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Bis[(2,3,6,7,12,13,16,17-octaethylporphycenato)oxomolybdenum(V)] hexamolybdate(VI)

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The title compound, $[Mo(C_{36}H_{44}N_4)O]_2[Mo_6O_{19}]$, contains a five-coordinate molybdenum–porphycene cationic complex, accompanied by a centrosymmetric hexamolybdate counter-anion. This is the first structure for a molybdenum porphycene. The shape of the central N_4 cavity is rectangular, enlarged lengthwise by metal coordination, and the mean short and long N$\cdots$N distances defining the N_4 cavity are 2.582 (9) and 3.031 (9) Å, respectively.

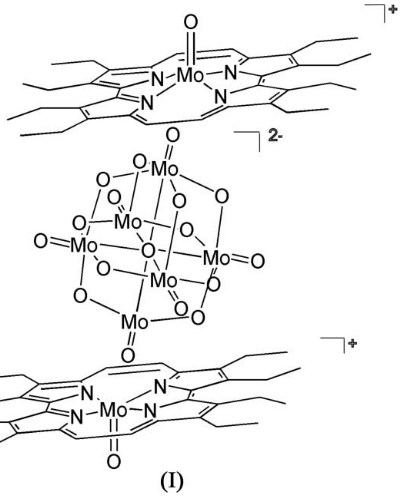
Key indicators

Single-crystal X-ray study
T = 223 K
Mean σ(C–C) = 0.014 Å
R factor = 0.064
wR factor = 0.168
Data-to-parameter ratio = 14.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Porphycene is one of the isomers of porphyrin first synthesized in 1986 (Vogel *et al.*, 1986). This isomer exhibits geometries of the N_4 coordination site which deviate noticeably from the ideal square shape of the porphyrin core. Recently, we prepared various porphycene derivatives (Aritome *et al.*, 2002; Baba, Shimakoshi, Aritome & Hisaeda, 2004, Baba, Shimakoshi, & Hisaeda, 2004). It was then shown that these unique structural properties result in interesting catalysis when they form complexes with metals (Hayashi *et al.*, 2001). Only a few metal complexes of porphycene have been reported; here we describe the title compound, (I), which is the first structure for a molybdenum porphycene.



(I)

The molecular structure of (I) and the atom-numbering scheme are shown in Fig. 1. In this compound, the shape of the central N_4 cavity is rectangular, enlarged by metal coordination lengthwise. The mean short and long N$\cdots$N distances defining the rectangle are 2.582 (9) and 3.031 (9) Å, respectively. The central molybdenum ion deviates by 0.524 (3)Å from the mean plane of the four coordinating pyrrole N atoms. The Mo1═O1 distance of 1.640 (7) Å is normal. The macrocyclic core of the porphycene is distorted and adopts a saddle form; this distortion may occur on complexation.

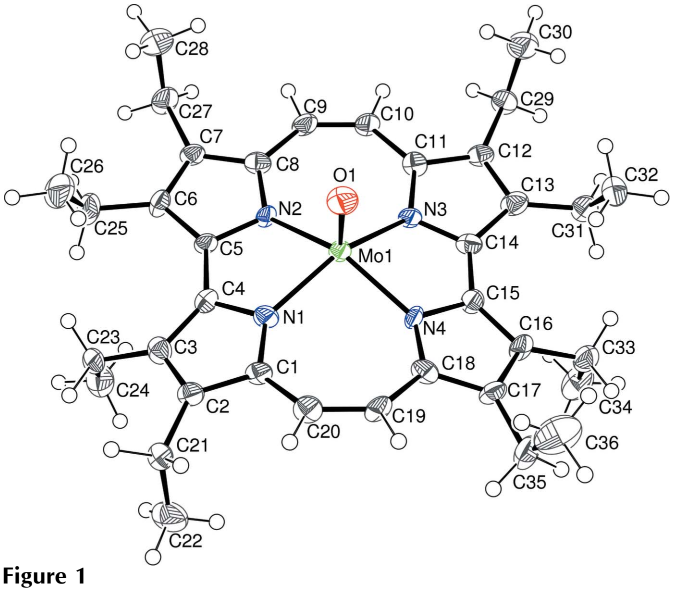


Figure 1
A view of the (2,3,6,7,12,13,16,17-octaethylporphycenato)oxomolybdenum(V) cation in (I), showing 50% displacement ellipsoids (arbitrary spheres for the H atoms).

