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Crystal Growth and Crystal Structure of $KTb(CrO_4)_2$

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Single crystals of $TbK(CrO_4)_2$ were grown hydrothermally from a mixture $K_2Cr_2O_7$ and Tb_2O_3 (molar ratio 10 : 1) at 127°C. They are orthorhombic, *P*212121, with a = 13.804(5), b = 5.735(1), c = 9.029(3) Å, Z = 4. The structure, different to the one observed for other members of the series $LnK(CrO_4)_2$ (Ln = La, Eu), consists of CrO_4 tetrahedra (mean Cr–O distance 1.66 Å) and TbO_8 bicapped trigonal prisms (mean Tb–O distance 2.40 Å) sharing corners and forming large channels parallel to the b axis, where the K atoms are located. The structure can also be described as a distorted CsCl-like arrangement where Tb and K atoms occupy alternate positions of the Cs substructure. The compound could be formulated as $(Tb,K)(CrO_4)$.

Introduction

Within a systematic study on the synthesis conditions and properties of the isomorphous series $KLn(CrO_4)_2$ (Ln = La, Eu), the synthesis, crystal structure, and magnetic properties of $KLa(CrO_4)_2$ were previously reported (*1–3*).

It is well known that lanthanide compounds can show different structures as a consequence of the decrease of the ionic radii which can lead to a decrease in the coordination number around the lanthanide cation (*4, 5*). Thus, five different structures are known in the series $KLn(MoO_4)_2$ (*6*) and $KLn(SO_4)_2$ (*7–9*). In contrast, only two are known of the type $KLn(WO_4)_2$ (*10, 11*).

We report here the crystal growth and crystal structure of $KTb(CrO_4)_2$ which shows structural differences with the other members of the series (Ln = La, Eu) reported previously (*1*). This work has been undertaken because of the potential application of these compounds as luminescent materials. A study of their magnetic and optical properties is actually in progress.

Experimental

Crystal Growth

Single crystals of $KTb(CrO_4)_2$ were grown by hydrothermal procedures using $K_2Cr_2O_7$ and Tb_2O_3 (molar ratio 10 : 1). The glass tubes were filled till 40% volume and sealed under N_2 atmosphere and heated at

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TABLE I

CRYSTAL DATA

Compound: $KTb(CrO_4)_2$
Molecular weight: 430
Space group: $P212121$
$a = 13.804(5)$ Å
$b = 5.735(1)$
$c = 9.029(2)$
$V = 714.79(1)$ Å^3
$Z = 4$
$D_c = 3.994$ g cm^{-3}
$\lambda(MoK\alpha) = 0.71069$
$\mu(MoK\alpha) = 0.71069$
$F(000) = 784$

TABLE II

COORDINATES AND THERMAL PARAMETERS AS $U_{eq} = (1/3) \cdot \Sigma[U_{ij} \cdot a_i^* \cdot a_j^* \cdot a_i \cdot a_j \cdot \cos(a_i, a_j)] \cdot 10^4$

Atom	x	y	z	U_{eq}
Tb	−0.1405(1)	0.2334(3)	0.0379(1)	155(3)
Cr(1)	0.1608(3)	0.2566(12)	−0.3408(4)	114(11)
Cr(2)	0.1162(3)	0.2442(18)	0.1845(5)	191(13)
K	0.4143(6)	0.2524(32)	0.4202(10)	400(26)
O(1)	0.2179(18)	0.2765(71)	−0.1850(28)	312(60)
O(2)	0.0967(20)	0.0171(52)	−0.3769(30)	171(58)
O(3)	0.0870(18)	0.4838(46)	−0.3345(28)	130(50)
O(4)	0.2320(20)	0.3193(53)	−0.4781(33)	351(72)
O(5)	0.0390(14)	0.2205(50)	0.0480(25)	196(44)
O(6)	0.2255(17)	0.2033(52)	0.1199(25)	217(53)
O(7)	0.1094(22)	0.4997(58)	0.2673(34)	262(66)
O(8)	0.0932(23)	0.0378(62)	0.3088(35)	305(71)

127°C during 15 days. After this treatment, orange, needle-shaped crystals of $KTb(CrO_4)_2$ formed on the walls of the tubes.

