Crystal Growth, Structure, and Properties of $KLa(CrO_4)_2$†

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The crystal growth and structure of $KLa(CrO_4)_2$, its spectroscopic properties, and thermal decomposition are reported. Crystals of $KLa(CrO_4)_2$ were obtained from an aqueous solution of $K_2Cr_2O_7$ + La_2O_3 (3:1), maintained at 150 °C for 1 month: space group $P2_1/c$, $Z = 4$, with a = 8.729(2), b = 7.4752(7), c = 11.049(6) Å, and β = 92.42(1)°. They consist of parallel layers of $[La(CrO_4)_2]_n^{n-}$ perpendicular to the a axis, the K^+ being situated between these layers. Of the possible 36 absorption bands, 16 were observed in the i.r. and Raman spectra, which were analysed using factor-group analysis. The thermal decomposition proceeds in one step at 720—760 °C according to $KLa(CrO_4)_2 \longrightarrow LaCrO_3 + KCrO_2 + \frac{3}{2}O_2$.

Polycrystalline samples of the double chromates $KLn(CrO_4)_2$ have been obtained previously.[1-3] From X-ray powder patterns their structure was related[4] to that of $PbCrO_4$, crocoite type, in which Pb^{2+} is ten-co-ordinated.

We considered it of interest to investigate the structure of $KLa(CrO_4)_2$ due to the increasing interest in the luminescence properties of lanthanides and, in particular, the recently observed[5-8] efficient luminescence in the host lattice $NaLn(SO_4)_2 \cdot H_2O$ in which nine-co-ordinated Ln^{3+} adopts C_2 symmetry. In this paper we report the hydrothermal growth of a single crystal of $KLa(CrO_4)_2$, the crystal structure (which implies nine-co-ordinated La), and thermal and optical properties.

Results and Discussion

Description of the Structure.—Table 1 shows the final atomic parameters, Table 2 the bond lengths and angles. The La atoms are co-ordinated to nine oxygen atoms (Figure 1).[9] The polyhedron around La is not regular but can be considered as an irregular pentagon with two additional oxygen atoms [O(3) and O(2)] above and another two [O(5) and O(6)] below the plane of the pentagon.

The crystal consists of parallel layers of composition $[La(CrO_4)_2]_n^{n-}$ perpendicular to the a axis (Figure 2). Each layer is formed by double rows of the independent CrO_4^{2-} tetrahedra linked to the La atom through the oxygen atoms. The K^+ ions are located between these layers. Each is surrounded by nine oxygen atoms at distances 2.722(5)—3.076(5), which are equal or less than the sum of the ionic radii, and can be thought of as chemically bonded.

This structure shows that $KLa(CrO_4)_2$ is not isostructural with crocoite as was suggested previously.[3] The X-ray powder pattern of $KLa(CrO_4)_2$ is included in Table 3.

I.r. and Raman Spectra.—In the spectral region between 1 260 and 250 cm^{-1}, absorption bands due to chromate anions are observed. The i.r. and Raman spectra were analysed using factor-group analysis. According to the structural results, the chromate group has C_1 site symmetry.

Table 4 illustrates the correlation of the internal vibrational modes for the CrO_4^{2-} group, which predicts 36 vibrations: 4 ν_1 in the region 830—847 cm^{-1}, 8 ν_2 in the region 330—358 cm^{-1}, 12 ν_3 in the region 860—984 cm^{-1}, and 12 ν_4 in the region 368—460 cm^{-1}. In Table 5 are included the observed vibrational frequencies, which do not contain all the 36 stretchings and bendings predicted by group theory.

