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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(*Received* 27 *January* 1993; *accepted* 30 *March* 1993)

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, Takahashi & Yamase, 1992; Ozeki & Yamase, 1993), nonasodium decatungstoeuropate (Sugeta & Yamase, 1993) and sodium tetrastrontium decatungstoeuropate (Yamase, Ozeki & Ueda, 1993) were all found to contain decatungstolanthanoate anions isostructural with that in the non-luminescent analogue, the tetravalent cerium complex $[\mathrm{Ce^{IV}W_{10}O_{36}}]^{8-}$ (Iball, Low & Weakley, 1974). The key to the above hypothesis for the uniqueness of the gadolinium compound is its crystal structure, which is reported here.

The pH of a 20 ml aqueous solution containing 8.3 g of $\mathrm{Na_2WO_4.2H_2O}$ was brought to 7.3 by adding $\mathrm{CH_3COOH}$. 1.15 g of $\mathrm{GdNO_3.4H_2O}$ dissolved in 2 ml $\mathrm{H_2O}$ and 0.24 g of KCl dissolved in 5 ml $\mathrm{H_2O}$ were then added and the solution was kept at 278 K. Crystals were obtained after a week.

Fig. 1 shows a packing diagram of the crystal viewed along the c^* axis. The crystal is almost isomorphous with $\mathrm{K_3Na_4H_2[TbW_{10}O_{36}].20H_2O}$ (Ozeki, Takahashi & Yamase, 1992) and $\mathrm{K_3Na_4H_2[SmW_{10}O_{36}].22H_2O}$ (Ozeki & Yamase, 1993). The only significant difference lies in a few of the water O atoms, which show large thermal displacement parameters and are apparently disordered.

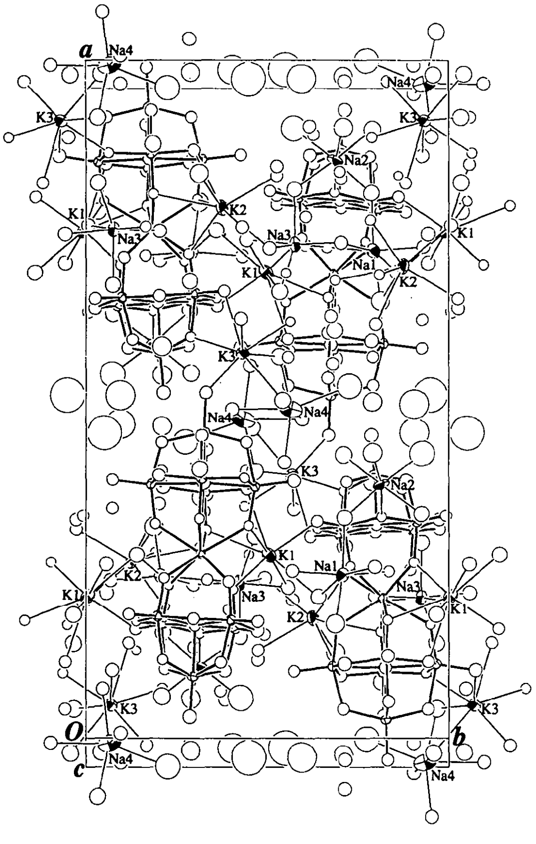

Fig. 1. Packing diagram of the unit cell viewed along the c^* axis. Thermal ellipsoids are shown at 50% probability levels. The K and Na atoms are shown as ellipsoids with shaded octants.

