

M₃X₁₃ Type of Equilateral-Triangular Metal Atom Cluster Compound with Several Unprecedented Features: [Mo₃(μ₃-CH₃C)(μ₂-Br)₃(η²,μ₂-CH₃CO₂)₃(H₂O)₃]ClO₄·4H₂O

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Abstract: From the reaction of Mo(CO)₆ with a refluxing mixture of acetic acid and acetic anhydride in the presence of NaBr and under nitrogen, the title compound is obtained after a suitable workup in which the reaction mixture is diluted with water and the trinuclear cation is adsorbed on a cation-exchange resin. The perchlorate salt was characterized by X-ray crystallography. It forms crystals in space group *P*2₁/*n* with *Z* = 4 and the following unit cell dimensions: *a* = 18.622 (5) Å, *b* = 9.182 (4) Å, *c* = 15.378 (5) Å; β = 97.54 (5)°; *V* = 2607 (3) Å³. The cation approaches very closely to having C_{3v} symmetry. There is an essentially equilateral triangle of molybdenum atoms with a mean Mo-Mo bond length of 2.594 [1] Å. Above this triangle is a capping μ₃-CH₃C group, and below each edge is a bridging μ₂-Br atom with an average Mo-Br distance of 2.595 [4] Å. Each edge of the Mo₃ triangle is also spanned by an η²,μ₂-CH₃CO₂ group, and the approximately octahedral coordination (not counting Mo-Mo bonds) about each Mo atom is completed by a water molecule. The metal cluster has an eight-electron count, an infrequent but theoretically permissible occurrence; it is also the first one of its type to have either μ₂-Br atoms or a μ₃-alkylidyne group.

The type of trinuclear metal atom cluster of which the title compound is an example was first shown to exist in the solid state more than a quarter century ago,² and studies of it in the solid-state context continue to appear.^{3,4} This type of cluster may be described in two ways: (1) It is an equilateral triangle of metal atoms with a capping (μ₃) atom (or group) on one side, three edge-bridging (μ₂) atoms on the opposite side, and three more atoms coordinated to each metal atom in outer positions. (2) It consists of three MX₆ octahedra fused together in such a way that all three share one vertex (the capping atom in the first description) and three shared edges radiate from the shared vertex. Each shared edge connects the μ₃ atom with one of the μ₂ atoms. A schematic drawing is presented in Figure 1.

In 1978 it was shown for the first time that this type of trimolybdenum cluster species could exist in discrete form and have an aqueous chemistry.⁵ In this instance, the cluster was sequestered as an oxalato complex. Subsequently, other sets of ligands have been used to obtain isolable (and X-ray characterized) complexes of the central Mo₃O₄⁴⁺ core,⁶⁻⁹ and a tungsten analogue has been reported.¹⁰ Finally, it should be noted that ready isolation of complexes of Mo₃O₄⁴⁺ from aqueous solutions of molybdenum(IV)⁴⁻⁸ as well as tracer¹¹ and EXAFS¹² data leave no doubt that the Mo₃O₄(H₂O)₉⁴⁺ ion, or one related to it by simple acid-base reactions, prevails in aqueous solutions of molybdenum(IV). It should be noted that there are also closely

related sulfur-containing trinuclear species.¹³⁻¹⁶

In this paper, we describe an M₃X₁₃-type cluster species that displays two features that are unusual and one that is unprecedented. It has been noted previously in one specific instance that such a cluster type could have μ₂-Cl atoms rather than μ₂-O atoms and further that the electron count within the metal atom cluster (for a more detailed explanation see the Discussion section) might be eight rather than six.¹⁷ The present compound also displays both of these unusual features, namely, it is an eight-electron cluster with halogen atoms in the μ₂-X positions. The halogen atoms in this case are bromine atoms, which have not previously been found in such a cluster. In addition, the μ₃-X position is occupied by an ethylidyne group; the occurrence of any alkylidyne group in this type of cluster is unprecedented although μ₃-alkylidyne groups have previously been found in one or both capping positions¹⁹ in the bicapped cluster species of the M₃(μ₃-X)(μ₃-Y)(O₂CR)₆L₃ type.

Experimental Section

Preparation of [Mo₃(CCH₃)(O₂CMe)₃Br₃(H₂O)₃]ClO₄·4H₂O. Molybdenum hexacarbonyl (0.5 g) and sodium bromide (0.5 g) were mixed with 30 mL of acetic acid and 30 mL of acetic anhydride. The mixture was refluxed for 12 h in an inert atmosphere and then cooled and filtered to remove Mo₂(O₂CCH₃)₄.

