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$K_3H(SeO_4)_2$ at 297 and 30 K

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Abstract

In tripotassium hydrogen bis(selenate), $K_3H(SeO_4)_2$, two selenate groups form a dimer through a hydrogen bond of 2.496 (2) Å, at 30 K (10 K above the low-temperature transition point). This is the shortest hydrogen bond among the members of the $M_3H(SeO_4)_2$-type crystals exhibiting the low-temperature phase transition.

Comment

Among the members of the $M_3H(XO_4)_2$-type crystals (M = K, Rb, Cs; X = S, Se) which exhibit a low-temperature (possibly antiferroelectric) phase transition, $K_3H(SeO_4)_2$ has the lowest transition temperature (T_c) of 20 K (Endo, Kaneko, Osaka & Makita, 1983).

In view of the low T_c of the title compound, the hydrogen-bond distance just above T_c is needed in order to examine the correlation between the transition temperature and hydrogen-bonding distances in the $M_3H(SeO_4)_2$-type crystals. Thus the structure determination at 30 K was undertaken. The data at 297 K were collected so that comparison may be made with previous work performed with a spherical shaped specimen (Ichikawa, Sato, Komukae & Osaka, 1992). An as-grown crystal was used in this work which had a hexagonal plate shape and was obtained by evaporation of a saturated solution.

The bond lengths and angles at 297 K agree with the previous results at 299 K (Ichikawa *et al.*, 1992) within 3σ, except for O(2)—Se—O(4) (4σ). The hydrogen-bond distance R [2.496 (2) Å] in $K_3H(SeO_4)_2$ at 30 K is the shortest among the members of the $M_3H(XO_4)_2$-type crystals exhibiting the low-temperature phase transition. By including the present results, the validity of a linear correlation between T_c and R is also established for $M_3H(SeO_4)_2$-type crystals with zero-dimensional hydrogen-bond networks (Ichikawa, Gustafsson & Olovsson, 1993).

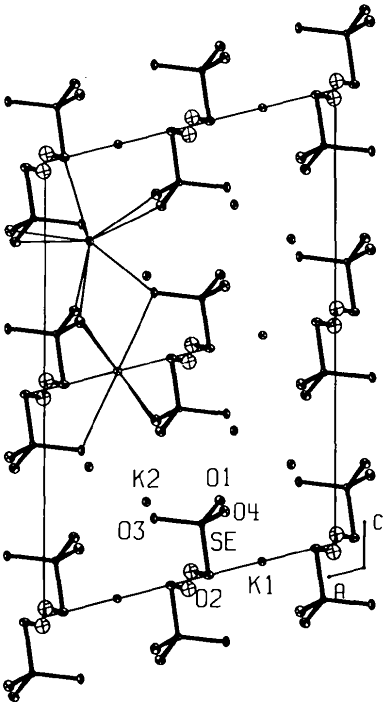

Fig. 1. The *b*-axis projection of the structure of $K_3H(SeO_4)_2$ at 30 K. Thermal ellipsoids are scaled to include 50% probability. The B value of the H atoms is set to 2.0 Å^2. Thick lines denote covalent bonds, thin lines indicate short K···O distances.

Experimental

At 30 K

Crystal data

$K_3H(SeO_4)_2$
M_r = 404.2
Monoclinic
$A2/a$
a = 10.0464 (8) Å
b = 5.8561 (4) Å
c = 14.8215 (13) Å
β = 103.629 (12)°
V = 847.44 (10) Å^3
Z = 4

D_x = 3.168 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 30 reflections
θ = 25.9-29.9°
μ = 9.86 mm^{-1}
Hexagonal plate
0.250 × 0.233 × 0.067 mm
Colourless

Data collection

Huber/Stoe/Aracor diffractometer
$\omega/2\theta$ scans
Absorption correction: *ABSSTOE* (Lundgren, 1983)
$T_{\min}$ = 0.287, $T_{\max}$ = 0.466

2543 observed reflections [All $I > 0$ and those $I < 0$ with $|I| < 15\sigma(I)$]
$R_{\rm int}$ = 0.017
$\theta_{\max}$ = 40.00°
$h = -18 \rightarrow 13$
$k = -10 \rightarrow 10$
$l = 0 \rightarrow 26$

4975 measured reflections
2543 independent reflections
6 standard reflections
frequency: 240 min
intensity variation: 0.03%

Refinement

Refinement on F^2
$R = 0.0549$
$wR = 0.0648$
$S = 1.41$
4967 reflections
65 parameters
All H-atom parameters refined
Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{\max} = 0.006$
$\Delta\rho_{\max} = 1.3$ e Å^{-3}
$\Delta\rho_{\min} = -1.4$ e Å^{-3}
Extinction correction: Becker & Coppens (1975) type 1 Lorentzian isotropic
Extinction coefficient: $0.35 (2) \times 10^4$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