Fig. 2 shows the structure of the $[\mathrm{GdW_{10}O_{36}}]^{9-}$ anion together with two proximate $\mathrm{K^+}$ cations. The $[\mathrm{GdW_{10}O_{36}}]^{9-}$ anion comprises a central $\mathrm{Gd^{3+}}$ cation and two $[\mathrm{W_5O_{18}}]^{6-}$ units, each of which may be regarded as derived by the removal of a $\mathrm{WO^{4+}}$ group from a $[\mathrm{W_6O_{19}}]^{2-}$ anion. It has a square array of O atoms at the lacunary site. Square arrays of O atoms from two $[\mathrm{W_5O_{18}}]^{6-}$ moieties face one another, rotated relative to each other by 45 ° to give a square antiprism, at the centre of which is located the $\mathrm{Gd^{3+}}$ ion. Each W atom is in a distorted octahedral coordination. This structure is essentially identical to those of the $[\mathrm{SmW_{10}O_{36}}]^{9-}$ and $[\mathrm{TbW_{10}O_{36}}]^{9-}$ anions. The Gd—O distances vary from 2.37 (2) to 2.49 (2) Å [average 2.43 (4) Å]. For comparison, the Sm—O and Tb—O distances in the corresponding anions are 2.42 (2)-2.52 (2) Å [average 2.47 (3) Å] and 2.40 (1)-2.44 (1) Å [average 2.42 (2)Å], respectively. The Gd—W distances are 3.812 (2)-3.875 (2) Å [average 3.84 (2) Å], compared with Sm—W and Tb—W distances of 3.820 (2)-3.889 (2) Å [average 3.85 (2) Å] and 3.807 (2)-3.866 (2) Å [average 3.83 (2) Å], respectively. The differences in the interatomic distances correlate with the change in ionic radius of the central lanthanoid resulting from the lanthanoid contraction, although the differences are not significant compared with their e.s.d.'s. In the present study the W—O distances *trans* to the Gd—O bonds were found to be 1.73 (2)-1.80 (2) Å [average 1.78 (2) Å]. This distance is shorter

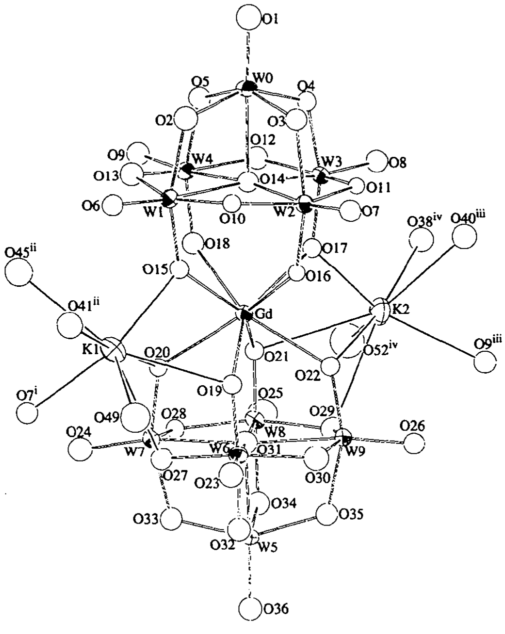

Fig. 2. *ORTEP* II (Johnson, 1976) drawing of the $[\mathrm{GdW_{10}O_{36}}]^{9-}$ anion and the coordination spheres of $\mathrm{K^+}$ cations in its proximity. Thermal ellipsoids are shown at 50% probability levels. Symmetry codes: (i) $\frac{3}{2}-x, -\frac{1}{2}+y, \frac{3}{2}-z$; (ii) $1-x, -y, 1-z$; (iii) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iv) $\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$.

than the corresponding value in the Tb^{3+} species [average 1.79 (2) Å] and longer than that of the Sm^{3+} compound [average 1.75 (1) Å]. These differences originate in the *trans* influence of the systematic changes in the Ln^{3+}—O distance in the three isomorphous crystals. We found W—O distances for the terminal O atom to be 1.71 (2)-1.80 (2) Å [average 1.76 (2) Å]. The W—O distances *trans* to the terminal W—O bond are 2.24 (2)-2.36 (3) Å [average 2.31 (4) Å] and the W—O distances for O atoms bridging two W atoms are 1.89 (3)-2.03(2) Å [average 1.96 (4) Å]. These distances show no systematic differences in the three isomorphous crystals.

