

Fig. 1. ORTEP (Johnson, 1965) drawing of the molecule with 35% thermal ellipsoids.

The coordination polyhedron of the Fe atom is tetragonal pyramidal. Four coordination sites are occupied by two CO and the midpoints *A* and *B* of the diene bonds C(13)–C(16) and C(14)–C(17), respectively. The fifth site is occupied by the apical C(18)–O(1) group. The apical Fe–CO bond makes an angle of 7 (1)° with the normal to the basal plane defined by *A*–*B*–C(19)–C(20). The diene is perpendicular to the basal plane and the Fe atom lies 0.5 (1) Å over it. The angles subtended at the Fe atom by the coordination polyhedron are listed in Table 2, and are comparable to those already discussed for analogous (exocyclic 1,3-diene)Fe(CO)₃ complexes (Pinkerton, Chapuis, Vogel, Hänisch, Narbel, Boschi & Roulet, 1979). The Fe atom is in an *exo* position with respect to the roof-shaped ligand, indicating that addition under Diels–Alder conditions does not cause epimerization at the

metal atom with respect to precursor (1) whose structure has been determined (Roulet *et al.*, 1981). Cyclization at C(10) is unambiguously confirmed. The position of the carbonitrile groups indicates that the Diels–Alder addition of TCE to (1) takes place with high *exo*-facial selectivity.

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The Structure of Tetramethylammonium μ_3 -Oxo-cyclo-tri- μ -bromo-tri- μ -formato-(*O,O'*)-tris(chloromolybdate)(3 *Mo*–*Mo*), [N(CH₃)₄][{MoBrCl(CHO₂)₃O}]

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Abstract. $M_r = 859.089$, triclinic, $P\bar{1}$, $a = 6.848$ (1), $b = 11.933$ (1), $c = 13.164$ (1) Å, $\alpha = 100.20$ (1), $\beta = 93.12$ (1), $\gamma = 101.14$ (1)°, $V = 1034.4$ (2) Å³, $Z = 2$, $D_m = 2.72$ (by flotation), $D_x = 2.76$ g cm⁻³, graphite-monochromated Mo $K\alpha$, $\lambda = 0.71073$ Å, μ

$= 79.102$ cm⁻¹, $F(000) = 804$, $T = 295$ K, final $R = 0.030$ for 3514 reflections. The crystal contains discrete cations and anions. The bond lengths and angles of the cation are normal. The mono-oxo-capped trinuclear Mo cluster anion consists of three Br atoms and HCO₂⁻

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Table 1. Atomic coordinates ($\times 10^5$ for Mo, Br, $\times 10^4$ for Cl, O, N, C) and equivalent isotropic temperature coefficients for the non-H atoms with e.s.d.'s in parentheses

	x	y	z	$B_{eq}(\text{\AA}^2)^\dagger$
Mo(1)	77496 (6)	21758 (4)	24486 (3)	1.988 (8)
Mo(2)	70195 (6)	42535 (4)	26590 (3)	1.879 (8)
Mo(3)	64397 (6)	29024 (4)	8458 (3)	2.031 (9)
Br(1)	54305 (8)	28428 (5)	37646 (4)	2.81 (1)
Br(2)	46850 (9)	9943 (5)	12910 (5)	3.01 (1)
Br(3)	36799 (8)	38603 (5)	15839 (4)	2.79 (1)
Cl(1)	7722 (2)	510 (1)	3275 (1)	3.56 (3)
Cl(2)	5882 (2)	5760 (1)	3805 (1)	3.03 (3)
Cl(3)	4417 (2)	2339 (2)	-799 (1)	3.66 (3)
O	8881 (5)	3505 (3)	1811 (2)	2.03 (7)
O(1)	10201 (5)	2953 (4)	3515 (3)	2.81 (8)
O(2)	9611 (5)	4750 (4)	3685 (3)	2.78 (8)
O(3)	8117 (6)	5565 (3)	1862 (3)	2.71 (8)
O(4)	7617 (6)	4410 (4)	297 (3)	3.21 (9)
O(5)	8497 (6)	2056 (4)	66 (3)	3.07 (9)
O(6)	9569 (5)	1395 (3)	1435 (3)	2.80 (8)
N	1684 (8)	8489 (5)	3390 (4)	3.4 (1)
C(1)	10682 (8)	4038 (5)	3861 (4)	2.8 (1)
C(2)	8250 (9)	5385 (5)	899 (4)	3.0 (1)
C(3)	9665 (9)	1558 (5)	525 (4)	3.0 (1)
C(4)	-98 (12)	8088 (7)	3939 (6)	5.1 (2)
C(5)	2583 (12)	9738 (8)	3870 (6)	5.3 (2)
C(6)	995 (15)	8468 (8)	2283 (5)	6.2 (2)
C(7)	3134 (14)	7727 (8)	3434 (8)	8.9 (2)

$$\dagger B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$$

groups that bridge three pairs of Mo atoms and three terminal Cl atoms. The coordination around Mo is distorted octahedral.

