O56	0.139 (1)	0.030 (2)	0.0786 (7)	0.036 (9)
O57	0.157 (2)	−0.175 (2)	0.0643 (7)	0.046 (9)
O58	0.047 (2)	0.075 (2)	0.0172 (8)	0.05 (1)
O59	0.103 (2)	−0.184 (2)	−0.0112 (9)	0.07 (1)
O60	0.266 (2)	−0.094 (3)	0.0208 (9)	0.09 (1)
O61	0.215 (1)	0.094 (2)	0.0184 (6)	0.030 (8)
O62	0.016 (2)	−0.096 (2)	0.0479 (7)	0.047 (9)
O63	0.451 (1)	0.827 (2)	−0.0179 (7)	0.037 (8)
O64	0.224 (1)	0.341 (2)	0.1853 (7)	0.035 (8)
O65	0.420 (2)	0.022 (2)	0.0088 (8)	0.05 (1)
O66	0.089 (2)	0.195 (2)	0.2453 (8)	0.05 (1)
O67	0.370 (2)	0.346 (2)	0.2297 (8)	0.06 (1)
O68	0.5	0.394 (4)	0.25	0.08 (2)
O69	0.212 (2)	0.421 (3)	0.0366 (10)	0.09 (1)
O70	0.152 (2)	0.576 (3)	0.0513 (10)	0.11 (2)
O71	0.052 (3)	0.352 (4)	0.222 (1)	0.17 (2)

Table 2. *Bond lengths* (Å)

W0—O1	1.72 (3)	W5—O33	1.91 (2)
W0—O3	1.86 (2)	W5—O23	2.26 (3)
W0—O4	1.90 (3)	W6—O28	1.70 (3)
W0—O5	1.90 (3)	W6—O19	1.78 (3)
W0—O2	1.95 (3)	W6—O27	1.93 (2)
W0—O14	2.32 (2)	W6—O24	2.00 (3)
W1—O6	1.70 (3)	W6—O32	2.08 (3)
W1—O15	1.74 (3)	W6—O23	2.29 (3)
W1—O13	1.92 (3)	W7—O29	1.68 (3)
W1—O10	1.94 (3)	W7—O20	1.82 (3)
W1—O2	1.99 (3)	W7—O24	1.87 (3)
W1—O14	2.42 (2)	W7—O25	1.93 (3)
W2—O7	1.69 (3)	W7—O33	2.02 (2)
W2—O16	1.83 (3)	W7—O23	2.36 (3)
W2—O10	1.96 (3)	W8—O30	1.72 (3)
W2—O11	2.02 (3)	W8—O21	1.83 (3)
W2—O3	2.06 (2)	W8—O26	1.92 (3)
W2—O14	2.27 (2)	W8—O25	1.98 (3)
W3—O8	1.75 (3)	W8—O34	2.04 (3)
W3—O17	1.76 (3)	W8—O23	2.34 (3)
W3—O12	1.88 (2)	W9—O31	1.71 (3)
W3—O11	1.95 (3)	W9—O22	1.76 (3)
W3—O4	2.06 (3)	W9—O27	1.93 (2)
W3—O14	2.20 (2)	W9—O26	1.96 (3)
W4—O9	1.70 (3)	W9—O35	2.08 (3)
W4—O18	1.79 (3)	W9—O23	2.27 (3)
W4—O13	1.90 (3)	Eu—O21	2.35 (3)
W4—O12	2.01 (2)	Eu—O18	2.37 (3)
W4—O5	2.04 (3)	Eu—O16	2.38 (3)
W4—O14	2.37 (2)	Eu—O22	2.39 (3)
W5—O36	1.75 (3)	Eu—O19	2.39 (3)
W5—O35	1.88 (3)	Eu—O20	2.42 (3)
W5—O32	1.88 (3)	Eu—O15	2.44 (3)
W5—O34	1.91 (3)	Eu—O17	2.50 (3)

Lists of structure factors, anisotropic thermal parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71172 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1050]

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Structure of $K_3Na_4H_2[SmW_{10}O_{36}].22H_2O$

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Abstract

Tripotassium tetrasodium dihydrogen decatungstosamarate docosahydrate, $K_3Na_4H_2[SmW_{10}O_{36}].22H_2O$, consists of a decatungstosamarate anion, three sevenfold or eightfold coordinated potassium cations, four octahedrally coordinated sodium cations, and water molecules. The decatungstosamarate anion is comprised of two $W_5O_{18}^{6-}$ moieties chelating to a central Sm^{3+} cation, which lies in a tetragonal antiprismatic coordination field. The Sm atom is not at the midpoint of the two $W_5O_{18}^{6-}$ groups. The Sm—W distances are 3.820-3.840 Å for the W atoms in one group and 3.855-3.888 Å for those in the other.

