

A Single-Crystal X-Ray Investigation of the Structures of $\text{La}_3(\text{OH})(\text{CrO}_4)_4 \cdot 3.5 \text{H}_2\text{O}$ and $\text{La}_2(\text{CrO}_4)_3 \cdot 7 \text{H}_2\text{O}$

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The unit cell of $\text{La}_3(\text{OH})(\text{CrO}_4)_4 \cdot 3.5 \text{H}_2\text{O}$ (**1**) is monoclinic, space group $C2/c$ (No. 15), with lattice parameters $a = 33.187(6)$, $b = 7.217(2)$, $c = 14.327(3)$ Å, $\beta = 97.34(1)^\circ$, $Z = 8$. $\text{La}_2(\text{CrO}_4)_3 \cdot 7 \text{H}_2\text{O}$ (**2**) forms monoclinic crystals, space group $P2_1/n$ (No. 14), with lattice parameters $a = 10.600(1)$, $b = 19.317(2)$, $c = 8.188(1)$ Å, $\beta = 90.88(1)^\circ$, $Z = 4$.

The structures of **1** and **2** were solved by direct methods from 2531 and 2911 independent diffractometer reflections and refined to R -values of 0.071 and 0.075, respectively. Both structures contain LaO_9 coordination polyhedra. In **1** the structure contains three independent LaO_9 coordination polyhedra forming alternating double and single layers of polyhedra parallel to the bc -plane. In **2** the structure contains two independent LaO_9 coordination polyhedra each forming a layer parallel to the ac -plane. All the LaO_9 coordination polyhedra in **1** and **2** are of the same type, a three-sided prism with the metal atom in the centre, six oxygen atoms in the corners and three oxygen atoms placed perpendicular to the three rectangular surfaces of the prism.

Solid rare-earth chromates can be precipitated from the $\text{CrO}_3\text{-RE}_2\text{O}_3\text{-H}_2\text{O}$ systems,¹ but the solids formed are often powders with crystals not sufficiently large for single-crystal X-ray diffractometry. Only in the case of cerium (IV) chromate was it possible at room temperature to obtain single crystals large enough for a detailed single-crystal structure investigation, in this case of $\text{Ce}(\text{CrO}_4)_2 \cdot 2 \text{H}_2\text{O}$.² Bueno *et al.*³ obtained single crystals of $\text{La}(\text{OH})\text{CrO}_4$ at 130°C in hydrothermal synthesis and solved the crystal structure by single-crystal X-ray diffractometry. By the use of hydrothermal synthesis single crystals of $\text{KLa}(\text{CrO}_4)_2$ ⁴ and $\text{KTb}(\text{CrO}_4)_2$ ⁵ were also obtained and the structures were solved using single-crystal X-ray diffractometry.

In the case of lanthanum the heterogeneous equilibria in the system $\text{CrO}_3\text{-La}_2\text{O}_3\text{-H}_2\text{O}$ were studied at 25°C by Bashilova *et al.*⁶ The hydrates $\text{La}_2(\text{CrO}_4)_3 \cdot 7 \text{H}_2\text{O}$, $\text{La}_2(\text{Cr}_2\text{O}_7)_3 \cdot 7 \text{H}_2\text{O}$ and $\text{La}_2(\text{Cr}_2\text{O}_7)_3 \cdot 10 \text{H}_2\text{O}$ were found and their X-ray powder patterns were reported. A basic lanthanum chromate was not found in the system.

For some time a sample of $\text{La}_2(\text{CrO}_4)_3 \cdot 7 \text{H}_2\text{O}$ has been available,⁷ but the crystals in the sample were not large enough for single-crystal X-ray diffractometry. As equipment for hydrothermal synthesis was present it was decided to investigate the system $\text{CrO}_3\text{-La}_2\text{O}_3\text{-H}_2\text{O}$ at room temperature, as well as at hydrothermal conditions, and single crystals of the following two compounds were found: $\text{La}_2(\text{CrO}_4)_3 \cdot 7 \text{H}_2\text{O}$ and $\text{La}_3(\text{OH})(\text{CrO}_4)_4 \cdot 3.5 \text{H}_2\text{O}$. The crystal structures of these compounds were unknown. The structures were then solved by single-crystal X-ray diffractometry, and the results are reported below.

