Synthesis, Thermal Behavior, Infrared Spectra, and Crystal Structure of $Yb_2(OH)_2(CrO_4)_2$ and $[Yb_2(OH)_2(CrO_4)_2(H_2O)_{2.5}] \cdot 0.5H_2O$

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The crystal structures of $Yb_2(OH)_2(CrO_4)_2$ and $Yb_2(OH)_2(CrO_4)_2 \cdot 3H_2O$ were determined by conventional single-crystal X-ray diffraction technique. Crystals of $Yb_2(OH)_2(CrO_4)_2$ are monoclinic, space group $P2_1/c$ (No. 14) with $a = 8.057(2)$ Å, $b = 11.297(1)$ Å, $c = 11.915(1)$ Å and $\beta = 136.67(3)$, $Z = 4$, $D_x = 5.46$ Mg m^{-3}. Crystals of $Yb_2(OH)_2(CrO_4)_2 \cdot 3H_2O$ are orthorhombic, space group $Pccn$ (No. 56) with $a = 10.884(2)$ Å, $b = 12.023(1)$ Å, $c = 16.033(8)$ Å, $Z = 8$, $D_x = 4.22$ Mg m^{-3}. In both compounds the coordination polyhedron of the eight oxygen atoms around ytterbium atoms is square antiprism. Structures form a three-dimensional network. Thermal behavior was investigated and IR spectra were recorded for both compounds. The thermal decomposition of $Yb_2(OH)_2(CrO_4)_2$ proceeds by a different mechanism than that of $Yb_2(OH)_2(CrO_4)_2 \cdot 3H_2O$. © 1992 Academic Press, Inc.
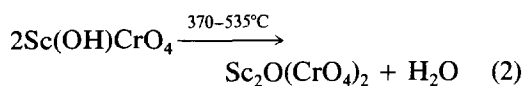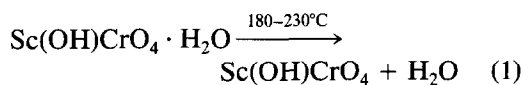
Introduction

There are several reports in the literature on lanthanoid hydroxide chromates (VI). Hydroxide chromates (VI) are prepared in solution. Bahilova and Nelyapina have synthesized the lanthanoid hydroxide chromates $Dy(OH)CrO_4 \cdot 2H_2O$ (*1*), $Er(OH)CrO_4 \cdot 1.5H_2O$ (*2*), $Tm(OH)CrO_4 \cdot 1.5H_2O$ (*3*), and $Yb(OH)CrO_4 \cdot 2H_2O$ (*4*). Bueno *et al.* have synthesized $Ln(OH)CrO_4$ ($Ln = Y$, Dy–Lu) (*5, 6*) and Habekost *et al.* report the synthesis of $La_3(OH)_2(CrO_4)_4 \cdot 3.5H_2O$ (*7*). Anoshina *et al.* report the rare earth compound $Sc(OH)(CrO_4) \cdot H_2O$ (*8*).

Five structures of lanthanoid chromates have been published: for $La(OH)CrO_4$ (*5*), $Ce(CrO_4)_2 \cdot 2H_2O$ (*9*), and $Ln_2[(CrO_4)_3(H_2O)_5] \cdot 2H_2O$ (where Ln is Nd or Eu) (*10*),

and for $La_3(OH)(CrO_4)_4 \cdot 3.5H_2O$ and $La_2(CrO_4)_3 \cdot 7H_2O$ (*7*). The last compound is isostructural with the corresponding Nd and Eu compounds. The structure of $Er(OH)CrO_4$ is the most recent to be published (*6*) and it is isostructural with one of our title compounds.

The only published thermal decomposition mechanism for basic rare earth chromates is that for $Sc(OH)(CrO_4) \cdot H_2O$. According to Anoshina *et al.* (*8*), $Sc(OH)(CrO_4) \cdot H_2O$ decomposes in three stages. The decomposition is the same in air and in an inert atmosphere and may be represented as follows:

$$Sc(OH)CrO_4 \cdot H_2O \xrightarrow{180–230°C} Sc(OH)CrO_4 + H_2O \quad (1)$$

$$2Sc(OH)CrO_4 \xrightarrow{370–535°C} Sc_2O(CrO_4)_2 + H_2O \quad (2)$$

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$$Sc_2O(CrO_4)_2 \xrightarrow{535-560°} Sc_2O_3 + Cr_2O_3 + 1.5O_2. \quad (3)$$
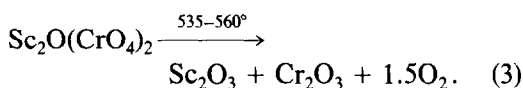
Experimental

Synthesis. Crystals of $Yb_2(OH)_2(CrO_4)_2$ and $Yb_2(OH)_2(CrO_4)_2 \cdot 3H_2O$ were synthesized in a steel autoclave with a Teflon lining. In the case of $Yb_2(OH)_2(CrO_4)_2$, 300 mg of Yb_2O_3 was mixed with 8 cm³ 0.6 mol dm⁻³ H_2CrO_4. The mixture was put in an autoclave and the temperature was raised to 140–160°C and then decreased slowly (5 degrees per day) to room temperature. The estimated maximum pressure in the autoclave was about 3.6×10^5–6.2×10^5 Nm⁻². In the case of $[Yb_2(OH)_2(CrO_4)_2(H_2O)_{2.5}] \cdot 0.5H_2O$, 300 mg of Yb_2O_3 was mixed with 8 cm³ 0.3 mol dm⁻³ H_2CrO_4. The mixture was put in an autoclave and the temperature was raised to 140°C (maximum pressure was about 3.6×10^5 Nm⁻²) and then decreased slowly (5 degrees per day) to room temperature. The crystals were filtered out without washing. The crystals of $Yb_2(OH)_2(CrO_4)_2$ were brown parallelepipedon and the crystals of $Yb_2(OH)_2(CrO_4)_2 \cdot 3H_2O$ yellow needles.

