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The Crystal Structure of Neodymium and Europium Chromate Heptahydrate: Synthesis, Infrared Spectra, and Thermal Behavior of Lanthanoid Chromate Heptahydrates, $[Ln_2(CrO_4)_3(H_2O)_5] \cdot 2H_2O$ (Ln = La, Pr, Nd, Sm, Eu, Gd)

JAAKKO LEPPÄ-AHO* AND JUSSI VALKONEN

University of Jyväskylä, Department of Chemistry,
SF-40100 Jyväskylä, Finland

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The crystal structures of $Nd_2(CrO_4)_3 \cdot 7H_2O$ and $Eu_2(CrO_4)_3 \cdot 7H_2O$ were determined by the conventional single-crystal X-ray diffraction technique. In addition, unit cell dimensions were measured for $La_2(CrO_4)_3 \cdot 7H_2O$ and $Sm_2(CrO_4)_3 \cdot 7H_2O$. All these compounds are isostructural. Crystals are monoclinic, space group $P2_1/c$. For $Nd_2(CrO_4)_3 \cdot 7H_2O$, a = 8.052(4) Å, b = 19.143(4) Å, c = 13.326(6) Å, β = 128.15(4)°, Z = 4, D_x = 3.14 Mg · m^{-3}, T = 296(1); and for $Eu_2(CrO_4)_3 \cdot 7H_2O$, a = 7.965(3) Å, b = 18.985(4) Å, c = 13.185(4) Å, β = 128.00(2)°, Z = 4, D_x = 3.29 Mg · m^{-3}, T = 296(1). Ln atoms are nine-coordinated so that the coordination polyhedron is a tricapped trigonal prism for *Ln*1 and a monocapped square antiprism for *Ln*2. Structures form a three-dimensional network. Unit cell dimensions for $La_2(CrO_4)_3 \cdot 7H_2O$ are a = 8.181(6) Å, b = 19.294(6) Å, c = 13.436(8) Å, β = 128.09(6)° and those for $Sm_2(CrO_4)_3 \cdot 7H_2O$ are a = 7.975(9) Å, b = 19.00(1) Å, c = 13.18(3) Å and β = 127.5(2)°. Thermal behavior was investigated and IR spectra were recorded for $Ln_2(CrO_4)_3 \cdot 7H_2O$ (Ln = La, Pr, Nd, Sm, Eu, Gd). © 1991 Academic Press, Inc.

Introduction

The oxidation states VI, V, and III of the chromium atom are of interest in compounds containing lanthanoids. The compounds synthesized and determined in this study have chromium in oxidation state VI. Chromium(VI), which exists in species such as CrO_3, CrO_4^{2-}, and $Cr_2O_7^{2-}$, is strongly oxidizing. The coordination number is 4 and the geometry around chromium is tetrahedral (*1*).

The heterogeneous equilibria of the CrO_3–Ln_2O_3–H_2O system have been investigated at 25 ± 0.1°C, to determine the composition and solubility of the lanthanoid chromates and the conditions under which they crystallize. The investigations established the formation of lanthanoid chromates(VI) (Ln = La, Nd, Sm, Gd) containing seven molecules of water (*2–5*).

Lanthanoid chromates containing crystal water decompose to $LnCrO_3$ and Cr_2O_3 when the temperature rises above 900°C. Water molecules are lost in two earlier stages according to Bashiolova *et al.* (*2, 3*). In lanthanum chromate heptahydrate, one H_2O molecule is split off at 110–145°C, and the rest of the water molecules are lost at 150–190°C (*2*). In the case of neodymium

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* To whom correspondence should be addressed.

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chromate heptahydrate, four molecules of water are split off at 100–180°C, and three at 205–230°C (*3*). There is a phase transformation in the temperature range 450–480°C according to Bashiolova *et al.* (*2*). This exothermic effect represents the crystallization of anhydrous $Ln_2(CrO_4)_3$. The anhydrous $Ln_2(CrO_4)_3$ subsequently decomposes to $LnCrO_4$ and Cr_2O_3, and finally $LnCrO_4$ decomposes to $LnCrO_3$ (*2, 3*).

Only two crystal structures of lanthanoid chromates have been published: those of $La(OH)CrO_4$ (*6*) and $Ce(CrO_4)_2 \cdot 2H_2O$ (*7*). $La(OH)CrO_4$ crystallizes in the monoclinic space group $P2_1/n$. The CrO_4 tetrahedra are nearly regular with Cr–O distances ranging from 1.613 to 1.696 Å (average 1.645 Å). The La atoms are coordinated to nine oxygens (*6*). $Ce(CrO_4)_2 \cdot 2H_2O$ crystallizes in the monoclinic space group $P2_1/m$. The average Cr–O distance is 1.642 Å and the O–Cr–O angles range between 108.8 and 111.1°. In the Ce compound, Ce atoms are coordinated to eight oxygens, and the coordination polyhedron is a bicapped trigonal prism (*7*). We have recently synthesized compounds of the same type containing ytterbium: $Yb_2(OH)_2(CrO_4)_2$ and $Yb_2(OH)_2(CrO_4)_2 \cdot 3H_2O$ (*8*).

Another group of lanthanoid compounds are the double chromates like $KLa(CrO_4)_2$ and $NH_4Ln(CrO_4)_2 \cdot nH_2O$ (Ln = lanthanoid, n = 0 or 1). Bueno *et al.* (*9*) have investigated the structure of $KLa(CrO_4)_2$ and its thermal behavior. $KLa(CrO_4)_2$ crystallizes in space group $P2_1/c$. The La atom can be considered to form an irregular pentagon with five oxygen atoms, with two additional oxygen atoms above and another two below the plane of the pentagon. The K^+ ions are located between parallel $[La(CrO_4)_2]_n^{n-}$ layers (*9*).