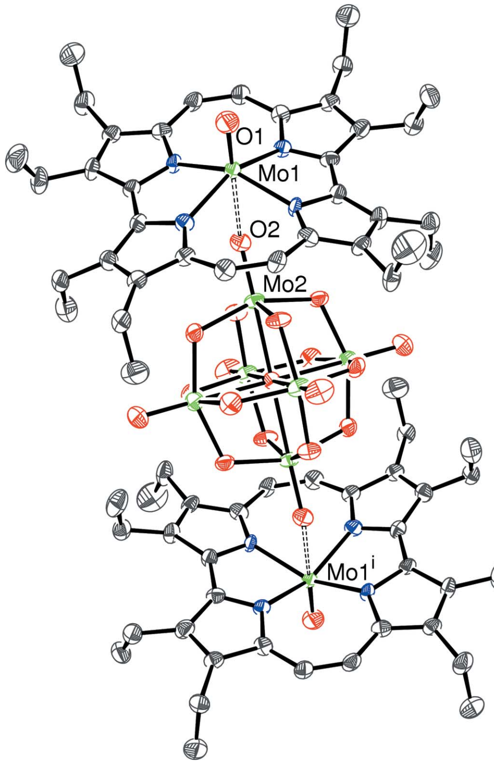


Figure 2
The association of two (2,3,6,7,12,13,16,17-octaethylporphycenato)oxomolybdenum(V) cations and one $[Mo_6O_{19}]^{2-}$ anion in (I), showing 50% displacement ellipsoids (H atoms have been omitted for clarity). The long Mo1···O2 contact is indicated by a dashed line. [Symmetry code: (i) $-x$, $2 - y$, $1 - z$.]

The crystal packing of (I) involves $[Mo_6O_{19}]^{2-}$ ions sandwiched between pairs of cations, the whole assemblage being generated by an inversion centre coinciding with the central O atom of the anion (Fig. 2). The long Mo1···O2 distance of 2.593 (7) Å suggests that this is best regarded as a combination of $[Mo(C_{36}H_{44}N_4)O]^+$ cations and hexamolybdate anions, rather than a neutral molecule.

Experimental

2,3,6,7,12,13,16,17-Octaethylporphycene [H_2(OEPc)] (10 mg, 1.87 mmol; Vogel *et al.*, 1993) was dissolved in dry decalin (13 ml) and $MoCl_5$ (100 mg, 3.66 mmol) and CH_3COONa (150 mg, 1.83 mmol) were added to it. After the solution was refluxed in an oil bath under a nitrogen atmosphere for 2 h, the reaction mixture was cooled and filtered. The mixture was then evaporated to dryness *in vacuo* to obtain a dark-green powder. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated dichloromethane/cyclohexane (75:25) solution. Plate-shaped crystals of (I) grew within one week in about 25% yield.

Crystal data

$[Mo(C_{36}H_{44}N_4)O]_2[Mo_6O_{19}]$
$M_r = 2169.02$
Triclinic, $P\bar{1}$
$a = 11.5979$ (11) Å
$b = 13.4762$ (13) Å
$c = 14.5563$ (15) Å
$\alpha = 62.426$ (2)°
$\beta = 77.652$ (2)°
$\gamma = 79.594$ (2)°
$V = 1961.2$ (3) Å^3
$Z = 1$
$D_x = 1.836$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 1.31$ mm^{-1}
$T = 223$ (2) K
Thick plate, purple
0.18 × 0.14 × 0.08 mm

Data collection

Bruker SMART CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.798$, $T_{max} = 0.902$
11847 measured reflections
7157 independent reflections
4809 reflections with $I > 2\sigma(I)$
$R_{int} = 0.048$
$\theta_{max} = 25.4°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.064$
$wR(F^2) = 0.168$
$S = 0.98$
7157 reflections
501 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0945P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 2.93$ e Å^{-3}
$\Delta\rho_{min} = -0.74$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mo1—O1	1.640 (7)	Mo1—N1	2.060 (6)
Mo1—N3	2.052 (6)	Mo1—N2	2.065 (7)
Mo1—N4	2.058 (6)		
N2—C8—C9	126.2 (8)	N4—Mo1—N1	94.6 (3)
O1—Mo1—N3	104.2 (3)	O1—Mo1—N2	104.0 (3)
O1—Mo1—N4	105.3 (3)	N3—Mo1—N2	95.0 (3)
N3—Mo1—N4	77.7 (3)	N4—Mo1—N2	150.7 (3)
O1—Mo1—N1	105.6 (3)	N1—Mo1—N2	77.6 (3)
N3—Mo1—N1	150.3 (3)		

H atoms were positioned geometrically (C—H = 0.94–0.98 Å) and refined as riding, with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}$(methyl C). The residual electron-density map contains one significant peak at 0.92 Å from atom Mo2.

Acta Cryst. (2006). E**62**, m1272–m1274 Maeda *et al.* • $[Mo(C_{36}H_{44}N_4)O]_2[Mo_6O_{19}]$ **m1273**

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

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