Thermal analysis and IR spectra. Thermal behavior was determined with a Perkin–Elmer TG-2 thermobalance. Sample size was 4.462 mg for $Yb_2(OH)_2(CrO_4)_2$ and 4.182 mg for $Yb_2(OH)_2(CrO_4)_2 \cdot 3H_2O$, heating rate 1.0° min⁻¹ and air flow 70 cm³ min⁻¹. The IR spectra were recorded with a Perkin–Elmer 283 IR spectrometer. The KBr method was used with a scan time of 12 min and scan range of 4000 to 200 cm⁻¹.

Crystal structure determination. X-ray determinations were made for $Yb_2(OH)_2(CrO_4)_2$ and $Yb_2(OH)_2(CrO_4)_2 \cdot 3H_2O$ using an Enraf–Nonius CAD4 automatic four-circle diffractometer equipped with a graphite monochromator ($MoK\alpha$-radiation = 0.71073 Å).

Cell constants were obtained from a least-squares refinement. Conditions for unit cell determination and data collection are summarized in Table IV. 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 and an empirical absorption (ϕ-scan) correction was measured for $Yb_2(OH)_2(CrO_4)_2$. For $Yb_2(OH)_2(CrO_4)_2 \cdot 3H_2O$, absorption correction was calculated using the program DIFABS (*11*).

All calculations were done with a micro VAX II computer using the Enraf–Nonius structure determination package SDP-plus (*12*). Scattering factors for neutral atoms and anomalous dispersion corrections for all atoms were taken from International Tables for X-Ray Crystallography (*13*). The SDP-plus package incorporates the direct methods program MULTAN (*14*) and the plotting programs ORTEP (*15*) and PLUTO (*16*).

Positions of ytterbium and chromium atoms were established by direct methods and the 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. The thermal behaviour of the investigated compounds is described in Tables I and II and Figs. 1 and 2. $Yb_2(OH)_2(CrO_4)_2$ dissociates to $YbCrO_3$ in two endothermic reactions. First, in temperature range 480–595°C, two OH groups are split off as one H_2O molecule and one oxygen (Eq. (4)). The remaining $YbCrO_4$ then dissociates to $YbCrO_3$ (Eq. (5)) before 725°C. Decomposition mechanisms are based solely on the TGA results and have not been verified by identification of the intermediate products. The thermal decomposition of $Yb_2(OH)_2(CrO_4)_2$ pro-

TABLE I
THERMAL DECOMPOSITION OF $Yb_2(OH)_2(CrO_4)_2$

T (°C)	Weight loss (%) Δ Obs.	Δ Theor.	Lost in reaction	Eq. No.
30–480	1.49[a]	0		
480–595	5.83	5.56	H_2O, $0.5O_2$	(4)
595–725	5.25	5.23	O_2	(5)
30–725	12.57	10.79	[b]	(6)

[a] Crystals are not pure, the most probable impurity is CrO_3. In the case of CrO_3 the reaction $CrO_3 \rightarrow Cr_2O_3 + 1.5O_2$ takes place in temperature range 30–400°C.
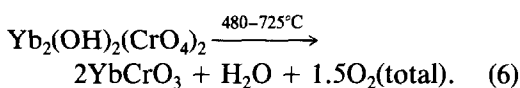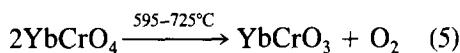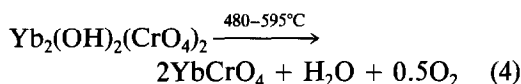
[b] Total reaction.

TABLE II
THERMAL DECOMPOSITION OF $Yb_2(OH)_2(CrO_4)_2 \cdot 3H_2O$

T (°C)	Weight loss (%) Δ Obs.	Δ Theor.	Lost in reaction	Eq. No.
30– 85	1.79	1.35	$0.5H_2O$	(7)
85–130	3.79	4.06	$1.5H_2O$	(7)
130–295	2.67	2.70	H_2O	(7)
295–470	2.65	2.70	H_2O	(8)
470–605	2.29	2.40	$0.5O_2$	(9)
607–725	4.68	4.80	O_2	(10)
30–725	17.87	18.02	[a]	(11)

[a] Total reaction.

ceeds by a mechanism not reported previously.

$$Yb_2(OH)_2(CrO_4)_2 \xrightarrow{480-595°C} 2YbCrO_4 + H_2O + 0.5O_2 \quad (4)$$

$$2YbCrO_4 \xrightarrow{595-725°C} YbCrO_3 + O_2 \quad (5)$$

$$Yb_2(OH)_2(CrO_4)_2 \xrightarrow{480-725°C} 2YbCrO_3 + H_2O + 1.5O_2(total). \quad (6)$$

