

Synthesis and Crystal Structure of $Ln_3(OH)(CrO_4)_4 \cdot 3.5H_2O$ ($Ln = Pr, Nd$) and $Ln_2(OH)_2(CrO_4)_2$ ($Ln = Tb, Gd$): Thermal Behavior and Infrared Spectra of $Pr_3(OH)(CrO_4)_4 \cdot 3.5H_2O$ and $Gd_2(OH)_2(CrO_4)_2$

JAAKKO LEPPÄ-AHO

University of Jyväskylä, Department of Chemistry, P.O. Box 35, SF-40351 Jyväskylä, Finland

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Crystal structures of $Ln_2(OH)_2(CrO_4)_2$ ($Ln = Gd, Tb$) and $Ln_3(OH)(CrO_4)_4 \cdot 3.5H_2O$ ($Ln = Pr, Nd$) were determined by a conventional single-crystal X-ray diffraction technique. Crystals of $Ln_2(OH)_2(CrO_4)_2$ ($Ln = Gd, Tb$) are monoclinic, space group $P2_1/c$ (no. 14) with lattice parameters $a = 8.2454(4)$ Å, $b = 11.3834(5)$ Å, $c = 12.1420(8)$ Å, and $\beta = 136.590(5)^\circ$, $Z = 4$, $D_x = 4.92$ mg · m⁻³ for $Gd_2(OH)_2(CrO_4)_2$ and $a = 8.214(1)$ Å, $b = 11.348(1)$ Å, $c = 12.094(2)$ Å, and $\beta = 136.59(1)^\circ$, $Z = 4$, $D_x = 5.01$ Mg · m⁻³ for $Tb_2(OH)_2(CrO_4)_2$. Crystals of $Ln_3(OH)(CrO_4)_4 \cdot 3.5H_2O$ ($Ln = Pr, Nd$) are monoclinic, space group $C2/c$ (No. 15) with lattice parameters $a = 32.779(3)$ Å, $b = 7.137(1)$ Å, $c = 14.183(4)$ Å, and $\beta = 97.41(1)^\circ$, $Z = 8$, $D_x = 3.90$ mg · m⁻³ for $Pr_3(OH)(CrO_4)_4 \cdot 3.5H_2O$ and with lattice parameters $a = 32.643(3)$ Å, $b = 7.1093(7)$ Å, $c = 14.122(1)$ Å, and $\beta = 97.421(8)^\circ$, $Z = 8$, $D_x = 3.99$ Mg · m⁻³ for $Nd_3(OH)(CrO_4)_4 \cdot 3.5H_2O$. In $Ln_3(OH)(CrO_4)_4 \cdot 3.5H_2O$ ($Ln = Pr, Nd$) the coordination polyhedron of the nine oxygen atoms around Ln atoms is a tricapped trigonal prism. In $Ln_2(OH)_2(CrO_4)_2$ ($Ln = Gd, Tb$) the coordination polyhedron of the eight oxygen atoms around Ln atoms is a square antiprism. Structures form a three-dimensional network. Thermal behavior was investigated and IR spectra were recorded for $Pr_3(OH)(CrO_4)_4 \cdot 3.5H_2O$ and $Gd_2(OH)_2(CrO_4)_2$. Thermal decomposition of $Pr_3(OH)(CrO_4)_4 \cdot 3.5H_2O$ begins by the loss of water molecules and follows by the mechanism described for $Yb_2(OH)_2(CrO_4)_2$ and $Ln_2(CrO_4)_3 \cdot 7H_2O$ ($Ln = La, Pr, Nd, Sm, Eu, Gd$).

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Introduction

In this study of the CrO_3 - Ln_2O_3 - H_2O system, four compounds of lanthanoid chromates were synthesized. The previously known structures are $Ln_2(CrO_4)_3 \cdot 7H_2O$ ($Ln = La, Nd, Eu$) (1, 2), $Ln_2(OH)_2(CrO_4)_2$ ($Ln = Er, Yb$) (3,4), $Yb_2(OH)_2(CrO_4)_2 \cdot 3H_2O$, (3), $La(OH)CrO_4$ (5), $La_3(OH)(CrO_4)_4 \cdot 3.5H_2O$ (2), and $Ce(CrO_4)_2 \cdot 2H_2O$ (6). The title compounds are isomorphous with compounds reported in Refs. (2-4).

Two difficulties in particular are encountered in synthesizing lanthanoid (rare-earth) chromates: first, the product crystals are small and second, mixtures of different

kinds of crystals very often result. Only a few crystals might be of interest, and it is sometimes impossible to obtain enough crystals for analyses other than for single-crystal equipment, such as single-crystal x-ray diffractometers.

Leppä-aho and Valkonen (1, 3), Bashio-lova *et al.* (7), Tananaev *et al.* (8), and Anoshina *et al.* (9) have studied the thermal decomposition of rare-earth chromates. In general, normal lanthanoid chromates decompose to $LnCrO_3$ and Cr_2O_3 releasing possible waters and oxygen. In the thermal decomposition of basic lanthanoid chromates ($Ln_2(OH)_2(CrO_4)_2 \cdot nH_2O$ $n = 0, 3$), Cr_2O_3 is not formed.

Experimental

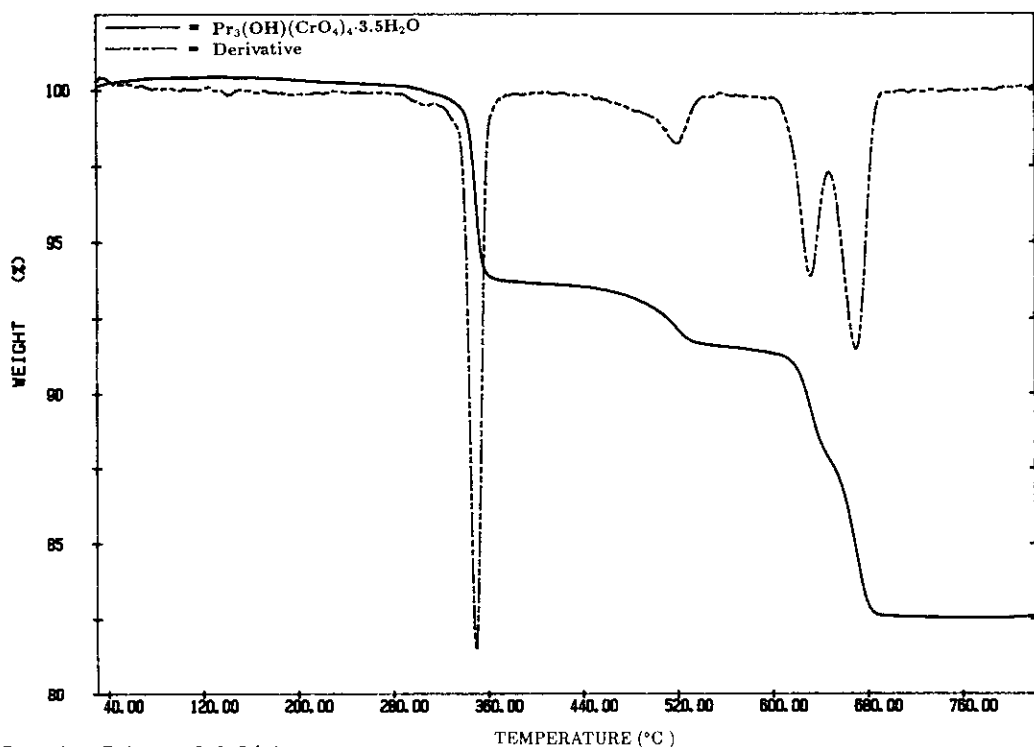
Synthesis. $Ln_3(OH)(CrO_4)_4 \cdot 3.5H_2O$ ($Ln = Pr, Nd$) and $Ln_2(OH)_2(CrO_4)_2$ ($Ln = Tb, Gd$) were synthesized in a steel autoclave with a Teflon lining. From 390 to 500 mg of lanthanoid oxides was mixed with $6 \text{ cm}^3 0.6 \text{ mole dm}^{-3} H_2CrO_4$. The mixtures were put in an autoclave and the temperature was raised to $152^\circ C$, then decreased slowly (5 degrees per day) to room temperature. The estimated maximum pressure in the autoclave was about $5.0 \cdot 10^5 \text{ N m}^{-2}$. Mixtures of crystals were filtered out without washing. The crystals of $Ln_3(OH)(CrO_4)_4 \cdot 3.5H_2O$ ($Ln = Pr, Nd$) and $Ln_2(OH)_2(CrO_4)_2$ ($Ln = Gd, Tb$) were brown parallelepipedon.

