

A decanuclear oxomolybdenum(V,VI) cluster with 4-isopropylpyridine

Barbara Modec,^{a*} Jurij V. Brenčič^a and Gerald Giester^b

^aFaculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5, PO Box 537, 1000 Ljubljana, Slovenia, and ^bInstitut für Mineralogie und Kristallographie, Universität Wien, Geozentrum, Althanstrasse 14, A-1090 Vienna, Austria

Correspondence e-mail: barbara.modec@guest.arnes.si

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The title centrosymmetric cluster octakis(4-isopropylpyridine-*N*)-di- μ_4 -oxo-hexa- μ_3 -oxo-octa- μ_2 -oxo-decaoxooctamolybdenum(V)dimolybdenum(VI), $[\text{Mo}_{10}\text{O}_{26}(\text{C}_8\text{H}_{11}\text{N})_8]$, consists of ten Mo atoms connected together by bridging oxo groups. Pentavalent Mo atoms are linked into four Mo_2^{V} pairs by metal–metal single bonds with lengths of 2.5637 (6) and 2.6132 (6) Å.

Comment

Recent years have witnessed a growing interest in the coordination chemistry of polyoxomolybdates (Khan & Zubieta, 1995). A well known moiety in molybdenum(V) chemistry, the $\text{Mo}_2\text{O}_4^{2+}$ unit, in which the metal centres participate in a metal–metal bond with an average length of 2.5–2.6 Å, serves as the main building block in the formation of larger aggregates (Chae *et al.*, 1993). Linkage of two, three, four or six units through oxygen-donor ligands has resulted, for example, in the tetranuclear complex $[\text{Mo}_4\text{O}_6(\text{OC}_2\text{H}_5)_4\text{Cl}_4(\text{PMe}_3)_2]$ (Limberg *et al.*, 1997), the hexanuclear moiety $[\text{Mo}_6\text{P}_4\text{O}_{24}(\text{OH})_7]^{5-}$, which has been identified as the basic structural unit of the molybdenum phosphate $(\text{Et}_4\text{N})_6[\text{Na}_{14}\text{Mo}_{24}\text{P}_{17}\text{O}_{97}(\text{OH})_{31}] \cdot x\text{H}_2\text{O}$ (Haushalter & Lai, 1989), the cyclic octanuclear $[\text{Mo}_8(\mu_2\text{-O})_8\text{O}_8(\mu_2\text{-OCH}_3)_8]$ framework found in $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Mo}_8\text{O}_{16}(\text{OCH}_3)_8(\text{C}_2\text{O}_4)]$ (Chen *et al.*, 1988) or in $[\text{Mo}_8\text{O}_{16}(\text{OCH}_3)_8\text{py}_4]$ (py is pyridine, $\text{C}_5\text{H}_5\text{N}$; Modec, Brenčič, Rotar *et al.*, 1998), and the dodecanuclear complex $[\text{Mo}_{12}\text{O}_{28}(\text{OCH}_3)_2\text{Cl}_2(3\text{-MePy})_8]$ (3-MePy is 3-methylpyridine, $\text{C}_6\text{H}_7\text{N}$; Modec *et al.*, 2000), respectively. In this paper, we present the structure of the title complex, (I), which was obtained by the solvothermal reaction of $(\text{PyH})_2[\text{MoOCl}_5]$ with 4-isopropylpyridine in methanol. It belongs to a class of polynuclear oxomolybdenum(V,VI) compounds whose representatives are, for example, $(\text{NBu}_4)_4[\text{Mo}_{10}\text{O}_{28}(\text{SCH}_2\text{-CH}_2\text{O})_2(\text{HOCH}_2)_2 \cdot 2\text{CH}_3\text{OH}]$ (Liu *et al.*, 1988), which consists of two Mo_2^{V} pairs and six Mo^{VI} sites, $[\text{Mo}_8(\text{pz})_6\text{-O}_{18}(\text{pzH})_6] \cdot 2\text{pzH}$ (pzH is pyrazole, $\text{C}_3\text{H}_4\text{N}_2$, and pz is pyrazolate, $\text{C}_3\text{H}_3\text{N}_2^-$; Ehler *et al.*, 1993), which contains three Mo_2^{V} pairs and two Mo^{VI} sites, and $[\text{Mo}_5\text{O}_{11}(\text{OCH}_3)_4\text{-py}_4] \cdot \text{CH}_3\text{OH}$ (Modec, Brenčič & Leban, 1998), which consists of two Mo_2^{V} pairs and one Mo^{VI} site.

