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Synthesis, Crystal Growth, and Structure of $La(OH)CrO_4$

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Single crystals of the new compound $La(OH)CrO_4$ were grown by hydrothermal synthesis. $La(OH)CrO_4$ crystallizes in the monoclinic system, space group $P2_1n$, $Z = 4$, with $a = 4.7234(8)$, $b = 13.222(3)$, $c = 7.019(1)$ Å, and $\beta = 107.28(1)°$. The structure has been solved by X-ray single-crystal techniques to a final R value of 0.027 using 1013 observed reflections. $La(OH)CrO_4$ has a three-dimensional array in which the tetrahedral CrO_4 groups alternate with LaO_9 polyhedra. ^1H NMR and IR spectra and X-ray powder-diffraction data are given.

Introduction

In the course of our study of the system Ln_2O_3–CrO_3–M_2O (*1, 2*) (Ln = rare earth, M = alkali metal) under hydrothermal conditions we have isolated single crystals of a new phase of formula $La(OH)CrO_4$ and determined its structure.

From previous hydrothermal investigations on the lanthanide hydroxide anion compounds various phases were obtained. The structure of that with formula $Ln(OH)X$ where X^- is CO_3^{2-} (*3, 4*) is closely related with those corresponding to the phases $Ln(OH)_2X$, where X is fluoride (*5*), chloride (*6*), and nitrate (*7, 8*). The structural feature common to all these phases appears to be the existence of alternate sheets of dihydroxo species $Ln(OH)_2^+$ and X^- anions, in the sequence $Ln(OH)_2^+ \ldots X^- \ldots Ln(OH)_2^+ \ldots$, with predominant $OH \ldots X$ hydrogen bonds.

On the other hand, the phases with formula $M^{III}(OH)CrO_4$ are known when M^{III} is Fe^{3+} (*9–12*) or Bi^{3+} (*13*).

$Fe(OH)CrO_4$ crystallizes in the orthorhombic system and the structure consists of parallel chains in which the metal atoms are octahedrally coordinated to two hydroxo groups and four chromate oxygens. The hydroxo groups are shared between octahedra forming infinite Fe–OH–Fe chains along the a axis.

$Bi(OH)CrO_4$ is dimorphous (*14, 15*) having one orthorhombic form and one monoclinic form. The structure of these two modifications are closely related and both can be considered to be formed by layers of $Bi(OH)CrO_4$ perpendicular to the a axis. The bismuth atoms form a puckered, two-

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dimensional network of condensed hexagons, each having two bismuth atoms in the hexagonal array bridged by oxygen atoms or hydroxide groups, forming square aggregates of formula $Bi_2O_2^{2+}$ or $Bi_2(OH)_2^{4+}$. The Bi atom has nine-coordination in a polyhedron coordination that can be considered to be a distorted monocapped square antiprism.

Although a few Bi^{3+} compounds are isostructural with those corresponding to La^{3+}, e.g., halides and oxohalides, the new phase of lanthanum is not isostructural with the analogous phase of bismuth, but some relationships can exist between them, as will be shown in this work.

Experimental

1. Crystal Growth

Yellow needle-shaped single crystals of La(OH)CrO$_4$ were obtained from La_2O_3, CrO_3, and Li(OH) in molar ratios 1 : 4 : 3, by hydrothermal synthesis for 40 hr at 130°C in sealed Pyrex glass tubes.

The La content of the crystals was determinated by complexometry, that of CrO_4^{2-} as $PbCrO_4$ by a gravimetric procedure, and that of OH^- by difference. (Found: La, 51.30; CrO_4^{2-}, 42.71; OH^-, 5.99. Calc: La, 51.10; CrO_4^{2-}, 42.65; OH^-, 6.25.)

2. IR and NMR Spectra

Infrared spectra were recorded on a Perkin–Elmer spectrophotometer Model 580 B, using CsI pellets.

The ^1H NMR spectra were obtained with a pulse spectrometer SXP 4/100 (Brucker) with a Fourier transform unit, Aspect-2000. The employed NMR frequency of proton was 70 MHz. The spectra were recorded at room temperature and the number of accumulations in each experiment was chosen such that the signal-to-noise ratio was higher than 30. Pretreatment of the sample was carried out in a special greaseless stopcocks vacuum cell, capable of maintaining a dynamic vacuum of Ca 1×10^{-3} N m^{-2}.