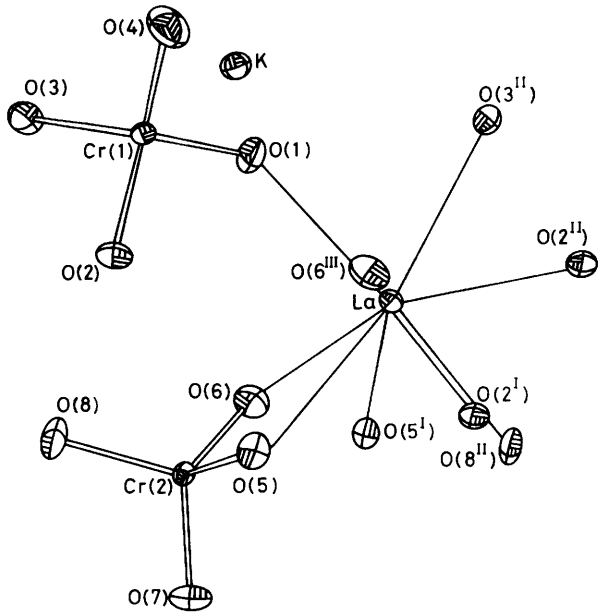


Figure 1. Co-ordination polyhedron of the lanthanum atoms

Thermal Decomposition.—Figure 3 shows the results of differential thermal analysis and thermal gravimetry for a powdered sample. The compound $KLa(CrO_4)_2$ remains stable up to 720 °C and it decomposes in one step, between 720 and 760 °C.

Contrary to previous work[10] in which the decomposition was said to occur through the steps $KLa(CrO_4)_2 \xrightarrow{-\frac{1}{2}O_2} LaCrO_4 + 0.5K_2Cr_2O_7 \xrightarrow{-\frac{1}{2}O_2} LaCrO_3 + 0.5K_2Cr_2O_7$, the reaction $KLa(CrO_4)_2 \longrightarrow LaCrO_3 + KCrO_2 + \frac{3}{2}O_2$ is postulated. The observed weight loss of 11.53% is in good agreement with the theoretical weight loss of 11.71%. However, $KCrO_2$ could not be identified because of its extreme sensitivity to air and humidity.[11] For this reason the X-ray pattern of the product of thermal decomposition of $KLa(CrO_4)_2$ shows a mixture of several phases.

