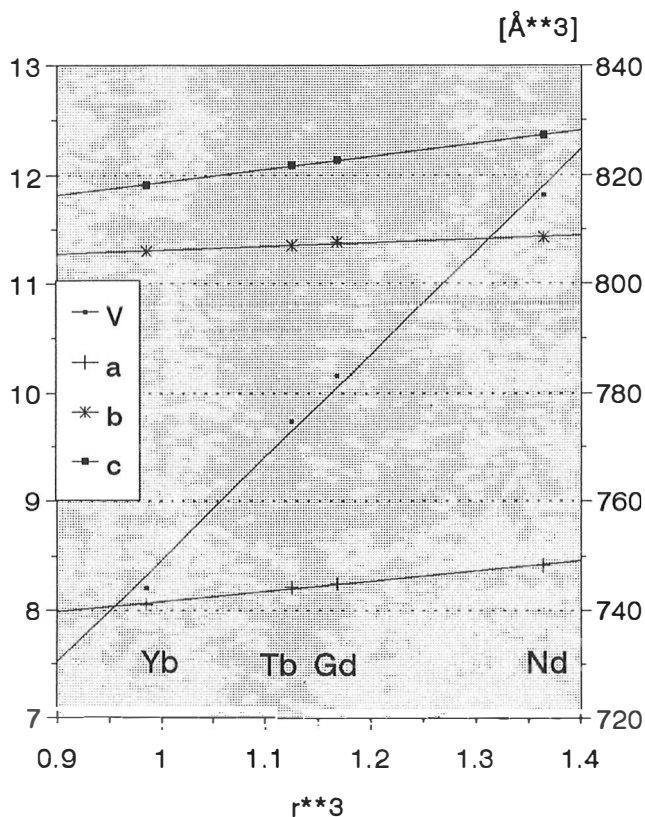


Fig. 7. Crystal data for  $\text{Ln}_2(\text{OH})_2(\text{CrO}_4)_2$ ,  $\text{Ln}=\text{Nd, Gd, Tb, Yb}$ , as a function of the third power of the Ln ionic radius.

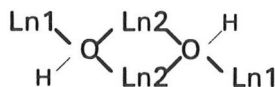
Comparing compounds of the same Ln atom but with different CN, we find that the differences in the mean bond distances are not very considerable. Sometimes there is no difference at all, as in the case of the mean Ln-O(OH) distances for  $\text{Nd}_2(\text{OH})_2(\text{CrO}_4)_2$  (CN=8) and  $\text{Nd}_3(\text{OH})(\text{CrO}_4)_4(\text{H}_2\text{O})_{3.5}$  (CN=9), which are 2.463(8) Å and 2.464(4) Å, respectively. This

is in accordance with the conclusions of Leskelä and Niinistö.<sup>41</sup> In the rare earth complexes the ionic radii of the Ln atom (and the bond distances) do not always give an indication of the coordination number in the solid state.

Figure 7 presents crystal data for  $\text{Ln}_2(\text{OH})_2(\text{CrO}_4)_2$ , Ln=Nd, Gd, Tb, Yb, as a function of the third power of the Ln ionic radius. The plot of unit cell volumes very clearly shows the lanthanoid contraction.

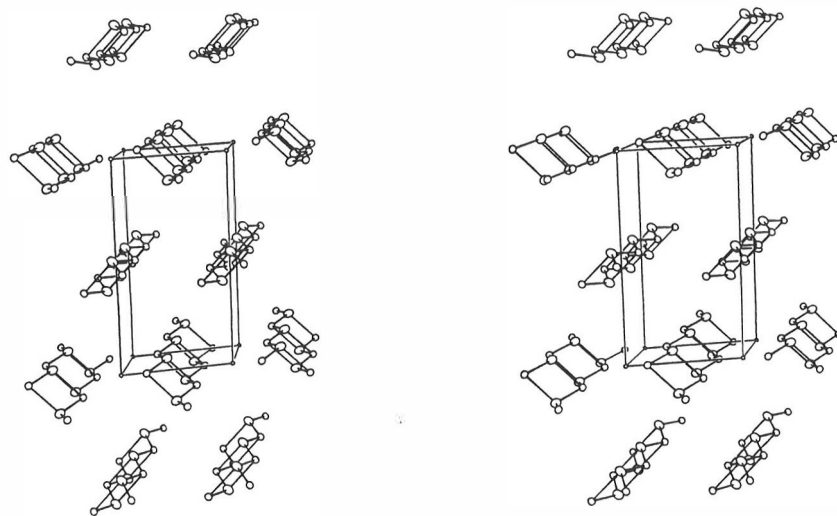
$\begin{array}{c} \text{H} \quad \text{H} \\ \vdots \quad \vdots \\ (-\text{Ln}-\ddot{\text{O}}-\text{Ln}-\ddot{\text{O}}-) \end{array}$  *structures of rare earth hydroxide chromates(VI)*