Comment

Photoluminescence of polyoxotungstolanthanoates and polyoxomolybdolanthanoates has been studied extensively for various kinds of polyoxometallates, among which are $Na_7H_2[LnW_{10}O_{36}].xH_2O$ (Ln = Pr^{3+}, Nd^{3+}, Eu^{3+} and Ho^{3+}) and $K_{13}[Eu(SiW_{11}O_{39})_2].xH_2O$ (Stillman & Thomson, 1976), $Na_9[LnW_{10}O_{36}].xH_2O$ (Ln = Sm^{3+}, Eu^{3+}, Tb^{3+} and Dy^{3+}) and $K_{17}[Eu(P_2W_{17}O_{61})_2].xH_2O$ (Blasse, Dirksen & Zonnevijlle, 1981), $K_{15}H_3[Eu_3(H_2O)_3(SbW_9O_{33})(W_5O_{18})_3].25.5H_2O$ (Yamase, Naruke & Sasaki, 1990), $(NH_4)_{12}H_2[Eu_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4].13H_2O$ (Naruke, Ozeki & Yamase, 1991; Naruke & Yamase, 1991), $Eu_2(H_2O)_{12}[Mo_8O_{27}].6H_2O$ (Yamase & Naruke, 1991), and $K_3Na_4H_2[TbW_{10}O_{36}].$-

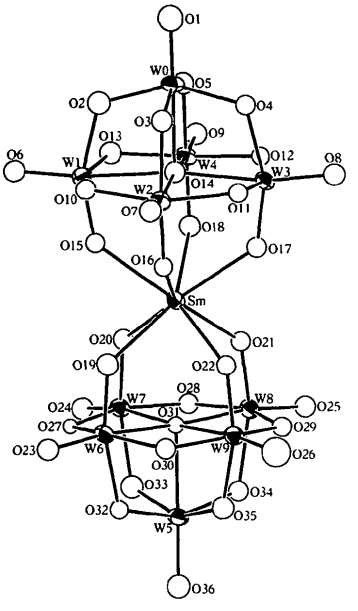

Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the $[SmW_{10}O_{36}]^{9-}$ anion. Thermal ellipsoids are shown at 50% probability levels.

$20H_2O$ (Ozeki & Yamase, 1993; Ozeki, Takahashi & Yamase, 1992). The crystal structures of the last four compounds have been analyzed by X-ray diffractometry. Although various lanthanide elements can substitute for the lanthanide atoms in the polyoxometallolanthanoates listed above, the crystal structures of the polyoxometallates with lanthanide elements other than Eu have been investigated little; there are a limited number of studies for $Na_6H_2[Ce^{IV}W_{10}O_{36}].30H_2O$ (Iball, Low & Weakley, 1974) and $K_3Na_4H_2[TbW_{10}O_{36}].20H_2O$ (Ozeki, Takahashi & Yamase, 1992). The crystal structure analysis of the title compound was undertaken to investigate the effect of substitution of the central lanthanide atom of the decatungstolanthanoate anion on its molecular and crystal structure, which may influence its photoluminescence properties.

The pH of a 30 ml aqueous solution containing 16.4 g $Na_2WO_4.2H_2O$ was brought to 7 by adding CH_3COOH. To this solution, 2.00 g of $Sm(CH_3COO)_3.4H_2O$ in 20 ml H_2O and 1.12 g of KCl in 10 ml H_2O were added. Maintaining the solution at room temperature, colourless crystals of the title compound were obtained after two weeks.