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Experimental

Preparation of compounds. By precipitation of a solution of 17.3 g $\text{La}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$ (Merck, p.a.) in 80 ml water with a solution of 9.7 g Na_2CrO_4 (Merck, p.a.) in 90 ml water, small crystals of $\text{La}_2(\text{CrO}_4)_3 \cdot 7 \text{H}_2\text{O}$ were formed. By slow mixing of the two solutions in a diffusion experiment in a U-shaped tube, crystals large enough for X-ray diffractometry were obtained. The duration of this diffusion growth experiment was 2 months. Hydrothermal treatment of $\text{La}_2(\text{CrO}_4)_3 \cdot 7 \text{H}_2\text{O}$ with water at 200°C for 140 h yields single crystals of LaOHCrO_4 and $\text{La}_3\text{OH}(\text{CrO}_4)_4 \cdot 3.5 \text{H}_2\text{O}$, and hydrothermal treatment of a mixture of 17.3 g $\text{La}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$ in 80 ml water and 9.7 g Na_2CrO_4 in 90 ml water at 120°C for 265 h yields small single crystals of $\text{La}_2(\text{CrO}_4)_3 \cdot 7 \text{H}_2\text{O}$.

The single crystals of $\text{La}_2(\text{CrO}_4)_3 \cdot 7 \text{H}_2\text{O}$ were yellow, and were board-shaped from the diffusion growth experiment and needle-shaped from the hydrothermal synthesis. The single crystals of $\text{La}_3(\text{OH})(\text{CrO}_4)_4 \cdot 3.5 \text{H}_2\text{O}$ were orange-yellow and had a plate-like morphology. Crystals of $\text{La}_3(\text{OH})(\text{CrO}_4)_4 \cdot 3.5 \text{H}_2\text{O}$ mixed with the yellow crystals of $\text{La}(\text{OH})\text{CrO}_4$ in the hydrothermal product represented less than 5% of the sample. By careful sorting of the crystals using a microscope and a pair of tweezers a sample of pure $\text{La}_3(\text{OH})(\text{CrO}_4)_4 \cdot 3.5 \text{H}_2\text{O}$ large enough for a Guinier photograph was obtained.

X-Ray diffraction. Guinier photographs were taken with a Guinier-Lenné camera with Si ($a = 5.43050$ Å) as internal standard using Cu $K\alpha_1$ radiation ($\lambda = 1.540598$ Å), and the powder patterns were also measured on a Stoe diffracto-

Table 1. Unit cell parameters, space groups and data for the single-crystal X-ray measurements of the two lanthanum chromates.

	La ₃ (OH)(CrO ₄) ₄ ·3.5 H ₂ O	La ₂ (CrO ₄) ₃ ·7 H ₂ O
Unit cell parameters:		
<i>a</i> /Å	33.187(6)	10.600(1)
<i>b</i> /Å	7.217(2)	19.317(2)
<i>c</i> /Å	14.327(3)	8.188(1)
β/°	97.34(1)	90.88(1)
Space group	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>Z</i>	8	4
Size of crystal/mm	0.125×0.0875×0.075	0.025×0.075×0.55
Density (calculated)/g cm ⁻³	3.75	2.98
Linear absorption coefficient, μ/cm ⁻¹	101	71
No. of measured and independent reflections	2766 and 2531	3253 and 2911
Scan method	ω-2θ	ω-2θ
Scan range, Δ2θ	0.80 + 0.35 tan θ	1.20 + 0.35 tan θ
sin θ/λ (max)	0.704	0.704

meter with a curved position-sensitive detector, using Cu *K*α₁ radiation. The diffractometer was calibrated with a standard of Ag₆Ge₁₀P₁₂ (*a* = 10.312 Å).

Single-crystal X-ray diffraction. Precession and Weissenberg photographs were taken of single crystals of the two compounds, and the space groups were determined from these photographs. Single-crystal X-ray diffraction data were measured on a Huber four-circle diffractometer using Mo *K*α radiation (λ = 0.7107 Å). The unit cell parameters were calculated in a least-squares refinement using diffraction data from 120 reflections for La₃(OH)(CrO₄)₄·3.5 H₂O, and from 156 reflections for La₂(CrO₄)₃·7 H₂O. The unit cell parameters and data for the crystals investigated are listed in Table 1. The powder patterns of the two compounds were indexed with the unit cell parameters obtained in the single-crystal X-ray diffraction measurements. This indicates that the single crystals investigated were representative for the two compounds.