The  $\begin{array}{c} \text{H} \quad \text{H} \\ \vdots \quad \vdots \\ (-\text{Ln}-\ddot{\text{O}}-\text{Ln}-\ddot{\text{O}}-) \end{array}$  structures for the four rare earth hydroxide chromates(VI) discussed in papers 2-4 are shown in Fig. 8a-8d. A continuous chain  $\begin{array}{c} \text{H} \quad \text{H} \\ \vdots \quad \vdots \\ (-\text{Ln}-\ddot{\text{O}}-\text{Ln}-\ddot{\text{O}}-) \end{array}$  structure is running in the **a** direction in  $\text{Ln}(\text{OH})\text{CrO}_4$  and  $\text{Ln}_2(\text{OH})_2(\text{CrO}_4)_2$  but not in  $[\text{Ln}_2(\text{OH})_2(\text{CrO}_4)_2(\text{H}_2\text{O})_{2.5}] \cdot 0.5\text{H}_2\text{O}$  or  $\text{Ln}_3(\text{OH})(\text{CrO}_4)_4(\text{H}_2\text{O})_{3.5}$ . In the  $[\text{Ln}_2(\text{OH})_2(\text{CrO}_4)_2(\text{H}_2\text{O})_{2.5}] \cdot 0.5\text{H}_2\text{O}$  structure (Fig. 8c), four Ln and four O(OH) (hydroxyl oxygen) atoms form distorted baskets, while in  $\text{Ln}_3(\text{OH})(\text{CrO}_4)_4(\text{H}_2\text{O})_{3.5}$  (Fig. 8d) four Ln atoms and two O(OH) atoms are joined in discrete groups (see below).

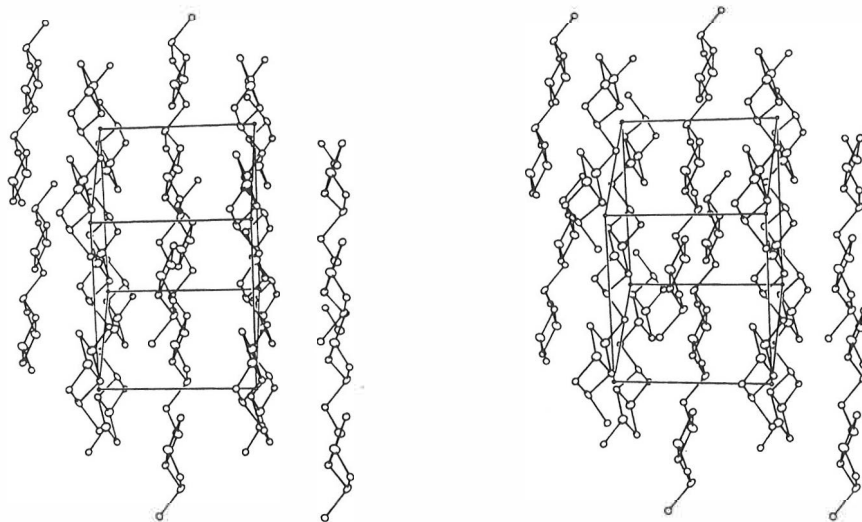


Although the  $\begin{array}{c} \text{H} \quad \text{H} \\ \vdots \quad \vdots \\ (-\text{Ln}-\ddot{\text{O}}-\text{Ln}-\ddot{\text{O}}-) \end{array}$  structures for  $\text{Ln}(\text{OH})\text{CrO}_4$  and  $\text{Ln}_2(\text{OH})_2(\text{CrO}_4)_2$  are alike, their thermal decomposition proceeds differently. Conversely, the  $\begin{array}{c} \text{H} \quad \text{H} \\ \vdots \quad \vdots \\ (-\text{Ln}-\ddot{\text{O}}-\text{Ln}-\ddot{\text{O}}-) \end{array}$  structures of  $[\text{Ln}_2(\text{OH})_2(\text{CrO}_4)_2(\text{H}_2\text{O})_{2.5}] \cdot 0.5\text{H}_2\text{O}$  and  $\text{Ln}(\text{OH})\text{CrO}_4$  are not alike, but the same intermediate product of rare earth oxochromate(VI) is found in their thermal decom-

position path. Evidently, then, the particular  $(-\text{Ln}-\overset{\text{H}}{\underset{\cdot\cdot}{\text{O}}}-\text{Ln}-\overset{\text{H}}{\underset{\cdot\cdot}{\text{O}}}-)$  structure does not explain why a rare earth hydroxide chromate(VI), upon decomposing, forms an oxochromate(VI) as an intermediate product. No direct correlation between the  $(-\text{Ln}-\overset{\text{H}}{\underset{\cdot\cdot}{\text{O}}}-\text{Ln}-\overset{\text{H}}{\underset{\cdot\cdot}{\text{O}}}-)$  structures and the thermal decomposition of these compounds could be demonstrated.