At 297 K

Crystal data

$K_3H(SeO_4)_2$
$M_r = 404.2$
Monoclinic
$A2/a$
$a = 10.1325 (5)$ Å
$b = 5.9042 (3)$ Å
$c = 14.9620 (7)$ Å
$\beta = 103.638 (7)°$
$V = 869.86 (6)$ Å^3
$Z = 4$
$D_x = 3.086$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 31 reflections
$\theta = 25.7$-$29.7°$
$\mu = 9.86$ mm^{-1}
Hexagonal plate
$0.250 \times 0.233 \times 0.067$ mm
Colourless

Data collection

Huber/Stoe/Aracor diffractometer
$\omega/2\theta$ scans
Absorption correction: *ABSSTOE* (Lundgren, 1983)
$T_{\min} = 0.287$, $T_{\max} = 0.466$
5495 measured reflections
2697 independent reflections
2697 observed reflections [All $I > 0$ and those $I < 0$ with $|I| < 15\sigma(I)$]
$R_{\rm int} = 0.0222$
$\theta_{\max} = 39.94°$
$h = -18 \rightarrow 17$
$k = -10 \rightarrow 10$
$l = 0 \rightarrow 26$
6 standard reflections
frequency: 240 min
intensity variation: 1.4%

Refinement

Refinement on F^2
$R = 0.0855$
$wR = 0.0561$
$S = 1.20$
5483 reflections
65 parameters
All H-atom parameters refined
Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{\max} = 0.04$
$\Delta\rho_{\max} = 0.8$ e Å^{-3}
$\Delta\rho_{\min} = -0.9$ e Å^{-3}
Extinction correction: Becker & Coppens (1975) type 1 Lorentzian isotropic
Extinction coefficient: $0.74 (3) \times 10^4$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *at* 30 K

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
K(1)	1/4	0.75972 (5)	0	0.00729
K(2)	0.65161 (2)	0.73825 (3)	0.19635 (2)	0.00796
Se	0.45991 (1)	0.23336 (2)	0.11623 (1)	0.00482
O(1)	0.39793 (8)	0.01108 (12)	0.15819 (6)	0.00929
O(2)	0.43454 (8)	0.18081 (14)	0.00090 (6)	0.01023
O(3)	0.62550 (8)	0.25116 (12)	0.15454 (6)	0.00898
O(4)	0.38165 (8)	0.46782 (12)	0.13066 (6)	0.00989

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *at* 297 K

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
K(1)	1/4	0.75530 (5)	0	0.0236
K(2)	0.65188 (2)	0.73694 (4)	0.19666 (2)	0.0277
Se	0.46017 (1)	0.23222 (1)	0.11600 (1)	0.0162
O(1)	0.39807 (8)	0.01316 (12)	0.15738 (5)	0.0305
O(2)	0.43537 (9)	0.18101 (15)	0.00208 (5)	0.0302
O(3)	0.62379 (8)	0.24914 (12)	0.15450 (7)	0.0301
O(4)	0.38288 (8)	0.46464 (12)	0.12963 (6)	0.0313

Table 3. *Selected geometric parameters* Å, °)

	30 K	297 K	299 K*
K-atom cooordination			
K(1)—O(1$^{\rm i}$)	2.8689 (9)	2.9065 (8)	2.909 (2)
K(1)—O(2$^{\rm i}$)	3.0833 (8)	3.1335 (9)	3.131 (3)
K(1)—O(2$^{\rm ii}$)	3.1914 (8)	3.2175 (9)	3.222 (2)
K(1)—O(3$^{\rm ii}$)	2.8575 (9)	2.8938 (9)	2.894 (2)
K(1)—O(4)	2.6860 (8)	2.6996 (9)	2.696 (3)
K(2)—O(1$^{\rm i}$)	2.9477 (8)	2.9843 (8)	2.977 (3)
K(2)—O(1$^{\rm iii}$)	3.0427 (8)	3.0718 (8)	3.077 (3)
K(2)—O(1$^{\rm iv}$)	2.7447 (8)	2.7797 (8)	2.782 (3)
K(2)—O(2$^{\rm ii}$)	2.8859 (9)	2.9357 (8)	2.930 (2)
K(2)—O(3)	2.9177 (7)	2.9477 (8)	2.944 (3)
K(2)—O(3$^{\rm i}$)	3.0656 (7)	3.0886 (8)	3.092 (3)
K(2)—O(3$^{\rm v}$)	2.7517 (10)	2.7828 (9)	2.785 (2)
K(2)—O(4)	3.0931 (8)	3.1194 (8)	3.124 (3)
K(2)—O(4$^{\rm iii}$)	2.9674 (8)	3.0014 (8)	3.000 (3)
K(2)—O(4$^{\rm vi}$)	3.1705 (8)	3.2273 (8)	3.236 (3)
SeO_4			
Se—O(1)	1.6283 (8)	1.6235 (7)	1.620 (2)
Se—O(2)	1.6959 (8)	1.6906 (8)	1.694 (2)
Se—O(3)	1.6295 (8)	1.6248 (8)	1.623 (2)
Se—O(4)	1.6212 (7)	1.6165 (8)	1.614 (2)
O(1)—O(2)	2.6386 (12)	2.6341 (11)	2.635 (3)
O(1)—O(3)	2.6953 (11)	2.6871 (11)	2.682 (3)
O(1)—O(4)	2.7048 (10)	2.6966 (10)	2.696 (3)
O(2)—O(3)	2.6414 (12)	2.6372 (12)	2.641 (3)
O(2)—O(4)	2.6995 (12)	2.6847 (11)	2.677 (3)
O(3)—O(4)	2.7070 (11)	2.6995 (11)	2.696 (3)
O(1)—Se—O(2)	105.05 (4)	105.26 (4)	105.3 (1)
O(1)—Se—O(3)	111.65 (4)	111.63 (4)	111.6 (1)
O(1)—Se—O(4)	112.68 (4)	112.66 (4)	113.0 (1)
O(2)—Se—O(3)	105.16 (4)	105.38 (5)	105.5 (1)
O(2)—Se—O(4)	108.92 (4)	108.52 (4)	108.0 (1)
O(3)—Se—O(4)	112.76 (4)	112.78 (4)	112.8 (1)
Hydrogen bond			
O(2)···O(2$^{\rm vii}$)	2.4965 (16)	2.5153 (18)	2.524 (5)