Besides the evidence of the peaks corresponding to $LaCrO_3$,

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

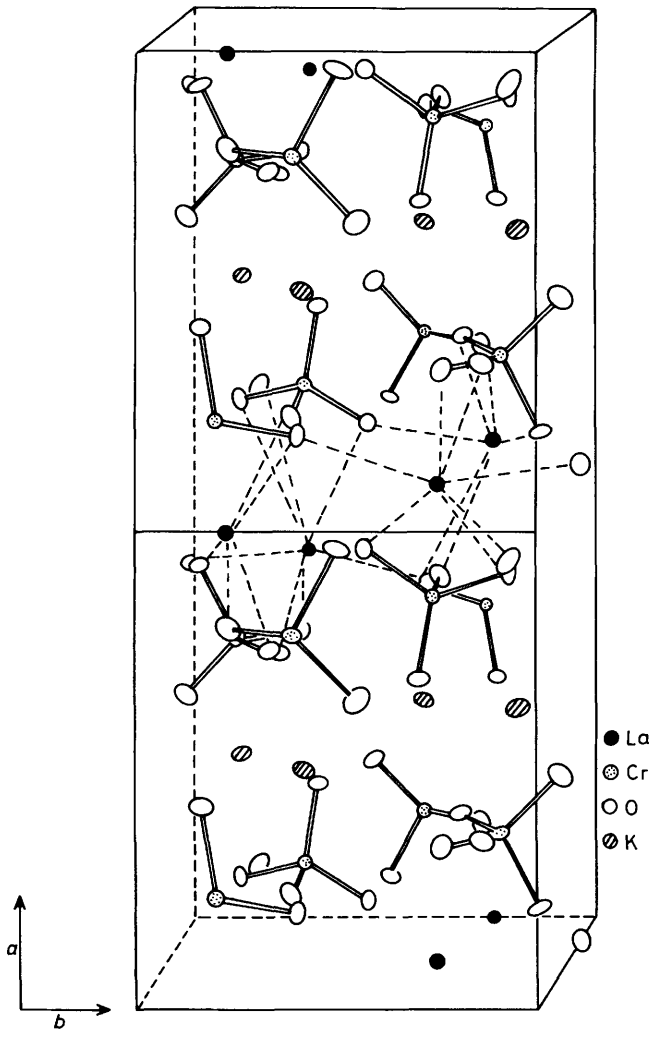


Figure 2. View of the two unit cells of $KLa(CrO_4)_2$

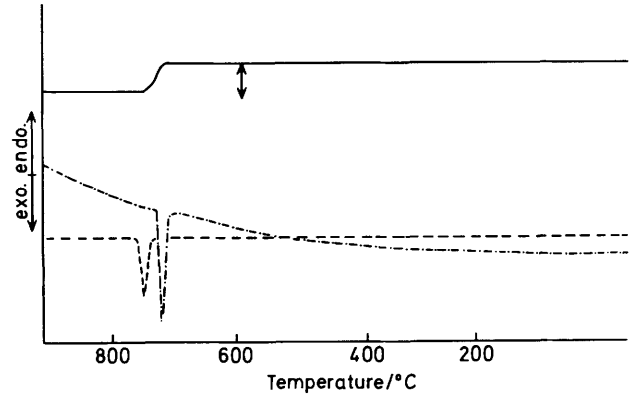


Figure 3. Thermal decomposition of $KLa(CrO_4)_2$: thermal gravimetry (——), differential thermal gravimetry (– – –), and differential thermal analysis (– • – • –)

orthorhombic form, many less intense reflections can be observed. These peaks corresponded to a mixture of Cr_2O_3, K_3CrO_4, and K_2CrO_4 which result from rapid oxidation of $KCrO_2$ due to humid air, according to $10KCrO_2 \xrightarrow{\frac{5}{2}O_2} 3Cr_2O_3 + 2K_3CrO_4 + 2K_2CrO_4$.

Table 1. Atomic parameters for $KLa(CrO_4)_2$

Atom	*X/a*	*Y/b*	*Z/c*
La	0.059 64(4)	0.160 75(5)	0.343 60(3)
Cr(1)	0.285 34(10)	0.334 44(16)	0.088 43(8)
Cr(2)	−0.194 08(10)	0.161 80(16)	0.106 09(8)
K	0.430 53(15)	−0.152 57(22)	0.164 06(13)
O(1)	0.267 63(55)	0.179 06(73)	0.194 06(42)
O(2)	0.115 88(51)	0.435 14(70)	0.062 46(43)
O(3)	0.313 82(52)	0.246 12(68)	−0.046 28(42)
O(4)	0.416 20(59)	0.477 05(75)	0.128 45(46)
O(5)	−0.148 74(51)	0.339 80(69)	0.192 77(39)
O(6)	−0.095 14(52)	−0.004 28(67)	0.176 54(43)
O(7)	−0.375 95(50)	0.128 09(66)	0.106 24(46)
O(8)	−0.141 39(55)	0.189 09(68)	−0.034 18(40)

Experimental

The compound $KLa(CrO_4)_2$ was synthesized in sealed glass tubes at 150 °C from a mixture of $K_2Cr_2O_7$ and La_2O_3 in molar ratio 3:1. After 1 month, greenish yellow crystals appeared at the top of the tube, the precipitate at the bottom comprising a very well crystallized powder of the same colour.

The content of La in the crystals was determined by complexometry, that of K by atomic absorption spectroscopy, and the CrO_4 as $PbCrO_4$ by a gravimetric procedure (Found: K, 9.55; La, 33.7; CrO_4, 56.5. Cr_2KLaO_8 requires K, 9.50; La, 33.9; CrO_4, 55.55%).