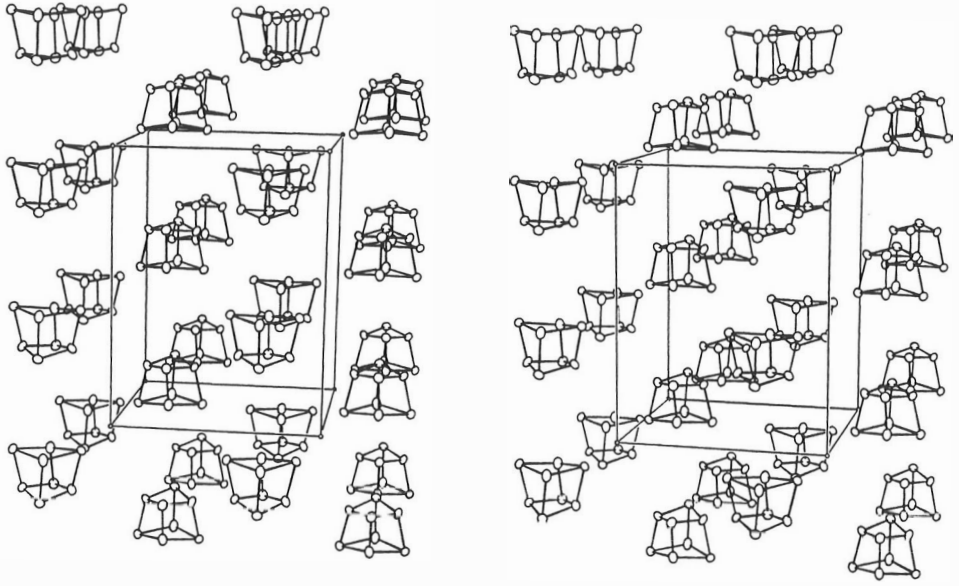


a)

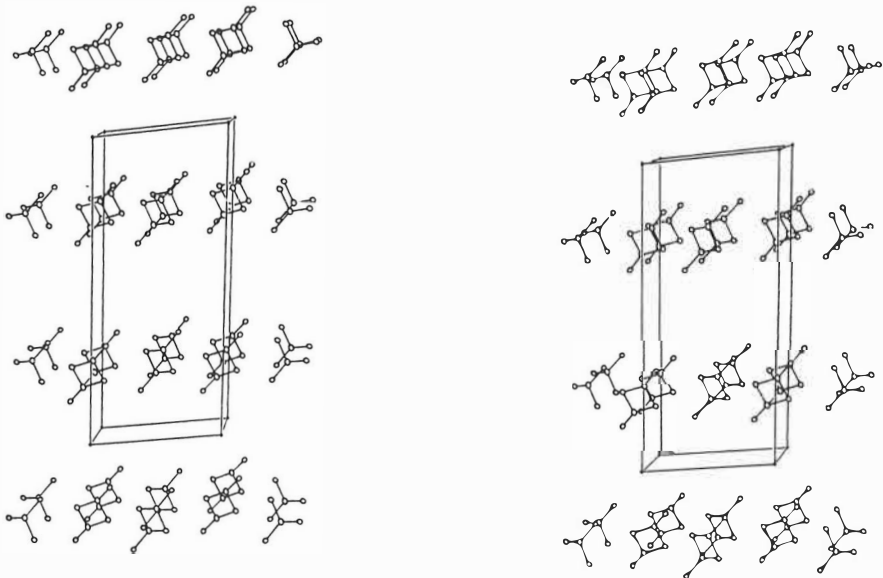


b)

$$\begin{array}{c} \text{H} \quad \text{H} \\ \vdots \quad \vdots \\ (-\text{Ln}-\text{O}-\text{Ln}-\text{O}-) \end{array}$$
 Fig. 8. A stereo view of the  $(-\text{Ln}-\text{O}-\text{Ln}-\text{O}-)$  structure for a)  $\text{Ln}(\text{OH})\text{CrO}_4$ , b)  $\text{Ln}_2(\text{OH})_2(\text{CrO}_4)_2$ , c)  $[\text{Ln}_2(\text{OH})_2(\text{CrO}_4)_2(\text{H}_2\text{O})_{2.5}]0.5\text{H}_2\text{O}$ , d)  $\text{Ln}_3(\text{OH})(\text{CrO}_4)_4(\text{H}_2\text{O})_{3.5}$ .



c)



d)

Fig. 8. Continued . . .

### *CrO<sub>4</sub> tetrahedra*

Figure 9 illustrates the different ways in which the CrO<sub>4</sub> tetrahedra are connected in the rare earth chromate(VI) structures studied in this work. Table 12 presents the standard deviation ( $\sigma_n$ ) of the mean O-Cr-O (ideal 109.5°) angle (°) values for the CrO<sub>4</sub> tetrahedra.

