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Structure of a Photoluminescent Polyoxotungstoantimonate

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Abstract. $K_{5.5}H_{1.5}[SbW_6O_{24}].6H_2O$, $M_r = 1933.48$, trigonal, $P\bar{3}m1$, $a = 13.672\,(3)$, $c = 12.908\,(5)$ Å, $V = 2089\,(1)$ Å^3, $Z = 2$, $D_m = 3.20$, $D_x = 3.07$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 182.25$ cm^{-1}, $F(000) = 1706$, $T = 298$ K, final $R = 0.060$ and $wR = 0.080$ for 1089 independent reflections. The $[SbW_6O_{24}]^{7-}$ anion shows the Anderson-type structure with the SbO_6 octahedron edge-shared by six WO_6 octahedra. K^+ cations and lattice water molecules bind the anions by ionic and hydrogen-bond networks, respectively. A column-like cavity exists around the *c* axis.

Introduction. Photoluminescence of polyoxotungstolanthanoates has been studied for $Na_9[Ln(W_5O_{18})_2].18H_2O$ ($Ln = Sm^{3+}$, Tb^{3+}, Dy^{3+} and Eu^{3+}), $K_{13}[Eu(SiW_{11}O_{39})_2].30H_2O$, $K_{17}[Eu(W_{17}O_{61})_2].48H_2O$ and $K_{15}H_3[Eu_3(H_2O)_3(W_5O_{18})_3(SbW_9O_{33})].25.5H_2O$ (Stillman & Thomson, 1976; Blasse, Dirksen & Zonnevijlle, 1981*a*; Ballardini, Chiorboli & Balzani, 1984; Yamase, Naruke & Sasaki, 1990). These compounds give luminescence due to *f*→*f* transitions within Ln^{3+} on photoexcitation into the O→W ligand-to-metal charge transfer (LMCT) bands, demonstrating that the photoexcitation energy migrates from polyoxotungstate groups to Ln^{3+}. However, there is no observable luminescence from the O→W LMCT states for the above compounds. Although the photoluminescence of the polyoxotungstates consisting of WO_6 octahedra can be expected, only one polyoxotungstate $Na_9[Gd(W_5O_{18})_2].18H_2O$ (Blasse, Dirksen & Zonnevijlle, 1981*b*) does photoluminesce and the photoluminescence from the O→W LMCT state peaks around 510 nm with a broad band. Recently we found a photoluminescent polyoxotungstate, $K_{5.5}H_{1.5}[SbW_6O_{24}].6H_2O$, which exhibits green emission on O→W LMCT photoexcitation below room temperature. In this paper, we describe the crystal structure of $K_{5.5}H_{1.5}[SbW_6O_{24}].6H_2O$, to give a better understanding of the energy transfer from the O→W LMCT excited state to the lanthanide site in the lattice.

Experimental. All the chemicals of reagent grade were used without further purification. 1.0 g of $KSb(OH)_6$ was dissolved into a hot aqueous solution (40 ml) containing WO_3 (5.2 g) and KOH (3.0 g). Solution pH was adjusted to 7.5 with HNO_3 or HCl. The crude product was formed on standing at room temperature and recrystallized from hot water. Found: K, 11.7; H_2O, 6.0%. Calculated for $SbW_6O_{24}K_{5.5}H_{1.5}(H_2O)_6$: K, 11.12; H_2O, 5.59%. Archimedes' principle was applied to measure D_m using a pycnometer.

A single crystal (0.2 × 0.2 × 0.3 mm) was sealed in a glass capillary and mounted on a Rigaku AFC-5R four-circle diffractometer. Lattice parameters were refined from 15 reflections with $13.8 < 2\theta < 29.4°$ using least-squares methods. Intensity data were collected in the range $5 < 2\theta < 60°$ using the 2θ–ω-scanning technique with a scan rate of 16° min^{-1}, $\Delta\omega = (1.00 + 0.14\tan\theta)°$, and $-16 \leq h \leq 16$, $0 \leq k \leq 19$, $0 \leq l \leq 18$. Intensities of three standard reflections measured every 150 observations showed little variation throughout the collection. Of 4483 reflections measured, 2280 were independent. 1089 data with $I > 3\sigma(I)$ from the unique reflections were used for the refinement of the structure. $R_{\rm int}$ was 0.068. Lorentz and polarization corrections were applied and an absorption correction was made by the program *DIFABS* (Walker & Stuart, 1983). The correction factors were from 0.80 to 1.54. All calculations were carried out using the *TEXSAN* (Molecular Structure Corporation, 1989) program which incorporates *MITHRIL* (Gilmore, 1984) for structure solution by direct methods. W and Sb atoms were refined with anisotropic thermal parameters. A short distance [1.59 (7) Å] between K(3) and its symmetry equivalent ($2 - x$, $1 - y$, z) position let us propose the occupancy of 0.25 for K(3) throughout the refinements. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Refinements were carried out by the full-matrix least-squares method for 47

