

Nonasodium decatungstodysprosate pentatriacontahydrate

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In the crystal structure of the title compound, $\text{Na}_9[\text{Dy}(\text{W}_5\text{O}_{18})_2]\cdot 35\text{H}_2\text{O}$, the complex anion has approximate D_{4d} symmetry, with Dy–O and W–O distances in the ranges 2.355 (6)–2.405 (6) and 1.715 (7)–2.369 (5) Å, respectively.

Comment

To date, the emission spectra of various polyoxometalates have been studied. In particular, trivalent Eu^{3+} ions in polyoxometallates exhibit strong red emissions under excitation of the oxygen-to-metal ($M = \text{Mo}, \text{W}$ or Nb) polyoxometallate charge-transfer bands ($\text{O} \rightarrow M$ ligand-to-metal charge transfer, LMCT), and their emission properties have been examined in order to gain a molecular insight into the intramolecular energy transfer to the 5D_0 and 5D_1 states of Eu^{3+} (Yamase, 1998).

In recent years, we have studied dysprosium oxide solids, which emit in the yellow and blue regions with a resultant white light (Su *et al.*, 1995). Powdered solids of decatungstodysprosate containing trivalent Dy^{3+} show a white or yellow luminescence on irradiation light of wavelength 320 nm, corresponding to the $\text{O} \rightarrow \text{W}$ LMCT band excitation. In the present study, the crystal structure of nonasodium decatungstodysprosate, $\text{Na}_9[\text{Dy}(\text{W}_5\text{O}_{18})_2]$, as the pentatriacontahydrate, (I), has been determined and it is compared with that of another decatungstodysprosate complex, $\text{K}_3\text{Na}_4\text{H}_2[\text{Dy}-\text{W}_{10}\text{O}_{36}]\cdot 21\text{H}_2\text{O}$, (II), previously reported by Ozeki & Yamase (1994a).

The structure of the complex anion in the title compound, (I), with the atomic numbering, is shown in Fig. 1, the arrangement of the Na polyhedra is shown in Fig. 2 and the crystal structure is shown in Fig. 3. There is one decatungstodysprosate anion, nine Na^+ cations and 35 water molecules in the asymmetric unit.

The metal–oxygen framework of (I) is almost the same as that found in (II). The Dy–O distances in the two $[\text{W}_5\text{O}_{18}]^{6-}$ groups of (I) are in the range 2.355 (6)–2.392 (6) Å [average 2.38 (1) Å] for O atoms attached to atoms W1–W4 and 2.391 (6)–2.405 (6) Å [average 2.40 (1) Å] for O atoms

attached to atoms W6–W9; nearly identical values were observed for (II) [average values 2.39 (2) and 2.40 (2) Å, respectively]. The Dy–W distances in (I), which range from 3.7725 (6) to 3.8242 (5) Å [average 3.801 (2) Å], are slightly shorter than those in (II) [average 3.83 (2) Å]. A similar trend has been reported in other decatungstolanthanoate complexes, with $\text{Ln} = \text{Sm}^{3+}$ (Ozeki & Yamase, 1994) and Gd^{3+} (Yamase *et al.*, 1994). The slight differences originate from the crystal packing of the compounds. The O atoms bonded by the lanthanide atoms in (II) also coordinate to the K^+ cations in

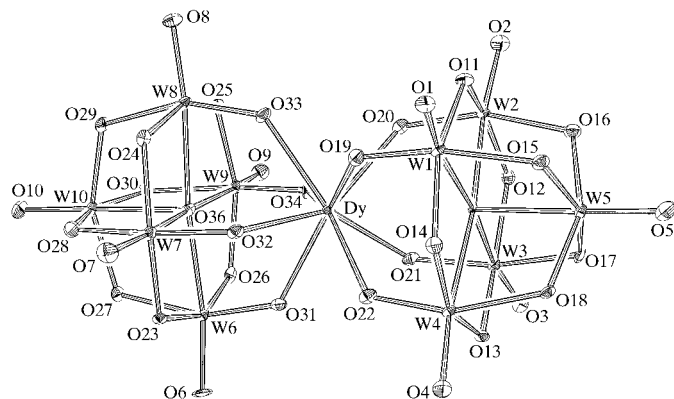


Figure 1

A view of the decatungstodysprosate anion in (I). Displacement ellipsoids are drawn at the 50% probability level.