The Tb and K contents, in the crystals, were determined by atomic absorption spectroscopy and CrO_4 as $PbCrO_4$ by a gravimetric procedure. (Found: K, 9.03; Tb, 36.87; CrO_4, 53.67; required: K, 9.07; Tb, 36.96; CrO_4, 53.96.)

Structure Solution and Refinement

The crystal data are collected in Table I. A needle-shaped crystal was used to collect

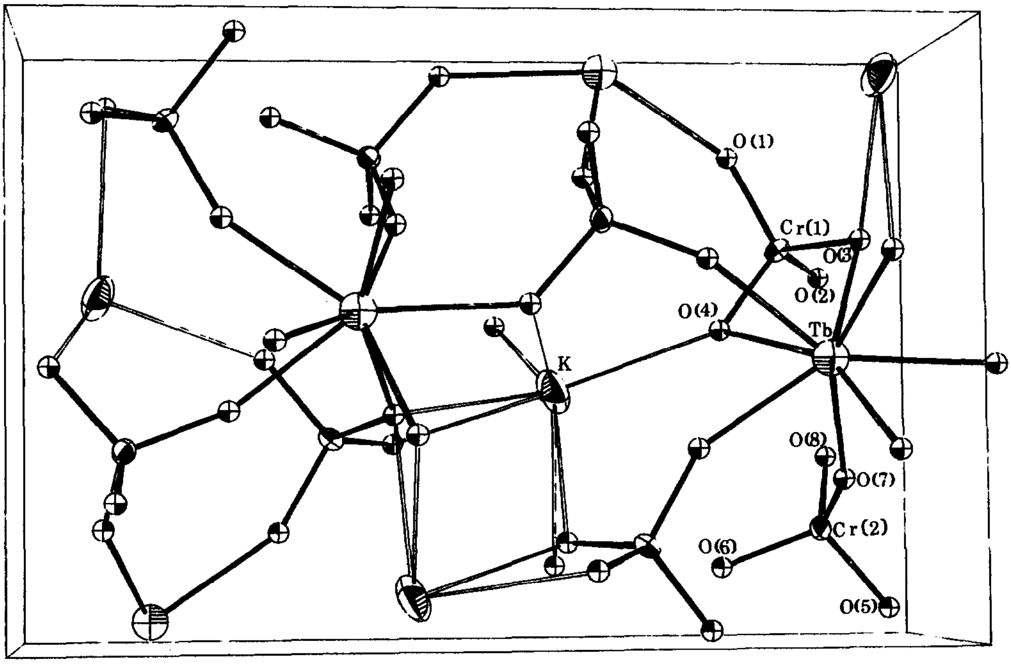

FIG. 1. ORTEP drawing (*17*) of the unit cell, viewed along the *b* axis, showing the CrO_4 tetrahedra, TbO_8 bicapped trigonal prisms, and the seven-coordination polyhedron around the K atom.

the X-ray diffraction data on a CAD-4 diffractometer, using graphite-monochromated MoKα radiation. A total of 1191 reflexions were measured in the $\omega/2\theta$ scan mode, up to maximum $\sin \theta/\lambda = 0.70$ Å^{-1}. Of that total, 360 were considered unobserved after the criterion $I < 3\sigma(I)$. The intensities were corrected by Lorentz and polarization factors. Atomic scattering factors for neutral atoms and anomalous dispersion corrections for Tb, K, Cr were taken from International Tables (*12*).

The Tb atom was located from the Patterson map, the remaining atoms being found in further Fourier synthesis calculated with the phases given by Tb.

After isotropic refinement an empirical absorption correction was applied (*13*) (min and max absorption corrections: 0.72 and 1.71, respectively; mean absorption correction: 1.04).

