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Structure of $NaSr_4[EuW_{10}O_{36}].34.5H_2O$

TOSHIHIRO YAMASE, TOMOJI OZEKI AND KYOTA UEDA

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 227 Japan

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Abstract

Sodium tetrastrontium decatungstoeuropate 34.5-hydrate, $NaSr_4[EuW_{10}O_{36}].34.5H_2O$, consists of a decatungstoeuropate anion, an octahedrally coordinated sodium cation, and four eightfold or ninefold coordinated strontium cations. Eu—O distances and W—O distances in the decatungstoeuropate anion are 2.35–2.50 and 1.68–2.42 Å, respectively. Sr—O distances are 2.50–3.00 Å and Na—O distances are 2.28–2.62 Å.

Comment

Luminescent polyoxotungstolanthanoates and molybdolanthanoates have been studied extensively for various kinds of compounds, including $Na_7H_2[LnW_{10}O_{36}].xH_2O$ (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*a*), $K_3Na_4H_2[TbW_{10}O_{36}].20H_2O$ (Ozeki & Yamase, 1993; Ozeki, Takahashi & Yamase, 1992), and $Na_9[EuW_{10}O_{36}].32H_2O$ (Sugeta & Yamase, 1993). Recently we found that decatungstoeuropates show electroluminescence when a large AC field is applied to their thin dispersion layer, which was fabricated by the deposition of a water-insoluble Sr^{2+} or Ba^{2+} salt of $[EuW_{10}O_{36}]^{9-}$ on the transparent SnO_2/In_2O_3 electrode (Yamase & Naruke, 1991*b*). Structure analysis of the title compound was undertaken in order to establish both the anion structure and the crystal packing of the Sr^{2+} salt in the dispersion layer.

To a 2 ml aqueous solution containing 0.2 g (0.072 mmol) of $Na_9[EuW_{10}O_{36}].32H_2O$ (Sugeta & Yamase, 1993), 0.1 g (0.81 mmol) of $SrCl_2$ in 8 ml H_2O was added. White powder was formed immediately after the addition of $SrCl_2$. The suspended solution was filtered off and the filtrate was kept at room temperature. Colourless crystals of the title compound were obtained after 24 h.

Fig. 1 shows the structure of the decatungstoeuropate anion with the coordination spheres of the Sr^{2+} and Na^+ cations. Fig. 2 shows crystal packing of the title com-

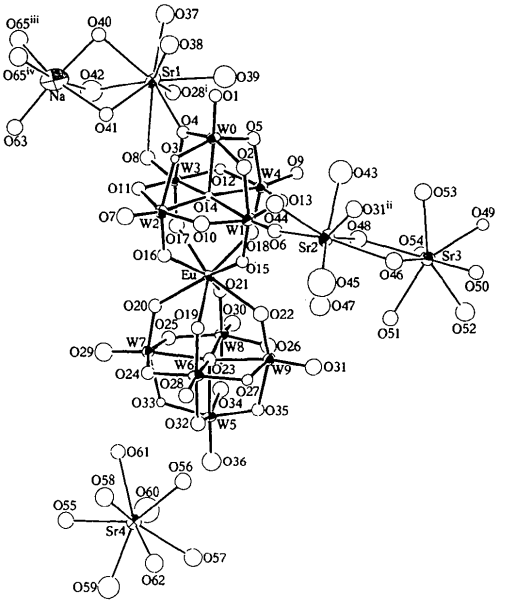

Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the $[EuW_{10}O_{36}]^{9-}$ anion and the coordination spheres of Sr^{2+} and Na^+ ions. Thermal ellipsoids are shown at 50% probability levels. Symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}+y, z$; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $1-x, 1-y, -z$; (iv) $x, 1+y, z$.

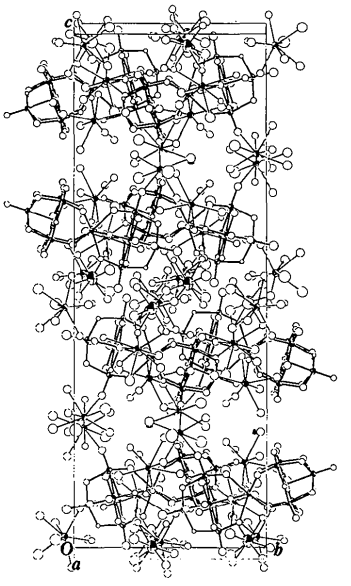

Fig. 2. Packing diagram of the unit cell viewed down the a^* axis.

pound viewed down to the a^* axis. Each W atom in the anion is octahedrally coordinated by six O atoms, of which one is the terminal O atom with W—O distances of 1.68 (3)-1.75 (3) Å. The O atoms, O14 and O23, *trans* to the terminal O atoms are shared by five W atoms with W—O distances of 2.26 (3)-2.42 (2) Å. The W—O distances for the O atoms which are shared by a W and an Eu atom are 1.74 (3)-1.83 (3) Å. The Eu—O distances are 2.35 (3)-2.50 (3) Å. These values agree well with those observed in the $Na_9[EuW_{10}O_{36}].32H_2O$ crystal (Sugeta & Yamase, 1993). Sr1 is coordinated by nine O atoms and the other three Sr atoms are coordinated by eight O atoms. Sr1 shares two O atoms with an $[EuW_{10}O_{36}]^{9-}$ anion and another O atom with a symmetry-related $[EuW_{10}O_{36}]^{9-}$ anion. Sr2 bridges two $[EuW_{10}O_{36}]^{9-}$ anions by sharing an O atom with each of them. The Na atom is coordinated by six O atoms in a distorted octahedral configuration.

