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Structure of $LaCr(CN)_6.5H_2O$

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Abstract. Lanthanum chromium hexacyanide pentahydrate, $M_r = 437{\cdot}09$, hexagonal, $P6_3/m$, $a = 7{\cdot}7053\ (4)$, $c = 14{\cdot}8155\ (9)$ Å, $V = 761{\cdot}8\ (2)$ Å^3, $Z = 2$, $D_x = 1{\cdot}909\ (8)$, $D_m = 1{\cdot}897\ (4)$ g cm^{-3}, $\lambda(\text{Mo}\ K\bar{\alpha}) = 0{\cdot}71073$ Å, $\mu = 34{\cdot}9$ cm^{-1}, $F(000) = 398$, $T = 295$ K, final $R = 0{\cdot}024$ for 430 unique reflections. The structure is of the $LaFe(CN)_6.5H_2O$ type. The La atom is nine coordinated by six N atoms, forming a trigonal prism, and three H_2O molecules in the equatorial plane of the N prism. The Cr atom is located at the center of a C octahedron. Two uncoordinated H_2O molecules occupy holes above and below the triangular N prism faces. Bonding distances are: La—N 2·619 (5), La—O 2·591 (5), Cr—C 2·065 (4), C—N 1·138 (6) Å.

Introduction. Some years ago we reported on the synthesis of the series $LnCr(CN)_6.nH_2O$ (Ln = La–Lu, Y; $n = 4$ or 5) (Hulliger, Landolt & Vetsch, 1976). These compounds are of some theoretical interest due to their relatively high magnetic ordering temperatures (11·7 K in the case of the Tb compound). The hexagonal modification with five water molecules per formula unit ($n = 5$) is stable at room temperature only with the larger rare-earth elements while from Ln = Sm through to Lu the orthorhombic modification with four water molecules ($n = 4$) is formed, in analogy to the corresponding iron and cobalt compounds (orthorhombic structure, see Petter, Gramlich & Hulliger, 1989; Mullica & Sappenfield, 1989). Based on the similarity of their X-ray powder diffraction patterns with those of the iron and cobalt analogs we assigned to them the same crystal structures. To place our assignment for the whole series on safer ground we decided to carry out a full structure determination for one representative of each modification. In the following we report the data obtained for hexagonal $LaCr(CN)_6.5H_2O$.

Experimental. As starting materials for the synthesis of $LaCr(CN)_6.5H_2O$ we used purified $K_3Cr(CN)_6$, prepared according to Brauer (1981) from CrO_3 (p. A., Fluka, Buchs), and $LaCl_3$ prepared from La_2O_3 (4N; Research Chemicals, Phoenix, AZ) and hydrochloric acid. The growth procedure is as follows. A 1–2 *M* neutral aqueous solution of $LaCl_3$ is added to an equal volume of clear, light yellow 1 *M* $K_3Cr(CN)_6$ solution saturated at room temperature. After keeping the mixture in the dark at room temperature for 1–2 days small crystals can be filtered from the solution. High-quality crystals can be obtained only if the growth proceeds very slowly. The crystallization time, however, is limited by the gradual decomposition of $K_3Cr(CN)_6$ to $Cr(OH)_3$. The resulting crystals of size 0·1–1 mm have the shape of squat hexagonal prisms, in most cases with pyramids on both ends. Their density was measured by the flotation method in a mixture of *para*-xylene and bromoform. The water content was checked by thermogravimetric measurements to be 4·9 (2) H_2O per formula unit. The unit-cell dimensions of $LaCr(CN)_6.5H_2O$ crystals of the same batch were derived from a Guinier powder pattern taken with Fe $K\alpha_1$ radiation and silicon (assuming $a = 5{\cdot}43047$ Å) as internal calibration. For the structure determination a small, nearly spherical and optically perfect crystal with edge length 0·04 mm and height 0·05 mm was chosen.

