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Poly[diaquahexakis(dimethyl sulfoxide-*κO*)cerium [(μ_2-hexacosaoxooctamolybdate)sodium]]

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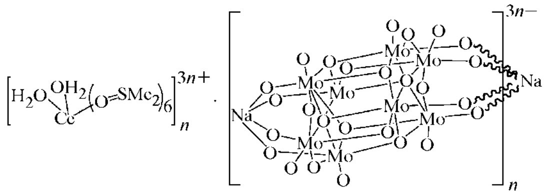
The title compound, $\{[Ce(C_2H_6OS)_6(H_2O)_2][NaMo_8O_{26}]\}_n$, contains an infinite chain of β-octamolybdate moieties linked by Na^+ ions, and further linked into a two-dimensional network by $[Ce(DMSO)_6(H_2O)_2]^{3+}$ (DMSO is dimethyl sulfoxide) groups *via* hydrogen-bond interactions. The Ce and Na atoms are located on a twofold axis and an inversion centre, respectively.

Comment

Polyoxometalates are currently receiving increasing attention in the domain of solid-state material chemistry, owing to their intriguing structural and topological properties and their many potential applications in catalysis, biology, medicine, photochemistry and magnetism (Pope & Müller, 1991; Pope, 1983). In the past decade, chemists have made great efforts in the design and synthesis of new polyoxometalates. To find suitable subunits and then link them into one-, two- or even three-dimensional extended networks in appropriate ways remains a great challenge. Recently, a series of octamolybdate-supported complexes with multi-dimensional frameworks has been synthesized by hydrothermal methods (Hagrman *et al.*, 1997, 1998; Wu *et al.*, 2002). To the best of our knowledge, only three octamolybdate-supported compounds with one- or two-dimensional extended structures have so far been reported as being synthesized *via* a direct route, using $(Bu_4N)_4[Mo_8O_{26}]$ or $(Bu_4N)_4[Mo_6O_{19}]$ as the starting materials (Qin *et al.*, 2004; Chen *et al.*, 2004*a*,*b*). We have succeeded in obtaining the title novel octamolybdate-supported compound having a two-dimensional framework, $\{[Ce(DMSO)_6(H_2O)_2][NaMo_8O_{26}]\}_n$ (DMSO is dimethyl sulfoxide), (I), which was also prepared *via* a direct route, but using Na_2MoO_4 as the Mo source. This is the first reported such octamolybdate-based compound with an infinitely extended structure to be synthesized by applying this 'one-step' method. It is also the first case of Mo–Na bimetallic oxide chains linked into a two-dimensional network *via* hydrogen-bonding interactions between β-$[Mo_8O_{26}]^{4-}$ units and coordinated rare earth ions.



(I)

Compound (I) consists of an infinite anionic chain framework built up of $[Mo_8O_{26}]^{4-}$ entities linked *via* Na^+ ions, and eight-coordinated (six DMSO and two water molecules) Ce atoms as charge-compensating cations (Fig. 1). The Ce atom occupies a special position across a twofold axis, and the Na atom lies on an inversion centre at ($\frac{3}{4}$, $\frac{1}{4}$, $\frac{1}{2}$).

As shown in Fig. 2, the $[Mo_8O_{26}]^{4-}$ moiety is built up of eight edge-sharing MoO_6 octahedra and displays the characteristic β-octamolybdate arrangement, which contains two μ_5-O atoms, O13 and O13^{iii} [symmetry code: (iii) $-x + \frac{3}{2}$, $-y + \frac{3}{2}$, $-z + 1$]. The Mo—O bond lengths and O—Mo—O