The thermal reaction is violent: when the temperature is raised above 390°C the sample splashes about. To determine the thermal behavior, the sample therefore, must be
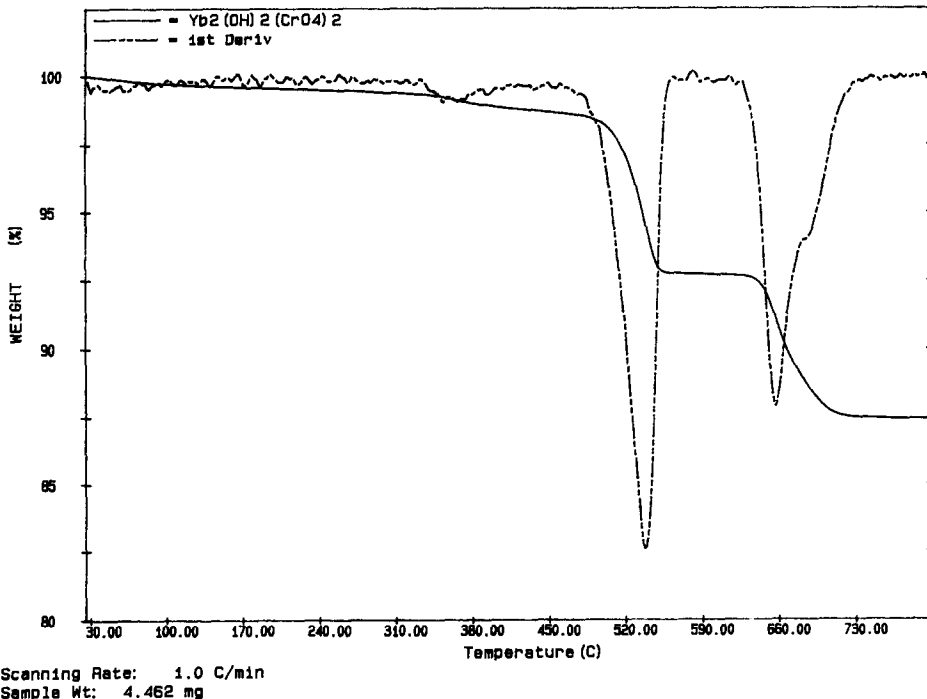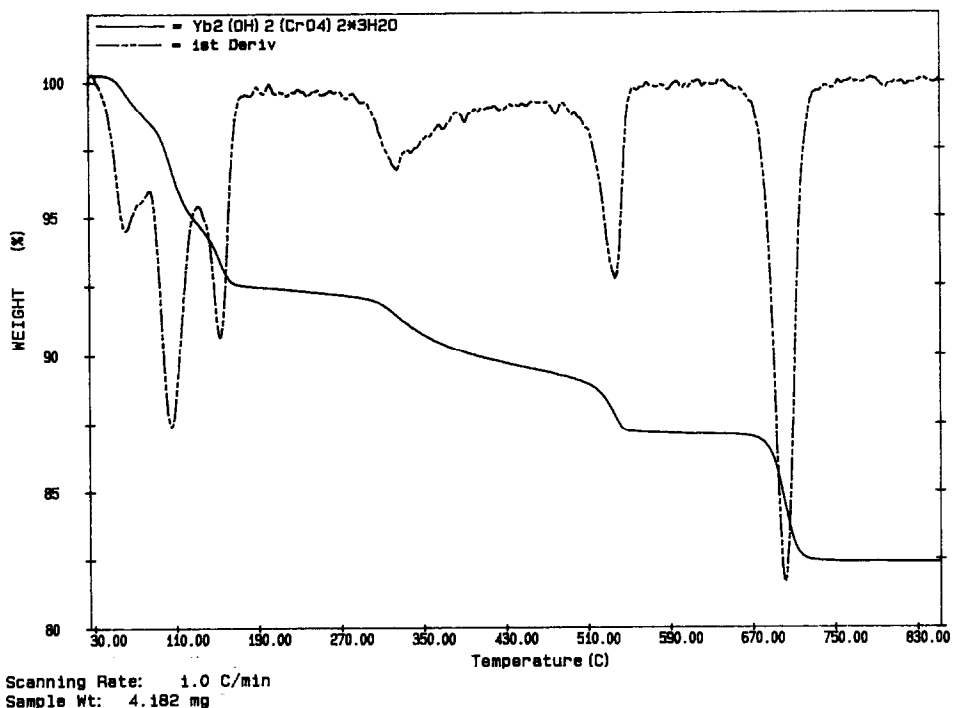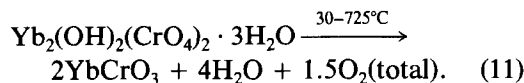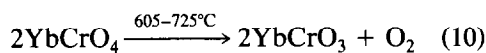

Scanning Rate: 1.0 C/min
Sample Wt: 4.462 mg

FIG. 1. TG and DTG curves for $Yb_2(OH)_2(CrO_4)_2$.

FIG. 2. TG and DTG curves for $Yb_2(OH)_2(CrO_4)_2 \cdot 3H_2O$.

covered with a cap. There was some mass loss between 30 and 400°C, due to possible CrO_3 impurity, that was crystallized with the product. CrO_3 decomposes to Cr_2O_3 releasing oxygen (see Table I).