Water (100 mL) was added to the filtrate and the resulting solution stirred for 1 h during which time the color changed to brown-green. The filtered solution was passed through a Dowex 50W × 2 (100-200 mesh)

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(3) By the expression "in the solid-state context" we mean in situations where the individual M₃X₁₃ units are not discrete but share some of the ligands, X, among themselves; i.e., the M₃X₁₃ units are fused together.

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(18) While the X-ray data cannot provide proof that the capping group is CCH₃ rather than OCH₃, there can be no reasonable doubt about this, since only μ₃-alkylidyne groups, but never μ₃-OR, group has been found in compounds prepared under these conditions. It would be difficult to see how an OCH₃ group could be generated. Moreover, and perhaps most persuasive, is the fact that if the capping group was OCH₃, we would have a ten-electron cluster which is unprecedented and inconsistent with the molecular orbital treatments of the cluster bonding.^{13,21,22}

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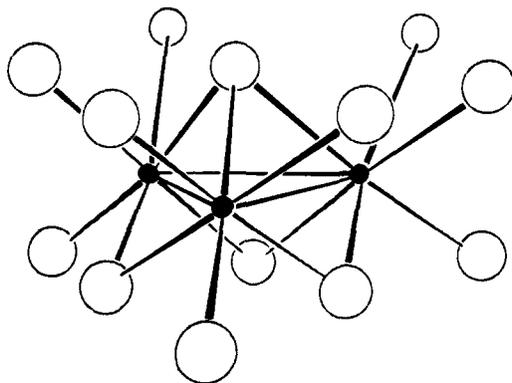


Figure 1. Generalized representation of the M_3X_{13} type of cluster, which is found in the cation of the title compound.

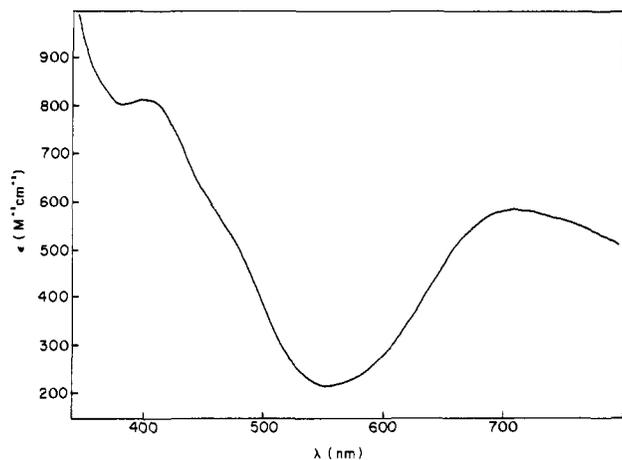


Figure 2. Visible absorption spectrum of the title compound in aqueous 0.3 M $HClO_4$ solution.

cation-exchange column. The column was then washed with 0.01 M oxalic acid and 0.1 M $HClO_4$ to remove the known Mo^V -aquo ion and the $\{Mo_3(\mu-CCH_3)_2(O_2CMe)_6(H_2O)_3\}^+$ cluster ion, respectively. After washing with H_2O , a green zone was eluted by 0.3 M $HClO_4$. The title compound was isolated in crystalline form by slow evaporation of the green solution. This procedure is useful only to obtain single crystals suitable for X-ray crystallography. In all cases, the green crystals are accompanied by substantial amounts of a noncrystalline blue substance. The identity of the blue solid has not been established. Since hydrolysis of the ethylidene cap is a distinct possibility, this blue product might contain the $[Mo_3(\mu_3-O)(O_2CCH_3)_3Br_3(H_2O)_3]^{2+}$ ion or something similar.

A modified workup, designed to avoid or minimize decomposition, was devised. The green band on the column was eluted with 0.3 M HCl and the eluate collected in a 250-mL round flask. The round part of this flask was then immersed in liquid N_2 , and the flask was tilted nearly 90° and then rapidly rotated. In this way, the liquid was frozen into a thin, uniform coating over most of the inside of the flask. The flask was then connected to a high-vacuum line, with a liquid nitrogen-cooled condenser in between. When the liquid N_2 bath was removed from the flask, the solvent was efficiently stripped from the flask without any melting. This freeze-drying procedure afforded a uniform but noncrystalline green product in about 30% yield.