The CrO<sub>4</sub> tetrahedra are seen to be more distorted in the compounds designated [6], [7] and [8], where a double oxygen bridge



is present between the Cr and Ln atoms. This distortion is clearly evident in the values of Table 12.

Table 12 also reveals that, for Ln<sub>2</sub>(OH)<sub>2</sub>(CrO<sub>4</sub>)<sub>2</sub>, the CrO<sub>4</sub> tetrahedra are more distorted in the Yb compound than in the Nd compound. The values of the decomposition temperatures seem to correlate with the distortion of the CrO<sub>4</sub> tetrahedra: the more distorted the CrO<sub>4</sub> tetrahedra in a Ln<sub>2</sub>(OH)<sub>2</sub>(CrO<sub>4</sub>)<sub>2</sub> compound, the lower the temperature at which the decomposition begins. The DTG temperatures for Nd<sub>2</sub>(OH)<sub>2</sub>(CrO<sub>4</sub>)<sub>2</sub> and Yb<sub>2</sub>(OH)<sub>2</sub>(CrO<sub>4</sub>)<sub>2</sub> are 575°C and 535°C, respectively.

Inspection of Table 12 may suggest the reason for the formation of Cr<sub>2</sub>O<sub>3</sub> during the thermal decomposition of [Ln<sub>2</sub>(CrO<sub>4</sub>)<sub>3</sub>(H<sub>2</sub>O)<sub>5</sub>].2H<sub>2</sub>O and Ln<sub>3</sub>(OH)(CrO<sub>4</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>3.5</sub>. In both these structures, there is one CrO<sub>4</sub> tetrahedron which is very near the ideal geometry, while the other tetrahedra are more or less distorted. This kind of situation creates a strong net (-O-Cr-O-Ln-O-Cr-O-) in the structure, through the nearly regular CrO<sub>4</sub> tetrahedra. The thermal decomposition begins at the more distorted CrO<sub>4</sub> tetrahedra, and some of these Cr atoms are reduced to oxidation state +3, forming Cr<sub>2</sub>O<sub>3</sub>. Evidently, whenever very different kind of distorted CrO<sub>4</sub>



tetrahedra are present in a rare earth chromates(VI) structure the thermal decomposition will include the formation of  $\text{Cr}_2\text{O}_3$ :

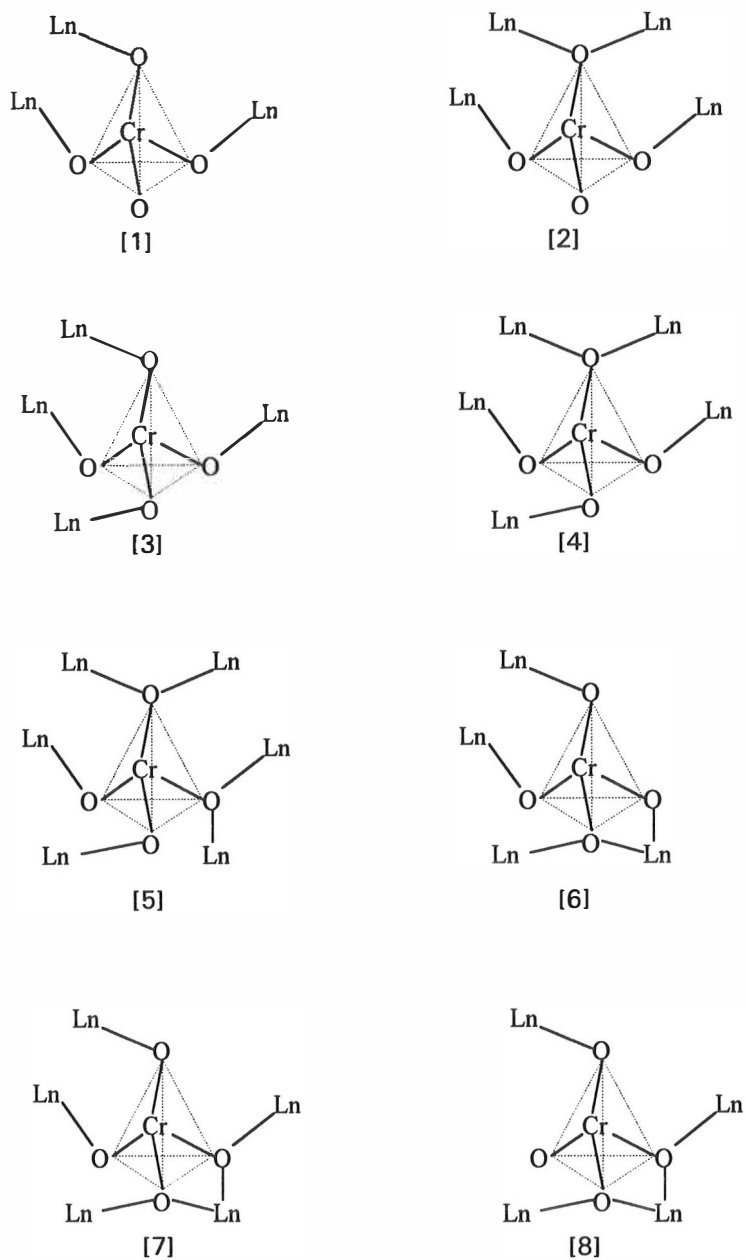
As mentioned above, within a compound group, the final R-value decreases with increasing Ln atomic number. The formation of crystals of rare earth chromates(VI) of different quality is not a random event but rather seems to correlate with the distortion of the  $\text{CrO}_4$  tetrahedra. The more regular the  $\text{CrO}_4$  tetrahedra the more difficult is the formation of perfect crystals.