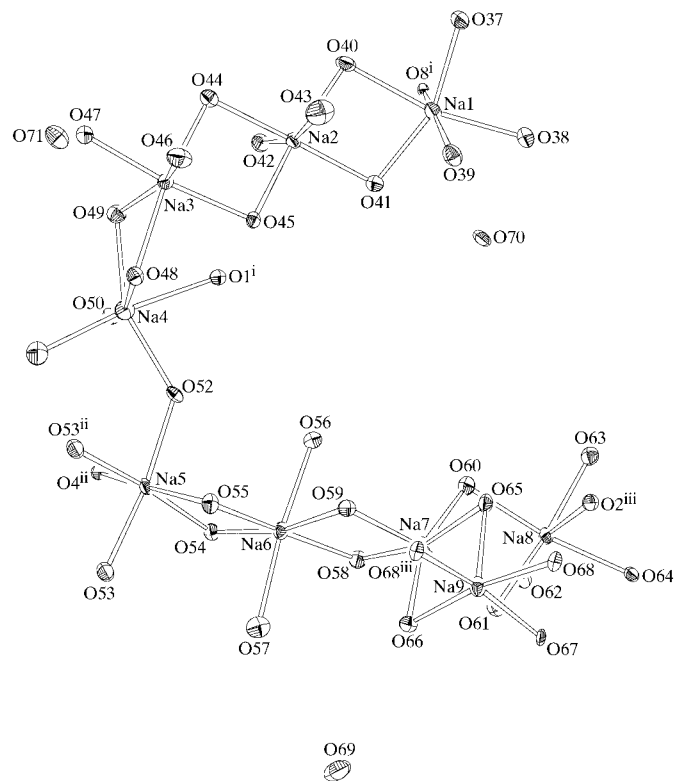


Figure 2

A view of (I), excluding the anion. Displacement ellipsoids are drawn at the 50% probability level [symmetry codes: (i) $x, y, 1+z$; (ii) $-x, -y, 1-z$; (iii) $-x, 1-y, 1-z$]. The Na^+ cations are octahedrally coordinated, except for Na_9 , which is coordinated square-pyramidally.

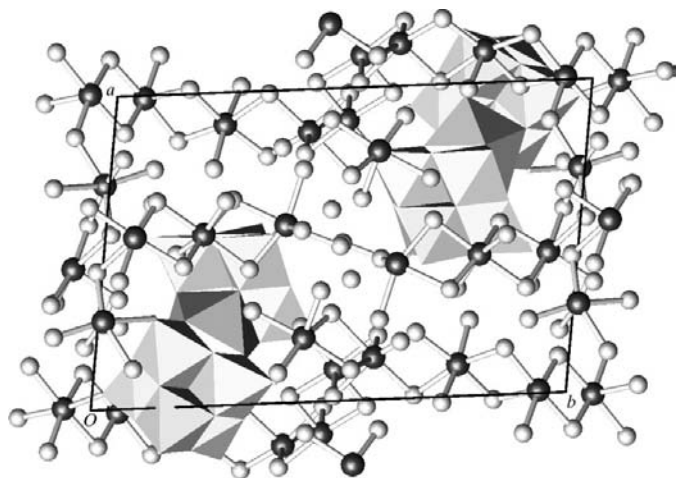


Figure 3
The crystal structure of (I), viewed down the c axis. Dark spheres denote Na^+ cations and white spheres denote water O atoms.

