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Key indicators

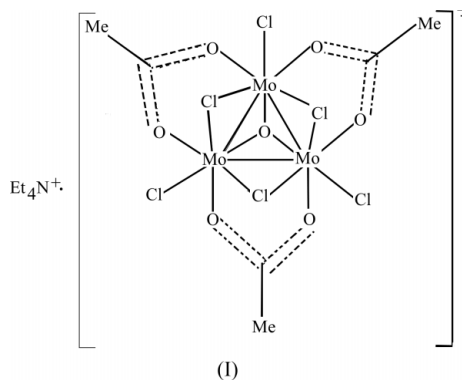
Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.020\text{ \AA}$
 R factor = 0.071
 wR factor = 0.157
Data-to-parameter ratio = 17.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.A new polymorph of tetraethylammonium tris(μ -acetato- O,O')tri- μ -chloro-trichloro- μ_3 -oxo-triangulo-trimolybdenum

The title compound, $[(\text{C}_2\text{H}_5)_4\text{N}][\text{Mo}_3\text{Cl}_6\text{O}(\text{C}_2\text{H}_3\text{O}_2)_3]$, has been synthesized by the reaction of $\text{MoCl}_3 \cdot 3\text{H}_2\text{O}$ with CH_3COOH . The structure is a polymorph of the structure reported by Chen, Lu, Huang, Huang & Huang [*Chin. J. Struct. Chem.* (1993), **12**, 117–123]. The crystal contains discrete cations and anions. The mono-oxo-capped trinuclear Mo cluster anion consists of three Cl atoms and three acetate groups that bridge the three edges of the Mo triangle; each Mo atom is also coordinated by one terminal Cl atom. The coordination around Mo is a distorted octahedron.

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Comment

A series of trinuclear Mo_3 cluster compounds with the cluster anions $\{[\text{Mo}_3(\mu_3\text{-O})(\mu\text{-X})_3(\mu\text{-O}_2\text{R})_3\text{X}_3]^-$ ($R = \text{H}, -\text{CH}_3, -\text{C}_2\text{H}_5, X = \text{Cl}, \text{Br}$) have been synthesized and structurally characterized (Cotton *et al.*, 1991*a,b*; Zhuang *et al.*, 1985, 1996; Chen *et al.*, 1993; Wu *et al.*, 1984; Lin & Chen, 1988). As an extension of these studies, we here report the synthesis and crystal structure of the title compound, (I), which was synthesized in a similar way to that described by Chen *et al.* (1993). However, the two crystal structures are polymorphs.



A view of the structure of (I) is shown in Fig. 1. The three Mo atoms of the cluster anion form an approximately equilateral triangle. On one side of the Mo_3 plane, one $\mu_3\text{-O}$ atom binds the three Mo atoms together to form an Mo_3O mono-capped cluster skeleton. The three acetate (Ac) ligands and the $\mu_3\text{-O}$ atom are situated on the same side of the plane. In addition, three terminal Cl atoms and three bridging Cl atoms are situated on the other side of the Mo_3 plane. Each unit cell consists of four formula units of $[\text{Et}_4\text{N}][\text{Mo}_3\text{OCl}_6(\text{Ac})_3]$, existing as discrete ions. The synthetic route and chemical composition of the title complex is identical to that of the complex reported by Chen *et al.* (1993). However, both structures are polymorphs. This reflects the diversity of crystal

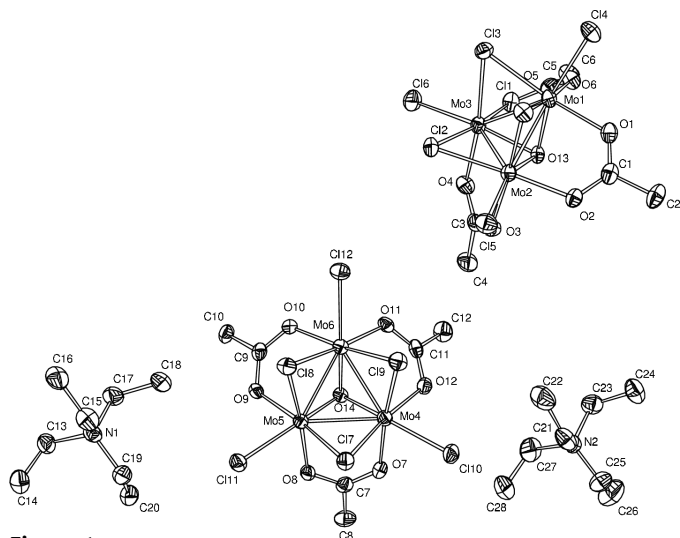


Figure 1
A view of the asymmetric unit of the title compound, showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

packing of this series of trinuclear Mo cluster compounds. The formal oxidation state of the Mo atoms is 3.33, so that the Mo₃ core possesses eight electrons to form three metal–metal bonds. The average Mo–Mo distance [2.5778 (14) Å] is consistent with an eight-electron system and the angles are normal.