From the Nd-compound synthesis, a mixture of $Nd_2(CrO_4)_3 \cdot 7H_2O$ and $Nd_3(OH)(CrO_4)_4 \cdot 3.5H_2O$ (only a few crystals) was obtained. The Pr-compound mixture con-

$T(^\circ C)$	Weight loss (%)		Lost in reaction	Eq. no.
	Δ Obs.	Δ Theor.		
280–375	6.40	6.52	$3.5H_2O$	(1)
450–540	2.11	1.76	$0.5H_2O, 0.25O_2$	(2)
600–650	3.95	4.14	$1.25O_2$	(3)
650–700	5.11	4.96	$1.5O_2$	(4)
30–700	17.57	17.38	^a	(5)

^a Total reaction.

tained different crystals; all the brown crystals were the same $Pr_3(OH)(CrO_4)_4 \cdot 3.5H_2O$ compound, but there were some green-yellow crystals ($Pr(OH)CrO_4$, perhaps) as well. In the $Gd_2(OH)_2(CrO_4)_2$ synthesis, pure, single crystals were obtained. In the $Tb_2(OH)_2(CrO_4)_2$ synthesis the product



Scanning Rate: 2.0 C/min
Sample Wt: 2.551 mg

FIG. 1. TG and DTG curves for $Pr_3(OH)(CrO_4)_4 \cdot 3.5H_2O$.

TABLE II
THERMAL DECOMPOSITION OF $Gd_3(OH)_2(CrO_4)_2$

T(°C)	Weight loss (%)		Lost in reaction	Eq. no.
	Δ Obs.	Δ Theor.		
440–640	5.76	5.86	H ₂ O, 0.5O ₂	(6)
640–840	5.28	5.51	O ₂	(7)
440–840	11.02	11.37	^a	(8)

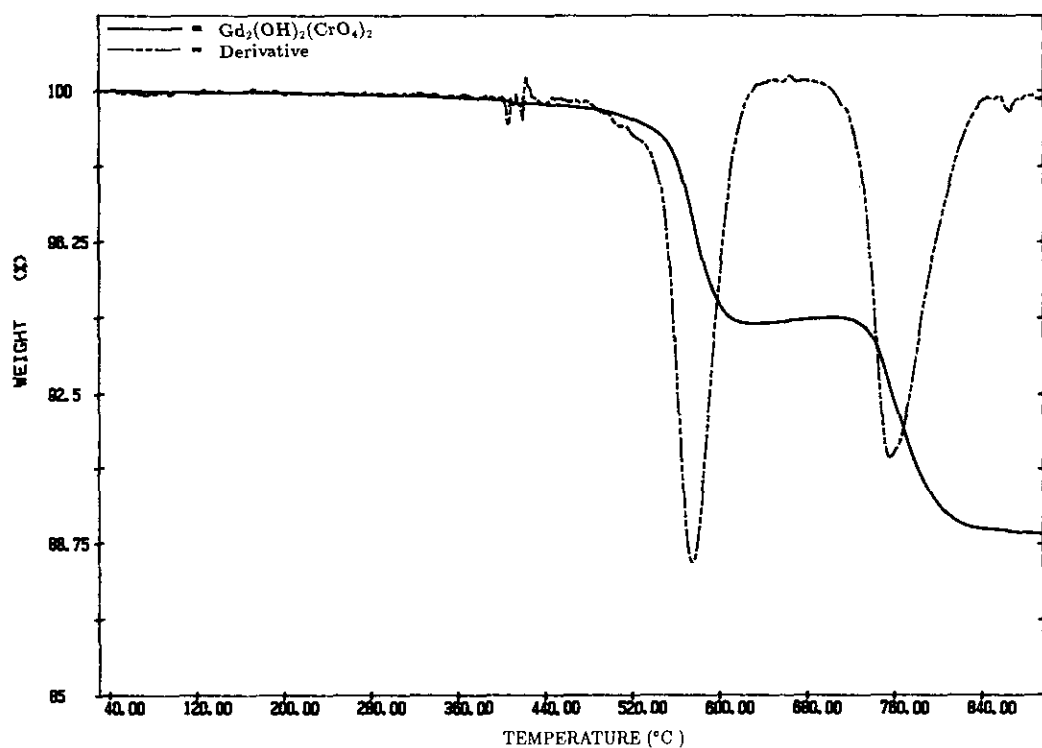
^a Total reaction.

crystals were mixed with a very fine powder.

Thermal analysis and IR spectra. Thermal behavior of $Pr_3(OH)(CrO_4)_4 \cdot 3.5H_2O$ and $Gd_2(OH)_2(CrO_4)_2$ was determined with a Perkin-Elmer thermogravimetric analyzer TGA 7. There were not enough crystals to determine the thermal decomposition of

$Nd_3(OH)(CrO_4)_4 \cdot 3.5H_2O$. Sample sizes were 2.551 and 8.912 mg for $Pr_3(OH)(CrO_4)_4 \cdot 3.5H_2O$ and $Gd_2(OH)_2(CrO_4)_2$, respectively, heating rate $2.0^\circ C \text{ min}^{-1}$ and air flow $70 \text{ cm}^3 \text{ min}^{-1}$. The IR spectra were recorded with Perkin-Elmer 283 IR spectrometer for $Pr_3(OH)(CrO_4)_4 \cdot 3.5H_2O$ and $Gd_2(OH)_2(CrO_4)_2$. The KBr method was used with a scan time of 12 min and a scan range of $4000 \text{ to } 200 \text{ cm}^{-1}$.

Crystal structure determination. X-ray determinations were made for all compounds using an Enraf-Nonius CAD4 automatic four circle diffractometer equipped with a graphite monochromator (MoK_α radiation = 0.71073 \AA). Cell constants were obtained from a least-squares refinement. Conditions for unit cell determination and data collection are summarized in Tables IV and V for $Ln_3(OH)(CrO_4)_4 \cdot 3.5H_2O$ ($Ln = Pr, Nd$) and $Ln_2(OH)_2(CrO_4)_2$ ($Ln = Gd,$



Scanning Rate: 2.0 C/min
Sample Wt: 8.912 mg

FIG. 2. TG and DTG curves for $Gd_2(OH)_2(CrO_4)_2$.