Experimental

Crystal data

$NaSr_4[EuW_{10}O_{36}].34.5H_2O$
M_r = 3561.432
Monoclinic
$C2/c$
a = 19.79 (1) Å
b = 15.609 (9) Å
c = 42.17 (4) Å
β = 92.63 (6)°
V = 13009 (38) Å^3
Z = 8
D_x = 3.64 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 9.1-12.0°
μ = 222.18 cm^{-1}
T = 298 K
0.47 × 0.10 × 0.08 mm
Colourless

Data collection

Rigaku AFC-5 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
T_{min} = 0.7231, T_{max} = 1.0000
15947 measured reflections
15947 independent reflections
6252 observed reflections [$I > 3\sigma(I)$]
θ_{max} = 27.5°
$h = -54 \rightarrow 54$
$k = 0 \rightarrow 20$
$l = 0 \rightarrow 25$
3 standard reflections monitored every 200 reflections
intensity variation: −9.2%

Refinement

Refinement on F
Final R = 0.0670
wR = 0.0589
S = 1.77
6205 reflections
427 parameters
Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{max}$ = 0.151
$\Delta\rho_{max}$ = 3.49 e Å^{-3}
$\Delta\rho_{min}$ = −3.21 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Data collection: *RCRYSTAN*85 (Rigaku Corporation, 1985). Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1984). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *ORTEP*II (Johnson, 1976).