The thermal decomposition of $NH_4Ln(CrO_4)_2 \cdot nH_2O$ (n = 0 or 1) compounds differs from the decomposition of $KLa(CrO_4)_2$. The $KLa(CrO_4)_2$ compound decomposes to $LaCrO_4$ and $K_2Cr_2O_7$ in a first stage, after which $LaCrO_4$ decomposes to $LaCrO_3$. In the case of $NH_4Ln(CrO_4)_2 \cdot nH_2O$ (*10*) compounds, the water is lost first and then the NH_3. Decomposition of the remaining $Ln_2(CrO_4)_3$ continues in the same way as for $Ln_2(CrO_4)_3 \cdot 7H_2O$ (*2, 3*) compounds.

The free CrO_4^{2-} ion belongs to the symmetry point group T_d and has normal vibrations with the following wavenumbers (cm^{-1}): $\nu_1(A_1) = 847$, $\nu_2(E) = 348$, $\nu_3(F_2) = 368$. Only stretching and deformation vibrations of type F_2 are seen in the infrared spectrum (*11*).

The infrared spectra of hydrated lanthanoid chromates are much more complex than the spectrum of free CrO_4^{2-} ion. There are several bands at wavenumbers over 3000 cm^{-1} and near 1600, 900, 830, and 450 cm^{-1}. Petrov *et al.* associate the bands below 850 cm^{-1} with the $\nu_1(A_1)CrO_4$ symmetric vibrations, the splitting of which can be due either to different coordination of the CrO_4 groups to metal or to the nonequivalence of the positions of the CrO_4 in the crystal cell. The two bands near 1600 cm^{-1} are due to the deformation vibration of water (*11*).

Experimental

Synthesis. $Ln_2(CrO_4)_3 \cdot 7H_2O$ ((Ln = La, Nd, Eu, Sm, Pr, Gd)) crystals were synthesized in an steel autoclave with Teflon lining. Ln_2O_3 (300 mg) was mixed with 8 cm^3 0.6 mole dm^{-3} H_2CrO_4. The mixtures were put in an autoclave and the temperature was raised to 160–170°C and then decreased slowly (5 degrees per day) to room temperature. The estimated maximum pressure in autoclave was about 6.2 10^5–7.9 10^5 Nm^{-2}. Finally the crystals were filtered out without washing. Yellow needles were obtained. The crystals of Nd and Eu compounds were good enough for crystal structure determination. The La and Sm compounds, but not the Pr and Gd compounds, allowed measurement of the unit cell dimensions.

Thermal analysis and IR spectra. Thermal behavior was determined with a Perkin–Elmer TG-2 thermobalance. Sample size was 5–10 mg, heating rate 10°C min^{-1}, and air flow 70 cm^3 min^{-1}. The temperature range was 25 to 850°C for the curves shown in Figs. 1–6. To investigate the splitting off of the water molecules, another set of curves were measured with sample size 3.1–3.3 mg. Heating rate was 2°C min^{-1} and air flow 70 cm^3 min^{-1} and the temperature range 25 to 400°C (Fig. 7.) Observed weight losses were calculated from both curves for each compound. 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 a scan range of 4000 to 200 cm^{-1}.

Crystal structure determination. X-ray determinations were made for $Nd_2(CrO_4)_3 \cdot 7H_2O$ and $Eu_2(CrO_4)_3 \cdot 7H_2O$ compounds using an Enraf-Nonius CAD4 automatic four circle diffractometer equipped with a graphite monochromator (Mo$K\alpha$ 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 III. 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 in the case of the Eu compound. For the Nd compound the absorption correction was calculated using the program DIFABS (*12*).

All calculations[1] were performed with a micro VAX II computer using the Enraf-Nonius structure determination package SDP-plus (*13*).This package incorporates the direct methods program MULTAN (*14*) and the plotting programs ORTEP (*15*) and PLUTO (*16*).

Positions of lanthanoid elements (Nd, Eu) 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. The thermal behavior of the investigated compounds are described in Table I and Figs. 1–7. As described above observed mass losses were calculated from two different curves for each compound. Our findings differed somewhat from those described in the literature (see Introduction). Pr, Nd, Sm, Eu, and Gd compounds (Figs. 2–7) lose three H_2O molecules between 25 and 94°C. A further H_2O molecule is split off in the temperature range 84–154°C and the final three water molecules are lost before 400°C. In the case of Nd, Sm, Eu, and Gd, further heating causes the remaining $Ln_2(CrO_4)_3$ part to decompose in two stages: $LnCrO_4$ (plus Cr_2O_3) is formed in a first stage (Eq. (2) below) and $LnCrO_3$ in the second (Eq. (3) below). Cr_2O_3 does not decompose further. $Pr_2(CrO_4)_3$ decomposes directly to $PrCrO_3$ without forming $PrCrO_4$, perhaps because of the oxidation of Pr, which reduces Cr^{VI} directly to Cr^{III}.

$La_2(CrO_4)_3 \cdot 7H_2O$ behaves differently from the other five compounds in losing water molecules in just two stages. Five molecules are split off between 25 and 116°C and the other before 400°C. $La_2(CrO_4)_3$ decomposes according to Eqs. (2) and (3), as can be confirmed from the DTG curve (two peaks between 660 and 750°C). On the basis of the unit cell determinations and the reasonable inference that the structures of all six com-

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[1] Tables containing F_{obs}, F_{calc}, and temperature factors have been deposited as supplementary material. See NAPS Document No. 00000 for 00 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 or for photocopy, $7.75 up to 20 pages plus $0.30 for each additional page. All orders must be prepaid.

