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catena-Poly[[heptakis(dimethylformamide-κO)di-μ_4-oxo-tetra-μ_3-oxo-hexadeca-μ_2-oxo-tetraoxolanthanum(III)octamolybdenum(IV)]-μ-sodium(I)]

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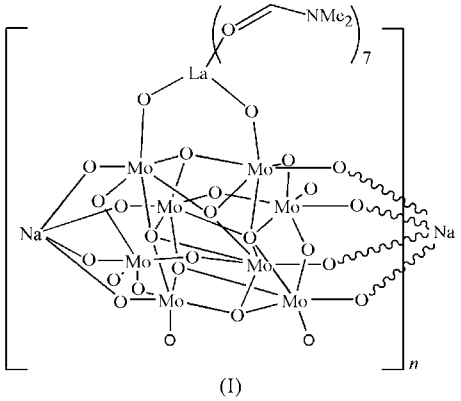
The title compound, $[NaLaMo_8O_{26}(C_3H_7NO)_7]_n$, contains infinite chains of $[Mo_8O_{26}]^{4-}$ units supporting dimethylformamide-coordinated La^{III} cations and linked by Na^+ cations. The lanthanum center adopts a nine-coordinate geometry and the Na atom is sandwiched between two β-$[Mo_8O_{26}]^{4-}$ units.

Comment

In the past decade, considerable progress has been made in the rational design and synthesis of new polyoxometalates (POMs), which are of interest owing to their intriguing topological structures and applicable properties (Müller *et al.*, 1995, 1998; Pope & Müller, 1991). One of the most challenging tasks is to obtain POM building blocks and link them into larger discrete clusters, or one-, two- or even three-dimensional extended frameworks in appropriate ways. We are



(I)

currently making great efforts to link basic building blocks, such as $[Mo_6O_{19}]^{2-}$, with rare earth salts to form new interesting extended compounds. We report here the synthesis and characterization of the title compound, (I).

The title compound consists of an infinite chain framework built up of octamolybdate-supported dimethylformamide-coordinated La^{III} and Na^+ ions (Fig. 1). The lanthanum center adopts a nine-coordinate geometry, and the locally centrosymmetric β-$[Mo_8O_{26}]^{4-}$ anion is linked to the La^{III} ion through two terminal O atoms (O4 and O19). The most interesting feature is that the La^{III} ions are located on only one side of the infinite chain, thus producing a locally noncentrosymmetric anionic cluster. Finally, seven O atoms from dimethylformamide (DMF) molecules complete the nine-coordinate environment of the La atom, with La—O distances in the range 2.474 (4)–2.618 (4) Å and O—La—O bond angles in the range 66.61 (13)–83.97 (14)° (Table 1). In the plumb direction, the β-$[Mo_8O_{26}]^{4-}$ units are linked by Na^+ cations so that the structure is extended into a one-dimensional infinite chain. The Na center is eight-coordinate and one β-$[Mo_8O_{26}]^{4-}$ unit supports four terminal O atoms; the Na atom is

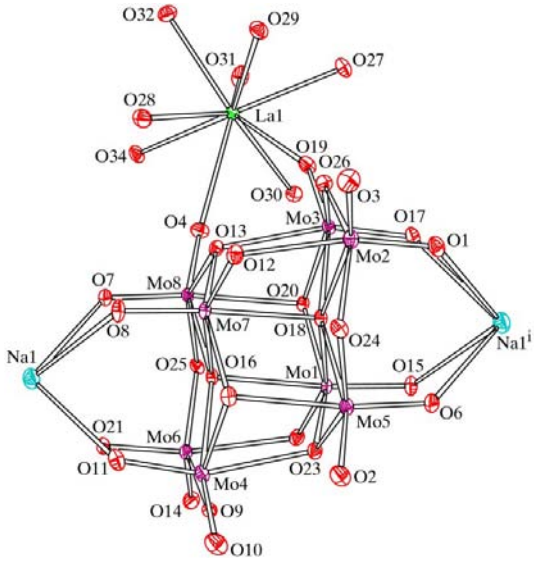


Figure 1
A molecular drawing of (I), showing 30% probability displacement ellipsoids. All C, N and H atoms have been omitted for clarity. [Symmetry code: (i) $x-1, y, z$.]

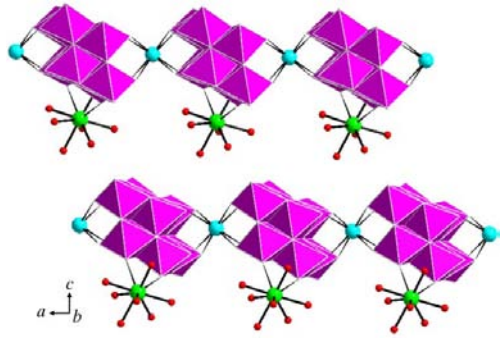


Figure 2
A polyhedral representation of the infinite chain in (I). All C, N and H atoms have been omitted for clarity.