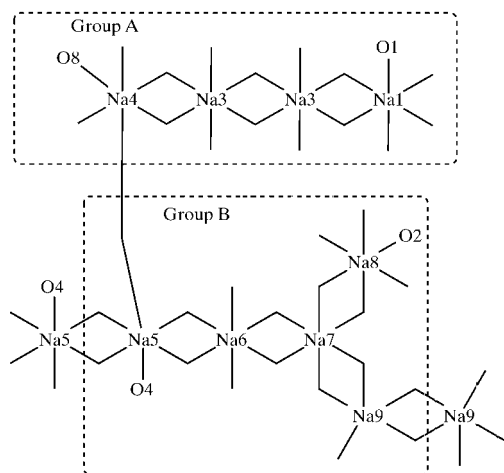


Figure 4
A schematic diagram of the NaO_n ($n = 5-6$) polyhedra linkage system. Single lines indicate $\text{Na}-\text{O}$ bonds. All water atom labels have been omitted for clarity. There are two groups of edge-shared NaO_n polyhedra, $\text{Na1}-\text{Na4}$ (Group A) and $\text{Na5}-\text{Na9}$ (Group B). Group B is connected to other B groups at each end by edge-sharing. Four O atoms of the decatungstodysprosate anion are connected to atoms Na1 , Na4 , Na5 and Na8 .

their vicinity. Such a bipolar interaction of these O atoms reduces their electron densities, with a resultant elongation of the $\text{Ln}-\text{W}$ distances in these salts.

Other lanthanide-incorporating compounds show similar structures, with a variety of $\text{Ln}-\text{W}$ distances due to the lanthanoid contraction; the $\text{Ce}-\text{W}$ distances in $\text{Na}_6\text{H}_2[\text{Ce}(\text{W}_5\text{O}_{18})_2]\cdot 30\text{H}_2\text{O}$ (Iball *et al.*, 1974) are in the range 3.784–3.797 Å (average 3.79 Å), slightly shorter than the $\text{Dy}-\text{W}$ distances in (I) [average 3.801 (2) Å]. Similarly, the actinide-incorporating compound $\text{Na}_8[\text{Th}(\text{W}_5\text{O}_{18})_2]\cdot 28\text{H}_2\text{O}$ (Griffith *et al.*, 2000) has long $\text{Th}-\text{W}$ distances (average 3.822 Å) compared with those in (I).

The Na^+ cations in (I), except for atom Na9 , are octahedrally coordinated by O atoms, with $\text{Na}-\text{O}$ distances in the

range 2.658 (8)–2.708 (8) Å [average 2.44 (6) Å], while atom Na9 is square-pyramidally coordinated by O atoms, with $\text{Na}-\text{O}$ distances in the range 2.286 (8)–2.346 (9) Å [average 2.33 (2) Å]. These NaO_n ($n = 5-6$) polyhedra are connected by an edge-sharing linkage for $\text{Na1}-\text{Na4}$ and $\text{Na5}-\text{Na9}$, and by a corner-sharing linkage between Na4 and Na5 sites (Fig. 4). Such hydrated Na^+ cations interact with the highly charged $[\text{LnW}_{10}\text{O}_{36}]^{9-}$ anions to balance the charge, leading to a large number of water molecules in the lattice, as exemplified by other sodium salts of decatungstolanthanoate, namely $\text{Na}_6\text{H}_2[\text{Ce}(\text{W}_5\text{O}_{18})_2]\cdot 30\text{H}_2\text{O}$ (Iball *et al.*, 1974), $\text{Na}_6\text{H}_3[\text{Sm}(\text{W}_5\text{O}_{18})_2]\cdot 28\text{H}_2\text{O}$ (Ozeki & Yamase, 1994b) and $\text{Na}_8\text{H}[\text{Gd}(\text{W}_5\text{O}_{18})_2]\cdot 30\text{H}_2\text{O}$ (Yamase *et al.*, 1994).

Experimental

The title compound was synthesized according to the method of Yamase *et al.* (1994) and recrystallized from an aqueous solution at 277 K.

Crystal data

$\text{Na}_9[\text{Dy}(\text{W}_5\text{O}_{18})_2]\cdot 35\text{H}_2\text{O}$
 $M_r = 3414.54$
 Triclinic, $P\bar{1}$
 $a = 13.0914$ (8) Å
 $b = 20.5067$ (12) Å
 $c = 12.7721$ (6) Å
 $\alpha = 105.519$ (1)°
 $\beta = 91.231$ (2)°
 $\gamma = 82.789$ (2)°
 $V = 3277.4$ (3) Å³

$Z = 2$
 $D_x = 3.460$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 27 035 reflections
 $\theta = 1.6-27.5^\circ$
 $\mu = 18.78$ mm⁻¹
 $T = 296$ (2) K
 Prism, colourless
 0.14 × 0.12 × 0.08 mm

Table 1

Selected bond distances (Å).