TABLE I

THERMAL DECOMPOSITION OF LANTHANOID CHROMATE HEPTAHYDRATES $Ln_2(CrO_4)_3 \cdot 7H_2O$, ($Ln$ = La, Pr, Nd, Sm, Eu, Gd)

Ln	Temperature *T* (°C)	Weight Loss (%)		Lost in reaction
		Δ Observed	Δ Theoretical	
La	25–116	11.4	12.0	5 H_2O
	116–395	5.4	4.8	2 H_2O
	510–710	5.0	5.3	1.25 O_2
	710–810	4.6	4.3	1.0 O_2
	25–810	26.3	26.3	[a]
Pr	25– 96	8.4	7.1	3 H_2O
	96–135	3.1	2.4	1 H_2O
	135–398	5.1	7.1	3 H_2O
	600–755	9.5	9.4	2.25 O_2
	25–755	26.2	25.9	[a]
Nd	25– 94	6.8	7.1	3 H_2O
	94–142	2.2	2.4	1 H_2O
	142–396	6.9	7.1	3 H_2O
	570–707	5.3	5.2	1.25 O_2
	707–810	4.2	4.2	1.0 O_2
	25–810	26.0	25.5	[a]
Sm	25– 89	7.1	7.0	3 H_2O
	89–147	2.5	2.3	1 H_2O
	147–396	6.5	7.0	3 H_2O
	575–715	5.2	5.2	1.25 O_2
	715–840	4.1	4.3	1.0 O_2
	25–840	25.0	26.6	[a]
Eu	25– 89	6.8	7.0	3 H_2O
	89–152	2.9	2.3	1 H_2O
	152–396	5.6	7.0	3 H_2O
	520–660	5.1	5.1	1.25 O_2
	710–787	4.1	4.1	1.0 O_2
	25–787	24.9	25.5	[a]
Gd	25– 84	7.0	6.9	3 H_2O
	84–154	3.2	2.3	1 H_2O
	154–398	5.7	6.9	3 H_2O
	573–678	5.1	5.0	1.25 O_2
	744–800	4.1	4.1	1.0 O_2
	25–800	24.9	25.1	[a]

[a] Total reaction.

pounds are the same, one would expect thermal dehydration to take place through the same stages. Perhaps lanthanum's large ionic radius causes it to behave differently.

As can be seen from the TG curves of the $Ln_2(CrO_4)_3 \cdot 7H_2O$ compounds, the heavier the lanthanoid, the lower the temperature at which the water molecules are lost. These temperature differences amount to a few degrees (2 to 7°C) between consecutive lanthanoid compounds.

$$Ln_2(Cr^{VI}O_4)_3 \cdot 7H_2O \xrightarrow{25\text{–}400^\circ C} Ln_2(Cr^{VI}O_4)_3 + 7H_2O \quad (1)$$

$$Ln_2(Cr^{VI}O_4)_3 \xrightarrow{510\text{–}715^\circ C} 2LnCr^{V}O_4 + 0.5Cr_2^{III}O_3 + 1.25O_2 \quad (2)$$

$$2LnCr^{V}O_4 \xrightarrow{707\text{–}840^\circ C} 2LnCr^{III}O_3 + O_2 \quad (3)$$

$$Ln_2(Cr^{VI}O_4)_3 \cdot 7H_2O \xrightarrow{25\text{–}840^\circ C} 2LnCr^{III}O_3 + 0.5Cr_2^{III}O_3 + 2.25O_2 + 7H_2O \quad \text{(total)} \quad (4)$$

IR spectra. IR spectral data for all six compounds are listed in Table II. Assignments were made according to the literature (*10*). The data are very similar to those reported by Petrov *et al.* The two bands with wavenumbers near 1600 cm^{-1} (from 1590 to 1636) are due to the deformation vibration of water. The splitting shows the nonequivalence of the water molecules entering into the composition of the compounds. Two of the seven molecules are not fixed in the structure, as seen in structure determination. According to Petrov *et al.*, the bands near wavenumber 850 cm^{-1} indicate a different coordination of the CrO_4 group by Nd and Eu atoms.

Crystal structure. Crystal data and constants for neodymium and europium chromate heptahydrates are given in Table III. Fractional coordinates are listed in Tables IV and V, bond distances in Table VI and O–Cr–O bond angles in Table VII.

There are two kinds of *Ln* atoms in the structure, with different environments (see Fig. 8). Both atoms are nine-coordinated but the coordination polyhedron for the *Ln*1 atom is a tricapped trigonal prism (Fig. 9) while that for the *Ln*2 atom is a capped square antiprism (Fig. 9). This situation can be explained by the coordination of a different number of water molecules, four molecules coordinated to the *Ln*1 atom and only one to the *Ln*2 atom and the bidental coordination of the CrO_4^{2-} group.

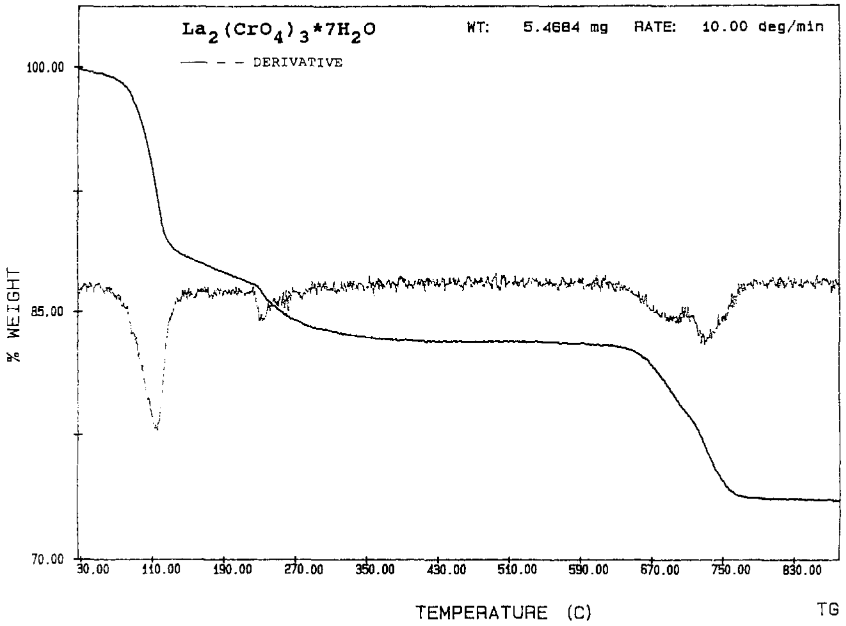

FIG. 1. TG and DTG curves for $La_2(CrO_4)_3 \cdot 7H_2O$.