In the case of $Yb_2(OH)_2(CrO_4)_2 \cdot 3H_2O$, water molecules leave the compound (Eq. (7)) in three stages (see Fig. 2): in the first stage a half molecule, then one-and-a-half molecules, and finally the rest of the water (0.5 H_2O). The structure of this anhydrous $Yb_2(OH)_2(CrO_4)_2$ is different compared to the synthesized anhydrous $Yb_2(OH)_2(CrO_4)_2$. The difference was confirmed using X-ray powder diffraction. This explains, why the thermal decomposition of this compound differs from that of $Yb_2(OH)_2(CrO_4)_2$ (see Eq. (8)). The further decomposition of $Yb_2(OH)_2(CrO_4)_2$ to $YbCrO_4$ occurs in two separate processes (Eqs. (8) and (9)), and the intermediate product is ytterbium oxochromate (VI).

$$Yb_2(OH)_2(CrO_4)_2 \cdot 3H_2O \xrightarrow{30-295°C}$$
$$Yb_2(OH)_2(CrO_4)_2 + 3H_2O \quad (7)$$

$$Yb_2(OH)_2(CrO_4)_2 \xrightarrow{295-470°C}$$
$$Yb_2O(CrO_4)_2 + H_2O \quad (8)$$

$$Yb_2O(CrO_4)_2 \xrightarrow{470-605°C} 2YbCrO_4 + 0.5O_2$$
$$(9)$$

$$2YbCrO_4 \xrightarrow{605-725°C} 2YbCrO_3 + O_2 \quad (10)$$

$$Yb_2(OH)_2(CrO_4)_2 \cdot 3H_2O \xrightarrow{30-725°C}$$
$$2YbCrO_3 + 4H_2O + 1.5O_2(\text{total}). \quad (11)$$
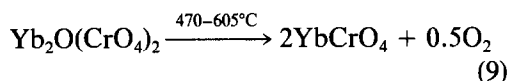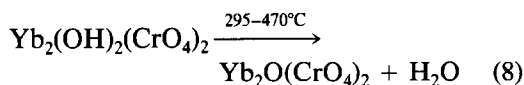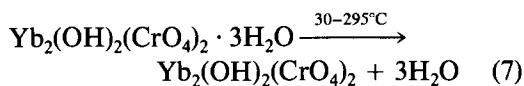
Evidently it is easier for an OH group to leave from $Yb_2(OH)_2(CrO_4)_2 \cdot 3H_2O$ than from $Yb_2(OH)_2(CrO_4)_2$ (see the temperature range), and it follows that the structures of the decomposition product $Yb_2(OH)_2(CrO_4)_2$ and the compound $Yb_2(OH)_2(CrO_4)_2$ (discussed above) are different. The reac-

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TABLE III

IR-SPECTRAL DATA (cm^{-1}) OF Yb$_2$(OH)$_2$(CrO$_4$)$_2$ AND
Yb$_2$(OH)$_2$(CrO$_4$)$_2$ · 3H$_2$O

Yb$_2$(OH)$_2$(CrO$_4$)$_2$ · nH$_2$O		
(n = 0)	(n = 3)	Assignment
3530 w	3480–3100 vb	} ν OH
3490 w,sp		
	1627 s	δ H$_2$O
	1580 sh,m	
946 sh		}
925 s	932 s	} ν_3 CrO$_4$
890 w,sp	910 sh	
853 m	857 m	} ν_1 CrO$_4$
797 b,s	780 w,b	
700 sp	732 w	} δ YbOH
672 sp		
400 s,sp	440 s,sp	} ν_4 CrO$_4$
327 m	316 m	
250 w,sp	250 w,sp	} T,L
220 m,sp	216 m,sp	

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

tion scheme for Yb$_2$(OH)$_2$(CrO$_4$)$_2$ · 3H$_2$O is the same as for Sc(OH)CrO$_4$ · H$_2$O (reactions (1)–(3)). (The stoichiometry of these reactions is the same.)

IR-spectral data for both compounds are listed in Table III. Assignments were made according to the literature.

Crystal structure. Crystal data and constants for Yb$_2$(OH)$_2$(CrO$_4$)$_2$ and Yb$_2$(OH)$_2$(CrO$_4$)$_2$ · 3H$_2$O are given in Table IV. Fractional coordinates are listed in Tables V and VI, bond distances in Table VII, and O–Cr–O bond angles in Table VIII.

In the structures of both compounds with different environments (see Figs. 3 and 4), there are two kinds of Yb atoms. In both compounds Yb atoms are coordinated to eight oxygens and the coordination polyhedra are square antiprisms.

Oxygens O1–O4 belong to Cr1 and O5–O8 to Cr2 atoms. O9 and O10 are OH group oxygens. In the case of Yb$_2$(OH)$_2$

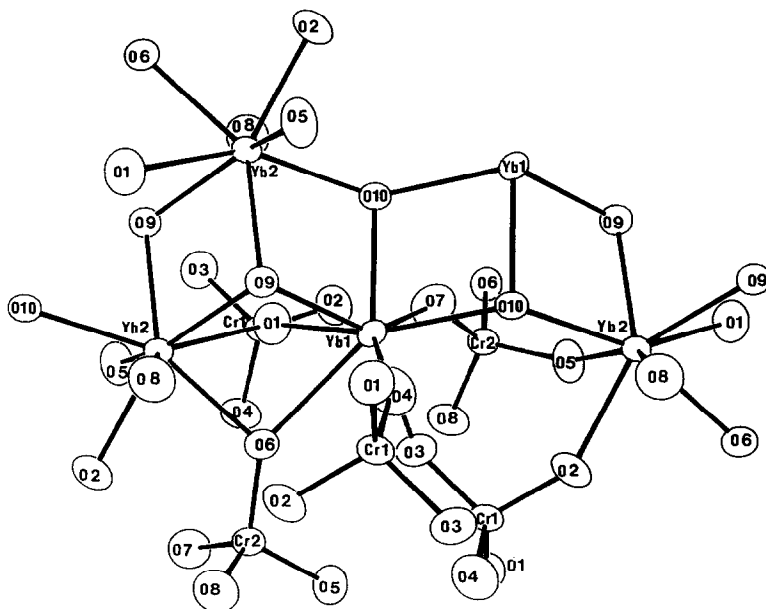FIG. 3. Environments of Yb1 and Yb2 atoms in Yb$_2$(OH)$_2$(CrO$_4$)$_2$.