Structure determination

The structures of the two compounds were solved by direct methods using the MULTAN⁸ program, which yielded the positions of all the metal atoms. Phased on this solution the oxygen atoms were located in Fourier map calculations, and the models of the structures were then refined in a least-squares procedure using the program LINUS.⁹

The structure of La₃(OH)(CrO₄)₄·3.5 H₂O. A total of 1511 reflections with *I* > 2σ(*I*) were used in the least-squares refinement of the structure with scattering contributions from neutral atoms.¹⁰ For the metal atoms anisotropic thermal parameters were refined, while oxygen atoms were kept isotropic. An isotropic extinction parameter *g* = 0.97 × 10⁻⁴ s of arcs was applied, and the least-squares refinements gave a final *R*-value of 7.1%. The weighting scheme used was *w* = 1/σ, where σ = [σ_{count}(*F*²) + 1.06*F*²]^{1/2} - |*F*| and σ_{count}(*F*²) = (number of counts)^{1/2}. *R*_w(*F*) was

8.4%. Table 2 is a list of atomic coordinates and the equivalent isotropic temperature factors, and Table 3 is a list of interatomic distances. Fig. 1 is a stereoscopic drawing showing the CrO₄²⁻ ions of the structure, and Fig. 2 shows the LaO₉ coordination polyhedra.

Table 2. Atomic coordinates and isotropic temperature factor parameters for La₃(OH)(CrO₄)₄·3.5 H₂O. For La and Cr the equivalent isotropic thermal parameters are given.^a

Atom	<i>x</i> / <i>a</i>	<i>y</i> / <i>b</i>	<i>z</i> / <i>c</i>	<i>U</i> _{eq} / <i>U</i> _{iso}
La1	0.1602(1)	0.1880(3)	0.1386(2)	0.012(1)
La2	0.2180(1)	0.1362(3)	-0.1104(1)	0.011(1)
La3	0.0234(1)	-0.1458(3)	-0.1117(1)	0.011(1)
Cr1	0.0596(2)	0.3458(8)	-0.0229(4)	0.014(3)
Cr2	0.2459(2)	-0.1533(8)	0.1713(4)	0.014(3)
Cr3	0.1465(2)	-0.1600(8)	-0.0800(4)	0.015(3)
Cr4	0.0614(2)	-0.1099(8)	0.1620(4)	0.013(3)
O11	0.1078(7)	0.2893(35)	0.0131(17)	0.006(2)
O12	0.0324(7)	0.3325(35)	0.0696(17)	0.008(2)
O13	0.0577(7)	0.4432(36)	0.4338(18)	0.008(2)
O14	0.4567(7)	0.3004(33)	0.1019(16)	0.006(2)
O21	0.2617(9)	0.0269(41)	0.1221(20)	0.013(3)
O22	0.2254(7)	0.3112(34)	0.2294(17)	0.008(2)
O23	0.3006(6)	0.3889(31)	0.2987(15)	0.004(2)
O24	0.2548(7)	0.1633(37)	0.3969(17)	0.008(2)
O31	0.1664(6)	0.1100(29)	0.3216(14)	0.003(2)
O32	0.0998(7)	0.1070(35)	0.4058(17)	0.007(2)
O33	0.1541(8)	0.3741(38)	0.4479(18)	0.010(2)
O34	0.3279(7)	0.4775(33)	0.4990(16)	0.005(2)
O41	0.4413(7)	0.1900(35)	0.2970(17)	0.008(2)
O42	0.3919(7)	0.4358(32)	0.3452(16)	0.004(2)
O43	0.0395(6)	0.0519(29)	0.2268(14)	0.000(2)
O44	0.4671(7)	0.4184(32)	0.4433(16)	0.006(2)
O(H)1	0.2109(7)	0.3267(34)	0.0286(17)	0.007(2)
O(W)1	0.0000	0.4145(46)	0.2500	0.006(3)
O(W)2	0.1016(7)	0.3330(33)	0.2214(16)	0.006(2)
O(W)3	0.3444(10)	0.0593(44)	0.3574(22)	0.016(3)
O(W)4	0.3500(8)	0.1939(38)	0.1580(18)	0.011(2)

$$^a U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

Table 3. Bond lengths in Å for the structure of $\text{La}_3(\text{OH})(\text{CrO}_4)_4 \cdot 3.5 \text{H}_2\text{O}$.