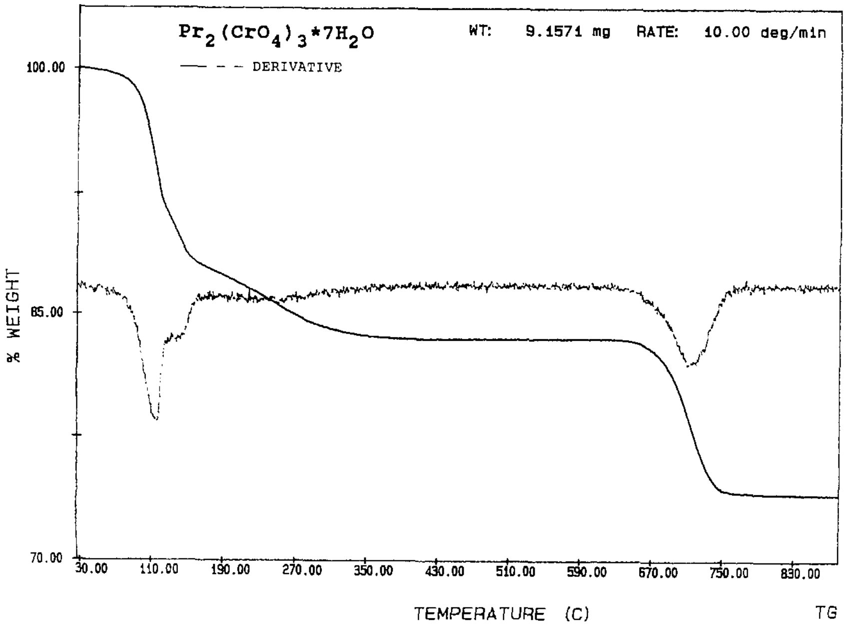

FIG. 2. TG and DTG curves for $Pr_2(CrO_4)_3 \cdot 7H_2O$.

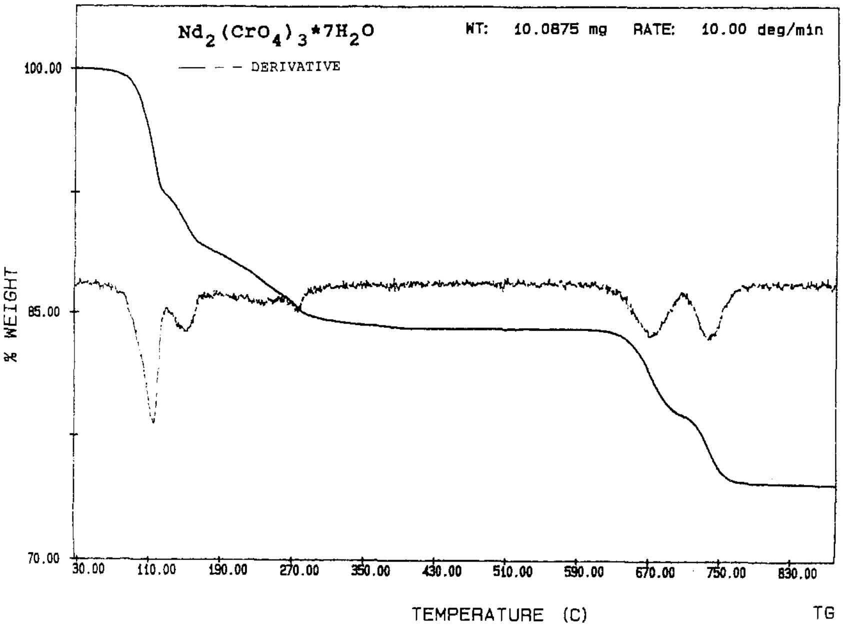

FIG. 3. TG and DTG curves for $Nd_2(CrO_4)_3 \cdot 7H_2O$.

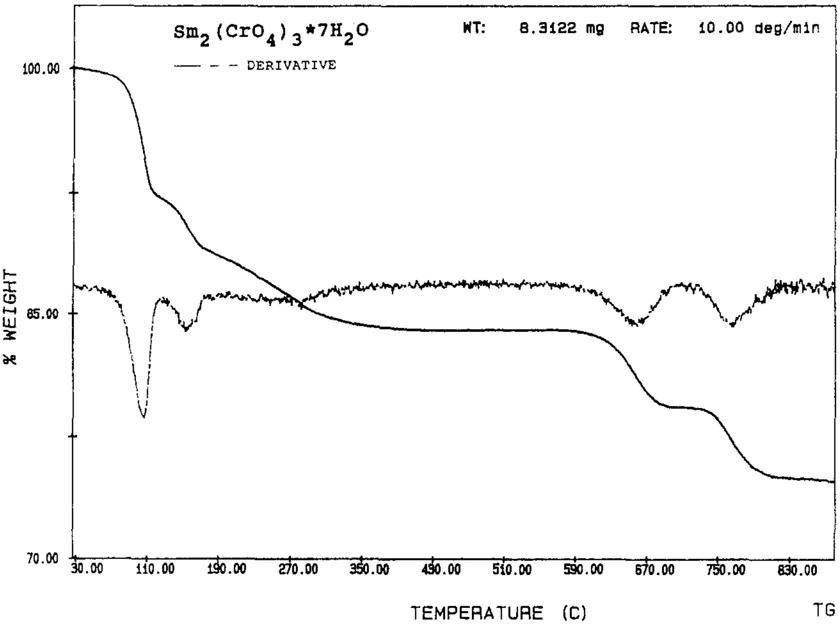

FIG. 4. TG and DTG curves for $Sm_2(CrO_4)_3 \cdot 7H_2O$.