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

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

	x	y	z	U_{eq}
W0	0.40658 (9)	0.7397 (1)	0.16131 (5)	0.0236
W1	0.31794 (10)	0.5667 (1)	0.18287 (5)	0.0245
W2	0.30804 (9)	0.6304 (1)	0.10837 (5)	0.0239
W3	0.47231 (9)	0.6159 (1)	0.10625 (4)	0.0205
W4	0.48228 (9)	0.5548 (1)	0.18013 (5)	0.0231
W5	0.34951 (9)	0.0698 (1)	0.09042 (4)	0.0214
W6	0.24754 (9)	0.2346 (1)	0.10336 (5)	0.0239
W7	0.36297 (9)	0.2547 (1)	0.05099 (4)	0.0225
W8	0.47985 (9)	0.2031 (1)	0.10552 (5)	0.0214
W9	0.36373 (10)	0.1828 (1)	0.15723 (4)	0.0228
Eu	0.3810 (1)	0.4072 (1)	0.12294 (5)	0.0206
Sr1	0.5537 (2)	0.8330 (3)	0.1018 (1)	0.0328
Sr2	0.1993 (2)	0.5502 (3)	0.2640 (1)	0.0348
Sr3	0.3204 (2)	0.3905 (3)	0.3309 (1)	0.0314
Sr4	0.1363 (2)	−0.0483 (3)	0.0244 (1)	0.0322
Na	0.497 (1)	0.907 (2)	0.0232 (6)	0.0816
O1	0.409 (1)	0.844 (2)	0.1739 (6)	0.022 (7)
O2	0.341 (1)	0.689 (2)	0.1894 (7)	0.033 (8)
O3	0.335 (1)	0.743 (2)	0.1308 (5)	0.009 (6)
O4	0.466 (1)	0.735 (2)	0.1273 (6)	0.023 (7)
O5	0.475 (1)	0.684 (2)	0.1870 (6)	0.027 (7)
O6	0.260 (1)	0.558 (2)	0.2115 (6)	0.030 (8)
O7	0.245 (2)	0.667 (2)	0.0836 (7)	0.040 (9)
O8	0.530 (1)	0.653 (2)	0.0792 (7)	0.030 (8)
O9	0.549 (1)	0.540 (2)	0.2063 (6)	0.024 (7)
O10	0.261 (2)	0.607 (2)	0.1473 (7)	0.039 (9)
O11	0.390 (1)	0.653 (2)	0.0828 (7)	0.026 (8)
O12	0.530 (1)	0.593 (2)	0.1416 (6)	0.016 (6)
O13	0.404 (1)	0.551 (2)	0.2048 (6)	0.026 (7)
O14	0.397 (1)	0.600 (2)	0.1426 (6)	0.012 (6)
O15	0.317 (1)	0.464 (2)	0.1662 (6)	0.020 (7)
O16	0.312 (1)	0.516 (2)	0.0988 (7)	0.027 (8)
O17	0.460 (1)	0.507 (2)	0.0969 (7)	0.033 (8)
O18	0.464 (1)	0.454 (2)	0.1612 (7)	0.031 (8)
O19	0.273 (1)	0.341 (2)	0.1144 (6)	0.023 (7)
O20	0.374 (1)	0.361 (2)	0.0681 (6)	0.024 (7)
O21	0.474 (1)	0.316 (2)	0.1165 (6)	0.025 (7)
O22	0.374 (1)	0.294 (2)	0.1608 (7)	0.033 (8)
O23	0.361 (1)	0.209 (2)	0.1042 (7)	0.025 (7)
O24	0.271 (1)	0.251 (2)	0.0580 (6)	0.025 (7)
O25	0.457 (1)	0.229 (2)	0.0603 (7)	0.027 (8)
O26	0.458 (1)	0.165 (2)	0.1471 (7)	0.034 (8)
O27	0.268 (1)	0.191 (2)	0.1454 (6)	0.017 (6)
O28	0.161 (1)	0.235 (2)	0.1014 (7)	0.032 (8)
O29	0.363 (2)	0.272 (2)	0.0117 (7)	0.05 (1)
O30	0.565 (1)	0.181 (2)	0.1061 (7)	0.037 (8)
O31	0.362 (2)	0.145 (2)	0.1951 (7)	0.039 (9)
O32	0.259 (1)	0.107 (2)	0.0905 (7)	0.031 (8)
O33	0.354 (1)	0.126 (1)	0.0503 (6)	0.012 (6)
O34	0.445 (1)	0.083 (2)	0.0944 (7)	0.036 (8)
O35	0.354 (1)	0.064 (2)	0.1351 (6)	0.024 (7)
O36	0.341 (2)	−0.039 (2)	0.0812 (8)	0.06 (1)
O37	0.656 (2)	0.938 (2)	0.1160 (7)	0.05 (1)
O38	0.490 (2)	0.950 (2)	0.1355 (7)	0.05 (1)
O39	0.594 (2)	0.789 (2)	0.1615 (9)	0.07 (1)
O40	0.537 (1)	0.980 (2)	0.0686 (7)	0.028 (8)
O41	0.432 (1)	0.832 (2)	0.0685 (7)	0.028 (8)
O42	0.587 (2)	0.815 (2)	0.0400 (8)	0.07 (1)
O43	0.289 (2)	0.662 (3)	0.2818 (9)	0.08 (1)
O44	0.149 (2)	0.685 (2)	0.2343 (7)	0.043 (9)
O45	0.071 (2)	0.509 (3)	0.2657 (10)	0.11 (2)
O46	0.196 (2)	0.465 (2)	0.3181 (7)	0.043 (9)
O47	0.188 (2)	0.390 (2)	0.2419 (8)	0.06 (1)
O48	0.322 (2)	0.468 (2)	0.2746 (7)	0.040 (9)
O49	0.404 (1)	0.408 (2)	0.3764 (6)	0.020 (7)
O50	0.249 (1)	0.373 (2)	0.3797 (7)	0.029 (8)
O51	0.254 (1)	0.292 (2)	0.2914 (7)	0.034 (8)
O52	0.340 (2)	0.230 (2)	0.3468 (8)	0.05 (1)
O53	0.330 (2)	0.555 (2)	0.3433 (7)	0.041 (9)
O54	0.438 (1)	0.339 (2)	0.3098 (7)	0.035 (8)
O55	0.132 (1)	−0.013 (2)	−0.0348 (7)	0.036 (9)

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]

References

Blasse, G., Dirksen, G. J. & Zonnevijlle, F. (1981). *J. Inorg. Nucl. Chem.* **43**, 2847-2853.

Gilmore, C. J. (1984). *J. Appl. Cryst.* **17**, 42-46.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Molecular Structure Corporation (1989). *TEXSAN. Single Crystal Structure Analysis Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Naruke, H., Ozeki, T. & Yamase, T. (1991). *Acta Cryst.* C**47**, 489-492.

Naruke, H. & Yamase, T. (1991). *J. Lumin.* **50**, 55-60.

Ozeki, T., Takahashi, M. & Yamase, T. (1992). *Acta Cryst.* C**48**, 1370-1374.

Ozeki, T. & Yamase, T. (1993). *J. Alloy. Compd.* **192**, 28-29.

Rigaku Corporation (1985). *RCRYSTAN. X-ray Analysis Program System*. Rigaku Corporation, Tokyo, Japan.

Stillman, M. J. & Thomson, A. J. (1976). *J. Chem. Soc. Dalton Trans.* pp. 1138-1144.

Sugeta, M. & Yamase, T. (1993). *Bull. Chem. Soc. Jpn*, **66**, 444-449.

Yamase, T. & Naruke, H. (1991*a*). *J. Chem. Soc. Dalton Trans.* pp. 285-292.

Yamase, T. & Naruke, H. (1991*b*). *Coord. Chem. Rev.* **111**, 83-90.

Yamase, T., Naruke, H. & Sasaki, Y. (1990). *J. Chem. Soc. Dalton Trans.* pp. 1687-1696.

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

TOMOJI OZEKI AND TOSHIHIRO YAMASE

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

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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 $K_3Na_4H_2[TbW_{10}O_{36}].$-