Experimental

Crystal data

$K_3Na_4H_2[GdW_{10}O_{36}].21H_2O$
M_r = 3161.3
Monoclinic
$P2_1/n$
a = 29.920 (5) Å
b = 16.103 (5) Å
c = 11.449 (3) Å
β = 96.36 (1)°
V = 5482 (4) Å^3
Z = 4

D_x = 3.83 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 10.0-12.5°
μ = 22.92 mm^{-1}
T = 298.15 K
Pillar
0.25 × 0.1 × 0.1 mm
Colourless

Data collection

Rigaku AFC-5*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (North, Phillips & Mathews, 1968)
$T_{\min}$ = 0.7582, $T_{\max}$ = 1.0000
13954 measured reflections
13036 independent reflections

6514 observed reflections [$I > 3\sigma(I)$]
$\theta_{\max}$ = 27.5°
$h = -38 \rightarrow 38$
$k = 0 \rightarrow 20$
$l = 0 \rightarrow 14$
3 standard reflections monitored every 100 reflections intensity variation: −3.1%

Refinement

Refinement on F
Final R = 0.0585
wR = 0.0519
S = 2.152
6512 reflections
391 parameters
H-atom parameters not determined

Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{\max}$ = 0.875
$\Delta\rho_{\max}$ = 2.79 e Å^{-3}
$\Delta\rho_{\min}$ = −3.18 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 Gd and W, respectively.

Data collection: *RCRYSTAN85* (Rigaku Corporation, 1985). Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). 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)

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

	x	y	z	U_{eq}
W0	0.58803 (5)	0.2050 (1)	0.4588 (1)	0.0252
W1	0.66490 (5)	0.08776 (9)	0.6178 (1)	0.0220
W2	0.67229 (5)	0.28896 (9)	0.6349 (1)	0.0211
W3	0.67210 (5)	0.30176 (9)	0.3514 (1)	0.0211
W4	0.66540 (5)	0.09982 (9)	0.3343 (1)	0.0216
W5	0.95575 (4)	0.1734 (1)	0.5816 (1)	0.0224
W6	0.87282 (5)	0.17274 (9)	0.7528 (1)	0.0209
W7	0.87302 (5)	0.03392 (9)	0.5439 (1)	0.0204
W8	0.87665 (4)	0.1811 (1)	0.3496 (1)	0.0208
W9	0.87705 (5)	0.32090 (9)	0.5585 (1)	0.0212
Gd	0.77270 (5)	0.1832 (1)	0.5143 (1)	0.0183
K1	0.7800 (3)	−0.0044 (6)	0.7405 (8)	0.0392
K2	0.7944 (3)	0.3740 (5)	0.2870 (8)	0.0388
K3	0.9222 (3)	−0.0684 (5)	0.2928 (8)	0.0370
Na1	0.2591 (5)	0.2078 (9)	0.480 (1)	0.0352
Na2	0.6224 (5)	0.186 (1)	0.911 (1)	0.0524
Na3	0.7514 (5)	0.0770 (9)	0.025 (1)	0.0354
Na4	0.9976 (6)	0.065 (1)	0.125 (1)	0.0674
O1	0.5293 (8)	0.214 (2)	0.446 (2)	0.037 (7)
O2	0.6014 (8)	0.117 (2)	0.574 (2)	0.034 (7)