Introduction. During an investigation on the reaction system of Mo^{III} in an $\text{EtOH}-\text{HX}$ ($X=\text{Cl}, \text{Br}$) medium, a series of trinuclear Mo cluster compounds with μ -bridged CH_3COO^- ligands have been synthesized and investigated by X-ray crystallography, including $[\text{Et}_4\text{N}]_2 [\text{Mo}_3(\mu_3\text{-O})(\mu\text{-Cl})_3(\mu\text{-OAc})_2\text{Cl}_3]$ (Shang Maoyu, Huang Jinling & Lu Jiayi, 1984), $[\text{C}_5\text{H}_7\text{S}_2][\text{Mo}_3(\mu_3\text{-O})(\mu\text{-X})(\mu\text{-OAc})_3\text{Cl}_3]$ ($X=\text{Cl}, \text{Br}$; $[\text{C}_5\text{H}_7\text{S}_2]^+ = 3,5$ -dimethyl-1,2-dithiolium cation) (Wu Dingming, Zhuang Honghui, Zheng Jianji, Huang Jinling, Huang Jianquan & Lu Jiayi, 1985) and $[\text{Et}_4\text{N}][\text{Mo}_3(\mu_3\text{-O})(\mu\text{-Cl})_3(\mu\text{-OAc})_3(\text{Cl}_{1/2}, \text{Br}_{1/2})_3]$ (Zhuang Honghui, Wu Dingming, Zheng Jianji, Huang Jinling & Huang Jianquan, 1985). It seemed interesting to use HCO_2^- instead of CH_3COO^- as a bridging ligand. In this paper we describe the results of an X-ray single-crystal structure determination for a trinuclear Mo cluster with an HCO_2^- group as a bridging ligand.

Experimental. Brown-black and pseudo-rhombohedral crystal, $0.25 \times 0.40 \times 0.12$ mm, by reaction of MoBr_3 , Me_4NBr and HCOOH in EtOH saturated with HCl gas. Enraf-Nonius CAD-4 diffractometer. 25 high-angle reflections used for refining lattice parameters. $2 \leq 2\theta \leq 52^\circ$. $h \bar{8}-8$, $k \bar{14}-14$, $l \bar{16}-0$. Three standard reflections ($\bar{1}69$, $0\bar{5}7$ and $4\bar{5}4$) with

decay factors min. 0.9786 and max. 1.0787 (from instrument instability). 4232 data, all unique, 3514 with $I \geq 3\sigma(I)$. SDP crystallographic computing package (Frenz, 1980). PDP-11/70 computer. Lp correction and empirical absorption correction based on ψ scans of 9 Bragg reflections (North, Phillips & Mathews, 1968) with transmission factors min. 0.3872 and max. 0.9986. Direct methods (*MULTAN80*; Main *et al.*, 1980). Anisotropic full-matrix refinement on F for 217 parameters and 3514 data. Final $R = 0.030$, $wR = 0.040$, $w = 1/\sigma^2(F_o)$. H atoms not determined. Max. $\Delta = 0.79 \sigma$. Max. height = 0.83 e \AA^{-3} in final difference

Table 2. Bond lengths (\AA) and angles ($^\circ$)