Symmetry codes: (i) $x, 1 + y, z$; (ii) $1 - x, 1 - y, -z$; (iii) $\frac{1}{2} + x, 1 - y, z$; (iv) $1 - x, \frac{1}{2} - y, \frac{1}{2} - z$; (v) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (vi) $1 - x, \frac{3}{2} - y, \frac{1}{2} - z$; (vii) $1 - x, -y, -z$.

* Ichikawa *et al.* (1992).

Data collection: *DIF*4 (Stoe & Cie, 1988). Cell refinement: *LATCON* (Lundgren, 1983). Data reduction: *STOEDATRED*, *ABSSTOE* (Lundgren, 1983). Program(s) used to refine structure: *DUPALS* (Lundgren, 1983). Molecular graphics: *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71628 (90 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1083]

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Structures of $LuFeO_3(ZnO)_m$ ($m = 1$, 4, 5 and 6)

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Abstract

The structures of the title compounds, iron lutetium zinc oxides, can be described as a close packing of O atoms, with Lu atoms in octahedral voids and Fe and Zn atoms in tetrahedral voids. Blocks constituting $m + 1$ layers of Fe and/or Zn atoms along the c axis are alternately stacked with single layers of Lu along the c axis.

Comment

In the process of establishing the phase diagrams of the R_2O_3–A_2O_3–MO (R = Sc, Y, In, Ho, Er, Tm, Yb, Lu; A = Al, Fe, Ga; M = Mg, Mn, Fe, Co, Cu, Zn, Cd) system, Kimizuka, Mohri, Matsui & Siratori (1988) and Kimizuka & Mohri (1989) identified several new homologous compounds of $RAO_3(MO)_m$ (m = integer), and estimated that these compounds have $InFeO_3(ZnO)_m$-type structures through both X-ray powder diffraction and electron-diffraction analysis. However, the compounds, including $LuFeO_3(ZnO)_m$, have not been studied by the single-crystal X-ray method and structural details were not known. We have, therefore, determined the structure of the title compounds by the single-crystal method to understand the crystal chemistry of the $LuFeO_3$–ZnO system. The crystals were grown through the solid-state reaction between Lu_2O_3, Fe_2O_3 and ZnO powder in platinum tubes at 1823 K for three days.

$LuFeO_3(ZnO)$ (Kimizuka & Takayama, 1981) is isostructural with the compounds In_2ZnS_4 (Lappe, Niggli, Nitsche & White, 1962) and $YbFe_2O_4$ (Kato, Kawada, Kimizuka & Katsura, 1975; Malaman *et al.*, 1975). As for these compounds, the structures of $LuFeO_3(ZnO)_m$ (Fig. 1) can be described as a close packing of O atoms, with Lu atoms in the octahedral voids of the cubic close-packed layers and Fe and Zn atoms (denoted M) in the tetrahedral voids of hexagonal close-packed layers. Commonly with these compounds, the basic structure consists of LuO_2^- and $(FeZn_m)O_{m+1}^+$ layers alternately stacked along the c axis. Bond lengths and angles in each coordination polyhedron (Fig. 2) are listed in Table 2. LuO_6 octahedra share edges forming a continuous layer on the c plane; O—Lu—O bond angles deviate by 10° from the ideal values of 90°. The M [excluding $M(1)$ for m = even] atoms shift from the centre of gravity of the coordination tetrahedra along the c axis in the opposite direction to the apical O atom to form trigonal bipyramids, resulting in long bonds to the apical O atoms [M—O^{ii} 2.215 (8)–2.990 (15) Å; Table 2]. For m = even, the $M(1)$ atom is on the centre of the equatorial triangle by the requirements of symmetry. The O—M—O angles are between 120 and 113°; these angles approach the ideal angle of 109.47° [110.8 (3)° in ZnO (Abrahams & Bernstein, 1969)] when their Zn content increases.

For the compound with $m = 1$, the displacement parameters U_{33} of Lu and O(1) were abnormally large; therefore, the X-ray photographs were exam-