TABLE IV

EXPERIMENTAL DATA FOR CRYSTALLOGRAPHIC ANALYSES

Formula	Yb$_2$(OH)$_2$(CrO$_4$)$_2$	Yb$_2$(OH)$_2$(CrO$_4$)$_2$ · 3H$_2$O
Unit cell determination		
F.W.	612.08	666.13
Crystal size (mm)	0.18 · 0.05 · 0.05	0.13 · 0.03 · 0.03
T(°K)	296 ± 1	296 ± 1
Refl. for latt. meas.	25	25
θ range for latt. meas. (°)	10–16	9–15
a(Å)	8.057(2)	10.884(2)
b(Å)	11.297(1)	12.023(1)
c(Å)	11.915(1)	16.033(8)
β (°)	136.67(3)	90
V(Å^3)	744.2(1)	2098.2(2)
Z	4	8
D_{calc}(Mg · m^{-3})	5.463	4.217
μ(cm^{-1})	276.6	196.6
MoKα	0.71073	0.71073
F(000)	1080	2400
Space group	$P2_1/c$ (No: 14)	$Pccn$ (No: 56)
Data collection and refinement		
θ range for data col. (°)	2.49–40.00	2.12–35.00
Scan method	$\omega/2\theta$	$\omega/2\theta$
Scan speed in ometa (° min^{-1})	0.87–16.50	0.92–16.50
Scan width in omega (°)	0.55 + 0.34 tan θ	0.60 + 0.34 tan θ
Variation of std. ref.	None	None
Refl. measured	4776	5134
Condition for obs. refl.	$I > 3\sigma(I)$	$I > 3\sigma(I)$
Refl. used in refinement	3499	2177
Abs. corr. (min/max)	0.61/1.00	0.94/1.06
Max. shift/error	0.00	0.00
Max. in final δ/eÅ^3	2.4(3)	1.5(3)
Number of param.	128	156
S	2.51	0.94
R	2.1	2.5
R_w	2.1	3.1

Note.

$$w = \frac{1}{(\sigma F_o)^2} \qquad s = \sqrt{\frac{\Sigma\, w(F_o - F_c)^2}{(m - n)}}.$$

(CrO$_4$)$_2$ · 3H$_2$O, oxygens O11–O14 belong to water molecules. O11 and O14 are in special positions and their population parameters are 0.5.

For Yb$_2$(OH)$_2$(CrO$_4$)$_2$ the average Cr–O distance is 1.653 (Table IX) Å and the O–Cr–O bond angles are between 106.5° and 113.6° (Table VIII). For Yb$_2$(OH)$_2$(CrO$_4$)$_2$ · 3H$_2$O, the average Cr–O distance is 1.650 Å (Table IX) and the O–Cr–O bond angles are between 107.9° and 112.3° (Table VIII). Cr–O bond lengths are normal for this kind of compound and the oxygen atoms form normal tetrahedra around Cr atoms.
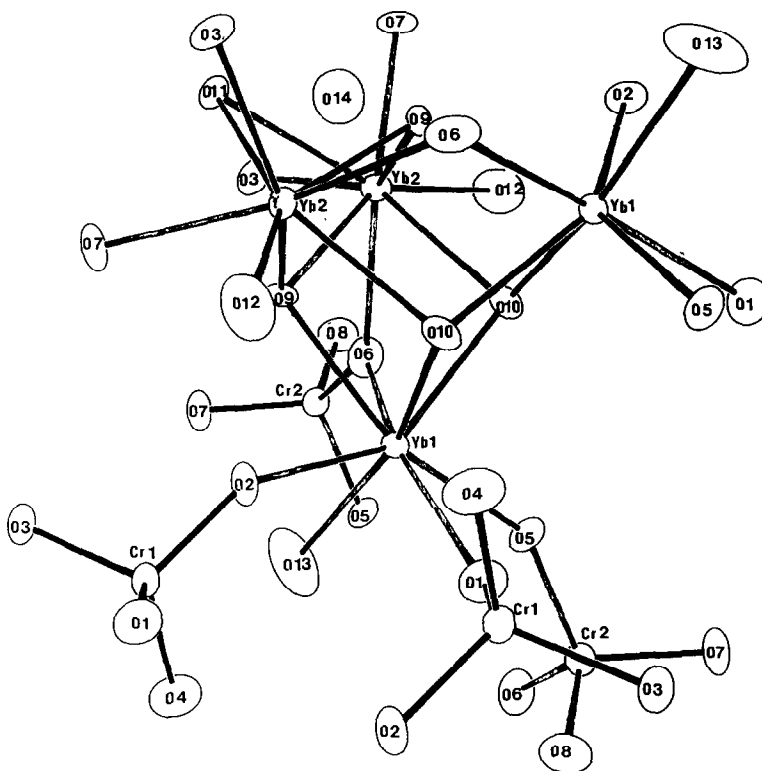
FIG. 4. Environments of Yb1 and Yb2 atoms in $Yb_2(OH)_2(CrO_4)_2 \cdot 3H_2O$.