Fig. 1 shows the structure of the $[SmW_{10}O_{36}]^{9-}$ anion. It consists of two $[W_5O_{18}]^{6-}$ moieties which can be derived by removing one WO_6 octahedron from the $[W_6O_{19}]^{2-}$ anion. The lacunary site of the resulting polyoxotungstate moiety becomes a tetradentate ligand, exhibiting twofold coordination to an Sm^{3+} atom to form a tetragonal antiprismatic SmO_8 configuration. The Sm—O distances are 2.42 (2)-2.52 (2) Å [average 2.47 (3) Å], which is 0.05 Å longer than the Tb—O distances in the $[TbW_{10}O_{36}]^{9-}$ anion [2.40 (1)-2.44 (1) Å, average 2.42 (2) Å (Ozeki, Takahashi & Yamase, 1992)]. This is explained by the smaller ionic radius of Tb^{3+} compared with that of Sm^{3+}, due to the lanthanide contraction. As a result of its *trans* influence, the W—O bonds *trans* to the Sm—O bonds are 1.72 (2)-1.77 (2) Å [average 1.75 (2) Å] which are shorter than the corresponding W—O distances in the $[TbW_{10}O_{36}]^{9-}$ anion [1.77 (2)-1.82 (1) Å, average 1.79 (2) Å]. The Sm—W distances are 3.820 (2)-3.888 (2) Å [average 3.85 (2) Å], which is also longer than the Tb—W distances [3.807 (2)-3.866 (2) Å, average 3.83 (3) Å]. The Sm atom is shifted to one $[W_5O_{18}]^{6-}$ moiety from the midpoint of the two $[W_5O_{18}]^{6-}$ groups. It lies at 3.113 (5) Å from the least-squares plane defined by W1, W2, W3 and W4, and 3.050 (3) Å from the plane defined by W6, W7, W8 and W9. The $[W_5O_{18}]^{6-}$ moieties in the $[SmW_{10}O_{36}]^{9-}$ anion are almost identical to those in the $[TbW_{10}O_{36}]^{9-}$ anion and the corresponding W—W distances are identical to within 0.011 Å (average 0.005 Å).

Fig. 2 shows a packing diagram of the crystal viewed along the c^* axis. The crystal is isomorphous with its Tb^{III} analogue except for the disordered water molecules which also were observed in the final difference Fourier map but could not be refined in the Tb^{III} analogue. K1 and K2 are coordinated by eight O atoms and K3 is coordinated by seven O atoms with K—O distances of 2.61 (2)-3.17 (2) Å. Each of the four Na atoms is coordinated by six O atoms with Na—O distances of 2.35 (2)-2.73 (3) Å in a distorted octahedral configuration. K1 and K2 bridge two symmetry-related $[SmW_{10}O_{36}]^{9-}$ anions and K3 bridges three anions, while no Na atoms have contact with more

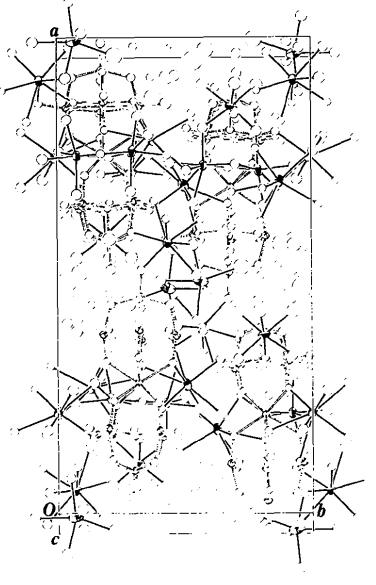

Fig. 2. Packing diagram of $K_3Na_4H_2[SmW_{10}O_{36}].22H_2O$ viewed along the c^* axis. Thermal ellipsoids are shown at 50% probability levels. Na and K atoms are shown as ellipsoids with shaded octants.

than one $[SmW_{10}O_{36}]^{9-}$ anion. The last nine O atoms of the water molecules (O54–O62) had large temperature factors and some of them were very close to each other (*e.g.* 1.78–1.92 Å). Because the interatomic distances are larger than 2.70 (4) Å for O54–O59 and O60–O62, a common site occupancy factor was applied to O54–O59 and its complement to unity was used as the site occupancy factors for O60–O62. After a successful refinement of this value which converged to 0.67 (2), the site occupancy factors for O54–O59 were fixed at $\frac{2}{3}$ and those for O60–O62 at $\frac{1}{3}$.