A further anisotropic refinement led to nonpositive defined temperature factors of O atoms, probably due to errors in the absorption correction. Thus, the refinement continued with anisotropic thermal parameters for Tb, K, and Cr and isotropic ones for O atoms. Final $R = 0.073$ for observed reflections only. The final atomic coordinates are collected in Table II. All the calculations[1] were performed using the XRAY80 System (*14*) running on a VAX 11/750 computer.

TABLE III

BONDS LENGTHS (Å) AND ANGLES (°)

Tb–O(1)v	2.36(2)	Cr(1)–O(1)	1.62(2)	K–O(2)iii	3.10(3)
Tb–O(2)vii	2.26(3)	Cr(1)–O(2)	1.67(3)	K–O(2)iv	2.87(3)
Tb–O(3)ix	2.44(3)	Cr(1)–O(3)	1.65(3)	K–O(3)ii	2.75(3)
Tb–O(4)ix	2.74(3)	Cr(1)–O(4)	1.62(3)	K–O(3)iv	2.85(3)
Tb–O(5)	2.48(2)	Cr(2)–O(5)	1.63(2)	K–O(4)i	2.71(3)
Tb–O(6)v	2.36(2)	Cr(2)–O(6)	1.63(2)	K–O(5)iii	3.02(3)
Tb–O(7)viii	2.25(3)	Cr(2)–O(7)	1.65(3)	K–O(5)ii	3.30(3)
Tb–O(8)vi	2.32(3)	Cr(2)–O(8)	1.66(3)		

O(1)vi–Tb–O(3)ix	131(1)	O(5)–Tb–O(6)v	144(1)
O(1)vi–Tb–O(4)ix	73(1)	O(5)–Tb–O(7)viii	76(1)
O(1)vi–Tb–O(7)viii	73(1)	O(5)–Tb–O(8)vi	74(1)
O(1)vi–Tb–O(8)vi	85(1)	O(6)v–Tb–O(7)viii	135(1)
O(1)vi–Tb–O(6)v	72(1)	O(6)v–Tb–O(8)vi	118(1)
O(1)vi–Tb–O(5)	144(1)	O(1)–Cr(1)–O(2)	119(2)
O(1)vi–Tb–O(2)vii	127(1)	O(1)–Cr(1)–O(3)	102(2)
O(2)vii–Tb–O(3)ix	82(1)	O(1)–Cr(1)–O(4)	111(1)
O(2)vii–Tb–O(4)ix	128(1)	O(2)–Cr(1)–O(3)	109(1)
O(2)vii–Tb–O(5)	77(1)	O(2)–Cr(1)–O(4)	111(1)
O(2)vii–Tb–O(6)v	73(1)	O(3)–Cr(1)–O(4)	103(1)
O(2)vii–Tb–O(7)viii	151(1)	O(5)–Cr(2)–O(6)	109(1)
O(2)vii–Tb–O(8)vi	77(1)	O(5)–Cr(2)–O(7)	112(1)
O(3)ix–Tb–O(4)ix	59(1)	O(5)–Cr(2)–O(8)	109(1)
O(3)ix–Tb–O(5)	73(1)	O(6)–Cr(2)–O(7)	110(1)
O(3)ix–Tb–O(6)v	83(1)	O(6)–Cr(2)–O(8)	108(1)
O(3)ix–Tb–O(7)viii	100(1)	O(7)–Cr(2)–O(8)	108(2)
O(3)ix–Tb–O(8)vi	144(1)		
O(4)ix–Tb–O(5)	116(1)		
O(4)ix–Tb–O(6)v	70(1)		
O(4)ix–Tb–O(7)viii	74(1)		
O(4)ix–Tb–O(8)vi	154(1)		
O(2)iii–K–O(2)iv	99(1)	O(3)ii–K–O(3)iv	92(1)
O(2)iii–K–O(3)ii	63(1)	O(3)ii–K–O(4)i	101(1)
O(2)iii–K–O(3)iv	64(1)	O(3)ii–k–O(5)iii	145(1)
O(2)iii–K–O(4)i	109(1)	O(3)ii–K–O(5)ii	78(1)
O(2)iii–K–O(5)iii	84(1)	O(3)iv–K–O(4)i	160(1)
O(2)iii–K–O(5)ii	140(1)	O(3)iv–K–O(5)iii	60(1)
O(2)iv–K–O(3)ii	69(1)	O(3)iv–K–O(5)ii	112(1)
O(2)iv–K–O(3)iv	57(1)	O(4)i–K–O(5)iii	101(1)
O(2)iv–K–O(4)i	143(1)	O(4)i–K–O(5)ii	86(1)
O(2)iv–K–O(5)iii	106(1)	O(5)ii–K–O(5)iii	130(1)
O(2)iv–K–O(5)ii	57(1)		