3. Data Collection

A crystal of dimensions 0.07 × 0.05 × 0.17 mm was mounted on a Nonius CAD-4 diffractometer. The cell dimensions were refined by least-squares fitting of the 2θ values of 25 reflections.

There was no appreciable change in the periodically monitored standard reflections. The intensities were corrected for Lorentz and polarization effects, and 1013 of these were considered as observed with $I > 2\sigma(I)$. Scattering factors for neutral atoms and anomalous dispersion correction for Cr and La were taken from "International Tables for X-Ray Crystallography" (*16*). The powder pattern was recorded using a Siemens Kristalloflex 810 diffractometer and a D-500 goniometer, with Cu$K\alpha$ radiation, at a scanning rate of 0.1° 2θ min^{-1} with Si (a = 5.43088(4) Å), as an international standard. The pattern was indexed using the parameters determined with the four-circle diffractometer.

4. Structure Determination

The heavy atoms were located from a three-dimensional Patterson map. The positions of the oxygen atoms were obtained from Fourier synthesis. An empirical absorption correction (*17*) was applied at the end of the isotropic refinement procedure. Anisotropic full-matrix least-squares refinement with unit weights led to $R = 0.027$ and $R_w = 0.035$. No trend in ΔF vs F_0 or sin θ/λ was observed.

The H atoms were located in a final difference Fourier synthesis as the highest peak of the map and their coordinates have been subsequently refined. The average shift-to-error ratio was 0.09. Most of the calculations were carried out with X-Ray 80 (*18*).

TABLE I

CRYSTAL DATA AND CONSTANTS OF La(OH)CrO$_4$

Formula weight: 271.9
Crystal system: monoclinic
Space group: $P2_1/n$
$a = 4.7234(8)$ Å
$b = 13.222(3)$ Å
$c = 7.019(1)$ Å
$\beta = 107.28(1)^\circ$
$V = 418.6(1)$ Å^3
$Z = 4$
$\rho_x = 4.41$ g cm^{-3}
$F(000) = 488$
Temperature: 295 K
Radiation Mo$K\alpha$: 0.71069 Å
Absorption factor (Mo$K\alpha$): 125.6 cm^{-1}
$R = 0.027$

Results and Discussion

Crystal data and constants for La(OH)CrO$_4$ are given in Table I. The cell parameters are those refined in the four-circles diffractometer. Table II lists the d-spacings and intensities measured in the powder pattern.

Table III shows the final atomic parameters, and Table IV gives bond lengths and angles.

The NMR spectrum shows a very sharp band centered at the resonance frequency, with a full width at half maximum (FWHM) of 2.5 G. This band denotes to the existence of OH groups.

TABLE II

POWDER PATTERN OF La(OH)CrO$_4$

$h\ k\ l$	d_o	d_c	I/I_o
0 2 0	6.642	6.624	100
0 2 1	4.737	4.721	6
1 1 0	4.283	4.273	7
$\bar{1}$ 1 1	4.187	4.177	13
1 2 0	3.734	3.731	12
0 3 1	3.696	3.692	13
$\bar{1}$ 2 1	3.670	3.666	10
0 0 2	3.372	3.365	9
1 0 1	3.319	3.321	30
0 1 2	3.269	3.262	7
1 1 1	3.228	3.221	8
$\bar{1}$ 3 0	3.160	3.157	25
$\bar{1}$ 1 2	3.107	3.101	20
0 4 1	2.975	2.972	40
$\bar{1}$ 2 2	2.875	2.874	10
0 3 2 1 4 0	2.673	2.677 2.671	9
$\bar{1}$ 4 1	2.647	2.647	6
$\bar{1}$ 3 2	2.586	2.586	3
1 4 1	2.345	2.345	4
$\bar{2}$ 1 1	2.324	2.325	9
$\bar{1}$ 4 2 $\bar{1}$ 0 3	2.296	2.297 2.299	4
$\bar{1}$ 5 1	2.269	2.270	14
0 6 0	2.206	2.208	17
0 6 1	2.297	2.098	17
$\bar{1}$ 5 2 $\bar{1}$ 3 3	2.037	2.038 2.039	5
2 3 0	2.009	2.010	5
$\bar{1}$ 6 1	1.970	1.973	5
2 1 1	1.949	1.950	4
1 4 2	1.934	1.933	17
2 2 1	1.888	1.889	3
$\bar{2}$ 1 3	1.875	1.878	4
0 6 2	1.845	1.846	2
$\bar{2}$ 2 3 0 7 1	1.821	1.824 1.822	7
1 7 0	1.743	1.745	14
$\bar{2}$ 3 3	1.741	1.743	13
$\bar{1}$ 7 1	1.736	1.738	12
2 5 0	1.716	1.718	8
2 4 1 $\bar{2}$ 5 2	1.692	1.694 1.693	7
0 8 0	1.655	1.656	14
0 2 4 $\bar{1}$ 7 2	1.627	1.630 1.628	4
1 6 2 $\bar{2}$ 6 1	1.616	1.619 1.613	5
1 8 0 2 3 2	1.552	1.555 1.554	3
$\bar{1}$ 8 1 $\bar{1}$ 4 4 $\bar{2}$ 2 4	1.549	1.550 1.552 1.550	6
$\bar{2}$ 7 1 1 8 1 1 7 2	1.479	1.477 1.482 1.482	5
0 6 4	1.334	1.338	7