Crystallography.—Crystal data. Cr_2KLaO_8, M = 410, space group $P2_1/c$, a = 8.729(2), b = 7.4752(7), c = 11.049(6) Å, β = 92.42(1)°, U = 720.3(2) Å^3, Z = 4, D_c = 3.789 g cm^{-3}, λ(Mo-K_α) = 0.710 69 Å, μ(Mo-K_α) = 93.3 cm^{-1}, T = 298 K, F(000) = 752.

Data collection. A prismatic crystal of dimensions 0.2 × 0.1 × 0.1 mm was mounted on a Nonius CAD-4 diffractometer. The cell dimensions were refined by least-squares fitting of the values of 25 reflections. The intensities of all 2 062 unique reflections with $1 < \theta < 30°$ and hkl −12,0,0 to 12,10,15 were measured at 295 K with monochromatic Mo-K_α radiation and the ω—2θ scan technique.

There was no appreciable change in the periodically monitored standard reflections. The intensities were corrected for Lorentz and polarization effects and 1 414 of these were considered as observed [$I > 3\sigma(I)$].

Scattering factors for neutral atoms and anomalous dispersion corrections for La, Cr, and K were taken from ref. 12.

Structure analysis and refinement. The heavy atoms were located from a three-dimensional Patterson map, and the positions of the O atoms obtained from a Fourier synthesis. An empirical absorption correction [13] was applied at the end of the isotropic refinement. Anisotropic full-matrix least-squares refinement with unit weights led to R = 0.024 and R' = 0.028.

No trend in F *vs.* F_o or (sin θ)/λ was observed. Maximum and average shift-to-error ratios were 0.03 and 0.004 respectively. A final difference synthesis showed an electron density of 2 e Å^{-3} located in the La atom position.

Most of the calculations were carried out with *X*-RAY 80.[14]

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

Other Measurements.—The *X*-ray powder patterns were recorded using a Siemens Kristalloflex 810 diffractometer and a D-500 goniometer with nickel-filtered copper radiation (λ = 1.540 598 Å) provided with a graphite monochromator. The *d*-

Table 2. Bond lengths (Å), angles (°), and principal contact distances for $KLa(CrO_4)_2$