O3	0.6046 (8)	0.282 (1)	0.591 (2)	0.027 (6)
O4	0.6088 (7)	0.288 (1)	0.362 (2)	0.022 (5)
O5	0.6040 (8)	0.128 (1)	0.345 (2)	0.028 (6)
O6	0.6602 (8)	0.007 (1)	0.717 (2)	0.027 (6)
O7	0.6701 (8)	0.362 (1)	0.750 (2)	0.028 (6)
O8	0.6708 (8)	0.381 (1)	0.245 (2)	0.028 (6)
O9	0.6588 (8)	0.026 (1)	0.219 (2)	0.030 (6)
O10	0.6624 (7)	0.185 (1)	0.721 (2)	0.019 (5)
O11	0.6704 (7)	0.361 (1)	0.496 (2)	0.016 (5)
O12	0.6641 (8)	0.203 (2)	0.245 (2)	0.030 (6)
O13	0.6554 (8)	0.026 (2)	0.466 (2)	0.033 (6)
O14	0.6641 (7)	0.199 (1)	0.484 (2)	0.026 (6)
O15	0.7248 (7)	0.096 (1)	0.617 (2)	0.021 (5)
O16	0.7307 (7)	0.270 (1)	0.629 (2)	0.016 (5)
O17	0.7310 (7)	0.284 (1)	0.383 (2)	0.022 (5)
O18	0.7249 (8)	0.106 (1)	0.361 (2)	0.028 (6)
O19	0.8155 (7)	0.168 (1)	0.712 (2)	0.022 (5)
O20	0.8144 (7)	0.051 (1)	0.523 (2)	0.019 (5)
O21	0.8175 (7)	0.187 (1)	0.354 (2)	0.021 (5)
O22	0.8177 (7)	0.308 (1)	0.542 (2)	0.021 (5)
O23	0.8763 (8)	0.168 (2)	0.910 (2)	0.035 (6)
O24	0.8811 (9)	−0.073 (2)	0.530 (2)	0.037 (7)
O25	0.8846 (9)	0.186 (2)	0.198 (2)	0.054 (8)
O26	0.8841 (8)	0.426 (1)	0.566 (2)	0.028 (6)
O27	0.8767 (8)	0.056 (1)	0.714 (2)	0.029 (6)
O28	0.8792 (7)	0.063 (1)	0.381 (2)	0.020 (5)
O29	0.8835 (8)	0.298 (2)	0.393 (2)	0.032 (6)
O30	0.8802 (8)	0.287 (2)	0.725 (2)	0.039 (7)
O31	0.8786 (8)	0.175 (2)	0.555 (2)	0.033 (6)
O32	0.9361 (8)	0.166 (2)	0.741 (2)	0.031 (6)
O33	0.9397 (8)	0.058 (1)	0.567 (2)	0.029 (6)
O34	0.9429 (7)	0.181 (2)	0.408 (2)	0.032 (6)
O35	0.9401 (8)	0.291 (1)	0.578 (2)	0.028 (6)
O36	1.0148 (8)	0.169 (2)	0.600 (2)	0.032 (6)
O37	0.7492 (7)	0.165 (1)	0.871 (2)	0.026 (6)
O38	0.2559 (8)	0.069 (2)	0.546 (2)	0.035 (7)
O39	0.7545 (8)	0.204 (2)	0.150 (2)	0.036 (6)
O40	0.7654 (8)	0.006 (2)	0.215 (2)	0.037 (7)
O41	0.2590 (9)	0.057 (2)	0.057 (2)	0.040 (7)
O42	0.0769 (8)	0.047 (2)	0.124 (2)	0.036 (7)
O43	0.0029 (9)	0.097 (2)	0.895 (2)	0.037 (7)
O44	0.669 (1)	0.075 (2)	0.991 (3)	0.048 (8)
O45	0.2836 (9)	0.141 (2)	0.317 (2)	0.047 (8)
O46	0.993 (1)	0.042 (2)	0.326 (3)	0.054 (9)
O47	0.920 (1)	0.033 (2)	0.102 (2)	0.055 (9)
O48	0.175 (1)	0.213 (2)	0.492 (2)	0.049 (8)
O49	0.818 (1)	0.034 (2)	0.976 (2)	0.053 (8)
O50	0.074 (1)	0.210 (2)	0.318 (2)	0.058 (9)
O51	0.582 (1)	0.210 (2)	0.084 (3)	0.07 (1)
O52	0.336 (1)	0.188 (2)	0.574 (2)	0.07 (1)
O53	0.963 (1)	0.226 (3)	0.091 (4)	0.12 (2)