TABLE III

ATOMIC PARAMETERS FOR La(OH)CrO$_4$ COORDINATES AND THERMAL PARAMETERS ($Å^2 \times 10^4$)

Atom	x/a	y/b	z/c	U_{eq}	U_{iso}
La	0.63372(8)	0.44372(3)	0.29735(6)	67(1)	
Cr	0.47817(24)	0.14932(8)	0.38126(16)	68(3)	
O(1)	0.7727(12)	0.0698(4)	0.4497(8)	130(15)	
O(2)	0.5737(14)	0.2591(4)	0.3175(9)	198(19)	
O(3)	0.3479(13)	0.1641(4)	0.5673(8)	167(17)	
O(4)	0.2264(12)	0.0967(4)	0.1924(8)	165(17)	
O(5)	0.1804(12)	0.4184(4)	0.4457(8)	117(15)	
H	0.182(26)	0.346(9)	0.480(18)		68

Note. For nonhydrogen atoms $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*a_ia_j \cos(a_i, a_j)$. For H atom U_{iso} value is listed.

TABLE IV

INTERATOMIC BOND DISTANCES (Å) AND ANGLES (°) IN La(OH)CrO$_4$

La polyhedron		Cr polyhedron	
La–O(1)^1	2.534(5)	Cr–O(1)	1.696(5)
La–O(1)^2	2.537(6)	Cr–O(2)	1.622(6)
La–O(2)	2.467(6)	Cr–O(3)	1.613(7)
La–O(3)^7	2.576(7)	Cr–O(4)	1.649(5)
La–O(4)^6	2.729(6)	O(1)–Cr–O(2)	111.2(3)
La–O(4)^3	2.658(6)	O(1)–Cr–O(3)	108.9(3)
La–O(5)	2.666(6)	O(1)–Cr–O(4)	107.5(3)
La–O(5)^4	2.503(5)	O(2)–Cr–O(3)	108.6(3)
La–O(5)^5	2.531(5)	O(2)–Cr–O(4)	110.4(3)
O(5)–H$_1$	0.99(1)	O(3)–Cr–O(4)	110.2(3)
O(1)^1–La–O(1)^2			65.9(2)
–O(2)			86.0(2)
–O(3)^7			68.6(2)
–O(4)^6			145.5(2)
–O(4)^3			80.0(2)
–O(5)			88.8(2)
–O(5)^4			135.0(2)
–O(5)^5			136.8(2)
O(1)^2–La–O(2)			137.4(2)
–O(3)^7			75.8(2)
–O(4)^6			144.6(2)
–O(4)^3			76.2(2)
–O(5)			132.3(2)
–O(5)^4			90.3(2)
–O(5)^5			85.4(2)
O(2)–La –O(3)^7			64.0(2)
–O(4)^6			74.5(2)
–O(4)^3			131.8(2)
–O(5)			74.6(2)
–O(5)^4			88.0(2)
–O(5)^5			133.9(2)
O(3)^7–La–O(4)^6			123.7(2)
–O(4)^3			144.3(2)
–O(5)			133.3(2)
–O(5)^4			68.8(2)
–O(5)^5			136.7(2)
O(4)^6–La–O(4)^3			91.9(2)
–O(5)			58.9(2)
–O(5)^4			73.6(2)
–O(5)^5			60.0(2)
O(4)^3–La–O(5)			59.4(2)
–O(5)^4			132.9(2)
–O(5)^5			61.4(2)
O(5)–La –O(5)^4			131.0(2)
–O(5)^5			87.8(2)
O(5)^4–La–O(5)^5			72.8(2)

Note. Symmetry code: 1, $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; 2, $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; 3, $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; 4, $1 + x, y, z$; 5, $1 - x, 1 - y, 1 - z$; 6, $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; 7, $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$.