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sandwiched between two β-$[Mo_8O_{26}]^{4-}$ units (Fig. 2). The distance between two adjacent La atoms is 9.418 (1) Å, along the *a* axis. The backbone framework of (I) is similar to that of $(NH_4)[La(\beta\text{–}Mo_8O_{26})(DMF)_7]$, (II) (Wu *et al.*, 2002), although the structure of (I) is extended into a one-dimensional infinite chain *via* the Na atoms, while the complex in (II) is discrete.

In the preparation, the β-$[Mo_8O_{26}]^{4-}$ unit was formed unexpectedly from $[Mo_6O_{19}]^{2-}$ and Na_2MoO_4. The structure of (I) may therefore suggest a route for the synthesis of other transition metal compounds, by linking appropriate basic building blocks in a controllable way.

Experimental

A solution of $(Bu_4N)_2[Mo_6O_{19}]$ (0.22 g, 0.16 mmol) and Na_2MoO_4 (0.10 g, 0.5 mmol) in DMF (7 ml) was added dropwise to a stirred ethanol solution (4 ml) of $La(NO_3)_3{\cdot}3H_2O$ (0.25 g, 0.7 mmol). The mixture was then stirred at 333 K for 1 h. Colorless crystals of (I) were obtained after the mixture had been filtered and the yellow filtrate had been kept in air for several days (yield 53% based on La). Analysis calculated: C 13.58, H 2.66, N 5.28%; found: C 13.61, H 2.52, N 5.33%.

Crystal data

$[NaLaMo_8O_{26}(C_3H_7NO)_7]$
M_r = 1857.09
Monoclinic, $P2_1/n$
a = 9.4180 (10) Å
b = 22.4088 (10) Å
c = 23.7508 (13) Å
β = 92.098 (3)°
V = 5009.2 (6) Å^3
Z = 4
D_x = 2.462 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12 241 reflections
θ = 1.8–25.0°
μ = 2.87 mm^{-1}
T = 293 (2) K
Prism, colorless
0.28 × 0.20 × 0.08 mm

Data collection

Bruker SMART *P*4 diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
T_{min} = 0.507, T_{max} = 0.795
29 069 measured reflections
8775 independent reflections
8115 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 25.0°
$h = -11 \rightarrow 10$
$k = -26 \rightarrow 25$
$l = -25 \rightarrow 28$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.097
S = 0.99
8775 reflections
654 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.046P)^2 + 34.1827P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.011
$\Delta\rho_{max}$ = 1.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.86 e Å^{-3}

All H atoms were positioned geometrically and refined using a riding model, with C—H distances of 0.93–0.96 Å and U_{iso}(H) values of $1.2U_{eq}$(C) or $1.5U_{eq}(C_{methyl})$. The maximum electron-density peak in the difference density map is located 1.14 Å from atom O5.

Table 1
Selected geometric parameters (Å, °).

La1—O32	2.474 (4)	Na1—O6^{ii}	2.520 (5)
La1—O27	2.498 (4)	Na1—O7	2.534 (5)
La1—O30	2.519 (4)	Na1—O21	2.573 (5)
La1—O34	2.532 (4)	Na1—O1^{ii}	2.611 (5)
La1—O29	2.557 (4)	Na1—O15^{ii}	2.651 (5)
La1—O28	2.560 (4)	Na1—O11	2.661 (5)
La1—O31	2.569 (4)	Na1—O17^{ii}	2.730 (5)
La1—O4	2.573 (4)	Na1—O8	2.776 (5)
La1—O19	2.618 (4)		
O32—La1—O4	131.90 (14)	O28—La1—O19	83.97 (14)
O27—La1—O4	128.28 (13)	O31—La1—O19	139.45 (13)
O30—La1—O4	68.46 (13)	O4—La1—O19	66.68 (12)
O34—La1—O4	66.61 (13)	O7—Na1—O21	72.70 (14)
O29—La1—O4	119.53 (13)	O7—Na1—O11	105.15 (15)
O28—La1—O4	66.93 (14)	O21—Na1—O11	68.76 (14)
O31—La1—O4	121.65 (14)	O7—Na1—O8	69.03 (14)
O32—La1—O19	137.87 (14)	O21—Na1—O8	107.92 (14)
O27—La1—O19	73.14 (13)	O1^{ii}—Na1—O8	70.79 (14)
O30—La1—O19	79.47 (14)	O15^{ii}—Na1—O8	178.68 (16)
O34—La1—O19	133.28 (13)	O11—Na1—O8	65.92 (14)
O29—La1—O19	68.03 (13)	O17^{ii}—Na1—O8	111.74 (15)

Symmetry code: (ii) $1 + x, y, z$.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART* and *SAINT* (Siemens, 1994); data reduction: *XPREP* in *SHELXTL* (Siemens, 1994); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1198). Services for accessing these data are described at the back of the journal.

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