TABLE V

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD
DEVIATIONS FOR $Yb_2(OH)_2(CrO_4)_2$

Atom	x	y	z	$B(\text{Å}^2)^a$
Yb1	0.51787(2)	0.44282(1)	0.15105(1)	0.628(2)
Yb2	0.09904(2)	0.42586(1)	0.17881(1)	0.634(2)
Cr1	0.13060(8)	0.17264(5)	−0.00262(5)	0.71(1)
Cr2	0.67577(8)	0.18874(5)	0.03861(5)	0.73(1)
O1	0.2178(4)	0.3143(2)	0.0601(3)	1.10(5)
O2	0.2145(4)	0.1257(3)	−0.0849(3)	1.30(5)
O3	−0.1667(4)	0.1696(3)	−0.1484(3)	1.25(6)
O4	0.2544(4)	0.0870(3)	0.1545(3)	1.35(5)
O5	0.9301(4)	0.2434(3)	0.1125(3)	1.18(5)
O6	0.5119(4)	0.1167(3)	−0.1394(2)	1.05(5)
O7	0.5195(4)	0.3005(3)	0.0111(3)	1.36(6)
O8	0.7527(4)	0.0969(3)	0.1762(3)	1.27(5)
O9	0.2262(3)	0.5506(2)	0.0967(2)	0.74(4)
O10	0.2297(3)	0.4939(2)	−0.1257(2)	0.84(5)

^{a} Anisotropically refined atoms are given in the form of the iso-
tropic 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 VI

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD
DEVIATIONS FOR $Yb_2(OH)_2(CrO_4)_2 \cdot 3H_2O$

Atom	x	y	z	$B(\text{Å}^2)^a$
Yb1	0.26421(2)	0.09308(2)	0.45244(2)	0.670(4)
Yb2	0.08407(2)	0.24561(3)	0.29703(2)	0.770(4)
Cr1	0.4955(1)	0.6057(1)	0.40062(7)	0.80(2)
Cr2	0.4227(1)	0.4867(1)	0.14913(8)	0.86(2)
O1	0.6397(5)	0.5850(5)	0.4313(4)	1.3(1)
O2	0.4137(5)	0.4910(5)	0.4028(3)	1.17(9)
O3	0.4960(5)	0.6562(5)	0.3043(4)	1.3(1)
O4	0.4334(5)	0.6960(5)	0.4639(4)	1.6(1)
O5	0.3978(5)	0.4188(4)	0.0600(4)	1.2(1)
O6	0.5192(6)	0.5903(5)	0.1304(4)	1.7(1)
O7	0.4804(5)	0.3980(5)	0.2168(4)	1.22(9)
O8	0.2936(6)	0.5336(5)	0.1863(4)	1.7(1)
O9	0.2471(5)	0.3656(4)	0.3142(3)	0.81(8)
O10	0.3655(5)	0.2595(4)	0.4371(3)	0.93(9)
O11	0.250	0.250	0.1726(5)	1.3(1)
O12	0.6088(6)	0.3052(6)	0.3523(5)	2.1(1)
O13	0.6807(6)	0.4086(5)	0.0543(6)	2.6(1)
O14	0.750	0.250	0.1732(8)	3.0(2)

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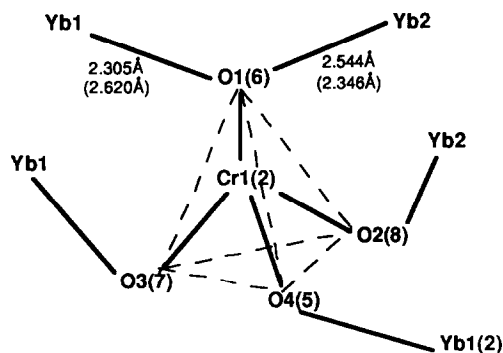

FIG. 5. Environments of Cr1 and Cr2 atoms in $Yb_2(OH)_2(CrO_4)_2$.

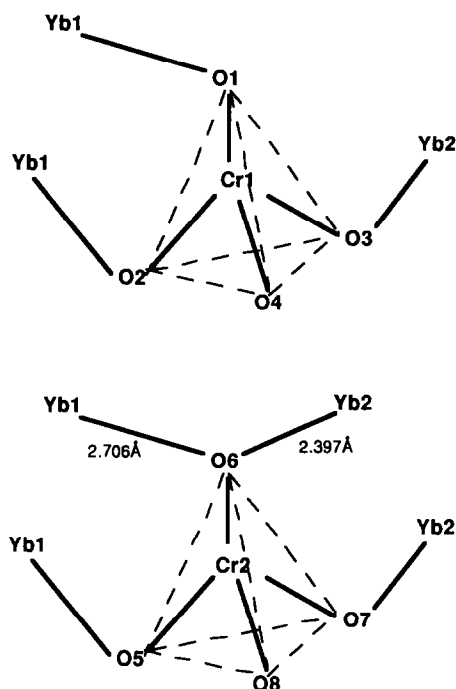FIG. 6. Environments of Cr1 and Cr2 atoms in $Yb_2(OH)_2(CrO_4)_2 \cdot 3H_2O$.