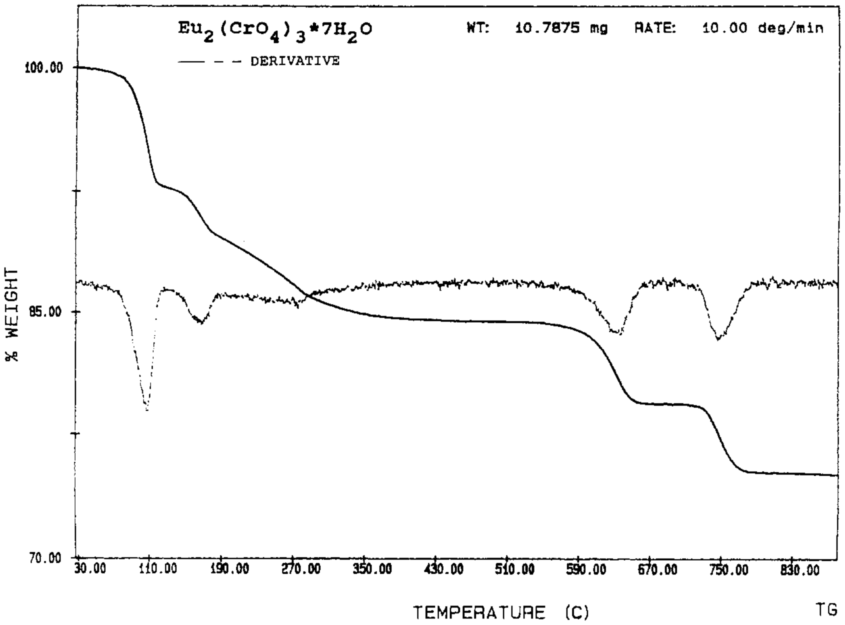

FIG. 5. TG and DTG curves for $Eu_2(CrO_4)_3 \cdot 7H_2O$.

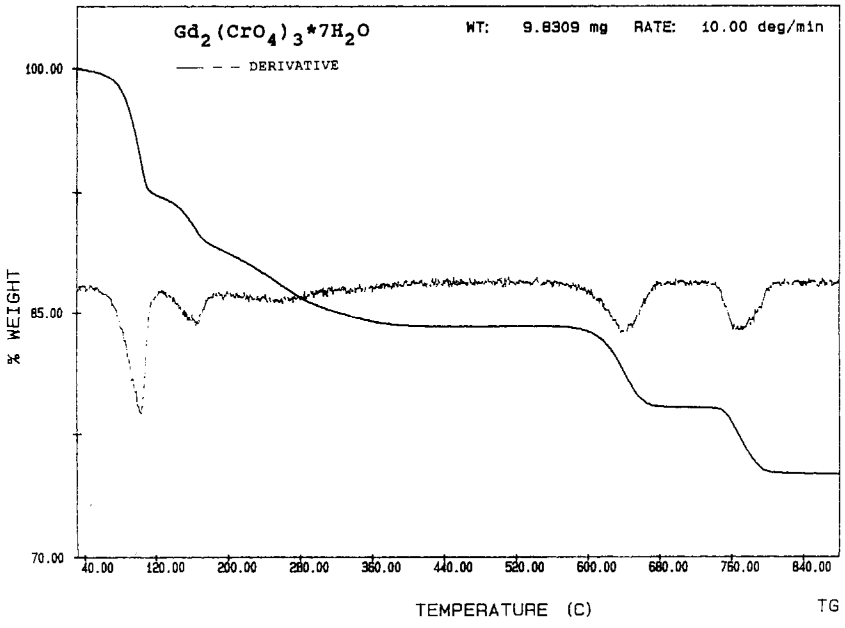

FIG. 6. TG and DTG curves for $Gd_2(CrO_4)_3 \cdot 7H_2O$.

TABLE II

IR Spectral Data (cm^{-1}) of $Ln_2(CrO_4)_3 \cdot 7H_2O$ (Ln = La, Pr, Nd, Sm, Eu, Gd) Compounds

$Ln_2(CrO_4)_3 \cdot 7H_2O$ (cm^{-1})						
La	Pr	Nd	Sm	Eu	Gd	Assignment
3000-3500 *s, vb*	3100-3500 *s, vb*	3085-3500 *s, vb*	3150-3500 *s, vb*	3100-3500 *s, vb*	3000-3500 *s, vb*	ν OH
1632 *s*	1636 *s*	1635 *s*	1632 *s, b*	1633 *s, b*	1630 *s,b*	δ H_2O
1600 *sh*	1590 *sh*	1600 *sh*	1600 *sh*	1600 *vw*	1600 *vw*	
911 *sh*	909 *sh*	910 *sh, sp*	917 *w, sh*	910 *m, sp*	914 *sh*	ν_3 CrO_4^{2-}
890 *sh*	890 *m, sh*	890 *w, sh*	890 *w, sh*	890 *sh*	890 *sh*	
855 *w, sp*	860 *m, sh*	860 *m, sp*	865 *w*	860 *m, sp*	867 *w, sp*	
840 *w, sp*	840 *w, sp*	832 *w, sp*	848 *w*	840 *w*	836 *sh*	ν_1 CrO_4^{2-}
817 *w, sh*	815 *w, sh*	820 *w, sp*	815 *w*	817 *w*	815 *sh*	
612 *b*	635 *b*	630 *b*	640 *b*	646 *w, sp*	635 *s, b*	ρ H_2O
590 *sh*	580 *w, b*		585 *w, b*			ν_4 CrO_4^{2-}
422 *sh, w*	425 *w, sh*	423 *w, sh*	430 *w, sp*	425 *w*	425 *w, b*	

Note. w = weak, m = medium, s = strong, v = very, b = broad, sp = sharp, sh = shoulder.