TABLE III
IR-SPECTRAL DATA (cm^{-1}) OF $\text{Gd}_2(\text{OH})_2(\text{CrO}_4)_2$ AND
 $\text{Pr}_3(\text{OH})(\text{CrO}_4)_4 \cdot 3.5\text{H}_2\text{O}$

$\text{Gd}_2(\text{OH})_2$ $(\text{CrO}_4)_2$	$\text{Pr}_3(\text{OH})$ $(\text{CrO}_4)_4 \cdot 3.5\text{H}_2\text{O}$	Assignment
3520 w	3350–3478 vb	} ν OH
3486 w		
	2926 w,sp	} ν H_2O
	1660 m,sp	
	1593 m	} δ H_2O
	972 sh	
940 sh	938 s	} ν_3 CrO_4^{2-}
915 m	915 sh	
892 w,sp	883 sp	} ν_1 CrO_4^{2-}
870 m	860 sh	
842 s,m	835 m	} ν_3 CrO_4^{2-}
810 w	809 m	
791 b,s		} ν_1 CrO_4^{2-}
	772 sh	
695 sh	708 sh	} ρ H_2O
650 s,b	640 sh	
	497 m	} δ LnOH
	429 w	
410 sh	412 w	} not assigned
391 sh	389 w	
376 s,sp	364 sh	} ν_4 CrO_4^{2-}
352 sh	348 w	
320 w,sh	324 w,b	} ν_2 CrO_4^{2-}
301 m		
	271 w	} T,L
215 m,sp	216 sh	

Note. w, weak; m, medium; s, strong; v, very; b, broad; sp, sharp; sh, shoulder, T,L, translational and librational modes.

Tb), respectively. Two test reflections measured hourly during data collection did not show any significant variation in intensity. Lorentz and polarization corrections were applied to the data. Absorption corrections were calculated for all compounds using the program DIFABS (10).

All calculations¹ were done with a micro

¹ Tables containing F_{obs} , F_{calc} and temperature factors have been deposited as supplementary material. See NAPS Document No. 05011 for 183 pages of supplementary materials from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance \$4.00 for microfiche copy of photocopy, \$7.75 up to 20 pages plus \$0.30 for each additional page. All orders must be prepaid.

VAX II computer using the Enraf-Nonius structure determination package SDP-plus (11). Scattering factors for neutral atoms and anomalous dispersion corrections for all atoms were taken from International Tables for X-Ray Crystallography (12). The SDP-plus package incorporates the direct methods program MULTAN (13) and the plotting programs ORTEP (14) and PLUTO (15).

Positions of lanthanoid and chromium atoms were established by direct methods and by remaining atoms were located in subsequent difference Fourier syntheses. Hydrogen atoms were not included in the calculations and refinements were based on structure factors. The function minimized was $\Sigma(|F_o| - |F_c|)^2$.

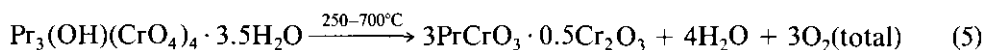
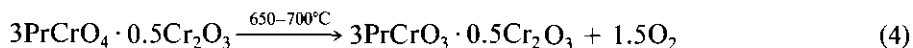
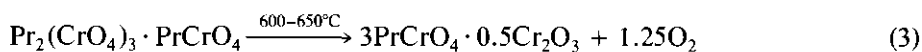
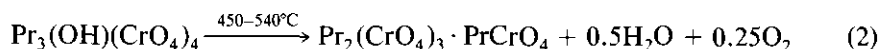
Results and Discussion

Thermal analysis and IR spectra. Thermal decomposition was determined for $\text{Pr}_3(\text{OH})(\text{CrO}_4)_4 \cdot 3.5\text{H}_2\text{O}$ and $\text{Gd}_2(\text{OH})_2(\text{CrO}_4)_2$. Table I and Fig. 1 give the results for thermal analysis of $\text{Pr}_3(\text{OH})(\text{CrO}_4)_4 \cdot 3.5\text{H}_2\text{O}$. The possible thermal decomposition mechanism can be expressed as in Eqs. (1–5) below.

In the first stage (Eq. (1)) H_2O molecules leave the compound between 280 and 375°C, quite high for water molecules. In the second stage (Eq. (2)) the OH-group leaves the compound forming H_2O and oxygen is split off. This is followed by the mechanism described for $\text{Yb}_2(\text{OH})_2(\text{CrO}_4)_2$ (3) and $\text{Gd}_2(\text{OH})_2(\text{CrO}_4)_2$ (see Eq. (6)). Equation (3) shows the formation of the PrCrO_4 and Cr_2O_3 from $\text{Pr}_2(\text{CrO}_4)_3$. The temperature range is the same as described for the decomposition of $\text{Ln}_2(\text{CrO}_4)_3 \cdot 7\text{H}_2\text{O}$ (1) compounds. The expression of the decomposition product is different in these two cases. The formation of PrCrO_3 in the last stage agrees with the decomposition described by Leppä-aho and Valkonen (3), but the temperature range is somewhat lower than that

in the formation of $LnCrO_3$ in the decomposition of $Ln_2(CrO_4)_3 \cdot 7H_2O$ compounds. The calculated and observed total mass loss

for $Pr_3(OH)(CrO_4)_4 \cdot 3.5H_2O$, 17.38% and 17.57%, respectively, confirms the accuracy of the decomposition mechanism.



The thermal decomposition of $Gd_2(OH)_2(CrO_4)_2$ proceeds by a mechanism reported previously by Leppä-aho and Valkonen (3). The thermal behavior of $Gd_2(OH)_2(CrO_4)_2$ is described in Table II and Fig. 2. $Gd_2(OH)_2(CrO_4)_2$ dissociates to $GdCrO_3$ in two endothermic reactions. First, in temperature range 440–640°C, two OH-groups are split off as one H_2O molecule and one oxygen (Eq. (6)). Then, the remaining $GdCrO_4$ dissociates to $GdCrO_3$ (Eq. (7)) before 840°C.

The only difference between these two compounds is the temperature range of the second process (Eq. (7)), which take place about 100 degrees higher in the case of the Gd-compound than in the case of the Yb-compound. This, difference cannot be explained by the scanning rate, but results because $Gd_2(OH)_2(CrO_4)_2$ has more stable structure than $Yb_2(OH)_2(CrO_4)_2$. $Tb_2(OH)_2(CrO_4)_2$ was not measured because of the impurity of the sample.

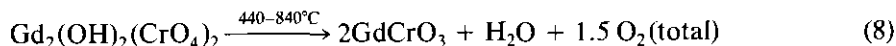
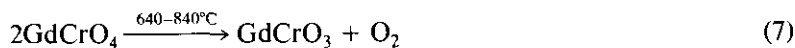
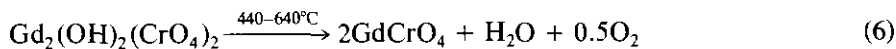


Table III gives the IR-spectral data for $Gd_2(OH)_2(CrO_4)_2$ and $Pr_3(OH)(CrO_4)_4 \cdot 3.5H_2O$. Assignments were made according to the literature (16–18). As previously stated, both compounds belong to the monoclinic system, space group $P2_1/c$ ($Z = 4$) and space group $C2/c$ ($Z = 8$) for $Gd_2(OH)_2$

$(CrO_4)_2$ and $Pr_3(OH)(CrO_4)_4 \cdot 3.5H_2O$, respectively. In both structures the CrO_4^{2-} ions are located on the general C_1 positions. Situation is equal to the structure $Ln(OH)CrO_4$ (Bueno *et al.* (18)). From the correlation between point group of the CrO_4^{2-} ions (T_d), their site group (C_1) and the factor