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TABLE VII

BOND DISTANCES (Å) AND THEIR ESTIMATED STANDARD
DEVIATIONS FOR $Yb_2(OH)_2(CrO_4)_2$ AND $Yb_2(OH)_2(CrO_4)_2 \cdot 3H_2O$

Compound					
$Yb_2(OH)_2(CrO_4)_2$			$Yb_2(OH)_2(CrO_4)_2 \cdot 3H_2O$		
Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Yb1	O1	2.305(3)	Yb1	O1	2.307(6)
Yb1	O3	2.224(2)	Yb1	O2	2.325(6)
Yb1	O4	2.281(2)	Yb1	O5	2.260(6)
Yb1	O6	2.620(4)	Yb1	O6	2.706(6)
Yb1	O7	2.323(4)	Yb1	O9	2.274(5)
Yb1	O9	2.283(3)	Yb1	O10	2.298(5)
Yb1	O10	2.337(2)	Yb1	O10	2.280(5)
Yb1	O10	2.373(3)	Yb1	O13	2.300(6)
Yb2	O1	2.544(4)	Yb2	O3	2.225(6)
Yb2	O2	2.306(3)	Yb2	O6	2.397(6)
Yb2	O5	2.272(3)	Yb2	O7	2.264(6)
Yb2	O6	2.346(2)	Yb2	O9	2.304(5)
Yb2	O8	2.268(3)	Yb2	O9	2.289(5)
Yb2	O9	2.334(3)	Yb2	O10	2.313(5)
Yb2	O9	2.280(2)	Yb2	O11	2.692(6)
Yb2	O10	2.409(3)	Yb2	O12	2.359(6)
Cr1	O1	1.688(3)	Cr1	O1	1.663(5)
Cr1	O2	1.633(4)	Cr1	O2	1.642(6)
Cr1	O3	1.644(2)	Cr1	O3	1.660(6)
Cr1	O4	1.649(3)	Cr1	O4	1.634(6)
Cr2	O5	1.653(3)	Cr2	O5	1.668(6)
Cr2	O6	1.682(3)	Cr2	O6	1.657(6)
Cr2	O7	1.639(3)	Cr2	O7	1.646(6)
Cr2	O8	1.634(3)	Cr2	O8	1.627(6)

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

Figure 5 shows the way Yb atoms are coordinated to the CrO_4 group in $Yb_2(OH)_2(CrO_4)_2$. It can be seen that the environments of the Cr1 and Cr2 atoms are equivalent. Because O1(6) (i.e., O1 and O6) forms a bridge between Yb1 and Yb2, one Yb–O bond is stretched (Yb1–O6 and Yb2–O1). In the case of $Yb_2(OH)_2(CrO_4)_2 \cdot 3H_2O$ the CrO_4 group environments are different (see Fig. 6). $Cr(2)O_4$ group (not $Cr(1)O_4$) acts as a bridging ligand between two Yb atoms and bonding is like that in $Yb_2(OH)_2(CrO_4)_2$.

In the $Yb_2(OH)_2(CrO_4)_2 \cdot 3H_2O$ structure, two-and-a-half of the three water molecules are coordinated to the structure. The uncoordinated half water molecule (oxygen O14) is located in holes of the structure. The formula of this compound should therefore be expressed as $[Yb_2(OH)_2(CrO_4)_2(H_2O)_{2.5}] \cdot 0.5H_2O$. As seen in the TG curve, and as expected the loss of the noncoordinated half water molecule occurs as separate process (first process).

The OH group oxygen can form a bridge between three metal atoms (expecially in the case of transition metals). It can be seen at the bond distance table and Figs. 7 and 8 that the hydroxyl oxygens O9 and O10 (in

TABLE VIII

O–Cr–O Bond Angles (°) and Their Estimated Standard Deviations for $Yb_2(OH)_2(CrO_4)_2 \cdot nH_2O$ ($n = 0$ or $n = 3$)

Atom 1	Atom 2	Atom 3	Angle (°)	
			$n = 0$	$n = 3$
O1	Cr1	O2	110.7(2)	112.3(3)
O1	Cr1	O3	107.8(1)	109.1(3)
O1	Cr1	O4	109.9(1)	107.9(3)
O2	Cr1	O3	106.3(1)	109.2(3)
O2	Cr1	O4	108.6(2)	108.7(3)
O3	Cr1	O4	113.6(2)	109.7(3)
O5	Cr2	O6	112.6(2)	108.4(3)
O5	Cr2	O7	107.1(2)	108.1(3)
O5	Cr2	O8	106.5(1)	110.1(3)
O6	Cr2	O7	109.6(1)	111.4(3)
O6	Cr2	O8	109.6(1)	110.7(3)
O7	Cr2	O8	111.4(2)	108.3(3)

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

both compounds) have three Yb neighbors arranged in pyramid form on one side of the hydroxyl oxygen. In $Yb_2(OH)_2(CrO_4)_2 \cdot 3H_2O$, the Yb–O–Yb bond angles are in the range of 101.22°–111.62° and the hydrogen atom is at the apex of the pyramid. In $Yb_2(OH)_2(CrO_4)_2$, two Yb–O–Yb angles are near the tetrahedral bonding (101.97° and
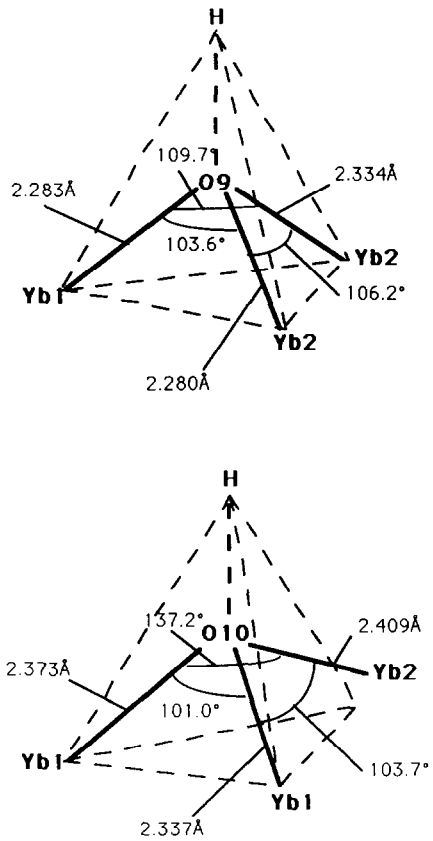

FIG. 7. Tetrahedra around hydroxo oxygens (O9 and O10) for $Yb_2(OH)_2(CrO_4)_2$.