W1–O1	1.729 (7)	W6–O27	2.029 (6)
W1–O19	1.800 (7)	W6–O36	2.300 (6)
W1–O11	1.950 (6)	W7–O7	1.722 (6)
W1–O14	1.958 (7)	W7–O32	1.795 (6)
W1–O15	2.039 (6)	W7–O24	1.943 (6)
W1–O35	2.315 (6)	W7–O23	1.960 (6)
W2–O2	1.725 (7)	W7–O28	2.041 (7)
W2–O20	1.792 (6)	W7–O36	2.338 (6)
W2–O11	1.935 (6)	W8–O8	1.738 (7)
W2–O12	1.947 (6)	W8–O33	1.778 (6)
W2–O16	2.009 (7)	W8–O24	1.942 (6)
W2–O35	2.301 (5)	W8–O25	1.960 (6)
W3–O3	1.738 (6)	W8–O29	2.021 (6)
W3–O21	1.797 (6)	W8–O36	2.320 (6)
W3–O13	1.947 (6)	W9–O9	1.736 (6)
W3–O12	1.969 (6)	W9–O34	1.786 (6)
W3–O17	1.999 (6)	W9–O26	1.935 (7)
W3–O35	2.305 (6)	W9–O25	1.949 (6)
W4–O4	1.715 (7)	W9–O30	2.025 (6)
W4–O22	1.792 (6)	W9–O36	2.310 (6)
W4–O14	1.943 (7)	W10–O10	1.731 (7)
W4–O13	1.946 (6)	W10–O29	1.882 (6)
W4–O18	2.023 (6)	W10–O28	1.906 (6)
W4–O35	2.369 (5)	W10–O27	1.925 (6)
W5–O5	1.726 (7)	W10–O30	1.940 (6)
W5–O15	1.892 (6)	W10–O36	2.254 (6)
W5–O18	1.893 (6)	Dy–O22	2.355 (6)
W5–O17	1.922 (6)	Dy–O19	2.378 (7)
W5–O16	1.957 (6)	Dy–O20	2.380 (6)
W5–O35	2.266 (6)	Dy–O34	2.391 (6)
W6–O6	1.730 (7)	Dy–O21	2.392 (6)
W6–O31	1.775 (6)	Dy–O32	2.393 (6)
W6–O23	1.935 (6)	Dy–O33	2.398 (6)
W6–O26	1.966 (6)	Dy–O31	2.405 (6)

Data collection

Rigaku R-AXIS RAPID diffractometer	14 785 independent reflections
ω scans	13 098 reflections with $I > 2\sigma(I)$
Absorption correction: numerical (NUMABS; Higashi, 1999)	$R_{\text{int}} = 0.052$
$T_{\text{min}} = 0.179$, $T_{\text{max}} = 0.315$	$\theta_{\text{max}} = 27.5^\circ$
33 444 measured reflections	$h = 0 \rightarrow 16$
	$k = -26 \rightarrow 26$
	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0579P)^2 + 24.6886P]$
$R[F^2 > 2\sigma(F^2)] = 0.036$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.104$	$(\Delta/\sigma)_{\text{max}} = 0.031$
$S = 1.18$	$\Delta\rho_{\text{max}} = 4.44 \text{ e } \text{\AA}^{-3}$
14 785 reflections	$\Delta\rho_{\text{min}} = -3.19 \text{ e } \text{\AA}^{-3}$
821 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters not defined	(Sheldrick, 1997)
	Extinction coefficient: 0.00070 (3)

The positions of the water H atoms were not determined. In a difference Fourier map, the highest peak was 0.77 Å from W5 and the deepest hole 1.15 Å from O19.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Molecular Structure Corporation & Rigaku, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to

refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1388). Services for accessing these data are described at the back of the journal.

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