Experimental

Crystal data

$K_3Na_4H_2[SmW_{10}O_{36}].22H_2O$
M_r = 3172.5
Monoclinic
$P2_1/n$
a = 29.894 (5) Å
b = 16.072 (3) Å
c = 11.446 (3) Å
β = 96.32 (2)°
V = 5466 (3) Å^3
Z = 4
D_x = 3.85 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 48 reflections
θ = 10.0–12.5°
μ = 22.847 mm^{-1}
T = 298 K
Plate
0.10 × 0.15 × 0.60 mm
Colourless

Data collection

Rigaku AFC-5 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
T_{min} = 0.3907, T_{max} = 1.0000
13625 measured reflections
12993 independent reflections
6752 observed reflections [$I > 3\sigma(I)$]
θ_{max} = 27.5°
$h = -38 \rightarrow 38$
$k = 0 \rightarrow 20$
$l = 0 \rightarrow 14$
3 standard reflections monitored every 100 reflections
intensity variation: −2.5%

Refinement

Refinement on F
Final R = 0.0528
wR = 0.0346
S = 2.03
6356 reflections
411 parameters
H atoms not included in the refinement
Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{max}$ = 0.0346
$\Delta\rho_{max}$ = 2.17 e Å^{-3}
$\Delta\rho_{min}$ = −2.47 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Coordinates for Tb and W atoms in the isomorphous $K_3Na_4H_2[TbW_{10}O_{36}].20H_2O$ crystal were used as the initial coordinates for Sm and W, respectively.

Data collection: *RCRYSTAN*85 (Rigaku Corporation, 1985). Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1989). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *ORTEP*II (Johnson, 1976).

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic thermal parameters* (Å^2)

O atoms isotropic; $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for other atoms.