Bond lengths of the CrO_4^{2-} ions	
Cr1—O11	1.667(23)
Cr1—O12	1.698(24)
Cr1—O13	1.642(26)
Cr1—O14	1.591(24)
Cr2—O21	1.599(29)
Cr2—O22	1.629(23)
Cr2—O23	1.681(21)
Cr2—O24	1.643(26)
Cr3—O31	1.672(21)
Cr3—O32	1.586(25)
Cr3—O33	1.608(27)
Cr3—O34	1.673(23)
Cr4—O41	1.566(26)
Cr4—O42	1.602(23)
Cr4—O43	1.710(21)
Cr4—O44	1.687(23)
Bond lengths of the LaO_9 polyhedra	
La1—O22	2.539(23)
La1—O31	2.664(20)
La1—O(H)1	2.646(24)
La1—O(W)2	2.621(23)
La1—O11	2.448(23)
La1—O(W)3	2.685(32)
La1—O23	2.620(22)
La1—O34	2.559(23)
La1—O42	2.539(23)
La2—O34	2.607(23)
La2—O(H)1	2.455(24)
La2—O21	2.534(30)
La2—O22	2.721(24)
La2—O23	2.695(21)
La2—O(H)1	2.511(23)
La2—O(W)4	2.584(26)
La2—O24	2.477(27)
La2—O31	2.572(21)
La3—O13	2.478(26)
La3—O32	2.530(25)
La3—O43	2.532(21)
La3—O14	2.578(24)
La3—O12	2.428(25)
La3—O43	2.580(20)
La3—O44	2.680(24)
La3—O44	2.438(24)
La3—O(W)1	2.810(23)

The structure of $\text{La}_2(\text{CrO}_4)_3 \cdot 7 \text{H}_2\text{O}$. In the least-squares refinement of the structure 1694 reflections with $I > 2\sigma(I)$ and scattering contributions from neutral atoms¹⁰ were used. The isotropic extinction parameter g was 0.46×10^{-4} s of arcs, and the final R -value was 7.5%. The weighting scheme used was $w = 1/\sigma$, where $\sigma = [\sigma_{\text{count}}(F^2) + 1.04F^2]^{1/2} - |F|$ and $\sigma_{\text{count}}(F^2) = (\text{number of counts})^{1/2}$. The $R_w(F)$ value was 8.0%. Table 4 contains the atomic coordinates and equivalent temperature factors of the model, and Table

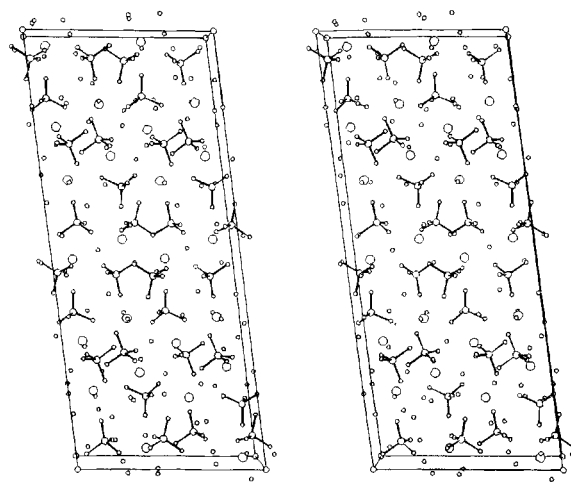


Fig. 1. Stereoscopic drawing of $\text{La}_3(\text{OH})(\text{CrO}_4)_4 \cdot 3.5 \text{H}_2\text{O}$ along the [010] direction showing packing of the CrO_4^{2-} ions.

5 gives the interatomic distances. Fig. 3 shows a stereoscopic drawing with the CrO_4^{2-} ions in the structure, and Fig. 4 shows the LaO_9 coordination polyhedra.

Discussion

$\text{La}_3(\text{OH})(\text{CrO}_4)_4 \cdot 3.5 \text{H}_2\text{O}$. The structure contains LaO_9 polyhedra forming alternating double and single layers of

Table 4. Atomic coordinates and equivalent isotropic temperature factor parameters for $\text{La}_2(\text{CrO}_4)_3 \cdot 7 \text{H}_2\text{O}$.