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Table 1. *Atomic coordinates and thermal parameters for* $K_{5.5}H_{1.5}[SbW_6O_{24}].6H_2O$

E.s.d.'s are indicated in parentheses.

$$B_{eq} = (\tfrac{8}{3})\pi^2\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq} or B (Å^2)
W	0.4278 (1)	0.0946 (1)	0.27090 (8)	1.43 (4)
Sb	$\frac{2}{3}$	$\frac{1}{3}$	0.2735 (4)	1.3 (1)
O(1)	0.520 (2)	0.260	0.352 (2)	1.7 (5)
O(2)	0.814 (2)	0.407	0.195 (2)	1.4 (4)
O(3)	0.390 (2)	0.195	0.199 (2)	2.1 (5)
O(4)	0.942 (2)	0.471	0.343 (2)	1.4 (4)
O(5)	0.326 (2)	0.040 (2)	0.365 (1)	2.3 (4)
O(6)	0.381 (2)	−0.005 (2)	0.174 (2)	3.0 (4)
K(1)	$\frac{2}{3}$	$\frac{1}{3}$	0.684 (1)	2.7 (3)
K(2)	0.3788 (9)	0.1894	0.5411 (7)	2.8 (2)
K(3)†	0.933 (3)	0.466	0.002 (3)	8.0 (9)
O*w*(1)	0.448 (2)	0.224	0.749 (2)	2.4 (5)
O*w*(2)	0.849 (1)	0.425	0.553 (2)	2.5 (6)

† Occupancy 0.25.

Table 2. *Selected interatomic distances* (< 3.5 Å) *and angles* (°)

E.s.d.'s are indicated in parentheses.

Sb—O(1)	2.01 (3)	K(2)—O(5)	2.89 (2)
Sb—O(2)	2.01 (3)	K(2)—O($5^{v,vi}$)	2.98 (2)
W—O(1)	2.22 (2)	K(2)—O*w*(1)	2.81 (3)
W—O(2^{ii})	2.19 (2)	K(2)—O*w*($2^{i,ii}$)	2.99 (1)
W—O(3)	1.93 (1)	K(3)—O(2)	2.86 (4)
W—O(4^{ii})	1.93 (1)	K(3)—O($6^{i,vii}$)	2.87 (4)
W—O(5)	1.72 (2)	K(3)—O($6^{viii,ix}$)	2.88 (4)
W—O(6)	1.72 (2)	O*w*(1)—O($5^{v,vi}$)	3.48 (3)
Sb—W	3.265 (1)	O*w*(1)—O($6^{v,vi}$)	2.85 (3)
W—W^{iii}	3.261 (3)	O*w*(1)—O*w*($2^{i,ii}$)	3.48 (3)
W—W^{iv}	3.269 (3)	O*w*(2)—O($1^{i,ii}$)	3.27 (3)
K(1)—O*w*(1)	2.72 (3)	O*w*(2)—O(4)	2.93 (4)
K(1)—O*w*(2)	2.74 (3)	O*w*(2)—O(4^{x})	2.81 (4)
K(2)—O(1)	2.96 (3)		

O(1)—W—O(2^{ii})	74.3 (8)	O(5)—W—O(2^{ii})	161.2 (9)
O(5)—W—O(6)	105.5 (9)	O(1)—W—O(6)	161.0 (9)
O(3)—W—O(5)	101.8 (10)	O(1)—Sb—O($1^{i,ii}$)	97.0 (9)
O(6)—W—O(4^{ii})	100.2 (10)	O(1)—Sb—O(2)	179.9 (11)
O(3)—W—O(4^{ii})	153.8 (10)	O(1)—Sb—O($2^{i,ii}$)	82.9 (6)