TABLE IV
 EXPERIMENTAL DATA FOR CRYSTALLOGRAPHIC ANALYSES

Formula	Pr ₃ (OH)(CrO ₄) ₄ · 3.5H ₂ O	Nd ₃ (OH)(CrO ₄) ₄ · 3.5H ₂ O
F.W.	966.76	976.76
Crystal size (mm)	0.05 · 0.05 · 0.1	0.05 · 0.08 · 0.1
T(°K)	296 ± 1	296 ± 1
Refl. for latt. meas.	25	25
θ range for latt. meas. (°)	7.09–13.77	5.86–13.30
<i>a</i> (Å)	32.779 (3)	32.643 (3)
<i>b</i> (Å)	7.137 (1)	7.1093 (7)
<i>c</i> (Å)	14.183 (4)	14.122 (1)
β (°)	97.41 (1)	97.421 (8)
<i>V</i> (Å ³)	3290 (1)	3249.9 (6)
<i>Z</i>	8	8
<i>D</i> _{calc} (Mg · m ⁻³)	3.90	3.99
μ (cm ⁻¹)	112.75	120.73
MoK α	0.71073	0.71073
<i>F</i> (000)	3560	3584
Space group	C2/c (No. 15)	C2/c (No. 15)
Data collection and refinement		
θ range for data col. (°)	2.04–40.00	2.04–35.00
Scan method	$\omega/2\theta$	$\omega/2\theta$
Scan speed (° min ⁻¹)	0.87–5.50	0.92–5.50
Scan width in omega (°)	0.55 + 0.34 tan θ	0.60 + 0.34 tan θ
Variation in std. ref.	none	none
Refl. measured	10,759	15,216
Condition for obs. refl.	$I > 3\sigma(I)$	$I > 3\sigma(I)$
Refl. used in refinement	4957	5576
Max. shift/error	0.01	0.01
Max. in final δ/e Å ⁻³	1.907	1.607
Number of param.	249	249
<i>S</i>	11.606	5.957
<i>R</i>	0.039	0.023
<i>R</i> _w	0.048	0.026

Note. $w = 1/(\sigma F_o)^2$. $s = \sqrt{(\sum w(F_o - F_c)^2)/(m - n)}$.

group (*C*_{2h}) we get the number of the possible components for the different vibrational modes: ν_1 symmetric stretching; 2 IR active bands, ν_2 symmetric bending; 4 IR active bands, ν_3 antisymmetric stretching; 6 IR active bands and ν_4 antisymmetric bending; 6 IR active bands. All of these bands cannot be seen in these structures. The observed frequencies assigned appear with similar frequencies found in the literature. The antisymmetric stretching ν_3 at 965–975 cm⁻¹ is only seen in the case of Pr₃(OH)(CrO₄)₄ · 3.5

H₂O. A band at 497 cm⁻¹ cannot be assigned. A weak band at 429 cm⁻¹ is assigned to be ν_4 antisymmetric CrO₄²⁻ bending for Pr₃(OH)(CrO₄)₄ · 3.5H₂O.

Crystal structure. Crystal data and lattice constants for Ln₃(OH)(CrO₄)₄ · 3.5H₂O (*Ln* = Pr, Nd) and Ln₂(OH)₂(CrO₄)₂ (*Ln* = Gd, Tb) are given in Tables IV and V, respectively. For Ln₃(OH)(CrO₄)₄ · 3.5H₂O (*Ln* = Pr, Nd) the fractional coordinates are listed in Tables VI and VII, bond distances in Table X and O–Cr–O bond angles in Ta-

TABLE V
 EXPERIMENTAL DATA FOR CRYSTALLOGRAPHIC ANALYSES

Formula	Gd ₂ (OH) ₂ (CrO ₄) ₂	Tb ₂ (OH) ₂ (CrO ₄) ₂
Unit Cell Determination		
F.W.	580.50	583.85
Crystal size (mm)	0.05 · 0.1 · 0.1	0.05 · 0.06 · 0.1
T (°K)	296 ± 1	296 ± 1
Refl. for latt. meas.	25	25
θ range for latt. meas. (°)	7.61–13.99	7.29–13.51
a (Å)	8.2454 (4)	8.214 (1)
b (Å)	11.3835 (5)	11.348 (1)
c (Å)	12.1420 (8)	12.094 (2)
β (°)	136.590 (5)	136.59 (1)
V (Å ³)	783.2 (1)	774.7 (2)
Z	4	4
D _{calc} (Mg · m ⁻³)	4.92	5.01
μ (cm ⁻¹)	194.89	209.29
MoKα	0.71073	0.71073
F (000)	1032	1040
Space group	P2 ₁ /c (No. 14)	P2 ₁ /c (No. 14)
Data collection and refinement		
θ range for data col. (°)	2.44–35.00	2.45–34.99
Scan method	ω/2θ	ω/2θ
Scan speed in omega (° min ⁻¹)	0.92–5.50	0.52–5.50
Scan width in omega (°)	0.60 + 0.34 tan θ	0.60 + 0.34 tan θ
Variation of std. ref.	none	none
Refl. measured	3588	3558
Condition for obs. refl.	I > 3σ (I)	I > 3σ (I)
Refl. used in refinement	2941	2599
Max. shift/error	0.00	0.00
Max. in final δ/e Å ⁻³	1.207	1.334
Number of param.	127	127
S	2.798	3.230
R	0.023	0.027
Rw	0.028	0.031

Note. $w = 1/(\sigma F_o)^2$, $s = \sqrt{(\sum w(F_o - F_c)^2)/(m - n)}$.

ble XII. The crystal structure determination of these compounds is more accurate than that expressed for La₃(OH)(CrO₄)₄ · 3.5H₂O by Habekost *et al.* (2). The final R's are 0.039 and 0.023 for Pr₃(OH)(CrO₄)₄ · 3.5H₂O and Nd₃(OH)(CrO₄)₄ · 3.5H₂O, respectively, while in the case of La₃(OH)(CrO₄)₄ · 3.5H₂O (2) the final R is 0.071. For Ln₂(OH)₂(CrO₄)₂ (Ln = Gd, Tb) the fractional coordinates are listed in Tables VIII and IX, bond distances in Table

XI, and O–Cr–O bond angles in Table XIII.

For Ln₃(OH)(CrO₄)₄ · 3.5H₂O (Ln = Pr, Nd) the average Cr–O distances are 1.648 and 1.646 Å for the Pr- and Nd-compounds, respectively (Table XIV). The O–Cr–O bond angles are between 102.3° and 112.4° and between 102.6° and 112.3° for the Pr- and Nd-compounds, respectively (Table XII). Cr–O bond lengths are normal for this kind of compound.