*Table 12.* The standard deviations ( $\sigma_n$ ) of the mean O-Cr-O angle ( $^\circ$ ) in  $\text{CrO}_4$  tetrahedra. Numbers in brackets refer to the structures in Fig. 9.

Compound	Cr1	Cr2	Cr3	Cr4
$\text{Nd}_2(\text{CrO}_4)_3 \cdot 7\text{H}_2\text{O}$	4.3 [6]	3.1 [6]	1.3 [1]	
$\text{Eu}_2(\text{CrO}_4)_3 \cdot 7\text{H}_2\text{O}$	3.3 [6]	3.1 [6]	1.1 [1]	
$\text{Tb}_2(\text{CrO}_4)_3 \cdot 7\text{H}_2\text{O}$	3.6 [6]	3.1 [6]	0.9 [1]	
$\text{Nd}_2(\text{OH})_2(\text{CrO}_4)_2$	1.8 [4]	1.8 [4]		
$\text{Gd}_2(\text{OH})_2(\text{CrO}_4)_2$	2.1 [4]	1.9 [4]		
$\text{Tb}_2(\text{OH})_2(\text{CrO}_4)_2$	2.1 [4]	2.0 [4]		
$\text{Yb}_2(\text{OH})_2(\text{CrO}_4)_2$	2.5 [4]	2.4 [4]		
$\text{Yb}_2(\text{OH})_2(\text{CrO}_4)_2 \cdot 3\text{H}_2\text{O}$	1.4 [1]	1.3 [2]		
$\text{Pr}_3(\text{OH})(\text{CrO}_4)_4(\text{H}_2\text{O})_{3.5}$	0.7 [3]	3.2 [7]	3.0 [8]	3.3 [8]
$\text{Nd}_3(\text{OH})(\text{CrO}_4)_4(\text{H}_2\text{O})_{3.5}$	0.6 [3]	3.1 [7]	3.0 [8]	3.3 [8]
$\text{Pr}(\text{OH})\text{CrO}_4$	1.4 [5]			

Numbering for chromium atoms as in papers 1-4

$$\sigma_n = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n}}$$



*Fig. 9.* Schemes showing the  $\text{CrO}_4$  coordination for all compounds discussed in papers 1-4.

#### 4.5. Powder diffraction studies

The powder diffraction studies show a very strong X-ray absorption for  $[\text{Ln}_2(\text{CrO}_4)_3(\text{H}_2\text{O})_5]\cdot 2\text{H}_2\text{O}$  compounds. Figure 10 presents the powder diffraction pattern for  $[\text{Nd}_2(\text{CrO}_4)_3(\text{H}_2\text{O})_5]\cdot 2\text{H}_2\text{O}$  as an example. Only a few of the peaks are more than two times the background, which shows that the compound is not perfectly crystallized. The peak indexing was difficult and laborious, carried out step by step. First some of the strongest peaks were indexed in the same way for each compound, then the next strongest, and so on, until most of the peaks had been indexed. Had there been just one compound instead of five of the same type, indexing probably would have been impossible for such bad quality crystalline material.