O54	0.496 (1)	0.210 (2)	0.820 (3)	0.07 (1)
O55	0.508 (2)	0.095 (3)	1.029 (5)	0.17 (2)
O56	0.573 (2)	0.073 (3)	0.838 (4)	0.13 (2)
O57	0.486 (2)	0.051 (4)	0.833 (5)	0.24 (3)

Table 2. *Bond lengths* (Å)

W0—O1	1.75 (2)	W5—O34	1.98 (2)
W0—O4	1.89 (2)	W5—O31	2.30 (2)
W0—O5	1.89 (2)	W6—O19	1.73 (2)
W0—O2	1.95 (2)	W6—O23	1.80 (2)
W0—O3	1.97 (2)	W6—O30	1.89 (3)
W0—O14	2.26 (2)	W6—O32	1.92 (2)
W1—O6	1.74 (2)	W6—O27	1.93 (2)
W1—O15	1.80 (2)	W6—O31	2.29 (2)
W1—O2	1.97 (2)	W7—O24	1.76 (2)
W1—O10	1.97 (2)	W7—O20	1.77 (2)
W1—O13	2.00 (2)	W7—O28	1.95 (2)
W1—O14	2.35 (2)	W7—O27	1.97 (2)
W2—O7	1.77 (2)	W7—O33	2.02 (2)
W2—O16	1.78 (2)	W7—O31	2.27 (3)
W2—O11	1.97 (2)	W8—O25	1.77 (3)
W2—O10	1.98 (2)	W8—O21	1.78 (2)
W2—O3	2.03 (2)	W8—O28	1.94 (2)
W2—O14	2.24 (2)	W8—O29	1.95 (3)
W3—O8	1.77 (2)	W8—O34	2.02 (2)
W3—O17	1.78 (2)	W8—O31	2.35 (2)
W3—O11	1.91 (2)	W9—O26	1.71 (2)
W3—O4	1.92 (2)	W9—O22	1.78 (2)
W3—O12	2.00 (2)	W9—O35	1.94 (2)
W3—O14	2.28 (2)	W9—O29	1.96 (2)
W4—O9	1.77 (2)	W9—O30	1.98 (2)
W4—O18	1.78 (2)	W9—O31	2.36 (3)
W4—O5	1.91 (2)	Gd—O16	2.37 (2)
W4—O12	1.95 (2)	Gd—O21	2.39 (2)
W4—O13	1.97 (2)	Gd—O15	2.41 (2)
W4—O14	2.35 (2)	Gd—O22	2.42 (2)
W5—O36	1.76 (2)	Gd—O17	2.45 (2)
W5—O33	1.93 (2)	Gd—O20	2.47 (2)
W5—O35	1.95 (2)	Gd—O18	2.47 (2)
W5—O32	1.98 (2)	Gd—O19	2.49 (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 71225 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1055]

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Structure of $La_5Mo_{32}O_{54}$ Containing *trans* Bicapped Mo_8 Octahedral Clusters and Tricluster Mo_7–Mo_{10}–Mo_7 Chain Fragments

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(*Received* 26 *October* 1992; *accepted* 10 *February* 1993)

Abstract

The crystal structure of $La_5Mo_{32}O_{54}$ contains the new *trans*-face bicapped Mo_8 cluster and a novel Mo_{24} tricluster chain fragment composed of one Mo_{10} and two Mo_7 clusters. The Mo_8 and Mo_{24} clusters are connected by bridging O atoms and are arranged in layers parallel to the *ac* plane. The three crystallographically distinct La^{3+} ions have coordination numbers of 11 or 12 with an environment in each case based on a distorted cubo-octahedron.

Comment

The present work constitutes part of our program in search of new reduced molybdenum oxides in combination with the rare-earth elements. Up to now, this study has led to the synthesis of six new structure types by solid-state reaction: $La_4Mo_2O_{11}$ (Gall & Gougeon, 1992) including isolated Mo_2 dimers, RMo_8O_{14} (R = La, Ce, Pr, Nd, Sm) (Leligny, Ledesert, Labbe, Raveau & McCarroll, 1990; Gougeon & McCarley, 1991) comprising Mo_8 clusters, $R_{16}Mo_{21}O_{56}$ (R = La, Ce, Pr, Nd) (Gall & Gougeon, 1993) showing isolated Mo_{10} clusters, RMo_5O_8 (R = La, Ce, Pr, Nd, Sm, Eu, Gd) (Hibble, Cheetham, Bogle, Wakerley & Cox, 1988; Gougeon, Gall & Sergent, 1991; Gall, 1990) containing chains of bioctahedral Mo_{10} clusters, $R_4Mo_4O_{11}$ (R = Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y) (Gougeon, Gall & McCarley, 1991*a*) characterized by infinite chains of *trans*-edge-shared Mo_6 octahedra, and $R_4Mo_{18}O_{32}$ (R = Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y) (Gougeon, Gall & McCarley, 1991*b*) which contains three kinds of infinite Mo chains, *i.e.* linear chains with alternate short and long Mo—Mo distances, chains of *trans*-edge-shared rhomboidal Mo_4 clusters and chains of *trans*-edge-shared octahedral Mo_6 clusters. We

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Acta Crystallographica Section C
ISSN 0108-2701 ©1993