Symmetry codes: (i) $1-y, x-y, z$; (ii) $1-x+y, 1-x, z$; (iii) $x, x-y, z$; (iv) $1-x+y, y, z$; (v) $x-y, x, 1-z$; (vi) $x-y, -y, 1-z$; (vii) $1-y, 1-x, z$; (viii) $1+y, 1-x+y, -z$; (ix) $1+y, x, -z$; (x) $2-x, 1-y, 1-z$.

parameters. Minimized quantity was $\sum w(F_o-F_c)^2$. H atoms were not included in the calculation. $R = 0.060$, $wR = 0.080$, $w^{-1} = \sigma^2(F_o)$, $(\Delta/\sigma)_{max} = 0.11$, $S = [\sum(|F_o|-|F_c|)/\sigma]/(n-m) = 2.31$, residual maximum and minimum Fourier peaks are 4.4 and -4.8 e Å^{-3}, respectively. Positional and thermal parameters for non-H atoms are listed in Table 1.*

Discussion. The crystal structure of $K_{5.5}H_{1.5}[SbW_6O_{24}].6H_2O$ viewed along the c axis is shown in Fig. 1. $[SbW_6O_{24}]^{7-}$ represents a Sb^VO_6 octahedron surrounded by six WO_6 octahedra, with a planar configuration of the seven edge-sharing metal oxide (MO_6) octahedra. This structure is known as an 'Anderson type', as reported for $K_5Na_2[SbW_6O_{24}].12H_2O$ (Lee & Sasaki, 1987), $K_6Na_2[PtW_6O_{24}].12H_2O$ (Lee, Ichida, Kobayashi & Sasaki, 1984), $Na_5[H_3PtW_6O_{24}].20H_2O$ (Lee,

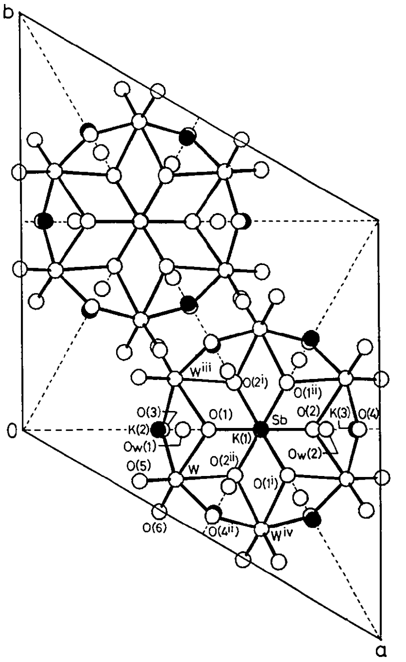

Fig. 1. Crystal structure of $K_{5.5}H_{1.5}[SbW_6O_{24}].6H_2O$ with the atom numbering, viewed along the c axis. Symmetry codes are listed in Table 2.

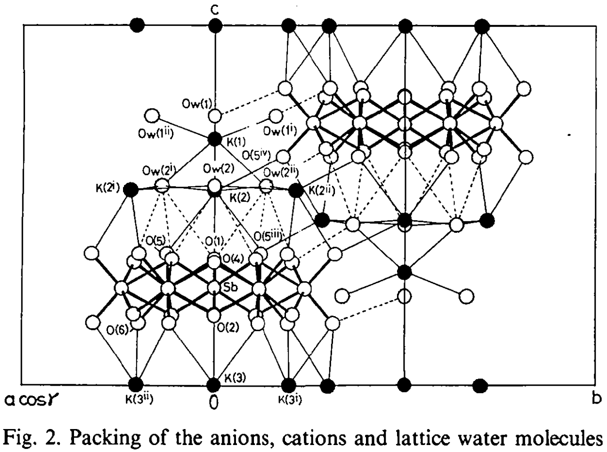

Fig. 2. Packing of the anions, cations and lattice water molecules in the unit cell projected onto the (100) plane. Thin and broken lines represent K—O and hydrogen bonds shorter than 3.3 Å, respectively. Symmetry codes are listed in Table 2.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54588 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0506]