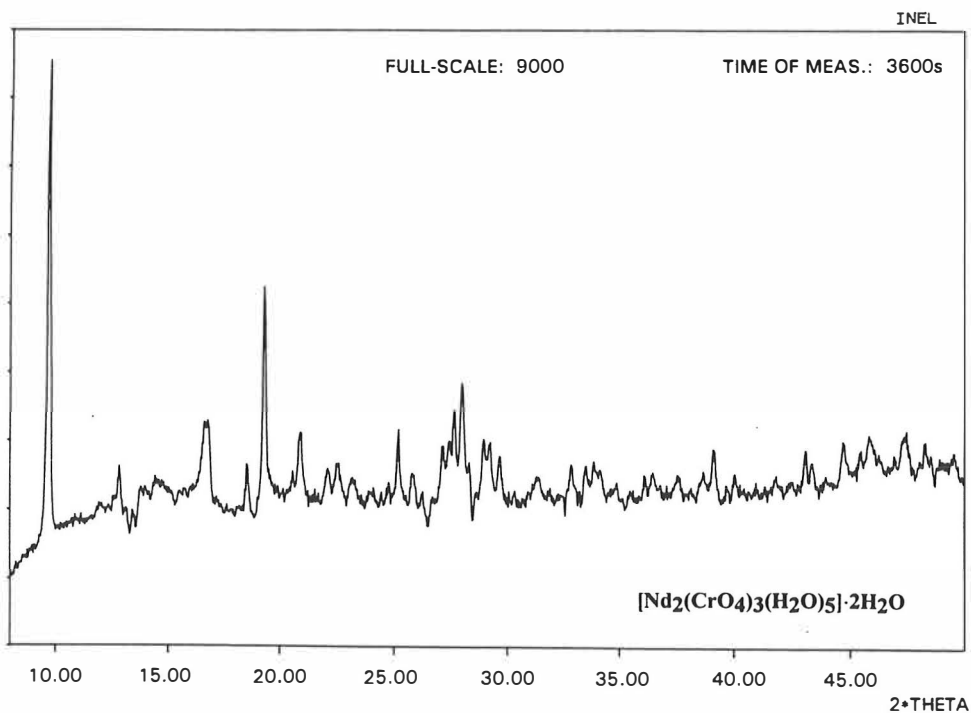


Fig. 10. Powder diffraction pattern of  $[\text{Nd}_2(\text{CrO}_4)_3(\text{H}_2\text{O})_5]\cdot 2\text{H}_2\text{O}$ .

The unit cell parameters determined by single crystal X-ray diffraction and powder diffraction methods are not the same, as can be seen in the plot of the unit cell volumes (Fig. 11). The difference, which is a consequence of the poorer crystals (on average) in the case of powder diffraction measurements, ranges from about 10 Å<sup>3</sup> for [La<sub>2</sub>(CrO<sub>4</sub>)<sub>3</sub>·(H<sub>2</sub>O)<sub>5</sub>]<sub>2</sub>·2H<sub>2</sub>O to 20 Å<sup>3</sup> for [Tb<sub>2</sub>(CrO<sub>4</sub>)<sub>3</sub>(H<sub>2</sub>O)<sub>5</sub>]<sub>2</sub>·2H<sub>2</sub>O (from 0.5% to 1.3%). A difference of 1.8 Å<sup>3</sup> (0.5%) was noted above for Pr(OH)CrO<sub>4</sub>.

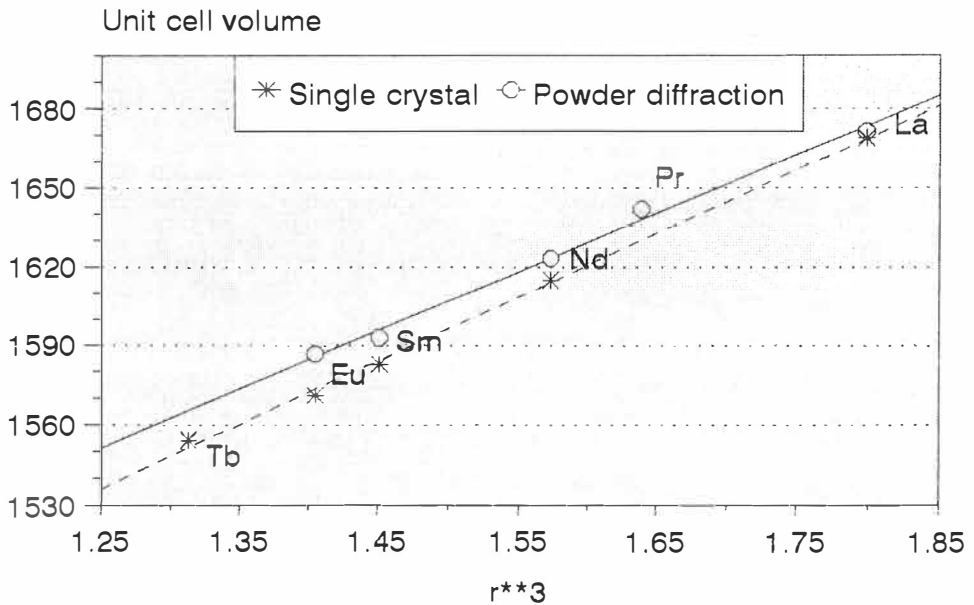


Fig. 11. Unit cell volumes of [Ln<sub>2</sub>(CrO<sub>4</sub>)<sub>3</sub>(H<sub>2</sub>O)<sub>5</sub>]<sub>2</sub>·2H<sub>2</sub>O (Ln= La, Pr, Nd, Sm, Eu, Tb), determined by single crystal X-ray diffraction and powder diffraction methods, as a function of the third power of the Ln ionic radius.