Atom	x/a	y/b	z/c	U_{eq}
La1	-0.0635(1)	0.0009(1)	0.2500(2)	0.012(1)
La2	0.2441(1)	0.2442(1)	0.3145(2)	0.014(1)
Cr1	-0.4465(4)	0.3539(2)	0.4526(5)	0.015(2)
Cr2	-0.0735(4)	0.1483(2)	0.4583(5)	0.015(2)
Cr3	0.2780(4)	0.0401(2)	0.3979(5)	0.019(2)
O11	0.1483(19)	0.1700(9)	0.0957(22)	0.024(11)
O12	-0.3698(18)	0.3693(9)	0.2845(21)	0.023(11)
O13	0.4467(19)	0.2934(9)	0.4277(24)	0.029(12)
O14	0.0150(18)	-0.0690(8)	0.0076(22)	0.017(9)
O21	0.1739(18)	-0.1741(10)	0.4078(22)	0.026(11)
O22	-0.0102(18)	0.0750(8)	0.5112(22)	0.018(9)
O23	0.0345(17)	0.2077(10)	0.4353(23)	0.028(12)
O24	-0.1478(17)	0.1300(8)	0.2800(18)	0.014(9)
O31	0.0854(18)	0.5123(9)	0.1628(20)	0.024(11)
O32	-0.2487(16)	-0.0067(9)	0.4200(19)	0.019(10)
O33	0.3332(16)	0.5159(10)	0.2377(21)	0.024(11)
O34	0.2858(18)	0.1271(9)	0.4147(23)	0.026(11)
OW1	-0.2451(17)	-0.4961(11)	0.4509(21)	0.025(10)
OW2	0.0575(19)	0.3083(10)	0.1629(22)	0.026(11)
OW3	-0.2328(21)	0.2649(10)	0.1351(18)	0.035(12)
OW4	0.4333(18)	0.1937(11)	0.1610(24)	0.033(12)
OW5	-0.4148(21)	0.1173(12)	0.3703(25)	0.044(14)
OW6	0.1852(22)	0.3592(11)	0.4463(22)	0.044(14)
OW7	-0.0520(26)	0.4249(13)	0.3586(31)	0.060(18)

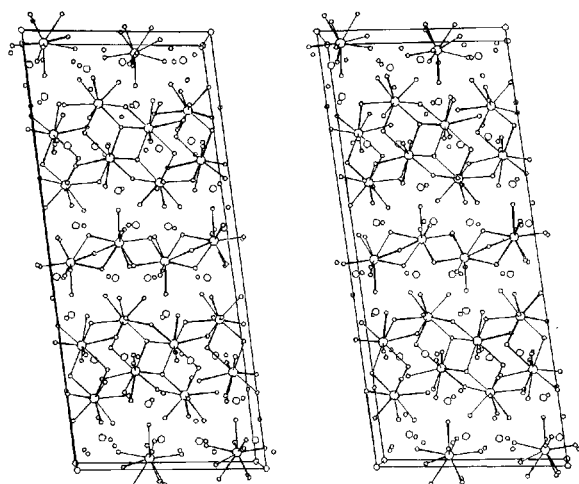


Fig. 2. Stereoscopic drawing of $\text{La}_3(\text{OH})(\text{CrO}_4)_4 \cdot 3.5\text{H}_2\text{O}$ along $[010]$ showing packing of the LaO_9 coordination polyhedra.

polyhedra parallel to the bc -plane. The oxygen atoms in the LaO_9 polyhedra belong for the La1 and La2 polyhedra to CrO_4^{2-} ions, water molecules and the OH^- ion. For the

Table 5. Bond lengths in Å for $\text{La}_2(\text{CrO}_4)_3 \cdot 7\text{H}_2\text{O}$.

Bond lengths of the CrO_4^{2-} ions

Cr1–O11	1.607(19)
Cr1–O12	1.636(18)
Cr1–O13	1.635(20)
Cr1–O14	1.691(17)
Cr2–O21	1.621(19)
Cr2–O22	1.624(17)
Cr2–O23	1.639(20)
Cr2–O24	1.688(17)
Cr3–O31	1.627(19)
Cr3–O32	1.658(18)
Cr3–O33	1.669(19)
Cr3–O34	1.685(19)

Bond lengths of the LaO_9 polyhedra

La1–OW1	2.585(18)
La1–O14	2.553(18)
La1–O22	2.626(18)
La1–O24	2.662(17)
La1–O32	2.429(17)
La1–O12	2.648(18)
La1–O22	2.555(18)
La1–O33	2.465(18)
La1–O14	2.543(18)
La2–O11	2.487(19)
La2–O13	2.518(20)
La2–O23	2.537(19)
La2–O34	2.447(19)
La2–O21	2.572(19)
La2–OW2	2.626(20)
La2–OW3	2.635(20)
La2–OW4	2.580(20)
La2–OW6	2.555(22)