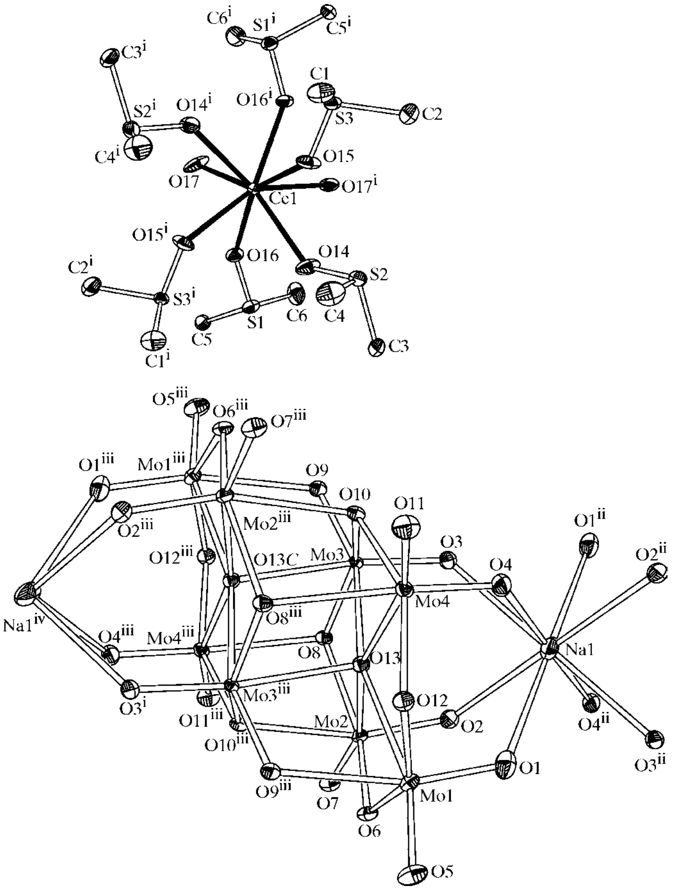


Figure 1
A molecular drawing of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. All H atoms have been omitted for clarity. [Symmetry codes: (i) $-x + 1$, y, $-z + \frac{3}{2}$; (ii) $-x + \frac{3}{2}$, $-y + \frac{1}{2}$, $-z + 1$; (iii) $-x + \frac{3}{2}$, $-y + \frac{3}{2}$, $-z + 1$; (iv) x, $y + 1$, z.]

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and Mo—O—Mo angles among the octamolybdate units are similar to those in other β-$[Mo_8O_{26}]^{4-}$ complexes (Luo *et al.*, 2003; Yang *et al.*, 2002; Hagrman & Zubieta, 2000). All Mo sites possess octahedral coordination geometry with different degrees of distortion and exhibit a +VI oxidation state, according to extensive bond-valence-sum calculations (Brown & Altermatt, 1985; Brese & O'Keeffe, 1991). Each $[Mo_8O_{26}]^{4-}$ unit forms covalent [Na—O = 2.426 (2)–2.445 (2) Å] or weak [Na—O = 2.820 (2)–2.841 (2) Å] interactions with Na^+ through eight terminal O atoms in opposite directions, thus forming a sandwich-like structure.

The coordination environment around the Ce centre is shown in Fig. 1. Each Ce^{3+} ion is coordinated by eight O atoms, of which six are from DMSO ligands and two from aqua ligands.

It is noteworthy that strong hydrogen-bond interactions exist in the solid-state structure of (I), and these might play an important role in the crystallization of (I). Each coordinated water molecule on the Ce atom forms two O—H$\cdots$O hydrogen bonds (Table 2) to a μ_2-bridging and a terminal O atom from the adjacent $[Mo_8O_{26}]_n$ chain. Therefore, the structure of (I) is finally extended into a two-dimensional network by strong hydrogen bonds (Fig. 3).

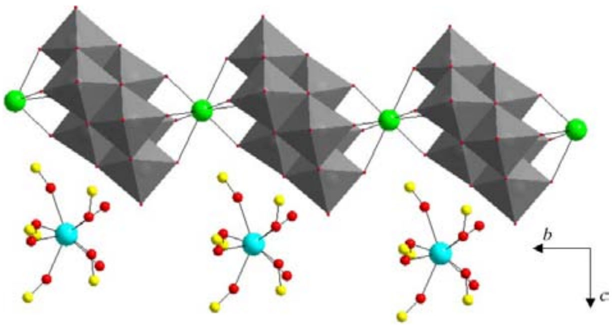

Figure 2
A polyhedral representation of the infinite chain in (I). All C and H atoms have been omitted for clarity.