## 5. CONCLUSIONS

The best way to prepare rare earth chromates(VI) is in a steel autoclave. Even then, however, it is difficult to obtain pure compounds; in most cases a mixture of two to four compounds is obtained. By this method five different rare earth chromate(VI) structures were crystallized. For four of these structures more than one rare earth was crystallized in this way, whereas for  $[\text{Ln}_2(\text{OH})_2(\text{CrO}_4)_2(\text{H}_2\text{O})_{2.5}] \cdot 0.5\text{H}_2\text{O}$  only the Yb compound was found. Many more compounds were obtained by the autoclave method than by the gel and evaporation methods, evidently because at raised temperature and pressure it is easy to get a concentrated  $\text{Ln}_2\text{O}_3$  solution – a prerequisite for the beginning of crystal growth for all the lanthanoid chromates(VI) and especially the hydroxide compounds.

For those rare earth chromate(VI) compounds whose crystal structures were determined by single crystal method, the Ln coordination number is eight or nine. The lanthanoid contraction is very clearly seen from the mean bond distances and unit cell volumes. However, the mean bond distances do not necessarily give an indication of the coordination number.

The standard deviation of the mean O-Cr-O angle values, indicating the distortion of the  $\text{CrO}_4$  tetrahedra, seems to correlate with the thermal decomposition of the  $\text{Ln}_2(\text{OH})_2(\text{CrO}_4)_2$  compounds. Comparison of crystal structures showed that, within a compound group, the distortion of the  $\text{CrO}_4$  tetrahedra varies systematically with the Ln atomic number. For  $\text{Ln}_2(\text{OH})_2(\text{CrO}_4)_2$  (Ln= Nd, Gd, Tb, Yb) compounds, the more regular the  $\text{CrO}_4$  tetrahedra, the higher the decomposition temperature for the same decomposition process. Another observation was that in the thermal decomposition of rare earth chromates(VI),  $\text{Cr}_2\text{O}_3$  will be obtained as a decomposition product when very different kinds of distorted tetrahedra are present in the structure.

The infrared spectra of these lanthanoid chromates(VI) are highly complex, as a consequence of the splitting and overlapping of  $\nu_1$   $\text{CrO}_4^{2-}$  and  $\nu_3$   $\text{CrO}_4^{2-}$  bands at frequencies from 950 to 780  $\text{cm}^{-1}$ .

The aim of this work, to synthesize and investigate the structures and thermal behaviour of new rare earth chromates(VI), was successfully accomplished. The synthesis of yet other new compounds (or even new structures) is not impossible, but the methods will have to be improved.

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## APPENDIX I

TABLE OF EXPERIMENTAL DATA FOR CRYSTALLOGRAPHIC STUDY OF Pr(OH)CrO<sub>4</sub>

Formula	Pr(OH)CrO <sub>4</sub>
UNIT CELL DETERMINATION	
<i>F.W.</i>	273.91
Crystal size (mm)	0.05-0.05-0.15
<i>T</i> (°C)	21 ± 1
Refl. for latt. meas.	25
θ range for latt. meas.(°)	7.18 -13.87
<i>a</i> (Å)	4.6877(7)
<i>b</i> (Å)	13.066(2)
<i>c</i> (Å)	7.0965(8)
β (°)	111.59(1)
<i>V</i> (Å <sup>3</sup> )	404.2(1)
<i>Z</i>	4
<i>D</i> <sub>calc</sub> (Mgm <sup>-3</sup> )	4.50
μ(cm <sup>-1</sup> )	144.09
MoK <sub>α</sub>	0.71073
<i>F</i> (000)	496
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> (No: 14)
DATA COLLECTION AND REFINEMENT	
θ range for data col. (°)	3.09 - 40.00
Scan method	ω/2θ
Scan speed in omega (°min <sup>-1</sup> )	0.79 - 5.50
Scan width in omega (°)	0.50 + 0.34tanθ
Variation of std. ref.	none
Refl. measured	2593
Condition for obs. refl.	I>3σ(I)
Refl. used in refinement	1913
Max. shift/error	0.00
Max in final Δ/eÅ <sup>-3</sup>	1.57
Number of param.	64
<i>S</i>	1.969
<i>R</i>	0.027
<i>R</i> <sub>w</sub>	0.034

$$w = \frac{1}{(\sigma F_0)^2}$$

$$s = \sqrt{\sum w(F_0 - F_c)^2 / (m - n)}$$

## APPENDIX II

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR Pr(OH)CrO<sub>4</sub>

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å) <sup>a</sup>
Pr	0.66465(5)	0.05470(2)	0.29792(3)	0.458(2)
Cr	0.0924(1)	0.65014(5)	0.61771(9)	0.445(8)
O1	0.3201(8)	0.5688(3)	0.5494(5)	0.88(5)
O2	0.2279(8)	0.3358(3)	0.5714(6)	1.15(6)
O3	0.0291(9)	0.5978(3)	0.8104(5)	1.10(5)
O4	0.2495(9)	0.7614(3)	0.6821(6)	1.28(6)
O(OH)	0.2685(8)	0.4201(3)	0.9434(5)	0.95(5)