The X-ray diffraction measurements for the structure determination were performed on a Picker FACS-1 diffractometer with STOE software and encoders using monochromatic molybdenum $K\alpha$ radiation. By the ω/θ scan method (learned profile version) we measured in four octants in the range $2\theta = 3$–$50°$ (range of h, k, l: -7–0, 0–9, 0–17) 2377 reflections of which 40 reflections with intensities $I < 2\sigma$ were finally omitted in the calculations (430 unique reflections). The intensities of three standard reflections, 220, 008 and 114, were checked every two hours revealing deviations less than 1% from the mean intensities. Since we made measurements in four octants we were able to test the symmetry conditions on equivalent reflections. The empirical absorption correction program revision 1.2 of the *XLS Structure Refinement Package* (Nicolet Instrument Corporation, 1988) was applied based on ψ scans for five reflections with $\chi > 60°$ ($\mu = 3{\cdot}49\ \text{mm}^{-1}$); maximum and minimum values of the absorption correction 0·60 and 0·80. No extinction corrections were applied. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The structure refinement was calculated with the *SHELXTL-PLUS* program of the same package on a DEC MicroVAX II. As starting parameters we used the values of $LaFe(CN)_6.5H_2O$ (Bailey, Williams & Milligan, 1973), with carbon surrounding the transition element and nitrogen bonded to the rare-earth element, in agreement with chemical arguments. The H atoms of the water molecules were neglected in the calculations. The full-matrix least-squares refinement of 32 variables on F_{hkl} values yielded the reliability values $R = 0{\cdot}024$ and $wR = 0{\cdot}027$, goodness of fit 0·626 {weighting scheme $w = [\sigma^2(F) + 0{\cdot}0068F^2]^{-1}$}. Maximum shift/e.s.d. = 0·04. No attempt was made to locate the H atoms *a posteriori* as the electron density $\Delta\rho$ in the final difference Fourier synthesis did not reveal any pronounced maxima ($\Delta\rho_{\max} = 1{\cdot}44$, $\Delta\rho_{\min} = -0{\cdot}36\ \text{e Å}^{-3}$). The resulting structure data are listed in Table 1.*

Table 1. *Atomic positions and thermal parameters* ($Å^2 \times 10^2$), *with e.s.d's in parentheses*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	Site	x	y	z	U_{eq}
La	2(*c*)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	1·2 (2)
Cr	2(*b*)	0	0	0	1·2 (2)
C	12(*i*)	0·1092 (6)	0·2516 (6)	0·0807 (3)	2·7 (3)
N	12(*i*)	0·2199 (6)	0·8302 (5)	0·1254 (4)	4·5 (3)
O1	4(*f*)	$\frac{1}{3}$	$\frac{2}{3}$	0·9097 (8)	6·9 (5)
O2	6(*h*)	0·4890 (7)	0·4365 (7)	$\frac{1}{4}$	5·8 (4)

Table 2. *Selected interatomic distances* (Å) *and bond angles* (°) *in* $LaCr(CN)_6.5H_2O$, *with e.s.d.'s in parentheses*

La—3 O2	2·591 (8)	N—1 C	1·137 (9)
6 N	2·619 (7)	1 La	2·619 (6)
6 O1	5·039 (6)	1 O2	2·950 (6)
2 O1	5·042 (12)	1 O2	2·969 (6)
		2 N	3·219 (9)
Cr—6 C	2·065 (4)	1 N	3·692 (8)
		1 O1	3·697 (12)
6 O1	4·646 (4)	1 O1	3·716 (4)
C—1 N	1·137 (9)	O1···3 O2	3·032 (11)
1 Cr	2·065 (4)	3 N	3·697 (12)
		3 N	3·716 (7)
2 C	2·917 (9)	3 C	3·756 (9)
2 C	2·925 (8)	3 C	3·767 (9)
1 O2	3·566 (6)	3 C	4·021 (9)
1 La	3·739 (4)	O2—1 La	2·591 (7)
1 O1	3·756 (9)		
1 O1	3·767 (6)	2 N	2·950 (7)
1 O2	3·786 (9)	2 N	2·969 (7)
		2 O1	3·032 (10)
		1 O2	3·284 (13)
O2—La—O2	120·0 (2)	C—Cr—C	89·8 (2)
N—La—O2	69·0 (2)		90·2 (2)
	69·5 (2)	Cr—C—N	179·6 (6)
	135·2 (2)	C—N—La	168·1 (5)
N—La—N	75·8 (2)	O2—O1—O2	65·6 (3)
	89·6 (2)	O1—O2—O1	102·6 (3)
	138·4 (2)		