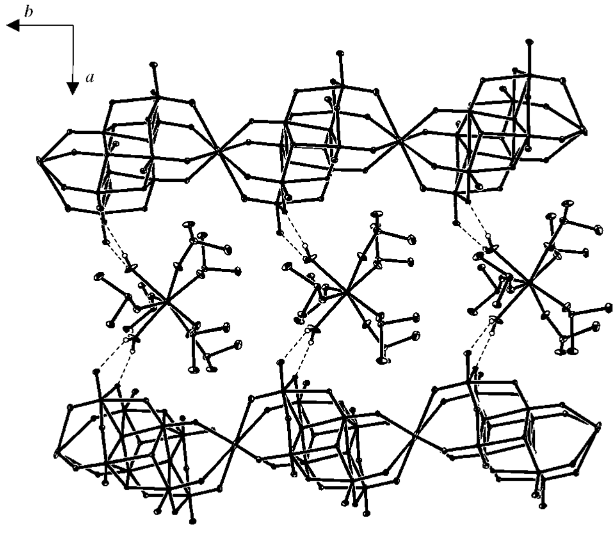

Figure 3
A packing diagram for (I), viewed along the *c* axis. Broken lines indicate hydrogen bonds. Displacement ellipsoids are shown at the 30% probability level. All H atoms have been omitted for clarity, except for those engaged in hydrogen bonding.

The backbone framework of (I) is similar to that of $[NaLa(\beta\text{-}[Mo_8O_{26}]^{4-})(DMF)_7]_n$ (DMF is dimethylformamide; Chen *et al.*, 2004*a*), (II), although in that compound, the $[La(DMF)_7]^{3+}$ moiety is covalently bound to the infinite one-dimensional chain.

Experimental

Na_2MoO_4 (0.964 g, 4 mmol) was dissolved in a mixture of water (5 ml) and dimethyl sulfoxide (10 ml), and then a solution of $CeCl_3$ (0.67 mmol) in water (2 ml) was added dropwise. The resulting solution was adjusted to about pH 3 with 10% hydrochloric acid. After stirring for about 15 min, the mixture was filtered and the filtrate was kept in air at ambient temperature. Orange crystals of (I) were separated from the mother liquor after one week (yield 45%, based on Ce).

Crystal data

$[Ce(C_2H_6OS)_6(H_2O)_2][NaMo_8O_{26}]$
$M_r = 1851.43$
Monoclinic, $C2/c$
$a = 22.7811$ (7) Å
$b = 9.2121$ (2) Å
$c = 22.8913$ (6) Å
$\beta = 97.829$ (2)°
$V = 4759.2$ (2) Å^3
$Z = 4$

$D_x = 2.584$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6634 reflections
$\theta = 3.0$–27.5°
$\mu = 3.34$ mm^{-1}
$T = 130.2$ (1) K
Prism, yellow
0.22 × 0.21 × 0.11 mm

Table 1
Selected geometric parameters (Å, °).

Ce1—O14	2.434 (2)	Na1—O1	2.841 (2)
Ce1—O15	2.445 (2)	Mo1—O5	1.7060 (19)
Ce1—O16	2.4630 (19)	Mo1—O1	1.707 (2)
Ce1—O17	2.517 (2)	Mo1—O6	1.9152 (18)
Na1—O2	2.4260 (19)	Mo1—O12	1.9430 (18)
Na1—O3	2.4453 (18)	Mo1—O9^{i}	2.3109 (18)
Na1—O4	2.830 (2)	Mo1—O13	2.4077 (17)