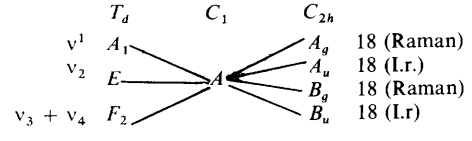
La–O(1)	2.510(5)	La–O(6^{III})	2.534(5)	Cr(2)–O(6)	1.684(5)	K–O(4^{VI})	2.780(5)
La–O(5)	2.761(5)	La–O(8^{II})	2.522(5)	Cr(2)–O(7)	1.607(5)	K–O(5^{I})	2.981(5)
La–O(6)	2.558(5)	Cr(1)–O(1)	1.658(5)	Cr(2)–O(8)	1.648(5)	K–O(7^{I})	3.076(5)
La–O(2^{I})	2.530(5)	Cr(1)–O(2)	1.674(5)	K–O(1)	2.884(5)	K–O(7^{VII})	2.785(5)
La–O(2^{II})	2.550(5)	Cr(1)–O(3)	1.656(5)	K–O(3^{IV})	2.722(5)	K–O(7^{VIII})	3.010(5)
La–O(3^{II})	2.581(5)	Cr(1)–O(4)	1.611(5)	K–O(4^{V})	2.799(6)	K–O(8^{VIII})	2.863(5)
La–O(5^{I})	2.559(5)	Cr(2)–O(5)	1.677(5)				
O(1)–La–O(5)	93.0(1)	O(2^{I})–La–O(2^{II})	61.3(1)	O(5)–Cr(2)–O(6)	102.5(2)	O(4^{V})–K–O(4^{VI})	118.6(2)
O(1)–La–O(6)	85.7(1)	O(2^{I})–La–O(3^{II})	120.6(2)	O(5)–Cr(2)–O(7)	109.5(2)	O(4^{V})–K–O(5^{I})	91.3(2)
O(1)–La–O(2^{I})	140.7(2)	O(2^{I})–La–O(5^{I})	68.5(1)	O(5)–Cr(2)–O(8)	111.7(2)	O(4^{V})–K–O(7^{I})	65.2(1)
O(1)–La–O(2^{II})	121.6(1)	O(2^{I})–La–O(6^{III})	140.6(2)	O(6)–Cr(2)–O(7)	111.8(2)	O(4^{V})–K–O(7^{VII})	137.5(2)
O(1)–La–O(3^{II})	70.4(1)	O(2^{I})–La–O(8^{II})	68.3(2)	O(6)–Cr(2)–O(8)	111.6(2)	O(4^{V})–K–O(7^{VIII})	85.2(1)
O(1)–La–O(5^{I})	73.4(2)	O(2^{II})–La–O(3^{II})	60.1(1)	O(7)–Cr(2)–O(8)	109.6(2)	O(4^{V})–K–O(8^{VIII})	78.6(2)
O(1)–La–O(6^{III})	78.1(2)	O(2^{II})–La–O(5^{I})	80.7(2)	O(1)–K–O(3^{IV})	133.9(2)	O(4^{VI})–K–O(5^{I})	87.0(1)
O(1)–La–O(8^{II})	150.1(2)	O(2^{II})–La–O(6^{III})	110.0(2)	O(1)–K–O(4^{V})	147.9(1)	O(4^{VI})–K–O(7^{I})	65.9(1)
O(5)–La–O(6)	58.9(1)	O(2^{II})–La–O(8^{II})	74.2(1)	O(1)–K–O(4^{VI})	80.1(2)	O(4^{VI})–K–O(7^{VII})	69.6(2)
O(5)–La–O(2^{I})	100.1(1)	O(3^{II})–La–O(5^{I})	93.8(1)	O(1)–K–O(5^{I})	62.2(1)	O(4^{VI})–K–O(7^{VIII})	148.9(2)
O(5)–La–O(2^{II})	143.5(1)	O(3^{II})–La–O(6^{III})	152.6(1)	O(1)–K–O(7^{I})	105.6(1)	O(4^{VI})–K–O(8^{VIII})	146.1(2)
O(5)–La–O(3^{II})	133.3(1)	O(3^{II})–La–O(8^{II})	103.4(1)	O(1)–K–O(7^{VII})	71.7(1)	O(5^{I})–K–O(7^{I})	52.1(1)
O(5)–La–O(5^{I})	123.8(1)	O(5^{I})–La–O(6^{III})	150.9(1)	O(1)–K–O(7^{VII})	90.2(1)	O(5^{I})–K–O(7^{VII})	131.2(2)
O(5)–La–O(6^{III})	63.1(1)	O(5^{I})–La–O(8^{II})	136.4(1)	O(1)–K–O(8^{VIII})	73.2(1)	O(5^{I})–K–O(7^{VIII})	151.3(1)
O(5)–La–O(8^{II})	150.1(2)	O(6^{III})–La–O(8^{II})	72.4(2)	O(3^{IV})–K–O(4^{V})	73.2(2)	O(5^{I})–K–O(8^{VIII})	62.2(1)
O(6)–La–O(2^{I})	70.4(1)	O(1)–Cr(1)–O(2)	109.1(2)	O(3^{IV})–K–O(4^{VI})	96.2(2)	O(7^{I})–K–O(7^{VII})	135.0(1)
O(6)–La–O(2^{II})	128.6(2)	O(1)–Cr(1)–O(3)	112.0(2)	O(3^{IV})–K–O(5^{I})	163.8(2)	O(7^{I})–K–O(7^{VIII})	145.9(1)
O(6)–La–O(3^{II})	152.6(1)	O(1)–Cr(1)–O(4)	110.9(2)	O(3^{IV})–K–O(7^{I})	114.6(1)	O(7^{I})–K–O(8^{VIII})	101.5(1)
O(6)–La–O(5)	65.7(1)	O(2)–Cr(1)–O(3)	101.0(2)	O(3^{IV})–K–O(7^{VII})	64.3(1)	O(7^{VII})–K–O(7^{VIII})	78.4(1)
O(6)–La–O(6^{III})	118.4(1)	O(2)–Cr(1)–O(4)	111.1(3)	O(3^{IV})–K–O(7^{VIII})	68.9(1)	O(7^{VII})–K–O(8^{VIII})	119.2(1)
O(6)–La–O(8^{II})	104.0(1)	O(3)–Cr(1)–O(4)	112.3(3)	O(3^{IV})–K–O(8^{VIII})	117.3(1)	O(7^{VIII})–K–O(8^{VIII})	53.8(1)