Discussion. Different views of this structure type can be found in the paper of Bailey, Williams & Milligan (1973) and in our report (Hulliger, Landolt & Vetsch, 1976). The interatomic distances in $LaCr(CN)_6.5H_2O$ are compiled in Table 2. In addition to the bonding distances we have also listed some longer distances that might be of interest for discussing the geometrical arrangement. Within the experimental accuracy the coordination polyhedron around the La atom – a trigonal prism made up of N atoms, three-capped by O2 atoms – is the same as in $LaFe(CN)_6.5H_2O$ (Bailey, Williams & Milligan, 1973) and $LaCo(CN)_6.5H_2O$ (Mullica, Milligan & Kouba, 1979). In these latter compounds La—O2 = 2·585 (5) and 2·602 (9) Å, La—N = 2·613 (4) and 2·618 (8) Å, respectively. The C octahedron around the Cr atom is virtually undistorted as in the Co analog, which is not surprising for a covalently bonded high-spin d^3 and a low-spin d^6 cation. The Cr—C distance lies within the range of observed values: 2·046 or 2·058 Å in cubic $Cs_2LiCr(CN)_6$ (Ryan & Swanson, 1974); 2·068–2·075 (4) Å in monoclinic elpasolite-type $Cs_2KCr(CN)_6$ (Figgis, Kucharski, Reynolds & White, 1983), and 2·038–2·099 Å in triclinic $K_3Cr(CN)_6$ at 4·2 K (Figgis, Reynolds & Williams, 1981). The C—N distance, 1·138 (6) Å, is shorter than that reported for $LaFe(CN)_6.5H_2O$, 1·155 (5) Å, and $LaCo(CN)_6.5H_2O$, 1·156 (11) Å, but it compares well with the distances observed in $Cs_2KCr(CN)_6$, 1·137–1·138 (6) Å, and in $Cs_3LiCr(CN)_6$, 1·138 (6) Å, as well as in $Zn_3[Co(CN)_6]_2.12H_2O$, 1·135 (13) Å (Mullica, Milligan, Beall & Reeves, 1978). The O1—O2 distances decrease on going from the Cr to the Fe and Co compounds. In parallel, the $[TC_6]$ octahedron is responsible not only for a decrease of

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* Lists of structure factors and anisotropic displacement factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53077 (4 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the lattice parameters *a* and *c*, but also of *c*/*a*. In hypothetical $LaV(CN)_6.5H_2O$ the hole between the $[FeC_6]$ octahedra and the $[LaN_6O_3]$ polyhedra might even be too large for the two non-bonded H_2O molecules.

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Synthesis and Structure of Magnesium Iron Thiosilicates $(Mg_{1-x}Fe_x)_2SiS_4$

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Abstract. $Mg_{1\cdot4}Fe_{0\cdot6}SiS_4$, M_r = 223·88, orthorhombic, *Pnma*, a = 12·633 (5), b = 7·348 (3), c = 5·901 (2) Å, V = 547·7 (4) Å^3, Z = 4, D_x = 2·715 g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 32·9 cm^{-1}, $F(000)$ = 442, T = 298 K, R = 0·025, wR = 0·022 for 690 unique reflections, $F_o > 4\sigma(F_o)$. $Mg_{1\cdot86}Fe_{0\cdot14}SiS_4$, M_r = 209·37, orthorhombic, *Pnma*, a = 12·677 (4), b = 7·405 (2), c = 5·913 (2) Å, V = 555·1 (3) Å^3, Z = 4, D_x = 2·505 g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 21·68 cm^{-1}, $F(000)$ = 416, T = 298 K, R = 0·029, wR = 0·025 for 1873 unique reflections, $F_o > 4\sigma(F_o)$. The two metal cations are not evenly distributed between the $M(1)$ and $M(2)$ positions of the olivine structure. The type of order [enrichment of Fe in the $M(1)$ position] is the same in both compounds. The degree of order is greater than in olivines of the forsterite–fayalite series.

Introduction. In the course of our studies of thiosilicates which crystallize in the olivine structure type we have carried out X-ray structure analyses of Mn_2SiS_4 (Fuhrmann & Pickardt, 1989*a*), $(Mn,Mg)_2SiS_4$, $(Mn,Fe)_2SiS_4$ and $(Mg,Fe)_2SiS_4$ (Fuhrmann & Pickardt, 1989*b*). The structure determination of the magnesium iron thiosilicate, combined with an electron microprobe analysis, yielded ordering effects of the metal cations in the two different positions of the olivine structure: the $M(1)$ position is enriched in Fe relative to $M(2)$. In order to verify these remarkable results [based on the cation size, Fe^{2+} should prefer the larger $M(2)$ octahedral site], we prepared single crystals of the solid-solution series Mg_2SiS_4–Fe_2SiS_4 and determined the crystal structures of $Mg_{1\cdot4}Fe_{0\cdot6}SiS_4$ and $Mg_{1\cdot86}Fe_{0\cdot14}SiS_4$. The formulae assigned to these compounds are based on the refined occupancies of the metal sites.

Experimental. Single crystals of the title compounds were obtained by chemical transport reactions carried out in sealed quartz ampoules at 1173/1073 K for two weeks using Mg_2Si, Fe, Si and S_8 as starting materials. A red, transparent $Mg_{1\cdot4}Fe_{0\cdot6}SiS_4$ crystal (0·22 × 0·18 × 0·2 mm) and a yellow transparent $Mg_{1\cdot86}Fe_{0\cdot14}SiS_4$ crystal (0·26 × 0·14 × 0·18 mm) were

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