	x	y	z	U_{iso}/U_{eq}
W0	0.58769 (4)	0.20415 (7)	0.4600 (1)	0.0281
W1	0.66496 (5)	0.08692 (6)	0.6182 (1)	0.0244
W2	0.67188 (4)	0.28889 (6)	0.6354 (1)	0.0235
W3	0.67153 (4)	0.30177 (6)	0.3518 (1)	0.0235
W4	0.66520 (4)	0.09923 (6)	0.3342 (1)	0.0238
W5	0.95640 (4)	0.17436 (7)	0.5813 (1)	0.0257
W6	0.87351 (4)	0.17325 (7)	0.7528 (1)	0.0233
W7	0.87381 (5)	0.03412 (6)	0.5431 (1)	0.0229
W8	0.87740 (4)	0.18187 (7)	0.34912 (9)	0.0234
W9	0.87745 (4)	0.32173 (7)	0.5583 (1)	0.0237
Sm	0.77299 (5)	0.18360 (8)	0.5139 (1)	0.0207
K1	0.7795 (3)	−0.0038 (4)	0.7419 (7)	0.0512
K2	0.7952 (3)	0.3739 (4)	0.2857 (6)	0.0427
K3	0.9221 (3)	−0.0681 (4)	0.2897 (7)	0.0442
Na1	0.2585 (5)	0.2070 (6)	0.484 (1)	0.0431
Na2	0.6222 (4)	0.1874 (8)	0.907 (1)	0.0471
Na3	0.7509 (4)	0.0769 (6)	0.027 (1)	0.0376
Na4	0.9973 (5)	0.0653 (9)	0.122 (1)	0.0672
O1	0.5309 (7)	0.210 (1)	0.448 (2)	0.042 (5)
O2	0.6027 (7)	0.116 (1)	0.576 (2)	0.032 (5)
O3	0.6061 (7)	0.2795 (9)	0.590 (2)	0.029 (5)
O4	0.6067 (6)	0.2883 (9)	0.361 (1)	0.024 (4)
O5	0.6001 (7)	0.125 (1)	0.343 (2)	0.030 (5)
O6	0.6593 (7)	0.009 (1)	0.715 (2)	0.028 (5)
O7	0.6681 (7)	0.361 (1)	0.748 (2)	0.031 (5)
O8	0.6675 (7)	0.381 (1)	0.247 (2)	0.029 (5)
O9	0.6584 (7)	0.028 (1)	0.218 (2)	0.029 (5)
O10	0.6633 (6)	0.183 (1)	0.720 (1)	0.025 (4)
O11	0.6689 (6)	0.3613 (9)	0.497 (2)	0.022 (4)
O12	0.6639 (6)	0.2049 (9)	0.245 (1)	0.020 (4)
O13	0.6587 (7)	0.029 (1)	0.465 (2)	0.030 (5)
O14	0.6626 (6)	0.197 (1)	0.482 (2)	0.028 (4)
O15	0.7232 (6)	0.0932 (9)	0.615 (2)	0.023 (4)
O16	0.7305 (6)	0.2722 (9)	0.634 (2)	0.022 (4)
O17	0.7293 (7)	0.2830 (9)	0.380 (2)	0.026 (5)
O18	0.7243 (7)	0.107 (1)	0.360 (2)	0.028 (5)
O19	0.8163 (6)	0.171 (1)	0.715 (1)	0.029 (4)
O20	0.8151 (7)	0.049 (1)	0.525 (2)	0.026 (5)
O21	0.8189 (5)	0.186 (1)	0.352 (1)	0.023 (4)
O22	0.8190 (6)	0.310 (1)	0.540 (1)	0.023 (4)
O23	0.8774 (6)	0.166 (1)	0.906 (1)	0.028 (5)
O24	0.8828 (7)	−0.0734 (9)	0.528 (2)	0.028 (5)
O25	0.8850 (6)	0.186 (1)	0.198 (1)	0.027 (4)
O26	0.8835 (8)	0.428 (1)	0.567 (2)	0.053 (7)
O27	0.8777 (6)	0.0530 (8)	0.708 (1)	0.013 (4)
O28	0.8786 (7)	0.0636 (9)	0.384 (2)	0.024 (4)
O29	0.8813 (6)	0.301 (1)	0.398 (1)	0.023 (4)
O30	0.8804 (6)	0.291 (1)	0.720 (1)	0.026 (5)
O31	0.8783 (6)	0.1778 (9)	0.555 (1)	0.017 (3)
O32	0.9400 (5)	0.1707 (9)	0.738 (1)	0.022 (4)
O33	0.9392 (7)	0.059 (1)	0.567 (2)	0.032 (5)
O34	0.9449 (5)	0.180 (1)	0.409 (1)	0.024 (4)
O35	0.9403 (6)	0.292 (1)	0.584 (2)	0.031 (5)
O36	1.0142 (6)	0.172 (1)	0.603 (2)	0.034 (5)
O37	0.7486 (6)	0.171 (1)	0.868 (1)	0.030 (4)
O38	0.2532 (7)	0.069 (1)	0.549 (2)	0.031 (5)
O39	0.7535 (7)	0.203 (1)	0.147 (2)	0.040 (5)
O40	0.7687 (7)	0.008 (1)	0.212 (2)	0.041 (5)
O41	0.2591 (8)	0.057 (1)	0.058 (2)	0.050 (6)
O42	0.0795 (7)	0.047 (1)	0.123 (2)	0.038 (5)
O43	0.0049 (8)	0.095 (1)	0.900 (2)	0.047 (6)
O44	0.6696 (8)	0.075 (1)	0.987 (2)	0.044 (6)
O45	0.2856 (7)	0.141 (1)	0.316 (2)	0.042 (6)
O46	0.9935 (7)	0.047 (1)	0.325 (2)	0.042 (6)
O47	0.9183 (8)	0.033 (1)	0.100 (2)	0.053 (6)
O48	0.1768 (8)	0.213 (1)	0.494 (2)	0.046 (6)
O49	0.8241 (7)	0.036 (1)	0.974 (2)	0.041 (5)
O50	0.0718 (9)	0.212 (1)	0.317 (2)	0.065 (8)
O51	0.5806 (8)	0.204 (1)	0.096 (2)	0.069 (7)
O52	0.3355 (7)	0.187 (1)	0.575 (2)	0.044 (5)
O53	0.966 (1)	0.224 (2)	0.097 (3)	0.11 (1)
O54	0.4947 (9)	0.201 (2)	0.823 (2)	0.028 (7)

O55	0.571 (1)	0.075 (2)	0.818 (3)	0.07 (1)
O56	0.427 (2)	0.069 (2)	0.781 (3)	0.08 (1)
O57	0.413 (2)	0.121 (3)	0.466 (4)	0.12 (2)
O58	0.506 (2)	0.086 (2)	1.045 (4)	0.11 (2)
O59	0.512 (2)	0.037 (3)	0.626 (5)	0.16 (2)
O60	0.496 (2)	0.057 (2)	0.850 (4)	0.01 (1)
O61	0.422 (2)	0.036 (3)	0.565 (5)	0.05 (2)
O62	0.451 (2)	0.131 (3)	0.342 (5)	0.03 (1)

Table 2. *Bond lengths* (Å)