Symmetry codes: I $\bar{x}$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$; II x, $\frac{1}{2}-y$, $\frac{1}{2}+z$; III $\bar{x}$, $\frac{1}{2}+y$, $\frac{1}{2}-z$; IV $1-x$, $\bar{y}$, $\bar{z}$; V x, $-1+y$, z; VI $1-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$; VII $1+x$, y, z; VIII $\bar{x}$, $\bar{y}$, $\bar{z}$.

Table 3. *X*-Ray powder data (Å) for $KLa(CrO_4)_2$

hkl	$d_{obs.}$	$d_{calc.}$	$I_{obs.}$	*hkl*	$d_{obs.}$	$d_{calc.}$	$I_{obs.}$
100	8.716	8.738	31	312	2.397	2.396	3
011	6.181	6.189	4	130		2.396	
110	5.673	5.680	6	−204	2.378	2.380	7
002	5.515	5.518	2	131	2.335	2.336	8
−111	5.106	5.111	13	−321	2.265	2.265	10
111	4.997	4.993	4	024	2.223	2.220	13
−102	4.758	4.761	11	−230	2.166	2.164	5
012	4.446	4.440	2	410	2.096	2.096	3
−112	4.015	4.016	11	−402	2.061	2.062	25
112	3.907	3.902	8	−133	2.017	2.019	5
020	3.739	3.738	20	133	1.997	1.997	23
−202	3.496	3.501	74	−323	1.978	1.980	19
202	3.356	3.354	7	−314		1.976	
−121	3.296	3.297	100	−421	1.870	1.871	23
−212	3.171	3.171	24	040		1.869	
212	3.062	3.060	80	331	1.857	1.857	29
220	2.841	2.840	3	−413		1.855	
004	2.761	2.759	29	−422	1.805	1.805	9
−212	2.684	2.685	11	−141		1.805	
311	2.611	2.610		−142	1.739	1.739	4
104	2.592	2.597	15	−206	1.722	1.722	10
014		2.588		−234		1.721	
−222	2.554	2.555	8	510	1.701	1.701	17
−123	2.533	2.533	4	−241		1.702	
222	2.492	2.496	6	315	1.679	1.679	5
123		2.490		−216		1.678	

Table 4. Correlation table



spacing measurements were made at a scanning rate of 0.1° 2θ m^{-1} using Si (a = 5.430 881 4 Å) as an internal standard.

Infrared spectra were recorded on a Perkin-Elmer model 580B spectrometer using the KBr pellet technique, Raman spectra with a Jobin Ivon Spectrometer Romanor U-1000 double monochromator using the Ar 514.5 nm exciting line.

Table 5. Observed vibrational bands (cm^{-1}) and assignments for $KLa(CrO_4)_2$

I.r.	Raman	
	976m	ν_3
968s	952m	
953s	912w	
940s	900m	
907s	883s	
883m	864vs	
840s	848s	
822vs	825vw	ν_1
810vw	814w	
450vw	447vw	ν_4
434m	440vw	
392vw	429m	
383w	391w	
353w	361m	ν_2
336w	339w	
	331w	

The thermal decomposition was studied on a Stanton 781 thermoanalyser in a flow of nitrogen at a heating rate of 5° min^{-1}, using platinum–rhodium crucibles and Al_2O_3 as the reference.

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