The structure of (I), illustrated in Fig. 1, is seen to consist of discrete centrosymmetric $[\text{Mo}_{10}(\mu_4\text{-O})_2(\mu_3\text{-O})_6(\mu_2\text{-O})_8\text{O}_{10}\text{-}(\text{C}_8\text{H}_{11}\text{N})_8]$ moieties. Among the ten Mo atoms, eight are grouped into four Mo_2^{V} pairs with short Mo–Mo distances [$\text{Mo}1\text{—Mo}2 = 2.6132$ (6) and $\text{Mo}4\text{—Mo}5 = 2.5637$ (6) Å] and two ($\text{Mo}3$ and its symmetry equivalent) are Mo^{VI} centres. The 26 O atoms are of four distinct types, with ten coordinated as terminal ligands at distances of 1.683 (3)–1.694 (3) Å. Eight doubly bridging O atoms are found at distances of 1.814 (3)–2.067 (3) Å, six adopt a triply bridging mode, with O–Mo distances spanning the range 1.964 (3)–2.261 (3) Å, and two (O7 and its symmetry equivalent) are μ_4 ligands coordinated to Mo atoms with unsymmetrical distances ranging from 1.988 (2) to 2.641 (3) Å.

A list of selected bond lengths and angles is given in Table 1. The hexavalent Mo atoms differ from their pentavalent counterparts with respect to the coordination environment, $[\text{MoO}_6]$ geometry being achieved through ligation to one terminal, two doubly bridging, two triply bridging and one quadruply bridging O atom. Owing to the pronounced *trans* influence of the multiply bonded terminal oxygen, O3, the coordination geometry around Mo3 approaches the square-pyramidal limit, with a weakly interacting sixth ligand, O7. The Mo^{V} centres display an $[\text{MoO}_5\text{N}]$ pseudo-octahedral geometry through coordination to oxo ligands and 4-isopropylpyridine, with two (an oxo group and the 4-isopropylpyridine) serving as terminal ligands. Nitrogen-donor ligands are coordinated to Mo atoms at an average distance of 2.230 (3) Å. Fig. 2 shows how the polyhedra are assembled.

The same structure was determined previously for $[\text{Mo}_{10}\text{O}_{26}\text{L}_8]$ (L is 3-methylpyridine or 3,5-lutidine; Modec *et al.*, 2000). The geometric parameters for all three compounds are nearly identical.

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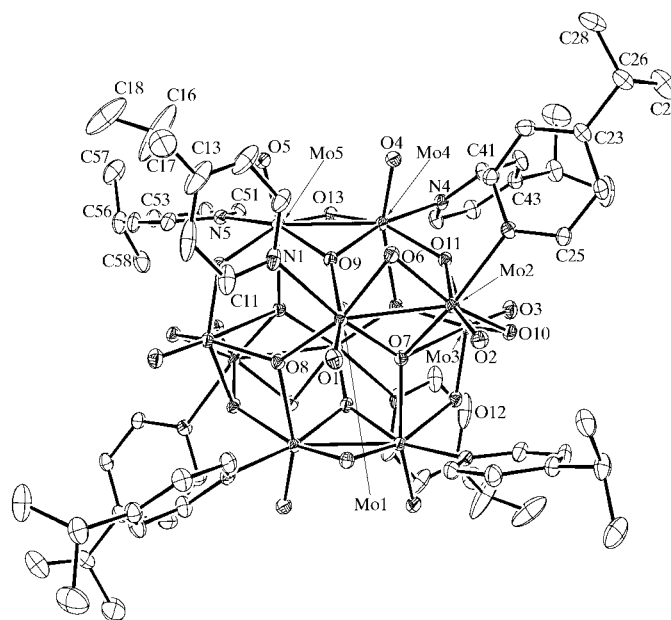


Figure 1
The molecular structure of (I) with displacement ellipsoids drawn at the 30% probability level. H atoms have been omitted for clarity.