TABLE VI

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR $\text{Pr}_3(\text{OH})(\text{CrO}_4)_4 \cdot 3.5\text{H}_2\text{O}$

Atom	x	y	z	$B[\text{\AA}^2]^a$
Pr1	0.16045(1)	0.18765(6)	0.13707(3)	0.622(5)
Pr2	0.21800(1)	0.13816(7)	-0.11098(3)	0.626(5)
Pr3	0.02331(1)	-0.14434(7)	-0.11296(3)	0.551(5)
Cr1	0.05912(4)	0.3455(2)	-0.02365(9)	0.62(2)
Cr2	0.24689(4)	-0.1555(2)	0.17157(8)	0.56(2)
Cr3	0.14645(4)	-0.1585(2)	-0.08180(9)	0.62(2)
Cr4	0.06164(4)	-0.1093(2)	0.16106(9)	0.57(2)
O1	0.1076(2)	0.288(1)	0.0147(5)	1.4(1)
O2	0.0318(2)	0.333(1)	0.0666(5)	1.3(1)
O3	0.0567(2)	0.441(1)	0.4317(6)	1.4(1)
O4	0.4591(2)	0.304(1)	0.1057(5)	1.3(1)
O5	0.2641(3)	0.025(1)	0.1215(6)	2.0(1)
O6	0.2260(2)	0.305(1)	0.2234(5)	1.5(1)
O7	0.2997(2)	0.390(1)	0.2992(5)	1.2(1)
O8	0.2537(2)	0.1610(9)	0.3966(4)	1.11(9)
O9	0.1673(2)	0.112(1)	0.3191(4)	1.2(1)
O10	0.0976(2)	0.105(1)	0.4057(5)	1.2(1)
O11	0.1534(3)	0.377(1)	0.4473(5)	1.6(1)
O12	0.3271(2)	0.482(1)	0.5014(5)	1.08(9)
O13	0.4410(2)	0.182(1)	0.2969(5)	1.5(1)
O14	0.3902(2)	0.439(1)	0.3441(5)	1.4(1)
O15	0.0402(2)	0.052(1)	0.2275(4)	1.1(1)
O16	0.4659(2)	0.415(1)	0.4451(4)	1.3(1)
O(OH)	0.2100(2)	0.3139(9)	0.0314(4)	0.91(9)
O(W)1	0.000	0.403(1)	0.250	1.4(2)
O(W)2	0.1032(2)	0.327(1)	0.2218(5)	1.5(1)
O(W)3	0.3445(3)	0.045(1)	0.3591(7)	2.3(2)
O(W)4	0.3503(3)	0.197(1)	0.1618(6)	2.1(1)

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

TABLE VII

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR $\text{Nd}_3(\text{OH})(\text{CrO}_4)_4 \cdot 3.5\text{H}_2\text{O}$

Atom	x	y	z	$B[\text{\AA}^2]^a$
Nd1	0.16066(1)	0.18676(3)	0.13641(1)	0.673(3)
Nd2	0.21807(1)	0.13859(3)	-0.11086(1)	0.650(3)
Nd3	0.02331(1)	-0.14404(3)	-0.11334(1)	0.515(2)
Cr1	0.05905(2)	0.34529(9)	-0.02392(4)	0.570(8)
Cr2	0.24709(2)	-0.15563(9)	0.17196(4)	0.567(8)
Cr3	0.14654(2)	-0.15860(9)	-0.08207(4)	0.629(8)
Cr4	0.06160(2)	-0.10938(9)	0.16060(4)	0.557(8)
O1	0.1077(1)	0.2880(5)	0.0145(2)	1.19(5)
O2	0.0315(1)	0.3322(5)	0.0661(2)	1.25(5)
O3	0.0567(1)	0.4410(5)	0.4314(3)	1.35(5)
O4	0.4593(1)	0.3040(5)	0.1060(2)	1.09(5)
O5	0.2647(1)	0.0267(5)	0.1220(3)	2.17(6)
O6	0.2258(1)	0.3047(6)	0.2231(2)	1.48(5)
O7	0.2997(1)	0.3911(5)	0.2994(2)	1.19(5)
O8	0.2536(1)	0.1603(5)	0.3971(2)	1.31(5)
O9	0.1671(1)	0.1119(5)	0.3186(2)	1.13(5)
O10	0.0978(1)	0.1022(5)	0.4056(3)	1.45(5)
O11	0.1534(1)	0.3756(5)	0.4480(3)	1.65(6)
O12	0.3263(1)	0.4825(5)	0.5007(2)	1.00(5)
O13	0.4414(1)	0.1811(5)	0.2985(3)	1.54(6)
O14	0.3897(1)	0.4405(5)	0.3442(3)	1.40(5)
O15	0.0399(1)	0.0516(5)	0.2270(2)	0.97(4)
O16	0.4660(1)	0.4141(5)	0.4460(2)	1.23(5)
O(OH)	0.21013(9)	0.3135(4)	0.0314(2)	0.83(4)
O(W)1	0.000	0.4015(6)	0.250	1.12(7)
O(W)2	0.1034(1)	0.3265(6)	0.2211(3)	1.85(6)
O(W)3	0.3445(2)	0.0426(6)	0.3590(3)	2.50(8)
O(W)4	0.3497(1)	0.1998(6)	0.1626(3)	1.89(6)

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

TABLE VIII

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR $\text{Gd}_2(\text{OH})_2(\text{CrO}_4)_2$

Atom	x	y	z	$B[\text{\AA}^2]^a$
Gd1	0.52380(3)	0.44374(2)	0.15525(2)	0.354(3)
Gd2	0.10124(3)	0.42429(2)	0.18101(2)	0.349(3)
Cr1	0.12982(9)	0.17562(7)	-0.00355(6)	0.40(1)
Cr2	0.67662(9)	0.18840(7)	0.03720(6)	0.38(1)
O1	0.2172(5)	0.3155(3)	0.0607(3)	0.76(6)
O2	0.2153(5)	0.1305(4)	-0.0821(3)	1.09(7)
O3	-0.1576(5)	0.1737(4)	-0.1455(3)	0.91(6)
O4	0.2441(6)	0.0889(4)	0.1464(4)	1.29(7)
O5	0.9291(5)	0.2377(4)	0.1135(4)	1.02(7)
O6	0.5189(5)	0.1185(4)	-0.1375(3)	0.85(6)
O7	0.5269(5)	0.3015(4)	0.0093(4)	1.03(7)
O8	0.7397(5)	0.0977(4)	0.1683(3)	1.09(7)
O(OH)1	0.2264(4)	0.5539(3)	0.0975(3)	0.51(5)
O(OH)2	0.2248(4)	0.4914(3)	-0.1276(3)	0.58(5)

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

TABLE IX
POSITIONAL PARAMETERS AND THEIR ESTIMATED
STANDARD DEVIATIONS FOR $Tb_2(OH)_2(CrO_4)_2$

Atom	x	y	z	$B[\text{Å}^2]^a$
Tb1	0.52229(3)	0.44376(2)	0.15410(2)	0.445(4)
Tb2	0.10096(3)	0.42458(2)	0.18051(2)	0.451(4)
Cr1	0.1296(1)	0.17488(8)	-0.00371(8)	0.49(1)
Cr2	0.6755(1)	0.18832(8)	0.03678(8)	0.51(1)
O1	0.2159(6)	0.3165(4)	0.0598(4)	0.84(8)
O2	0.2150(6)	0.1300(5)	-0.0828(4)	1.17(8)
O3	-0.1602(6)	0.1730(5)	-0.1460(4)	1.08(9)
O4	0.2460(7)	0.0887(5)	0.1481(4)	1.28(9)
O5	0.9282(6)	0.2396(5)	0.1129(5)	1.18(9)
O6	0.5173(6)	0.1176(4)	-0.1390(4)	0.87(8)
O7	0.5267(6)	0.3008(4)	0.0102(4)	1.00(8)
O8	0.7407(7)	0.0981(5)	0.1694(4)	1.21(9)
O(OH)1	0.2249(5)	0.5532(4)	0.0966(4)	0.55(7)
O(OH)2	0.2253(6)	0.4918(4)	-0.1280(4)	0.64(7)

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

The tetrahedra around Cr1 atom is normal, but the other Cr atoms have one disordered O–Cr–O angle caused by the oxygen double-bridge between Cr and Ln atoms. Environments of Cr atoms are described in Fig. 3. Only the environments of Cr3 and Cr4 atoms are alike. The Cr4 atom is coordinated to three different Ln3 atoms by O15 and O16 as seen in Fig. 4. One of the distances (O16–Ln3) is stretched and is about 0.2 Å longer than the average (see Table XIV) Ln–O distance. If we compare the environments of these four Cr atoms with environments of Cr atoms in $Ln_2(CrO_4)_3 \cdot 7H_2O$ and $Yb_2(OH)_2(CrO_4)_2$ compounds, we find similarities only in one case. Thus, it is very difficult to find evidence for thermal decomposition from the structural similarities. There is one additional difference between these three compounds, $Ln_3(OH)(CrO_4)_4 \cdot 3.5H_2O$ and $Ln_2(CrO_4)_3 \cdot 7H_2O$ structures contain a LnO_9 coordination polyhedra, but the $Ln_2(OH)_2(CrO_4)_2$ structure contains a LnO_8 coordination polyhedron.