Mo(1)—Mo(2)	2.593 (1)	Mo(1)—Mo(3)	2.598 (1)
Mo(2)—Mo(3)	2.596 (1)	Mo(1)—Br(1)	2.541 (1)
Mo(1)—Br(2)	2.542 (1)	Mo(2)—Br(1)	2.543 (1)
Mo(2)—Br(3)	2.539 (1)	Mo(3)—Br(2)	2.542 (1)
Mo(3)—Br(3)	2.543 (1)	Mo(1)—Cl(1)	2.427 (2)
Mo(2)—Cl(2)	2.412 (1)	Mo(3)—Cl(3)	2.420 (1)
Mo(1)—O	1.972 (3)	Mo(2)—O	1.978 (3)
Mo(3)—O	1.977 (3)	Mo(1)—O(1)	2.080 (4)
Mo(1)—O(6)	2.095 (3)	Mo(2)—O(2)	2.092 (4)
Mo(2)—O(3)	2.080 (4)	Mo(3)—O(4)	2.090 (4)
Mo(3)—O(5)	2.098 (4)	C(1)—O(1)	1.267 (7)
C(1)—O(2)	1.267 (7)	C(2)—O(3)	1.259 (7)
C(2)—O(4)	1.269 (7)	C(3)—O(5)	1.271 (7)
C(3)—O(6)	1.250 (7)	N—C(4)	1.494 (8)
N—C(5)	1.507 (9)	N—C(6)	1.502 (8)
N—C(7)	1.476 (9)		

Mo(1)—Mo(2)—Mo(3)	60.09 (2)	Mo(2)—Mo(1)—Mo(3)	60.02 (2)
Mo(1)—Mo(3)—Mo(2)	59.90 (2)	Mo(1)—O—Mo(2)	82.06 (12)
Mo(1)—O—Mo(3)	82.29 (13)	Mo(2)—O—Mo(3)	82.07 (13)
Mo(1)—Mo(2)—Br(1)	59.29 (2)	Mo(2)—Mo(1)—Br(1)	59.38 (2)
Mo(1)—Br(1)—Mo(2)	61.33 (2)	Mo(1)—Mo(3)—Br(2)	59.27 (2)
Mo(3)—Mo(1)—Br(2)	59.28 (2)	Mo(1)—Br(2)—Mo(3)	61.46 (2)
Mo(2)—Mo(3)—Br(3)	59.19 (2)	Mo(3)—Mo(2)—Br(3)	59.36 (2)
Mo(2)—Br(3)—Mo(3)	61.44 (2)	O—Mo(1)—Cl(1)	157.63 (11)
Br(1)—Mo(1)—O(6)	171.72 (11)	Br(2)—Mo(1)—O(1)	171.86 (12)
Cl(1)—Mo(1)—O(1)	84.11 (12)	Cl(1)—Mo(1)—O(6)	84.52 (12)
Cl(1)—Mo(1)—Br(1)	87.42 (4)	Cl(1)—Mo(1)—Br(2)	87.86 (5)
O—Mo(1)—O(1)	80.17 (15)	O—Mo(1)—O(6)	80.02 (15)
O—Mo(1)—Br(1)	108.25 (10)	O—Mo(1)—Br(2)	107.91 (10)
Br(2)—Mo(1)—Br(1)	88.45 (2)	Br(2)—Mo(1)—O(6)	89.36 (11)
O(1)—Mo(1)—Br(1)	89.89 (10)	O(1)—Mo(1)—O(6)	91.16 (15)
Cl(2)—Mo(2)—O	157.79 (11)	Br(3)—Mo(2)—O(2)	171.93 (11)
Br(1)—Mo(2)—O(3)	172.35 (10)	Cl(2)—Mo(2)—O(3)	85.10 (11)
Cl(2)—Mo(2)—O(2)	84.13 (11)	Cl(2)—Mo(2)—Br(1)	87.40 (4)
Cl(2)—Mo(2)—Br(3)	87.81 (4)	O—Mo(2)—O(2)	79.83 (14)
O(3)—Mo(2)—O	79.65 (14)	O—Mo(2)—Br(1)	107.98 (10)
O—Mo(2)—Br(3)	108.04 (10)	Br(1)—Mo(2)—Br(3)	88.42 (2)
Br(1)—Mo(2)—O(2)	90.78 (11)	O(3)—Mo(2)—Br(3)	89.78 (11)
O(3)—Mo(2)—O(2)	89.96 (15)	Cl(3)—Mo(3)—O	157.53 (10)
Br(3)—Mo(3)—O(5)	173.09 (11)	Br(2)—Mo(3)—O(4)	172.24 (11)
Cl(3)—Mo(3)—O(5)	85.01 (11)	Cl(3)—Mo(3)—O(4)	84.71 (12)
Cl(3)—Mo(3)—Br(2)	87.56 (5)	Cl(3)—Mo(3)—Br(3)	88.09 (4)
O—Mo(3)—O(5)	78.73 (14)	O—Mo(3)—O(4)	79.84 (15)
O—Mo(3)—Br(2)	107.76 (10)	O—Mo(3)—Br(3)	107.92 (10)
O(4)—Mo(3)—O(5)	89.66 (16)	O(4)—Mo(3)—Br(3)	89.71 (11)
Br(2)—Mo(3)—O(5)	90.33 (12)	Br(2)—Mo(3)—Br(3)	89.37 (2)
C(1)—O(1)—Mo(1)	123.42 (34)	C(1)—O(2)—Mo(2)	122.42 (36)
O(1)—C(1)—O(2)	123.67 (49)	C(2)—O(3)—Mo(2)	123.24 (39)
C(2)—O(4)—Mo(3)	122.31 (35)	O(3)—C(2)—O(4)	124.24 (55)
C(3)—O(5)—Mo(3)	122.24 (34)	C(3)—O(6)—Mo(1)	122.27 (36)
O(5)—C(3)—O(6)	124.78 (50)	C(4)—N—C(5)	108.64 (53)
C(4)—N—C(6)	108.53 (61)	C(4)—N—C(7)	110.49 (64)
C(5)—N—C(6)	106.90 (57)	C(5)—N—C(7)	112.04 (71)
C(6)—N—C(7)	110.11 (64)		