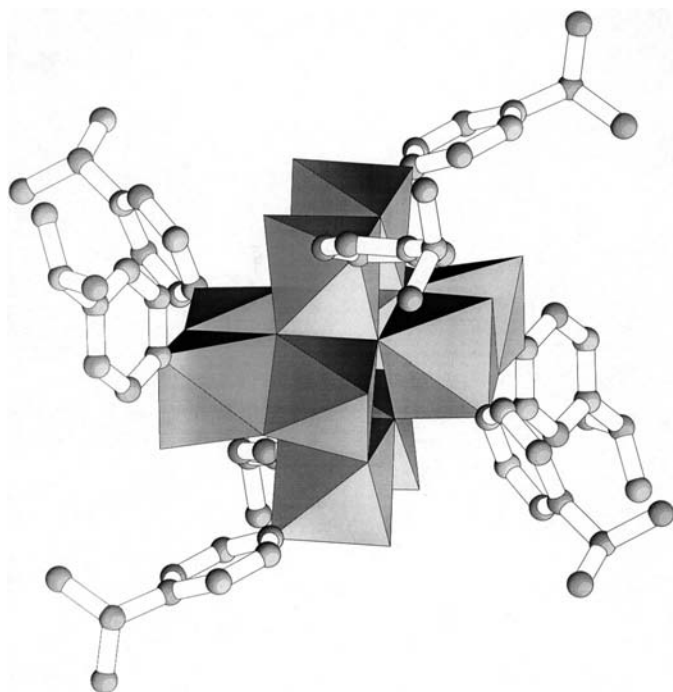


Figure 2
 ATOMS (Dowty, 1993) representation of (I), showing the assembly of the polyhedra.

Experimental

A solution of (PyH)₂[MoOCl₅] (428 mg, 0.95 mmol) in methanol (5 ml) and 4-isopropylpyridine (5 ml) was heated in a sealed glass tube in an autoclave at 403 K for 76 h. Red crystals of (I) were obtained in low yield. Analysis calculated (found): C 32.78 (32.49), H 3.78 (3.20), N 4.78% (4.90%). IR data (nujol, cm⁻¹): 1618 (*vs*), 1314 (*m*), 1250 (*w*), 1228 (*m*), 1212 (*w*), 1070 (*m*), 1058 (*m*), 1031 (*s*), 978 (*vs*), 958 (*vs*), 939 (*s*), 893 (*w*), 867 (*w*), 831 (*m*), 796 (*w*), 760 (*s*), 741 (*s*), 702 (*vs*), 669 (*m*), 651 (*w*), 618 (*m*), 582 (*w*), 544 (*w*), 517 (*s*), 419 (*w*), 400 (*w*), 362 (*w*), 349 (*w*), 335 (*w*), 311 (*m*), 266 (*w*).

Crystal data

[Mo₁₀O₂₆(C₈H₁₁N)₈]
M_r = 2344.82
 Monoclinic, *P*₂₁/*n*
a = 11.794 (2) Å
b = 20.179 (4) Å
c = 17.843 (4) Å
 β = 107.78 (3)°
V = 4043.6 (14) Å³
Z = 2

D_x = 1.926 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 21 096 reflections
 θ = 2.10–29.55°
 μ = 1.572 mm⁻¹
T = 150 (2) K
 Block, red
 0.11 × 0.11 × 0.11 mm

Data collection

Nonius KappaCCD diffractometer
 ω scans
 21 096 measured reflections
 11 238 independent reflections
 9113 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.030
 θ_{\max} = 29.55°
h = -16 → 16
k = -28 → 28
l = -24 → 24

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.041
wR(*F*²) = 0.092
S = 1.069
 11 238 reflections
 495 parameters
 H-atom parameters not refined

$w = 1/[\sigma^2(F_o^2) + (0.0282P)^2 + 11.8693P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.60 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -1.05 \text{ e } \text{Å}^{-3}$

Table 1
 Selected geometric parameters (Å).