Note. Symmetry codes:

i: $x, \quad y, \quad z + 1$ ii: $-x + 1/2, \quad -y + 1, \quad z + 1/2$

iii: $-x + 1/2, \quad -y, \quad z + 1/2$ iv: $x + 1/2, \quad -y + 1/2, \quad -z$

v: $x - 1/2, \quad -y + 1/2, \quad -z$ vi: $-x, \quad y + 1/2, \quad -z + 1/2$

vii: $-x, \quad y + 1/2, \quad -z - 1/2$ viii: $-x, \quad y - 1/2, \quad -z + 1/2$

ix: $-x, \quad y - 1/2, \quad -z - 1/2$

Description and Discussion of the Structure

All the interatomic distances and angles are summarized in Table III. Figure 1 is a perspective view of the unit cell contents, along the *b* axis, showing the coordination polyhedra around Tb and K.

The structure can be described as CrO_4 tetrahedra and TbO_8 bicapped trigonal prisms sharing corners and forming channels parallel to the *b* axis where the K atoms are located. They are coordinated to six oxygens at distances ranging from 2.70

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[1] A table containing F_{obsd} and F_{calcd} has been deposited as supplementary material. See NAPS Document No. 04743 for 6 pages of supplementary materials from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, New York 10163. Remit in advance \$4.00 for microfiche copy or for photocopy, \$7.75 up to 20 pages plus \$.30 for each additional page. All orders must be prepaid.