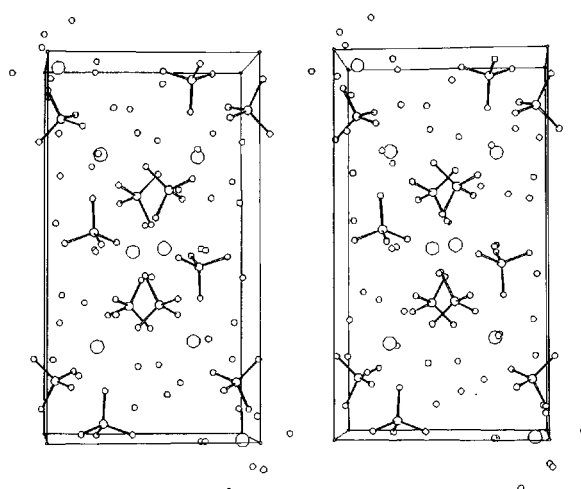


Fig. 3. Stereoscopic drawing of $\text{La}_2(\text{CrO}_4)_3 \cdot 7\text{H}_2\text{O}$ along $[001]$ showing packing of the CrO_4^{2-} ions.

LaO_9 polyhedron of La3, the oxygen atoms belong to CrO_4^{2-} ions and to a water molecule. Fig. 5 displays the three LaO_9 polyhedra and shows the interatomic La–O distances. The three LaO_9 polyhedra are all of the same type, a three-sided prism with the lanthanum atom in the centre, six oxygen atoms in the corners and three oxygen atoms placed perpendicular to the three rectangular surfaces of the prism. This coordination polyhedron is known from the crystal structure of $\text{La}(\text{OH})_3$.¹¹

The La–O distances in the polyhedra are 2.43(2) to 2.72(2) Å. The Cr–O distances in the CrO_4^{2-} ions are from 1.57(3) to 1.71(2) Å. These interatomic distances do not deviate significantly from the interatomic distances found in the structure of $\text{La}(\text{OH})\text{CrO}_4$.³ However, the standard deviations of atomic coordinates and interatomic distances are larger for the structure of $\text{La}_3(\text{OH})(\text{CrO}_4)_4 \cdot 3.5\text{H}_2\text{O}$ than for the structure of $\text{La}(\text{OH})\text{CrO}_4$.³ The crystals of $\text{La}_3(\text{OH})(\text{CrO}_4)_4 \cdot 3.5\text{H}_2\text{O}$ were all very small, and only a

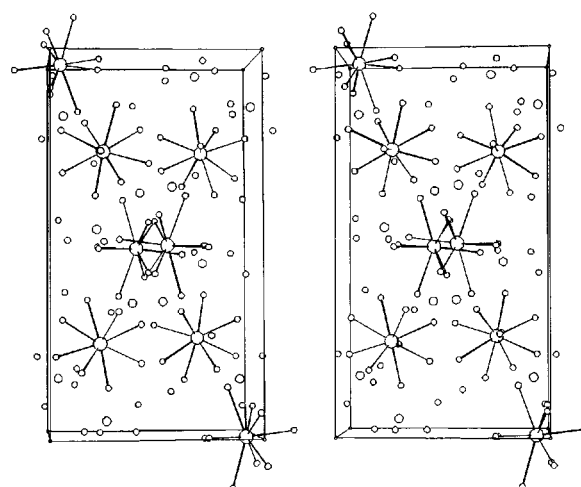


Fig. 4. Stereoscopic drawing of $\text{La}_2(\text{CrO}_4)_3 \cdot 7\text{H}_2\text{O}$ along $[001]$ showing packing of the LaO_9 coordination polyhedra.

limited number of reflections out to $\sin \theta/\lambda = 0.704$ could consequently be measured as significant reflections. This results in large standard deviations for coordinates and interatomic distances of the structure.