<sup>a</sup> Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter, defined as:  $(4/3)[u^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$

TABLE OF GENERAL DISPLACEMENT PARAMETER EXPRESSIONS, B-VALUES, FOR Pr(OH)CrO<sub>4</sub>

Name	<i>B</i> (1,1)	<i>B</i> (2,2)	<i>B</i> (3,3)	<i>B</i> (1,2)	<i>B</i> (1,3)	<i>B</i> (2,3)	<i>B</i> <sub>eqv</sub>
Pr	0.462(4)	0.471(5)	0.444(4)	0.009(6)	0.169(3)	0.044(5)	0.458(2)
Cr	0.40(1)	0.41(2)	0.51(1)	-0.02(1)	0.15(1)	-0.03(1)	0.445(8)
O1	1.03(8)	0.8(1)	1.00(8)	0.33(7)	0.60(6)	-0.00(7)	0.88(5)
O2	0.62(9)	1.3(1)	1.1(1)	-0.07(9)	-0.20(8)	-0.1(1)	1.15(6)
O3	1.39(9)	1.2(1)	0.89(8)	0.10(9)	0.65(6)	0.16(8)	1.10(5)
O4	1.0(1)	0.8(1)	1.6(1)	-0.17(9)	0.06(9)	-0.2(1)	1.28(6)
O(OH)	1.09(8)	0.81(9)	1.11(8)	-0.18(8)	0.59(6)	-0.22(8)	0.95(5)

The form of the anisotropic displacement parameter is:  $\exp[0.25\{h^2a^2B(1,1) + k^2b^2B(2,2) + l^2c^2B(3,3) + 2hkabB(1,2) + 2hlacB(1,3) + 2klbcB(2,3)\}]$  where *a*, *b* and *c* are reciprocal lattice constants

## APPENDIX III

**TABLE OF BOND DISTANCES (Å) FOR  
Pr(OH)CrO<sub>4</sub>**

Atom1	Atom2	Bond (Å)
Pr	O1	2.499(4)
Pr	O1'	2.495(3)
Pr	O2	2.530(4)
Pr	O3	2.677(3)
Pr	O3'	2.605(4)
Pr	O4	2.432(4)
Pr	O(OH)	2.477(4)
Pr	O(OH)'	2.456(4)
Pr	O(OH)''	2.653(4)
Cr	O1	1.698(4)
Cr	O2	1.614(3)
Cr	O3	1.650(4)
Cr	O4	1.618(4)

Note: Numbers in parentheses are estimated standard deviations in the least significant digits

**TABLE OF O-Cr-O BOND ANGLES (°) FOR Pr(OH)CrO<sub>4</sub>**

Atom 1	Atom 2	Atom 3	Angle (°)
O1	Cr	O2	108.9(2)
O1	Cr	O3	107.5(2)
O1	Cr	O4	112.0(2)
O2	Cr	O3	109.9(2)
O2	Cr	O4	108.7(2)
O3	Cr	O4	109.9(2)

Note: Numbers in parentheses are estimated standard deviations in the least significant digits

## APPENDIX IV

TABLE OF O-Pr-O BOND ANGLES (°) FOR Pr(OH)CrO<sub>4</sub>

Atom 1	Atom 2	Atom 3	Angle (°)
O1	Pr	O1'	66.2(1)
O1	Pr	O2	69.0(1)
O1	Pr	O3	144.1(1)
O1	Pr	O3'	80.4(1)
O1	Pr	O4	85.4(1)
O1	Pr	O5	137.9(1)
O1	Pr	O5	134.8(1)
O1	Pr	O5	87.8(1)
O1'	Pr	O2	75.8(1)
O1'	Pr	O3	146.1(1)
O1'	Pr	O3	77.0(1)
O1'	Pr	O4	136.9(1)
O1'	Pr	O5	86.4(1)
O1'	Pr	O5'	89.5(1)
O1'	Pr	O5''	132.5(1)
O2	Pr	O3	122.7(1)
O2	Pr	O3	145.2(1)
O2	Pr	O4	63.7(1)
O2	Pr	O5	136.4(1)
O2	Pr	O5'	68.3(1)
O2	Pr	O5''	132.5(1)
O3	Pr	O3	91.8(1)
O3	Pr	O4	73.6(1)
O3	Pr	O5	60.4(1)
O3	Pr	O5'	74.6(1)
O3	Pr	O5''	58.8(1)
O3'	Pr	O4	131.4(1)
O3'	Pr	O5	61.9(1)
O3'	Pr	O5'	132.5(1)
O3'	Pr	O5''	59.3(1)
O4	Pr	O5	133.2(1)
O4	Pr	O5'	88.7(2)
O4	Pr	O5''	74.0(1)
O5	Pr	O5'	72.1(1)
O5	Pr	O5''	88.5(1)
O5'	Pr	O5''	133.1(1)

Note: Numbers in parentheses are estimated standard deviations in the least significant digits

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