Spectroscopy. The electronic spectrum, which was recorded on doubly chromatographed material in aqueous solutions, is depicted in Figure 2.

The solutions used for NMR measurements were prepared by dissolving freeze-dried material in D_2O . Two peaks at 2.86 and 2.38 ppm (relative to internal DSS) with relative integrated intensities of 1 and 3.4, respectively, were observed at 90 MHz. Puzzled by what we considered too serious a deviation from the expected intensity ratio of 1:3, we reexamined the spectra at 200 MHz. This clearly revealed that the signal at 2.38 ppm consisted of two resonances, one of which had a peak height about 3.1 times that for the 2.86 ppm resonance. The sample was therefore rechromatographed on a column prepared with D_2O . The green eluate was measured without further treatment. This new 200-MHz spectrum showed a significant decrease of the contamination peak while the ratio of peak heights (approximately 1:3) of the remaining two resonances was unaffected.

Table I. Crystal Data and Experimental Details

form unit	$[Mo_3(CH_3CO_2)_3Br_3 \cdot C_2H_5 \cdot (H_2O)_3] \cdot ClO_4 \cdot 4H_2O$
fw	957.3
$F(000)$	1832
a	18.622 (5)
b	9.182 (4)
c , Å	15.378 (5)
β , deg	97.54 (5)
V , Å ³	2606.7
D_{meas}	
D_{calcd} , g·cm ⁻³	2.440
Z	4
space group	$P2_1/n$
μ , cm ⁻¹	64.3
radiation	Mo $K\alpha$
scan mode	$\omega/2\theta$
scan speed, °·min ⁻¹	3.0
scan width, ° ω	1.2
angular range in 2θ , deg	5–50
background time at each side of the peak, s	10
monitor reflections	$3\bar{1}\bar{1}$; 012; $20\bar{2}$
no. of unique reflections	4519
cutoff criterion	$F_o > 1.5\sigma F_o$
no. of reflects in the last refinement cycle	3648
no. of parameters refined	285
weighting scheme	$1.031/(\sigma^2 F_o + 0.001(F_o)^2)$
R_f	0.060
R_w	0.058

X-ray Crystallography. Crystals of the title compound grew as thin plates. Unit cell parameters, crystal class determination, and data collection were performed on a Phillips PW 1100/20 four-circle diffractometer. The general procedures and the computer programs involved have been described before.¹⁹ The perchlorate ion had to be refined isotropically as two differently oriented tetrahedra of oxygen atoms with a common Cl atom. Other than this, no special problems were encountered in solving and refining the structure. For the interested reader, a detailed description of the crystallographic procedure is available as part of the supplementary material. Information pertaining to data collection and refinement is given in Table I.

Results

Preparation. As reported previously,¹⁹ when $Mo(CO)_6$ is refluxed under an inert atmosphere with a mixture of acetic acid and acetic anhydride, trinuclear molybdenum cluster compounds containing the capping (μ_3) CH_3C group are obtained, but these products are of the bicapped type. The present work has shown that by having $NaBr$ present in the refluxing reaction mixture, bromine can be incorporated into the product with a concomitant change in structure to the monocapped, tribridged type. The cluster cation obtained is $[Mo_3(\mu_3-CH_3C)(\mu-Br)_3(O_2CCH_3)_3(H_2O)_3]^+$, and in this work it was isolated as its perchlorate salt with additional water of crystallization, namely, as $[Mo_3(CH_3C)Br_3(O_2CCH_3)_3(H_2O)_3]ClO_4 \cdot 4H_2O$. In aqueous solution, the cation tends to decompose, presumably by partial hydrolysis, to give a blue substance, which always accompanies the crystalline product when this is obtained by slow evaporation at room temperature. By a freeze-drying procedure, this blue contaminant can be avoided, but the product is then only microcrystalline.

Structural Results. The crystalline compound consists of an ordered array of the cluster cations, perchlorate anions, and molecules of water of crystallization. The trinuclear cation is depicted in Figure 3, where the atom-numbering scheme is defined. A stereorepresentation of the entire unit cell forms part of the supplementary material. Table II gives the atomic positional parameters and equivalent isotropic thermal parameters, while a list of the anisotropic thermal parameters is available as supplementary material.