O14—Ce1—O15	72.27 (7)	O7—Mo2—O13	161.09 (8)
O14—Ce1—O16	74.25 (7)	O2—Mo2—O13	92.68 (8)
O15—Ce1—O16	146.49 (7)	O6—Mo2—O13	77.75 (7)
O14—Ce1—O17	137.83 (7)	O8—Mo2—O13	74.56 (7)
O15—Ce1—O17	149.53 (7)	O3—Mo3—O9	106.05 (9)
O16—Ce1—O17	63.72 (7)	O3—Mo3—O8	101.18 (8)
O2^{ii}—Na1—O2	180	O9—Mo3—O8	97.85 (8)
O2—Na1—O3	75.47 (6)	O3—Mo3—O10	99.97 (8)
O2—Na1—O4	108.15 (6)	O9—Mo3—O10	96.78 (8)
O3—Na1—O4	68.53 (6)	O8—Mo3—O10	149.76 (7)
O2—Na1—O1	71.40 (6)	O3—Mo3—O13	95.68 (8)
O3—Na1—O1	108.80 (6)	O9—Mo3—O13	158.26 (8)
O5—Mo1—O1	105.91 (10)	O8—Mo3—O13	78.32 (7)
O5—Mo1—O6	102.22 (9)	O10—Mo3—O13	78.30 (7)
O1—Mo1—O6	99.12 (9)	O11—Mo4—O4	105.53 (10)
O5—Mo1—O12	100.87 (9)	O11—Mo4—O12	101.98 (9)
O1—Mo1—O12	98.43 (9)	O4—Mo4—O12	100.48 (8)
O6—Mo1—O12	145.78 (7)	O11—Mo4—O10	100.39 (8)
O5—Mo1—O13	160.74 (8)	O4—Mo4—O10	96.91 (8)
O1—Mo1—O13	93.32 (8)	O12—Mo4—O10	146.69 (7)
O6—Mo1—O13	75.01 (7)	O11—Mo4—O13	162.14 (8)
O12—Mo1—O13	74.84 (7)	O4—Mo4—O13	92.08 (8)
O7—Mo2—O2	105.99 (9)	O12—Mo4—O13	77.12 (7)
O7—Mo2—O6	101.14 (8)	O10—Mo4—O13	74.05 (7)
O2—Mo2—O6	100.76 (8)	Mo1—O1—Na1	126.74 (10)
O7—Mo2—O8	99.92 (8)	Mo2—O2—Na1	134.29 (10)
O2—Mo2—O8	96.21 (8)	Mo3—O3—Na1	131.35 (9)
O6—Mo2—O8	148.03 (7)	Mo4—O4—Na1	128.43 (10)

Symmetry codes: (i) $-x+\frac{3}{2}, -y+\frac{3}{2}, -z+1$; (ii) $-x+\frac{3}{2}, -y+\frac{1}{2}, -z+1$.

Table 2
Hydrogen-bond geometry (Å, °).

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
$\mathrm{O}17-\mathrm{H}17B\cdots\mathrm{O}5^{\mathrm{iii}}$	0.84 (4)	2.32 (4)	2.974 (3)	136 (5)
$\mathrm{O}17-\mathrm{H}17A\cdots\mathrm{O}12^{\mathrm{iii}}$	0.84 (2)	2.00 (2)	2.758 (3)	151 (4)

Symmetry code: (iii) $x-\frac{1}{2}, y-\frac{1}{2}, z$.

Data collection

Rigaku Mercury CCD area-detector diffractometer	5365 independent reflections
ω scans	5248 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2002)	$R_{\mathrm{int}} = 0.020$
	$\theta_{\max} = 27.5°$
	$h = -29 \rightarrow 27$
$T_{\min} = 0.524$, $T_{\max} = 0.693$	$k = -11 \rightarrow 8$
16 875 measured reflections	$l = -28 \rightarrow 29$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0302P)^2 + 15.179P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.021$	
$wR(F^2) = 0.055$	
$S = 1.05$	$(\Delta/\sigma)_{\max} = 0.003$
5365 reflections	$\Delta\rho_{\max} = 1.59$ e Å^{-3}
290 parameters	$\Delta\rho_{\min} = -0.84$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

The water H atoms were located in a difference Fourier map and refined with restrained O—H distances approximately equal to 0.84 (1) Å and H···H distances approximately equal to 1.4 (1) Å. H atoms bonded to C atoms were positioned geometrically, with C—H distances of 0.96 Å, and allowed to ride on their parent atoms, with $U_{\mathrm{iso}}(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{C})$.

Data collection: *CrystalClear* (Rigaku, 2002); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXL97*; software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1236). Services for accessing these data are described at the back of the journal.

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