W0—O1	1.69 (2)	W6—O30	1.94 (2)
W0—O4	1.89 (2)	W6—O27	2.01 (1)
W0—O5	1.92 (2)	W6—O32	2.01 (2)
W0—O3	1.95 (2)	W6—O31	2.29 (2)
W0—O2	1.96 (2)	W7—O24	1.76 (2)
W0—O14	2.23 (2)	W7—O20	1.76 (2)
W1—O6	1.69 (2)	W7—O28	1.90 (2)
W1—O15	1.75 (2)	W7—O27	1.91 (2)
W1—O2	1.93 (2)	W7—O33	1.98 (2)
W1—O10	1.93 (2)	W7—O31	2.32 (1)
W1—O13	1.97 (2)	W8—O21	1.76 (2)
W1—O14	2.36 (2)	W8—O25	1.77 (2)
W2—O7	1.74 (2)	W8—O28	1.94 (2)
W2—O16	1.77 (2)	W8—O29	2.00 (2)
W2—O11	1.96 (2)	W8—O34	2.06 (2)
W2—O3	1.98 (2)	W8—O31	2.35 (2)
W2—O10	1.99 (2)	W9—O26	1.71 (2)
W2—O14	2.28 (2)	W9—O22	1.75 (2)
W3—O8	1.74 (2)	W9—O29	1.88 (2)
W3—O17	1.75 (2)	W9—O30	1.90 (2)
W3—O11	1.93 (2)	W9—O35	1.93 (2)
W3—O4	1.97 (2)	W9—O31	2.31 (1)
W3—O12	1.97 (1)	Sm—O21	2.42 (2)
W3—O14	2.28 (2)	Sm—O16	2.44 (2)
W4—O9	1.74 (2)	Sm—O22	2.45 (2)
W4—O18	1.76 (2)	Sm—O15	2.46 (2)
W4—O13	1.90 (2)	Sm—O17	2.48 (2)
W4—O12	1.98 (1)	Sm—O18	2.49 (2)
W4—O5	2.00 (2)	Sm—O20	2.49 (2)
W4—O14	2.32 (2)	Sm—O19	2.52 (2)
W5—O36	1.72 (2)	Sm—W1	3.888 (2)
W5—O32	1.91 (2)	Sm—W2	3.855 (2)
W5—O33	1.93 (2)	Sm—W3	3.874 (2)
W5—O35	1.95 (2)	Sm—W4	3.872 (2)
W5—O34	1.96 (2)	Sm—W6	3.837 (2)
W5—O31	2.32 (2)	Sm—W7	3.840 (2)
W6—O19	1.72 (2)	Sm—W8	3.820 (2)
W6—O23	1.75 (2)	Sm—W9	3.820 (2)

Lists of structure factors, anisotropic thermal parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71170 (30 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.[CIF reference: AS1049]

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Structure of $K_3Na_4H_2[GdW_{10}O_{36}].21H_2O$

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Abstract

Tripotassium tetrasodium dihydrogen decatungstogadolinate henicosahydrate, $K_3Na_4H_2[GdW_{10}O_{36}].21H_2O$, consists of a decatungstogadolinate anion, three eight-nine coordinated K^+ cations, four octahedrally coordinated Na^+ cations, and water molecules of crystallization. The decatungstogadolinate anion is comprised of two $[W_5O_{18}]^{6-}$ units which chelate to a central Gd^{3+} cation to give a tetragonal antiprismatic coordination. The Gd—O distances and W—O distances in the decatungstogadolinate anion are 2.37 (2)-2.49 (2) and 1.71 (2)-2.36 (3) Å, respectively.

Comment

The decatungstogadolinate anion, $[GdW_{10}O_{36}]^{9-}$, is unusual in that it does not show photoluminescence from the Gd^{3+} centre but shows luminescence from the polyoxotungstate framework. In contrast, other decatungstate anions of trivalent lanthanoid elements, of general formula $[LnW_{10}O_{36}]^{9-}$ where Ln = Pr, Nd, Sm, Eu, Tb, Dy and Ho, show a luminescence associated with the lanthanoid atom's *f-f* transitions upon irradiation with UV light. This irradiation is into bands associated with, essentially, transitions within the polyoxotungstate framework (Stillman & Thomson, 1976; Blasse, Dirksen & Zonnevijlle, 1981). This unusual pattern suggests that the uniqueness of the $[GdW_{10}O_{36}]^{9-}$ anion may arise because it has a different crystal structure from those of the other anions. In the course of our crystallographic investigations on photoluminescent decatungstolanthanoate complexes, the tripotassium tetrasodium salts of the decatungstoterbate and decatungstosamarate anions (Ozeki,