Kobayashi & Sasaki, 1983) and $(Na,K)_8[NiW_6O_{24}]$.$12H_2O$ (Hau, 1970). The Sb atom lies on the C_3 axis in the anion and is positioned at a distance of 0.03 Å from the plane containing six W atoms. In addition, the Sb, O(1), O(2), O(3) and O(4) atoms are located on the mirror plane (Fig. 1). Table 2 lists selected interatomic distances and bond angles. There are three types of O atoms for the anion: three-coordinate bridging atoms, O(1) and $O(2^{ii})$, connected to Sb and two W atoms; two-coordinate bridging atoms, O(3) and $O(4^{ii})$, connected to two adjacent W atoms; terminal O atoms, O(5) and O(6), connected to each W atom. The average W—O distances for [O(1), $O(2^{ii})$], [O(3), $O(4^{ii})$] and [O(5), O(6)] are 2.21, 1.93 and 1.72 Å, respectively. The Sb—O bond length [2.01 (3) Å] is comparable to the values [1.894 (3)–2.102 (3) Å] for Sb^VO_6 octahedra of Sb_2O_5 (Jansen, 1979). There is little difference in the corresponding bond lengths and angles between crystals of $K_{5.5}H_{1.5}[SbW_6O_{24}]$.$6H_2O$ and $K_5Na_2[SbW_6O_{24}]$.$12H_2O$ (Lee & Sasaki, 1987).

Fig. 2 represents the crystal structure projected onto the (100) plane. K^+—O and O*w*—O distances less than 3.5 Å are also listed in Table 2. The anion is sandwiched between the two layers of K^+ cations: K(2)–$K(2^i)$–$K(2^{ii})$ and K(3)–$K(3^i)$–$K(3^{ii})$ planes (Fig. 2). K(1) achieves sixfold coordination with O*w*(1), O*w*(1^i), O*w*(1^{ii}), O*w*(2), O*w*(2^i) and O*w*(2^{ii}) atoms, forming a distorted $K(1)O_6$ octahedron. O*w*(1) and O*w*(2) atoms serve to bind anions together by hydrogen bonding. No atom can be found around the (00*z*) region (Fig. 1), which forms a column-like cavity lying around the *c* axis of the crystal. Such a cavity does not exist in the $K_5Na_2[SbW_6O_{24}]$.$12H_2O$ lattice (Lee & Sasaki, 1987).

The O→W LMCT photoexcitation of $K_{5.5}H_{1.5}[SbW_6O_{24}]$.$6H_2O$ results in a broad luminescence in the range 400–650 nm with a peak at 510 nm. A similar spectrum was reported for $Na_9[Gd(W_5O_{18})_2]$.$18H_2O$ (Blasse, Dirksen & Zonnevijlle, 1981*b*). The relative yield of the luminescence from the O→W LMCT state for $K_{5.5}H_{1.5}[SbW_6O_{24}]$.$6H_2O$ was 2.5 times higher than for $Na_9[Gd(W_5O_{18})_2]$.$18H_2O$, when the samples were exposed to 290 nm light at 77 K.

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Structure of Barium Perrhenate Tetrahydrate

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Abstract. $Ba(ReO_4)_2.4H_2O$, $M_r = 709.80$, monoclinic, $P2_1/n$, $a = 7.376\ (2)$, $b = 12.452\ (2)$, $c = 12.173\ (1)$ Å, $\beta = 90.04\ (1)°$, $V = 1118$ Å^3, $Z = 4$, $D_x = 4.216$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.70930$ Å, $\mu = 254.3$ cm^{-1}, $F(000) = 1240$, $T = 292$ K, $R = 0.038$ for 2591 observed reflections with $I > 3\sigma(I)$. The metrically pseudo-orthorhombic structure has the approximate space group symmetry *Pmnb* (No. 62). Ba cations constitute a distorted hexagonal close-packed motif with 12 Ba—Ba distances ranging from 7.115 to 7.601 Å. Along with Re atoms they are disposed on the pseudo-mirror plane ($d_{200} = 3.688$ Å). The coordination polyhedron of Ba is a distorted tetradecahedron with Ba—O distances within 2.831 (7)–2.953 (7) Å. Two non-equivalent ReO_4 tetrahedra have irregular geometry, Re—O 1.709 (8)–1.743 (8) Å for Re(1), 1.709 (8)–1.729 (9) Å for Re(2). The structure may be looked upon as composed of buckled ${}_\infty^2[Ba(ReO_4)_2]$ layers coinciding with the (002) plane ($d_{002} = 6.087$ Å). The layers are

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