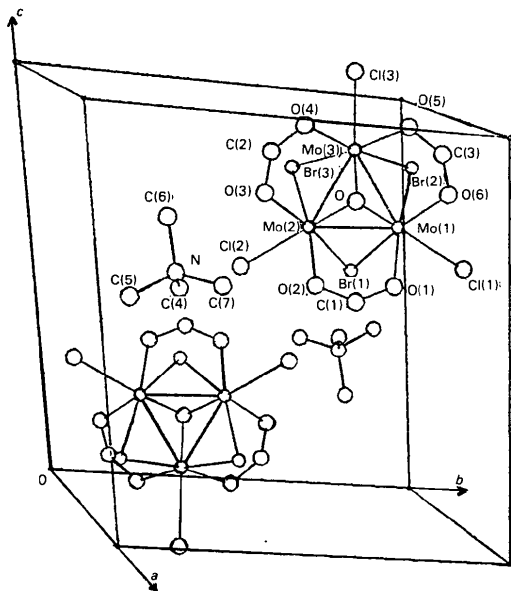


Fig. 1. Perspective view of the unit-cell contents.

Fourier map. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).^{*} Atomic coordinates and bonding geometry are in Tables 1 and 2. Fig. 1 shows the unit cell.

Discussion. The crystal is a discrete ionic one containing an Me₄N⁺ cation and an [Mo₃(μ₃-O)(μ-Br)₃(μ-O₂CH)₃Cl₃]⁻ cluster anion in each asymmetric unit.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42050 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Copper(I)–Olefin Complexes. Structure of (1-2-η-Cyclohexene)-(di-2-pyridylamine)copper(I) Perchlorate, [Cu(C₆H₁₀)(C₁₀H₉N₃)]ClO₄*

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Abstract. $M_r = 416.34$, monoclinic, $P2_1/c$, $a = 106.23 (1)^\circ$, $V = 1711.6 (6) \text{ \AA}^3$, $Z = 4$, $D_x = 7.478 (1)$, $b = 25.014 (6)$, $c = 9.530 (1) \text{ \AA}$, $\beta = 1.615 \text{ g cm}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$, $\mu = 14.608 \text{ cm}^{-1}$, $F(000) = 856$, $T = 173 \text{ K}$. Final $R = 0.047$ for 2946 unique observed reflections. The

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The bond lengths and angles of the cation are in conformity with those reported in the literature. In the cluster anion three Mo atoms form an approximately equilateral triangle with an average Mo–Mo bond distance of 2.596 (1) Å. On one side of the triangular plane one μ₃-O atom binds the three Mo atoms together to form a monocapped cluster core. Each pair of Mo atoms is further bridged by a Br ligand and an HCO₂⁻ group. The local coordination polyhedron around each Mo atom is a distorted octahedron. The symmetry of the cluster anion as a whole is approximately C_{3v}.

The formal oxidation state for each Mo atom is 3 $\frac{1}{3}$, so that the metal core (Mo₃) has eight electrons to form the metal–metal bonds. As a two-center molecular orbital, the order for each Mo–Mo bond may be regarded as 4/3, which is in good agreement with the bond lengths observed (2.593, 2.596 and 2.598 Å).

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