TABLE III

Experimental Data for Crystallographic Analyses

Formula:	$Nd_2(CrO_4)_3 \cdot 7H_2O$	$Eu_2(CrO_4)_3 \cdot 7H_2O$
	Unit cell determination	
F.W.	762.57	778.01
Crystal size (mm)	0.18 · 0.05 · 0.05	0.2 · 0.1 · 0.1
T(K)	296 ± 1	296 ± 1
No. of reflections for lattice measurements	25	23
θ range for lattice measurements (°)	4–17	10–13
a (Å)	8.052(4)	7.965(3)
b (Å)	19.143(4)	18.985(4)
c (Å)	13.326(6)	13.185(4)
β (°)	128.15(4)	128.00(2)
V (Å^3)	1615(1)	1571(1)
Z	4	4
D_{calc} ($Mg \cdot m^{-3}$)	3.14	3.29
$\mu[cm^{-1}]$	83.5	99.4
Mo$K\alpha$	0.71073	0.71073
F(000)	1432	1456
Space group	$P2_1/c$ (No: 14)	$P2_1/c$ (No: 14)
	Data collection and refinement	
θ range for data collection (°)	2–30	2–35
Scan method	$\omega/2\theta$	$\omega/2\theta$
Scan speed in omega (°min^{-1})	1.2–16.5	1.6–16.5
Scan width in omega (°)	$0.8 + 0.34 \tan\theta$	$1.0 + 0.34 \tan\theta$
Variation of std. ref.	None	None
Refl. measured	4848	7069
Condition for observing reflections	$I > 3\sigma(I)$	$I > 3\sigma(I)$
Reflections used in refinement	2235	4016
Abs. correction (min/max)	0.81/1.20	0.78/1.00
Max shift/error	0.00	0.00
Max in final δ/eÅ^3	2.8(6)	4.0(5)
Number of parameters	218	218
S	3.3	3.3
R	6.5	5.2
R_W	7.1	4.8

Note. $w = 1/(\sigma F_0)^2$, $s = \sqrt{\Sigma w(F_0 - F_c)^2/(m - n)}$.

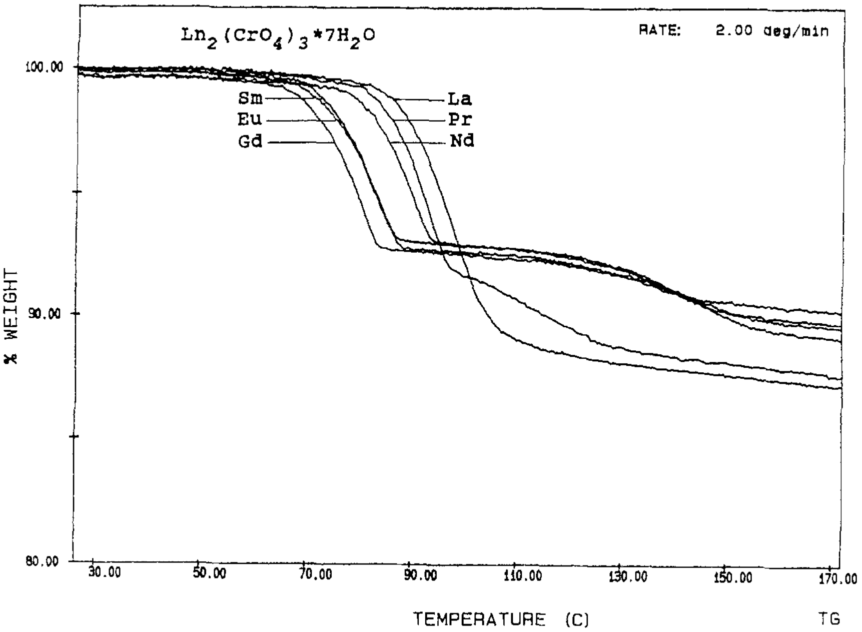

FIG. 7. TG data for $Ln_2(CrO_4)_3 \cdot 7H_2O$ (Ln = La, Pr, Nd, Sm, Eu, and Gd). Comparison of thermal dehydration in the temperature range 26 to 173°C.

TABLE IV

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR $Nd_2(CrO_4)_3 \cdot 7H_2O$

Atom	x	y	z	B (Å^2)[a]
Nd1	0.0587(2)	0.24366(6)	0.7458(1)	0.75(2)
Nd2	0.3139(2)	0.50124(8)	1.06322(9)	0.67(2)
Cr1	−0.1150(5)	0.3516(2)	0.9279(3)	0.85(8)
Cr2	0.4940(5)	0.6459(2)	0.9447(3)	0.77(7)
Cr3	0.1744(5)	0.4597(2)	1.2764(3)	1.09(8)
O1	0.002(2)	0.4316(7)	0.993(1)	0.7(3)
O2	−0.366(2)	0.3723(9)	0.856(2)	2.5(5)
O3	−0.089(2)	0.329(1)	0.824(1)	2.0(4)
O4	−0.028(2)	0.2907(9)	1.037(1)	1.3(4)
O5	0.524(2)	0.569(1)	1.017(1)	2.6(4)
O6	0.248(2)	0.6700(8)	0.847(1)	1.1(4)
O7	0.588(2)	0.6279(9)	0.866(1)	1.7(4)
O8	0.634(2)	0.7053(9)	1.053(1)	1.5(4)
O9	0.329(2)	0.4909(8)	1.246(1)	1.2(3)
O10	−0.074(2)	0.4858(9)	1.166(1)	1.3(4)
O11	0.248(2)	0.4885(9)	1.411(1)	2.1(4)
O12	0.191(2)	0.3718(8)	1.284(1)	1.7(3)
O13	−0.275(2)	0.3072(9)	0.561(1)	1.7(4)
O14	0.139(2)	0.360(1)	0.691(1)	2.9(5)
O15	0.085(2)	0.1909(9)	0.928(1)	2.0(4)
O16	0.399(2)	0.236(1)	0.771(1)	2.7(4)
O17	0.695(2)	0.504(1)	1.247(1)	2.1(4)
O18	0.176(3)	0.579(1)	1.545(2)	4.5(6)
O19	−0.542(2)	0.382(1)	0.589(2)	2.9(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 V