$\text{La}_2(\text{CrO}_4)_3 \cdot 7\text{H}_2\text{O}$. The structure contains two independent LaO_9 coordination polyhedra, each forming a layer that is separated by the CrO_4^{2-} ions. The layers are parallel to the ac -plane. The two coordination polyhedra are of the same kind as found in $\text{La}(\text{OH})_3$.¹¹ The oxygen atoms in the LaO_9 polyhedron belonging to La1 come from one water molecule, and the remaining oxygen atoms come from CrO_4^{2-} ions. The LaO_9 polyhedron of La2 has four oxygen atoms belonging to the water molecules, and the remaining five oxygen atoms come from CrO_4^{2-} ions. The two LaO_9 coordination polyhedra with the interatomic La–O distances are displayed in Fig. 6. Two water molecules OW5 and OW7 have La–O distances larger than 3 Å. The water molecule, OW5, is hydrogen-bonded in a tetrahedron to O31, O24, OW2 and OW4 with the distances 2.73(2), 2.95(2), 2.81(2) and 2.76(2) Å, respectively. The water molecule, OW7, is only hydrogen-bonded to O31, OW1 and OW6, with the distances 2.76(2), 2.67(2) and 2.90(2) Å, respectively. The La–O distances in the LaO_9 polyhedra are 2.45(2) to 2.66(2) Å and are comparable with the La–O distances in the structure of $\text{La}(\text{OH})\text{CrO}_4$.³ Also, in the structure of $\text{La}_2(\text{CrO}_4)_3 \cdot 7\text{H}_2\text{O}$ the standard deviations of coordinates and interatomic distances are larger than in the structure of $\text{La}(\text{OH})\text{CrO}_4$.³ Owing to the small crystal size of the compound only a rather limited number of reflections could be measured as significant reflections out to the limit $\sin \theta/\lambda = 0.704$.

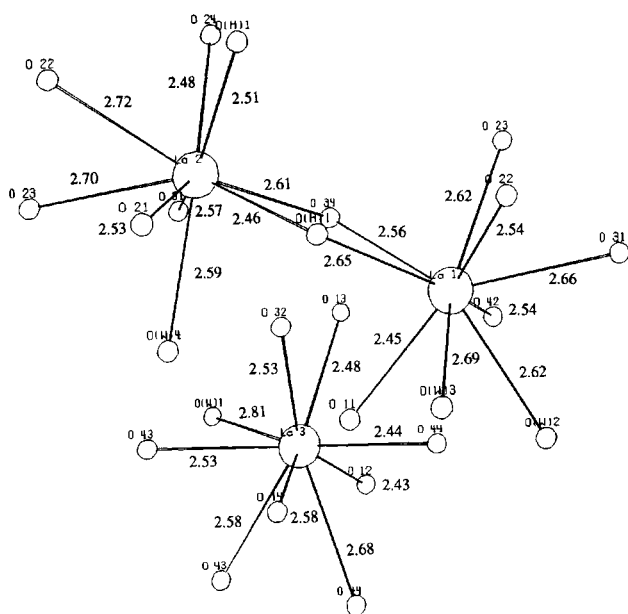


Fig. 5. LaO_9 coordination polyhedra with La–O distances in $\text{La}_3(\text{OH})(\text{CrO}_4)_4 \cdot 3.5\text{H}_2\text{O}$.

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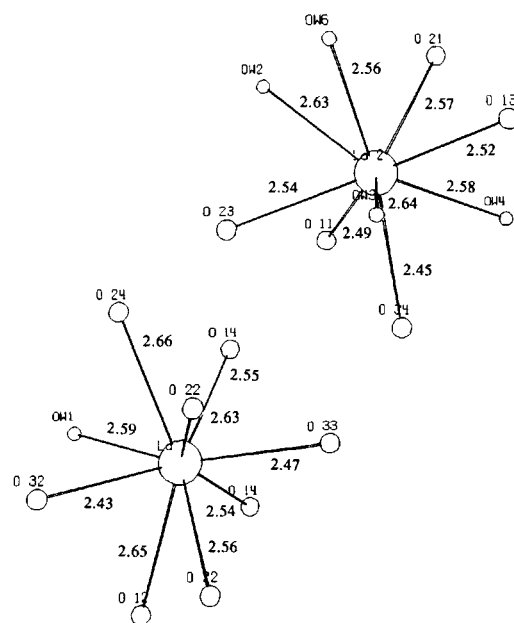


Fig. 6. LaO_9 coordination polyhedra with La–O distances in $\text{La}_2(\text{CrO}_4)_3 \cdot 7\text{H}_2\text{O}$.