Mo1—O1	1.689 (3)	Mo3—O8 ⁱ	1.995 (2)
Mo1—O6	1.949 (3)	Mo3—O11	2.002 (2)
Mo1—O7	1.997 (2)	Mo3—O7	2.641 (3)
Mo1—O8	2.091 (2)	Mo4—O4	1.694 (3)
Mo1—O9	2.215 (3)	Mo4—O13	1.926 (3)
Mo1—N1	2.243 (3)	Mo4—O9	1.964 (3)
Mo1—Mo2	2.6132 (6)	Mo4—O11	1.996 (2)
Mo2—O2	1.687 (3)	Mo4—N4	2.241 (3)
Mo2—O6	1.926 (3)	Mo4—O8 ⁱ	2.261 (3)
Mo2—O7	1.988 (2)	Mo4—Mo5	2.5637 (6)
Mo2—O10	2.067 (3)	Mo5—O5	1.683 (3)
Mo2—O11	2.207 (3)	Mo5—O13	1.944 (3)
Mo2—N2	2.210 (3)	Mo5—O9	1.969 (2)
Mo2—Mo3	3.0147 (9)	Mo5—O12 ⁱ	2.056 (3)
Mo3—O3	1.693 (3)	Mo5—N5	2.226 (3)
Mo3—O12	1.814 (3)	Mo5—O7 ⁱ	2.277 (3)
Mo3—O10	1.857 (3)		

Symmetry code: (i) $-x, -y, 1 - z$.

Although the data were collected at 150 K, the C atoms of one aromatic ring, *i.e.* C11–C15, exhibited large values of their atomic displacement parameters. For some of the propyl C atoms, C16, C18 and C28 from another 4-isopropylpyridine ligand, disorder over two positions was suggested. Refinement with the aforementioned C atoms partially occupying two positions was not successful. The parameters of the disordered atoms are therefore subject to some systematic error. Consequently, a final difference Fourier map showed five relatively large electron-density peaks of 1.60, 1.58, 1.55, 1.32 and 1.23 e Å⁻³ at distances of 0.78, 0.46, 2.63, 0.36 and 0.86 Å from atoms H16, H56, H12, C16 and C28, respectively. H atoms were placed in calculated positions (C–H = 0.93–0.98 Å) and were not refined.

Data collection: *DENZO* (Otwinowski & Minor, 1997); cell refinement: *DENZO*; data reduction: *DENZO*; program(s) used to solve structure: *SHELXS93* (Sheldrick, 1993); program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1493). Services for accessing these data are described at the back of the journal.

References

- Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
- Chae, H. K., Klempner, W. G. & Marquart, T. A. (1993). *Coord. Chem. Rev.* **128**, 209–224.
- Chen, Q., Liu, S. & Zubieta, J. (1988). *Angew. Chem. Int. Ed. Engl.* **27**, 1724–1725.
- Dowty, E. (1993). *ATOMS*. Version 2.0. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.
- Ehlert, M. K., Rettig, S. J., Storr, A., Thompson, R. C. & Trotter, J. (1993). *Inorg. Chem.* **32**, 5176–5182.
- Haushalter, R. C. & Lai, F. W. (1989). *Angew. Chem. Int. Ed. Engl.* **28**, 743–746.
- Khan, M. I. & Zubieta, J. (1995). *Prog. Inorg. Chem.* **43**, 1–149.
- Limberg, C., Büchner, M., Heinze, K. & Walter, O. (1997). *Inorg. Chem.* **36**, 872–879.
- Liu, S., Sun, X. & Zubieta, J. (1988). *J. Am. Chem. Soc.* **110**, 3324–3326.
- Modéc, B., Brenčić, J. V., Golič, L. & Daniels, L. M. (2000). *Polyhedron*, **19**, 1407–1414.
- Modéc, B., Brenčić, J. V. & Leban, I. (1998). *Inorg. Chem. Commun.* **1**, 161–163.
- Modéc, B., Brenčić, J. V., Rotar, R., Golič, L. & Prout, K. (1998). *Acta Cryst. C* **54**, 1573–1575.
- Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.
- Sheldrick, G. M. (1993). *SHELXL93* and *SHELXS93*. University of Göttingen, Germany.