The IR spectra exhibits a very sharp peak at 3514 cm^{-1}, corresponding to the stretching vibration of the hydroxyl group.

The La atoms are coordinated to nine oxygens (Fig. 1) (*19*), in a very irregular manner. Six of these oxygen atoms belong to six different CrO$_4$ groups, and the remaining three (O_5, O_5^1, O_5^4) are hydroxyl oxygens

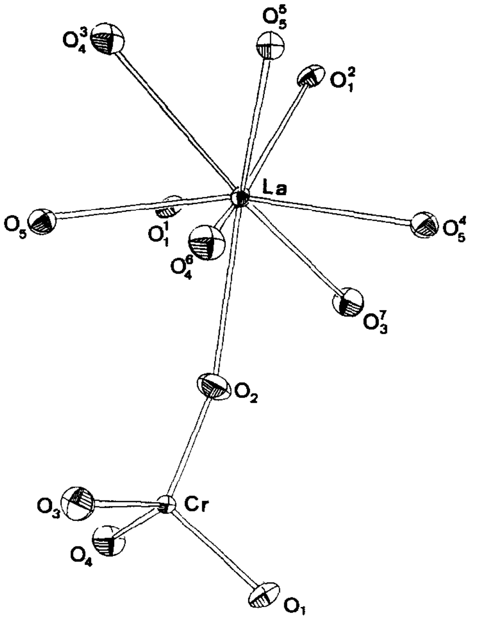

FIG. 1. Coordination polyhedron of the La atoms. ORTEP (*19*).

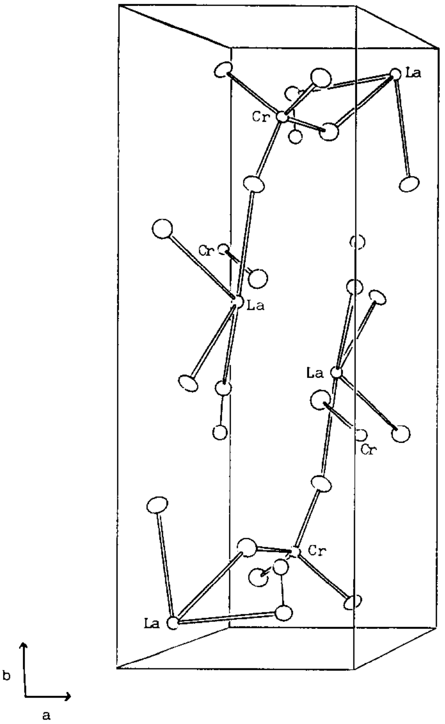

FIG. 2. A view of the unit cell of La(OH)CrO_4. ORTEP (*19*).

which are common to another two La atoms. There is not significant difference between the La–O and La–OH distances which average 2.584 and 2.567 Å, respectively.

The CrO_4 tetrahedra are nearly regular, with CrO_4 distances ranging from 1.613(7) to 1.696(5) Å.

The distances La–O are quite similar to those found in KLa(CrO_4) (*1*). In both compounds the coordination polyhedra of the La atom show one distance longer than the other eight.

In three-dimensional La(OH)CrO_4 (Fig. 2), the La ions are linked through O_5 atoms (O_5, O_5^1, O_5^4) to give infinite puckered layers of La polyhedra sharing vertices, perpendicular to the *b* axis. These layers alternate along the *b* axis with independent tetrahedra of chromate anions common oxygens, forming a three-dimensional array.

On the other hand, the H atom of the hydroxyl group (H_5) is surrounded by five O atoms with distances within 2.54 to 2.99 Å. The geometry of these oxygen atoms does not show clearly the existence of hydrogen bonds although some kind of interaction between these oxygens and the O_5 through the hydrogen is not to be excluded.

La(OH)CrO_4 can be related with the two Bi(OH)CrO_4 compounds (*14, 15*), because these three hidroxo-chromates of a trivalent metal are three-dimensional, with nine-coordinated *M* polyhedra, which are linked through hydroxyl oxygens giving infinite puckered layers.

Nevertheless, for M = Bi, there are two OH groups coordinated to Bi, and in La(OH)CrO_4 there are three of these groups which are coordinated. Thus, MO_9 polyhedra share two or three vertices for M = Bi, La, respectively. On the other hand, all the distances La–O are similar and there are two Bi–OH distances which are shorter than the other Bi–O distances.

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