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR $Eu_2(CrO_4)_3 \cdot 7H_2O$

Atom	x	y	z	B (Å^2)[a]
Eu1	0.05913(7)	0.24379(3)	0.74680(4)	0.836(9)
Eu2	0.31507(7)	0.50137(3)	1.06353(4)	0.741(8)
Cr1	−0.1124(2)	0.35234(9)	0.9301(1)	0.87(3)
Cr2	0.4930(2)	0.64585(9)	0.9425(1)	0.85(3)
Cr3	0.1724(2)	0.4594(1)	1.2747(1)	1.21(3)
O1	0.006(1)	0.4290(4)	0.9910(7)	1.3(2)
O2	−0.3645(9)	0.3713(4)	0.8602(6)	1.3(2)
O3	−0.083(1)	0.3242(5)	0.8251(6)	1.7(2)
O4	−0.025(1)	0.2929(4)	1.0420(6)	1.3(2)
O5	0.522(1)	0.5691(4)	1.0139(7)	1.7(1)
O6	0.246(1)	0.6710(5)	0.8473(7)	1.7(2)
O7	0.587(1)	0.6290(4)	0.8650(6)	1.6(2)
O8	0.635(1)	0.7067(4)	1.0513(6)	1.5(2)
O9	0.3310(9)	0.4929(4)	1.2446(6)	1.2(2)
O10	−0.0782(9)	0.4836(4)	1.1620(6)	1.3(2)
O11	0.244(1)	0.4891(5)	1.4100(6)	2.1(2)
O12	0.193(1)	0.3728(4)	1.2840(7)	2.3(2)
O13	−0.269(1)	0.3072(4)	0.5629(7)	1.8(2)
O14	0.138(1)	0.3563(5)	0.6960(8)	2.7(2)
O15	0.084(1)	0.1905(5)	0.9266(6)	1.8(2)
O16	0.406(1)	0.2340(5)	0.7750(8)	2.7(2)
O17	0.6911(9)	0.5042(5)	1.2468(5)	1.4(2)
O18	0.177(2)	0.5777(6)	1.5495(9)	4.5(3)
O19	−0.543(1)	0.3820(5)	0.5895(7)	2.6(2)

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

TABLE VI

BOND DISTANCES (Å) AND THEIR ESTIMATED STANDARD DEVIATIONS FOR $Nd_2(CrO_4)_3 \cdot 7H_2O$ and $Eu_2(CrO_4)_3 \cdot 7H_2O$

Compound					
$Nd_2(CrO_4)_3 \cdot 7H_2O$			$Eu_2(CrO_4)_3 \cdot 7H_2O$		
Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Nd1	O3	2.59(2)	Eu1	O3	2.47(1)
Nd1	O4	2.50(2)	Eu1	O4	2.450(8)
Nd1	O6	2.42(1)	Eu1	O6	2.374(8)
Nd1	O8	2.47(1)	Eu1	O8	2.433(6)
Nd1	O12	2.37(2)	Eu1	O12	2.373(8)
Nd1	O13	2.57(1)	Eu1	O13	2.522(6)
Nd1	O14	2.54(2)	Eu1	O14	2.43(1)
Nd1	O15	2.52(2)	Eu1	O15	2.471(9)
Nd1	O16	2.55(2)	Eu1	O16	2.56(1)
Nd2	O1	2.46(2)	Eu2	O1	2.442(8)
Nd2	O1	2.52(2)	Eu2	O1	2.556(8)
Nd2	O2	2.58(2)	Eu2	O2	2.553(8)
Nd2	O5	2.49(2)	Eu2	O5	2.47(1)
Nd2	O5	2.52(2)	Eu2	O5	2.48(1)
Nd2	O7	2.59(2)	Eu2	O7	2.592(8)
Nd2	O9	2.37(2)	Eu2	O9	2.316(9)
Nd2	O10	2.42(1)	Eu2	O10	2.362(6)
Nd2	O17	2.48(1)	Eu2	O17	2.429(5)
Cr1	O1	1.73(1)	Cr1	O1	1.650(7)
Cr1	O2	1.66(2)	Cr1	O2	1.653(7)
Cr1	O3	1.58(2)	Cr1	O3	1.63(1)
Cr1	O4	1.65(2)	Cr1	O4	1.634(8)
Cr2	O5	1.70(2)	Cr2	O5	1.671(8)
Cr2	O6	1.63(1)	Cr2	O6	1.624(7)
Cr2	O7	1.67(2)	Cr2	O7	1.62(1)
Cr2	O8	1.62(1)	Cr2	O8	1.635(7)
Cr3	O9	1.64(2)	Cr3	O9	1.665(9)
Cr3	O10	1.67(1)	Cr3	O10	1.658(6)
Cr3	O11	1.60(2)	Cr3	O11	1.604(9)
Cr3	O12	1.69(2)	Cr3	O12	1.649(8)

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

The average Cr–O distance is 1.65 Å. The geometry of the chromate groups is slightly distorted. O–Cr–O angles vary from 101.0 to 112.4° for the neodymium compound and from 102.0 to 112.9° for the europium compound. Two of the angles are very small: oxygens in the angles O1–Cr1–O2 and O5–Cr2–O7 are bound to the same *Ln* atom as the bidental ligand and this decreases the angle size (Fig. 8). Average bond distances are shown in Table VIII.