TABLE IX

AVERAGE BOND DISTANCES

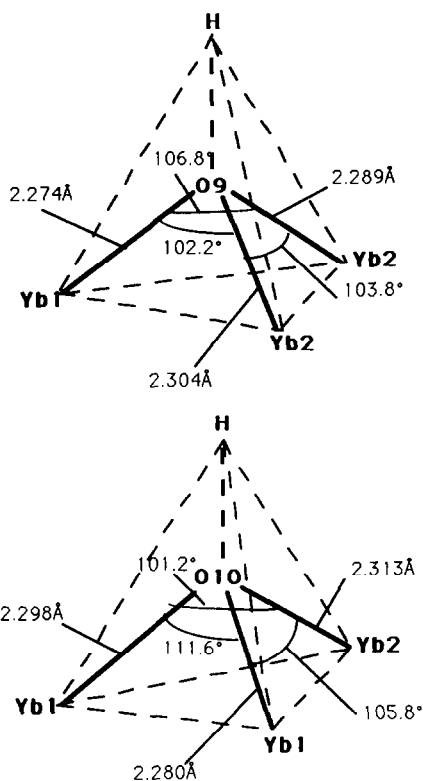| Compound	Bond (Å)			
	Cr–O	Ln–O(Cr)	Ln–O(H₂O)	Ref.
$Yb_2(OH)_2(CrO_4)_2$	1.653	2.344	—	This work
$Yb_2(OH)_2(CrO_4)_2 \cdot 3H_2O$	1.650	2.355	2.450	This work
$Nd_2(CrO_4)_3 \cdot 7H_2O$	1.65	2.49	2.52	*(10)*
$Eu_2(CrO_4)_3 \cdot 7H_2O$	1.65	2.45	2.48	*(10)*
$La_2(CrO_4)_3 \cdot 7H_2O$	1.65	2.54	2.60	*(7)*
$La_3(OH)(CrO_4)_4 \cdot 3.5H_2O$	1.64	2.56	2.60	*(7)*
$La(OH)CrO_4$	1.65	2.58	—	*(5)*
$Ce(CrO_4)_2 \cdot 2H_2O$	1.64	2.34	2.50	*(9)*
$KLa(CrO_4)_2$	1.65	2.57	—	*(17)*
$KTb(CrO_4)_2$	1.64	2.40	—	*(18)*

FIG. 8. Tetrahedra around hydroxo oxygens (O9 and O10) for $Yb_2(OH)_2(CrO_4)_2 \cdot 3H_2O$.

TABLE X

HYDROXYL OXYGEN–OXYGEN DISTANCES (LESS THAN 3.0 Å). ESTIMATION OF POSSIBLE HYDROGEN BONDS FOR $Yb_2(OH)_2(CrO_4)_2$

Oxygen–oxygen distances (Å)		
O9	O1	2.698(4)
	O1	2.984(4)
	O4	2.903(3)
	O5	2.943(4)
	O6	2.868(3)
	O8	2.636(5)
	O9	2.774(3)
	O10	2.749(5)
O10	O2	2.991(3)
	O4	2.912(5)
	O7	2.713(4)
	O7	2.706(4)
	O8	2.866(4)
	O9	2.749(5)
	O10	2.996(3)

TABLE XI

WATER MOLECULE OXYGEN–OXYGEN AND HYDROXYL OXYGEN–OXYGEN DISTANCES (LESS THAN 3.0 Å). ESTIMATION OF POSSIBLE HYDROGEN BONDS FOR $Yb_2(OH)_2(CrO_4)_2 \cdot 3H_2O$

Oxygen–oxygen distances (Å)		
O9	O2	2.752(8)
	O6	2.688(9)
	O8	2.924(8)
	O9	2.780(7)
	O10	2.678(7)
	O10	2.765(7)
	O11	2.663(8)
O10	O1	2.820(8)
	O2	2.884(8)
	O4	2.756(8)
	O5	2.932(8)
	O6	2.624(8)
	O9	2.678(7)
	O9	2.765(7)
	O10	2.539(6)
O11	O1	2.855(8)
	O9	2.663(8)
O12	O4	2.98(1)
	O6	2.950(9)
	O7	2.813(9)
	O8	2.861(9)
O13	O2	2.892(8)
	O4	2.856(9)
	O5	2.898(9)
	O14	2.80(1)
O14	O3	2.928(6)
	O13	2.80(1)

103.72°), while the third (Yb1–O10–Yb2) is opened to 137.21° due to a rigid double bridge (see Fig. 3) structure between these two Yb atoms. In $Yb_2(OH)_2(CrO_4)_2$ (see Table X), the hydroxyl group oxygen O9 is surrounded by eight O atoms at distances ranging from 2.636 to 2.984 Å, and O10 is surrounded by seven O atoms at distances ranging from 2.706 to 2.996 Å. In the case of $Yb_2(OH)_2(CrO_4)_2 \cdot 3H_2O$ (see Table XI), O9 atom is surrounded by seven O atoms at distances ranging from 2.663 to 2.924 Å, and the O10 atom is surrounded by eight O

atoms at distances ranging from 2.539 to 2.932 Å.

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