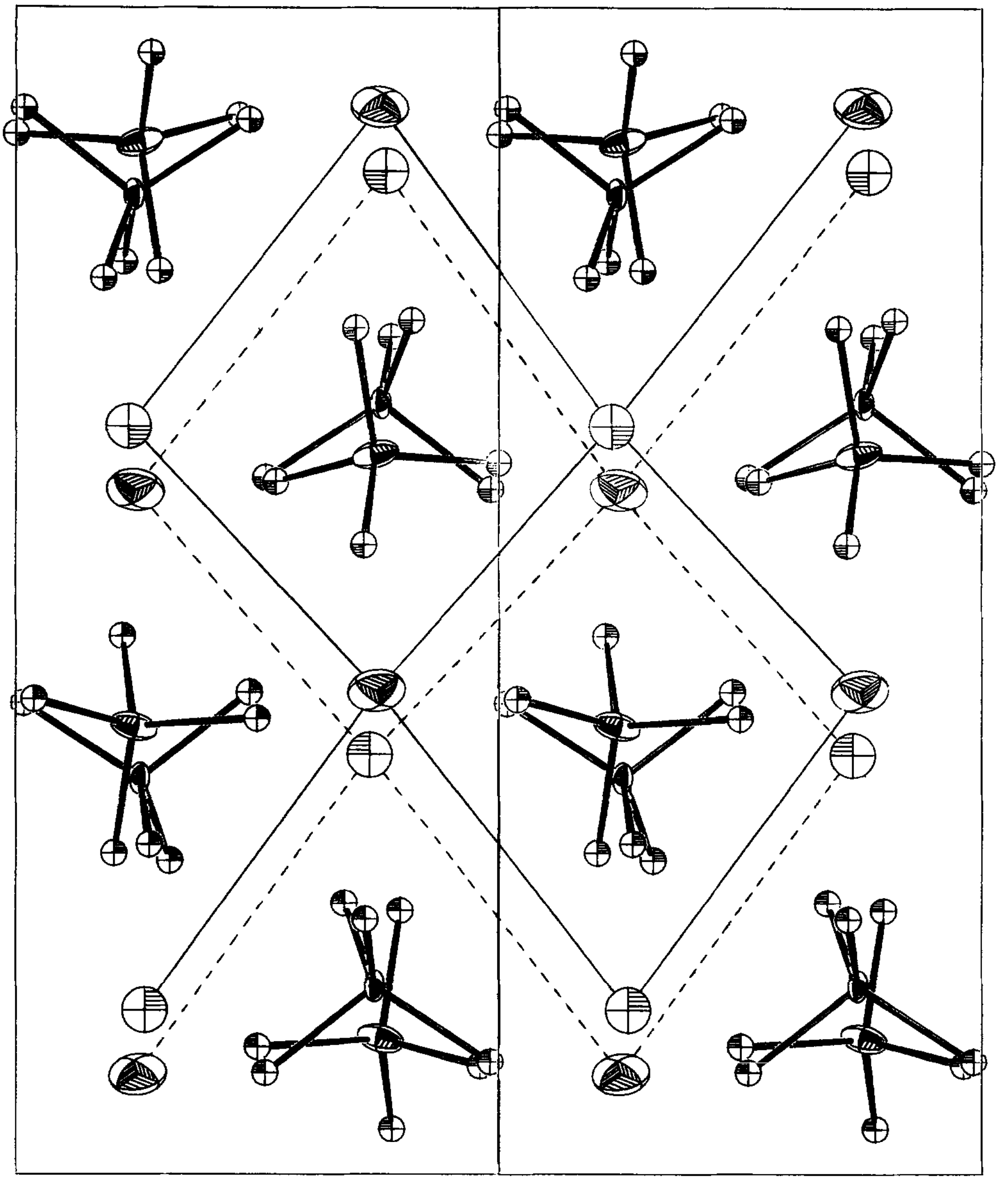

FIG. 2. Two unit cells of $TbK(CrO_4)_2$ viewed along the c axis to show the CsCl-type arrangement of Tb and K cations and CrO_4 anions. The edges of the hypothetical CsCl unit cell are marked.

to 3.10 Å and a seventh O atom at a longer distance of 3.30 Å which is represented by a single line in Fig. 1. This irregular polyhedron can be described as a distorted octahedron in which one of the apical positions is occupied by two O atoms belonging to the same CrO_4 group, Cr(1), which acts as a bidentate ligand, resulting in the irregular seven-coordination polyhedron mentioned above.

The eight oxygens of the asymmetric unit are involved in the coordination around the Tb atom. However, only four (O(2), O(3), O(4), and O(5) are linked to the K atoms. Consequently, the coordination around the oxygens is variable; i.e., O(1), O(6), O(7), and O(8) are only two-coordinated to Cr and Tb, O(4) is three-coordinated to Cr(1), Tb, and K. The three remaining oxygens are four-coordinated to Cr, Tb, and two K atoms.

The mean Cr–O and Tb–O bond lengths (1.64 and 2.40 Å, respectively) are as expected from the sum of ionic radii (1.66 and 2.40 Å) (*15*). However, the mean K–O distance (2.88 Å considering the six nearest neighbors) is greater than the expected value of 2.74 Å.

The structure can also be described, in a simpler way, on the basis of the cation packing (*16*). Tb, K, and Cr atoms form a distorted CsCl-type arrangement where Tb and K atoms are at the center of an irregular Cr_8 cube. Inversely, each Cr atom is at the center of a distorted Tb_4K_4 cube, with Tb and K atoms occupying alternate corners. This description can be better understood in Fig. 2; two unit cells have been represented viewed along the *c* axis and the distorted (Tb, K) cubes are marked.

Considering the CrO_4 anions as a whole, $TbK(CrO_4)_2$ could be also formulated as a CsCl-type compound of formula (Tb, K)(CrO_4).

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