TABLE X
BOND DISTANCES (Å) AND THEIR
ESTIMATED STANDARD DEVIATIONS
FOR $Pr_3(OH)(CrO_4)_4 \cdot 3.5H_2O$ and
 $Nd_3(OH)(CrO_4)_4 \cdot 3.5H_2O$

$Ln_3(OH)(CrO_4)_4 \cdot 3.5H_2O$			
Atom1	Atom2	Pr	Nd
Ln1	O1	2.399(7)	2.388(3)
	O6	2.477(7)	2.460(3)
	O7	2.593(7)	2.572(3)
	O9	2.619(6)	2.609(3)
	O12	2.527(7)	2.500(3)
	O14	2.467(7)	2.441(3)
	O(OH)	2.515(7)	2.498(3)
	O(W)2	2.536(8)	2.548(4)
Ln2	O(W)3	2.559(9)	2.536(4)
	O5	2.483(8)	2.455(4)
	O6	2.613(7)	2.604(4)
	O7	2.666(6)	2.659(3)
	O8	2.431(7)	2.415(3)
	O9	2.549(7)	2.550(3)
	O12	2.536(7)	2.517(3)
	O(OH)	2.420(6)	2.405(3)
Ln3	O(OH)	2.503(6)	2.488(3)
	O(W)4	2.550(9)	2.516(4)
	O2	2.409(7)	2.396(3)
	O3	2.432(7)	2.422(3)
	O4	2.493(8)	2.483(3)
	O10	2.430(6)	2.429(3)
	O15	2.556(6)	2.532(3)
	O15	2.487(7)	2.475(3)
Cr1	O16	2.398(6)	2.380(3)
	O16	2.705(8)	2.699(4)
	O(W)1	2.718(7)	2.697(3)
	O1	1.663(7)	1.662(3)
Cr2	O2	1.657(7)	1.652(3)
	O3	1.646(7)	1.643(3)
	O4	1.635(7)	1.628(3)
	O5	1.608(8)	1.617(4)
Cr3	O6	1.658(6)	1.649(3)
	O7	1.665(7)	1.663(3)
	O8	1.627(7)	1.630(3)
	O9	1.674(7)	1.665(3)
Cr4	O10	1.635(6)	1.630(3)
	O11	1.623(7)	1.608(4)
	O12	1.674(7)	1.688(3)
	O13	1.611(7)	1.605(4)
	O14	1.627(7)	1.639(3)
	O15	1.697(7)	1.692(3)
	O16	1.661(6)	1.660(3)

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

To estimate the possible hydrogen bonds, the hydroxyl oxygen–oxygen and water oxygen–oxygen distances less than 3.0 Å are listed in Table XV for $Ln_3(OH)(CrO_4)_4 \cdot$

TABLE XI

BOND DISTANCES (Å) AND THEIR ESTIMATED STANDARD DEVIATIONS FOR $Gd_2(OH)_2(CrO_4)_2$ AND $Tb_2(OH)_2(CrO_4)_2$

$Ln_2(OH)_2(CrO_4)_2$			
Atom 1	Atom 2	Gd	Tb
Ln1	O1	2.372(4)	2.357(5)
	O3	2.304(3)	2.290(4)
	O4	2.344(4)	2.331(4)
	O6	2.643(5)	2.628(6)
	O7	2.415(5)	2.400(6)
	O(OH)1	2.362(4)	2.353(5)
	O(OH)2	2.422(3)	2.406(3)
	O(OH)2	2.442(4)	2.429(6)
	Ln2	O1	2.571(5)
O2		2.370(4)	2.358(6)
O5		2.347(4)	2.326(5)
O6		2.435(3)	2.418(4)
O8		2.340(4)	2.332(5)
O(OH)1		2.406(4)	2.389(5)
O(OH)1		2.350(2)	2.328(3)
O(OH)2		2.457(4)	2.455(5)
Cr1	O1	1.687(4)	1.699(5)
	O2	1.627(5)	1.627(7)
	O3	1.629(3)	1.636(4)
	O4	1.639(4)	1.641(5)
Cr2	O5	1.644(4)	1.650(5)
	O6	1.678(3)	1.685(4)
	O7	1.639(4)	1.631(5)
	O8	1.634(4)	1.631(6)

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

TABLE XII

C-Cr-O BOND ANGLES (°) AND THEIR ESTIMATED STANDARD DEVIATIONS FOR $Pr_3(OH)(CrO_4)_4 \cdot 3.5H_2O$ AND $Nd_3(OH)(CrO_4)_4 \cdot 3.5H_2O$

$Ln_3(OH)(CrO_4)_4 \cdot 3.5H_2O$				
Atom 1	Atom 2	Atom 3	Pr	Nd
O1	Cr1	O2	108.9(4)	109.1(2)
O1	Cr1	O3	110.5(4)	110.3(2)
O1	Cr1	O4	108.5(4)	108.7(2)
O2	Cr1	O3	110.1(4)	110.2(2)
O2	Cr1	O4	109.2(4)	108.9(2)
O3	Cr1	O4	109.6(4)	109.5(2)
O5	Cr2	O6	110.8(4)	110.4(2)
O5	Cr2	O7	109.7(4)	109.6(2)
O5	Cr2	O8	111.2(4)	111.1(2)
O6	Cr2	O7	102.3(3)	102.6(2)
O6	Cr2	O8	111.2(4)	111.3(2)
O7	Cr2	O8	111.3(4)	111.4(2)
O9	Cr3	O10	111.3(3)	110.9(2)
O9	Cr3	O11	110.3(4)	110.9(2)
O9	Cr3	O12	102.7(3)	102.8(2)
O10	Cr3	O11	110.8(4)	111.4(2)
O10	Cr3	O12	110.4(4)	110.2(2)
O11	Cr3	O12	111.1(3)	110.3(2)
O13	Cr4	O14	108.2(4)	108.6(2)
O13	Cr4	O15	112.0(4)	112.3(2)
O13	Cr4	O16	112.4(4)	111.7(2)
O14	Cr4	O15	110.8(4)	110.8(2)
O14	Cr4	O16	110.7(4)	110.8(2)
O15	Cr4	O16	102.6(3)	102.6(2)