CrO_4 groups are not coordinated identically to the structure. Cr1 and Cr2 are coordinated identically but the coordination of the Cr3 atom differs. The main difference occurs for O11, which because it is not coordinated to any *Ln* atom slightly shortens the Cr3–O11 distance.

The structure forms a regular three-dimensional network, in which lanthanoid polyhedra are connected to chromium tetrahedra in all dimensions. There are also several hydrogen bonds in the structure. Every water oxygen atom (O13 . . . O19) has at least four oxygen–oxygen distances less than 3.0 Å.

In the $Ln_2(CrO_4)_3 \cdot 7H_2O$ structure, five of seven water molecules are coordinated to the metal atom (oxygens O13 . . . O17) and the two noncoordinated water molecules (oxygens O18 and O19) are located in holes of the structure. Thus the formulas of these compounds should properly be expressed

TABLE VII

O–Cr–O BOND ANGLES (°) AND THEIR ESTIMATED STANDARD DEVIATIONS FOR $Nd_2(CrO_4)_3 \cdot 7H_2O$ AND $Eu_2(CrO_4)_3 \cdot 7H_2O$.

			Angle (°)	
Atom 1	Atom 2	Atom 3	Nd	Eu
O1	Cr1	O2	99.8(8)	102.3(4)
O1	Cr1	O3	111(1)	111.4(5)
O1	Cr1	O4	112.4(6)	111.8(3)
O2	Cr1	O3	109.4(9)	111.0(4)
O2	Cr1	O4	112(1)	110.6(4)
O3	Cr1	O4	111(1)	109.6(4)
O5	Cr2	O6	112.3(8)	111.9(4)
O5	Cr2	O7	103(1)	103.0(5)
O5	Cr2	O8	109.2(8)	109.9(4)
O6	Cr2	O7	110.8(8)	112.3(4)
O6	Cr2	O8	110.4(8)	109.0(4)
O7	Cr2	O8	111.4(9)	110.6(5)
O9	Cr3	O10	110.6(8)	110.6(4)
O9	Cr3	O11	109.8(8)	109.2(4)
O9	Cr3	O12	109.6(9)	110.1(5)
O10	Cr3	O11	107.3(8)	107.9(4)
O10	Cr3	O12	111.1(7)	110.6(4)
O11	Cr3	O12	108.5(8)	108.4(4)

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

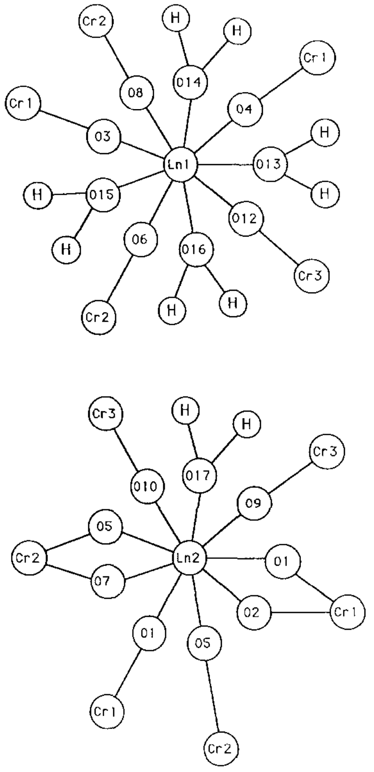

FIG. 8. Environments of *Ln*1 and *Ln*2 atoms in *Ln*2$(CrO_4)_3 \cdot 7H_2O$ (*Ln* = Nd, Eu) compounds.

as $[Ln_2(CrO_4)_3(H_2O)_5] \cdot 2H_2O$. Contrary to expectation, the loss of the two noncoordinated waters does not appear in the TG curves as a separate process. In the first stage three molecules of water are split off.

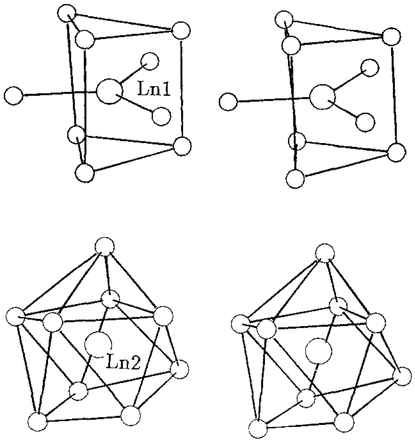

FIG. 9. A stereoview of the coordination polyhedra.

In addition to the crystal structure determination of neodymium and europium chromate heptahydrate, the lattice parameters were determined for lanthanum and samarium chromate heptahydrates. Unit cell dimensions for $La_2(CrO_4)_3 \cdot 7H_2O$ are a = 8.181(6) Å, b = 19.294(6) Å, c = 13.436(8) Å, β = 128.09(6)°, and V = 1669(2) Å^3 and for $Sm_2(CrO_4)_3 \cdot 7H_2O$ a = 7.975(9) Å, b = 19.00(1) Å, c = 13.18(1) Å, β = 127.5(2)°, and V = 1583(6) Å^3.

TABLE VIII

AVERAGE BOND DISTANCES

Compound	Bond [Å]			
	Cr–O	Ln–O (Cr)	Ln–O (H_2O)	Ref.
$Nd_2(CrO_4)_3 \cdot 7H_2O$	1.65	2.49	2.52	This work
$Eu_2(CrO_4)_3 \cdot 7H_2O$	1.65	2.45	2.48	This work
$La(OH)CrO_4$	1.65	2.58	—	(*6*)
$Ce(CrO_4)_2 \cdot 2H_2O$	1.64	2.34	2.50	(*7*)
$KLa(CrO_4)_2$	1.65	2.57	—	(*9*)

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