Experimental

A mixture of 5.2 g (20 mmol) of MoCl₃·3H₂O in 40 ml of acetic acid was refluxed at 353 K for 2 h. After cooling, 40 ml of ethanol saturated with HCl and 2.0 g (7.8 mmol) of (Et)₄NI was added and the mixture was stirred for 1 h. Several days later, crude crystals precipitated. On recrystallization from CH₂Cl₂, black single crystals were obtained.

Crystal data

(C₈H₂₀N)[Mo₃Cl₆O(C₂H₃O₂)₃]
M_r = 823.90
 Triclinic, *P* $\bar{1}$
a = 7.9356 (1) Å
b = 14.4258 (1) Å
c = 24.4415 (4) Å
 α = 96.613 (1)°
 β = 92.518 (1)°
 γ = 91.815 (1)°
V = 2774.80 (6) Å³

Z = 4
D_x = 1.972 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 6220 reflections
 θ = 0.8–25.1°
 μ = 1.95 mm⁻¹
T = 293 (2) K
 Prism, black
 0.84 × 0.20 × 0.02 mm

Data collection

Siemens SMART CCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.680, *T_{max}* = 1.000
 14579 measured reflections

9771 independent reflections
 7292 reflections with *I* > 2σ(*I*)
R_{int} = 0.041
 θ_{\max} = 25.1°
h = -9 → 9
k = -15 → 17
l = -29 → 26

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.071
wR (*F*²) = 0.157
S = 1.07
 9771 reflections
 559 parameters

H atom not refined
 $w = 1/[\sigma^2(F_o^2) + 55.1956P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.005$
 $\Delta\rho_{\max} = 0.80 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.81 \text{ e } \text{Å}^{-3}$

Table 1

Selected interatomic distances (Å).

Mo6—O14	1.995 (7)	Mo3—Cl2	2.417 (3)
Mo6—O10	2.071 (7)	Mo3—Mo1	2.5756 (13)
Mo6—O11	2.079 (7)	Mo5—O14	1.986 (7)
Mo6—Cl9	2.406 (3)	Mo5—O9	2.070 (7)
Mo6—Cl12	2.415 (3)	Mo5—O8	2.092 (7)
Mo6—Cl8	2.430 (3)	Mo5—Cl11	2.404 (3)
Mo6—Mo4	2.5746 (14)	Mo5—Cl7	2.411 (3)
Mo6—Mo5	2.5894 (14)	Mo5—Cl8	2.423 (3)
Mo2—O13	1.981 (7)	Mo5—Mo4	2.5751 (14)
Mo2—O2	2.078 (8)	Mo1—O13	1.985 (7)
Mo2—O3	2.089 (8)	Mo1—O6	2.070 (8)
Mo2—Cl2	2.405 (3)	Mo1—O1	2.080 (8)
Mo2—Cl5	2.406 (3)	Mo1—Cl4	2.406 (3)
Mo2—Cl1	2.418 (3)	Mo1—Cl3	2.409 (3)
Mo2—Mo3	2.5722 (14)	Mo1—Cl1	2.425 (3)
Mo2—Mo1	2.5798 (14)	Mo4—O14	1.997 (7)
Mo3—O13	1.992 (7)	Mo4—O12	2.063 (8)
Mo3—O5	2.068 (8)	Mo4—O7	2.070 (8)
Mo3—O4	2.068 (8)	Mo4—Cl9	2.417 (3)
Mo3—Cl3	2.413 (3)	Mo4—Cl10	2.419 (3)
Mo3—Cl6	2.414 (3)	Mo4—Cl7	2.422 (3)

H atoms were placed in calculated positions and not refined.

Data collection: SMART (Siemens, 1995); cell refinement: SAINT (Siemens, 1995); data reduction: XPREP in SHELXTL-Plus (Sheldrick, 1991); program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: XP in SHELXTL-Plus; software used to prepare material for publication: SHELXL97.

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References

- Chen, Q. H., Lu, S. F., Huang, J. Q., Huang, Z. X. & Huang, X. Y. (1993). *Chin. J. Struct. Chem.* **12**, 117–123.
 Cotton, F. A., Shang, M. Y. & Zhong, S. S. (1991a). *J. Am. Chem. Soc.* **113**, 3007–3011.
 Cotton, F. A., Shang, M. Y. & Zhong, S. S. (1991b). *J. Am. Chem. Soc.* **113**, 6917–6922.
 Lin, X. C. & Chen, G. (1988). *Acta Chim. Sin. (Chin.)*, **46**, 439–444.
 Sheldrick, G. M. (1990). *Acta Cryst. A* **46**, 467–473.
 Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
 Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
 Siemens (1995). *SMART* and *SAINTE*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Wu, D. M., Zhuang, H. H., Zheng, J. J., Huang, J. L. & Lu, J. X. (1984). *Chin. J. Struct. Chem.* **3**, 51–55.
 Zhuang, H. H., Wu, D. M., Huang, J. Q. & Huang, J. L. (1996). *Chin. J. Struct. Chem.* **15**, 257–260.
 Zhuang, H. H., Wu, D. M., Zheng, J. J., Huang, J. Q. & Huang, J. L. (1985). *Chin. Sci. Bull. (Chin.)*, 1220–1223.