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

TABLE XIII

O-Cr-O BOND ANGLES (°) AND THEIR ESTIMATED STANDARD DEVIATIONS FOR $Gd_2(OH)_2(CrO_4)_2$ AND $Tb_2(OH)_2(CrO_4)_2$

$Ln_2(OH)_2(CrO_4)_2$				
Atom 1	Atom 2	Atom 3	Gd	Tb
O1	Cr1	O2	110.4(2)	110.2(3)
O1	Cr1	O3	107.8(2)	107.4(2)
O1	Cr1	O4	110.3(2)	110.3(2)
O2	Cr1	O3	107.0(2)	107.4(2)
O2	Cr1	O4	108.5(2)	108.8(3)
O3	Cr1	O4	112.8(2)	112.8(3)
O5	Cr2	O6	112.0(2)	112.1(3)
O5	Cr2	O7	107.7(2)	107.1(3)
O5	Cr2	O8	106.9(2)	107.0(2)
O6	Cr2	O7	109.6(2)	110.2(2)
O6	Cr2	O8	109.8(2)	110.0(2)
O7	Cr2	O8	110.9(3)	110.4(3)

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

TABLE XIV

THE AVERAGE BOND DISTANCES (Å) FOR $Ln_3(OH)(CrO_4)_4 \cdot 3.5H_2O$ ($Ln = Pr, Nd$) AND $Ln_2(OH)_2(CrO_4)_2$ ($Ln = Gd, Tb$)

Bond	$Ln_3(OH)$ (CrO_4) ₄ · 3.5H ₂ O		$Ln_2(OH)_2$ (CrO_4) ₂	
	Pr	Nd	Gd	Tb
Cr-O	1.648	1.646	1.647	1.650
$Ln-O$	2.51	2.50	2.41	2.40
$Ln-O(H_2O)$	2.60	2.57	—	—
$Ln-O(OH)$	2.48	2.46	2.41	2.40

TABLE XV

HYDROXYL OXYGEN-OXYGEN AND WATER OXYGEN-OXYGEN DISTANCES (LESS THAN 3.0 Å)

Oxygen-oxygen distances [Å]				
		Pr	Nd	
O(OH)	O5	2.904(10)	2.896(5)	
	O5	2.686(11)	2.668(5)	
	O6	2.706(9)	2.691(4)	
	O8	2.877(9)	2.863(5)	
	O12	2.677(10)	2.650(4)	
	O(OH)		2.996(4)	2.996(4)
	O(W)3		2.989(6)	2.989(6)
O(W)1	O2	2.966(7)	2.956(3)	
	O3	2.989(7)	2.974(3)	
	O13	2.911(10)	2.902(5)	
	O15	2.867(12)	2.846(5)	
O(W)2	O1	2.973(11)	2.953(5)	
	O2		2.996(5)	
	O9	2.817(10)	2.795(5)	
	O13	2.914(11)	2.909(5)	
	O14	2.940(11)	2.914(6)	
	O15	2.861(10)	2.857(5)	
	O(W)3	2.679(13)	2.652(5)	
O(W)3	O1	2.883(12)	2.861(6)	
	O6	2.993(12)	2.963(6)	
	O7	2.973(12)	2.945(6)	
	O11	2.793(12)	2.779(6)	
	O(W)1		2.989(6)	
	O(W)2	2.679(13)	2.652(6)	
O(W)4	O9		2.999(6)	
	O11	2.749(12)	2.779(6)	

Note. Estimation of possible hydrogen bonds for $Ln_3(OH)(CrO_4)_4 \cdot 3.5H_2O$ ($Ln = Pr, Nd$).

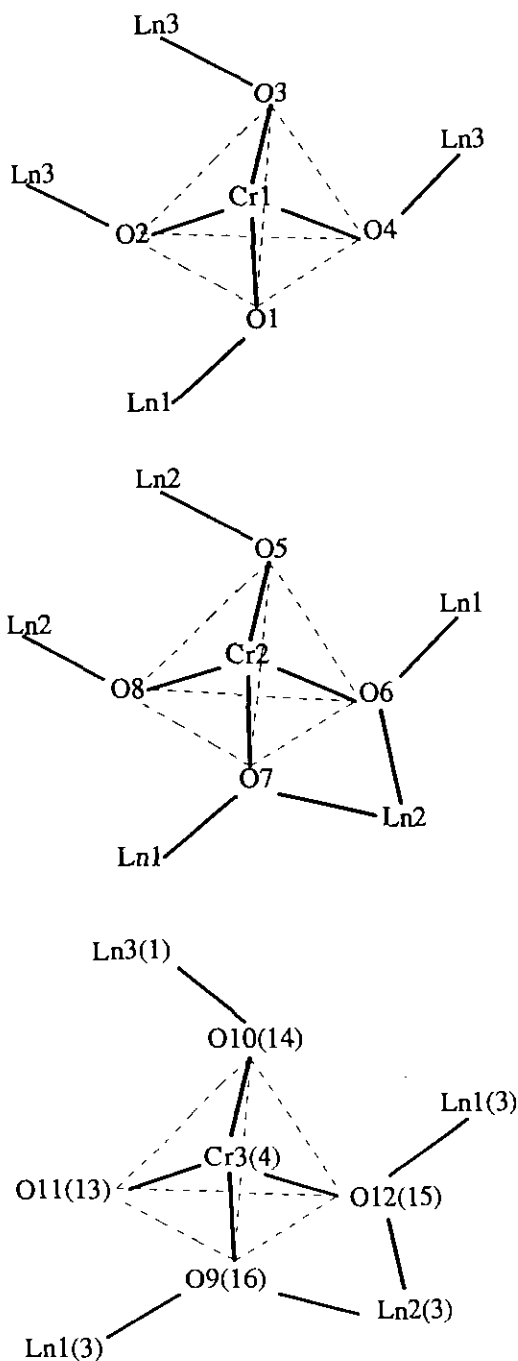


FIG. 3. Environments of Cr atoms in $Ln_3(OH)(CrO_4)_4 \cdot 3.5H_2O$ ($Ln = Pr, Nd$).

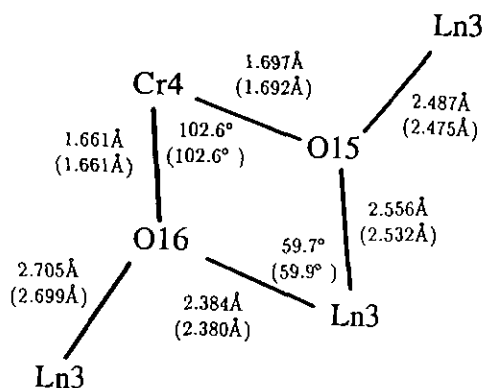


FIG. 4. Environment of Cr4 atom in $Ln_3(OH)(CrO_4)_4 \cdot 3.5H_2O$ ($Ln = Pr, Nd$). Values in parentheses are for Nd-compound.

$3.5H_2O$ ($Ln = Pr, Nd$). In $Pr_3(OH)(CrO_4)_4 \cdot 3.5H_2O$ and $Nd_3(OH)(CrO_4)_4 \cdot 3.5H_2O$, the hydroxyl groups are surrounded by five and seven oxygen groups, respectively at distances less than 3.0 \AA . The water oxygen atoms in $Pr_3(OH)(CrO_4)_4 \cdot 3.5H_2O$ are surrounded by one (O(W)4), four (O(W)1), five (O(W)3), and six (O(W)2) oxygen atoms at the distance less than 3.0 \AA . In $Nd_3(OH)(CrO_4)_4 \cdot 3.5H_2O$ the water oxygen atoms are surrounded by two (O(W)4), four (O(W)1), six (O(W)3), and seven (O(W)2) oxygen atoms at the distance

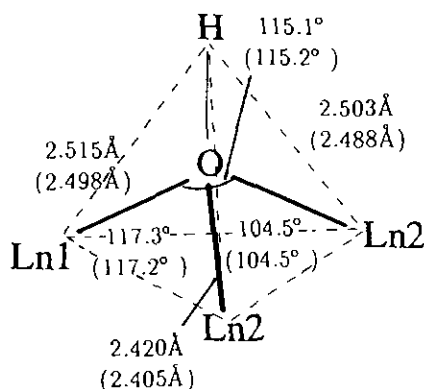


FIG. 5. Tetrahedra around hydroxyl oxygen for $Ln_3(OH)(CrO_4)_4 \cdot 3.5H_2O$ ($Ln = Pr, Nd$). Values in parentheses are for Nd-compound.

TABLE XVI
HYDROXYL OXYGEN-OXYGEN DISTANCES
(LESS THAN 3.0 \AA)

Oxygen-oxygen distances [\AA]		Gd	Tb
O(OH)1	O1	2.737 (5)	2.716 (6)
	O1		2.989 (6)
	O5		2.985 (7)
	O6	2.957 (4)	2.932 (5)
	O8	2.694 (7)	2.683 (8)
	O9	2.864 (4)	2.834 (5)
O(OH)2	O10	2.812 (6)	2.808 (8)
	O4		2.979 (9)
	O7	2.761 (5)	2.760 (6)
	O7	2.747 (5)	2.741 (6)
	O8	2.962 (5)	2.954 (6)
	O9	2.812 (6)	2.808 (8)

Note. Estimation of possible hydrogen bonds for $Ln_2(OH)_2(CrO_4)_2$ ($Ln = Gd, Tb$).

less than 3.0 \AA . All the water molecules are coordinated to the structure. O(W)1 is in a special position and has a population parameter of 0.5.

The OH-group oxygen forms a ridge between three metal atoms (see Fig. 5). The environments of OH atoms in these two compounds seem to be very much alike as expected from the similarities in the Ln^{3+} radii which happen to be 1.13 and 1.12 \AA for Pr^{3+} and Nd^{3+} , respectively.

The $Ln_2(OH)_2(CrO_4)_2$ ($Ln = Tb, Gd$) structure forms a regular three-dimensional network, in which lanthanoid atoms (eight coordinated) are connected to chromium tetrahedra in all dimensions. For $Ln_2(OH)_2(CrO_4)_2$ ($Ln = Gd, Tb$) the average Cr-O distances are 1.647 and 1.650 \AA for Gd- and Tb-compounds, respectively (Table XIV). The O-Cr-O bond angles are between 106.9° and 112.8° and between 107.0° and 112.8° for Gd- and Tb-compounds, respectively (Table XIII). If we compare the CrO_4 tetrahedras in $Gd_2(OH)_2(CrO_4)_2$, $Tb_2(OH)_2(CrO_4)_2$, and $Yb_2(OH)_2(CrO_4)_2$ (3), we find the maximum difference in O-Cr-O angles

(around the Cr atom) to be 5.8° for $\text{Gd}_2(\text{OH})_2(\text{CrO}_4)_2$, 5.4° for $\text{Tb}_2(\text{OH})_2(\text{CrO}_4)_2$ and 7.3° for $\text{Yb}_2(\text{OH})_2(\text{CrO}_4)_2$.

To estimate the possible hydrogen bonds, the hydroxyl oxygen–oxygen distances less than 3.0 Å are listed in Table XVI for $\text{Ln}_2(\text{OH})_2(\text{CrO}_4)_2$ ($\text{Ln} = \text{Gd}, \text{Tb}$). In $\text{Gd}_2(\text{OH})_2(\text{CrO}_4)_2$, the O(OH)1 and O(OH)2 are surrounded by five and four oxygen atoms, respectively at the distances less than 3.0 Å. In $\text{Tb}_2(\text{OH})_2(\text{CrO}_4)_2$ the O(OH)1 and O(OH)2 are surrounded by seven and five oxygen atoms, respectively at the distances less than 3.0 Å. If we compare the number of oxygen atoms around the hydroxyl oxygen atoms in $\text{Ln}_2(\text{OH})_2(\text{CrO}_4)_2$ ($\text{Ln} = \text{Gd}, \text{Tb}$) and in $\text{Yb}_2(\text{OH})_2(\text{CrO}_4)_2$ (3) we can see that the number of oxygen atoms around O(OH) atoms at the distances less than 3.0 Å increases with increasing atomic number. This effect can be seen in the case of $\text{Ln}_3(\text{OH})(\text{CrO}_4)_4 \cdot 3.5\text{H}_2\text{O}$ ($\text{Ln} = \text{Pr}, \text{Nd}$) compounds, as well.

References

1. J. LEPPÄ-AHO AND J. VALKONEN, *J. Solid State Chem.* **92**, 136 (1991).
2. S. HABEKOST, A. N. CHRISTENSEN, AND R. G. HAZELL, *Acta Chem. Scand.* **45**, 6 (1991).
3. J. LEPPÄ-AHO, AND J. VALKONEN, *J. Solid State Chem.* **99**, 364 (1992).
4. I. BUENO, C. PARADA, A. MONGE, AND C. R. VALLERO, *J. Solid State Chem.* **90**, 263 (1991).
5. I. BUENO, C. PARADA, O. GARCIA, E. G. PUEBLA, A. MONGE, AND C. R. VALLERO, *J. Solid State Chem.* **78**, 78 (1989).
6. O. LINDGREN, *Acta Chem. Scand. Ser. A* **31**, 167 (1977).
7. N. I. BASHILOVA, I. V. TANANAIEV, AND E. S. TAKHANOVA, *Russ. J. Inorg. Chem.* **16**, (9), 1368 (1971).
8. I. V. TANANAIEV, N. I. BASHILOVA, AND E. S. TAKHANOVA, *Russ. J. Inorg. Chem.* **16**(10), 1502 (1971).
9. N. P. ANOSHINA, T. S. BUCHENKOVA, L. N. KOMISSAROVA, AND V. M. SHATSKII, *Russ. J. Inorg. Chem.* **15**(7), 897 (1970).
10. N. WALKER AND D. STUART, *Acta Crystallogr. Sect. A* **39**, 158 (1983).
11. B. A. FRENZ, "Computing in Crystallography," (H. Schenk, R. Olthof-Hatzelkamp, H. van Konigveld, and G. C. Bassi, Eds.), p. 64, Delft University Press, Delft (1978).
12. International Tables for X-Ray Crystallography. Vol. IV, pp. 72–98. Kynoch Press, Birmingham (1974).
13. P. MAIN, S. J. FISKE, S. E. HULL, L. LESSINGER, G. GERMAIN, J.-P. DECLERCQ, AND M. M. WOOLFSON, "MULTAN11/82, System of Computer Programs for Automatic Solution of Crystal Structures," Universities of York and Louvain (1982).
14. C. K. JOHNSON, "ORTEPII," Report ORNL-5138. Oak Ridge National Laboratory, TN.
15. W. D. S. MOTHERWELL, AND W. CLEGG, "PLUTO 78," University of Cambridge (1978).
16. K. NAKAMOTO, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," 4th ed., Wiley, New York (1986).
17. K. I. PETROV, G. N. VORONSKAYA, N. I. BASHILOVA, AND E. S. TAKHANOVA, *Russ. J. Inorg. Chem.* **20**(1), 39 (1975).
18. I. BUENO, C. BARADA, R. S. PUCHE, I. L. BOTTO, AND E. J. BARAN, *J. Less-Common Met.* **169**, 105 (1991).