Table III lists the principal bond lengths and angles. The cluster cation contains an essentially equilateral triangle of molybdenum atoms, although no crystallographic symmetry is imposed upon it. The Mo–Mo distances are equal to within one standard de-

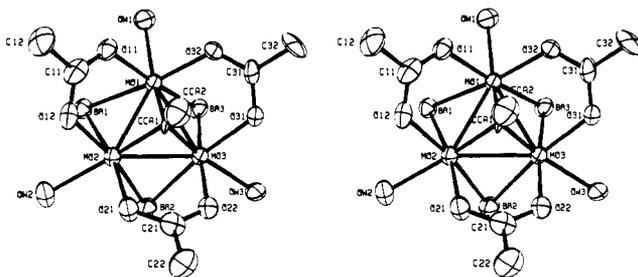


Figure 3. Stereoview of the trinuclear cation, showing the atom-numbering scheme. Atoms are represented by ellipsoids of thermal vibration at the 40% probability level.

Table II. Final Positional Parameters and Equivalent^a or Isotropic Temperature Factors^b

atom	X	Y	Z	U _{eq}
Mo(1)	5667 (1)	1625 (1)	8283 (1)	282 (2)
Mo(2)	4364 (1)	1715 (1)	7450 (1)	298 (2)
Mo(3)	5065 (1)	4115 (1)	7853 (1)	298 (2)
Br(1)	4616 (1)	259 (1)	8895 (1)	357 (3)
Br(2)	3776 (1)	3759 (1)	8293 (1)	403 (3)
Br(3)	5603 (1)	3616 (1)	9465 (1)	387 (3)
Cl	2841 (2)	-643 (5)	5006 (3)	65 (1)
O(11)	5785 (4)	-227 (9)	7534 (5)	36 (2)
O(12)	4663 (5)	-150 (10)	6816 (6)	43 (2)
C(11)	5292 (8)	-683 (13)	6922 (9)	44 (3)
C(12)	5464 (8)	-1965 (16)	6380 (10)	55 (4)
O(21)	3951 (4)	2790 (9)	6288 (5)	40 (2)
O(22)	4552 (5)	4862 (9)	6629 (6)	41 (2)
C(21)	4127 (7)	4070 (16)	6089 (8)	42 (3)
C(22)	3861 (9)	4669 (17)	5214 (9)	54 (4)
O(31)	5095 (4)	4752 (9)	7617 (6)	40 (2)
O(32)	6620 (4)	2597 (9)	8005 (5)	37 (2)
C(31)	6658 (7)	3885 (15)	7697 (10)	44 (4)
C(32)	7344 (6)	4411 (19)	7426 (12)	69 (5)
OW(1)	6434 (4)	365 (9)	9221 (6)	42 (2)
OW(2)	3294 (5)	587 (10)	7251 (6)	47 (2)
OW(3)	4994 (4)	6430 (9)	8155 (6)	42 (2)
CCa(1)	5300 (6)	2428 (11)	7090 (7)	24 (3)
CCa(2)	5614 (8)	2346 (16)	6235 (9)	56 (4)
OW(4)	3970 (5)	2461 (10)	550 (6)	55 (3)
OW(5)	1385 (5)	2522 (10)	-2789 (7)	62 (3)
OW(6)	2380 (5)	949 (12)	-1544 (7)	71 (3)
OW(7)	2097 (5)	3239 (13)	5731 (7)	75 (3)
atom	X	Y	Z	U _{iso}
OCl(1)	2540 (9)	305 (19)	5630 (11)	77 (5)
OCl(2)	3434 (11)	101 (22)	4703 (13)	105 (6)
OCl(3)	2304 (10)	-938 (23)	4271 (13)	93 (6)
OCl(4)	3081 (14)	-1845 (29)	5470 (18)	141 (8)
OCl(5)	2921 (29)	964 (60)	4694 (35)	134 (16)
OCl(6)	3597 (31)	-1162 (61)	5303 (37)	150 (18)
OCl(7)	2824 (36)	-1252 (78)	5875 (46)	175 (23)
OCl(8)	2570 (27)	-1911 (61)	4562 (34)	115 (16)

^a U_{eq} = $\frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$. Fractional coordinates ($\times 10^4$) for all atoms. U_{eq} ($\times 10^4$) for Mo and Br atoms and ($\times 10^3$) for the remaining atoms. Esd's are in parentheses.

viation, with a mean value of 2.594 [1] Å. Above the metal atom plane (as it appears in Figure 3) are found the capping CH₃C group and three edge-bridging acetate groups. Well below the plane of the metal atoms are the three μ_2 -Br atoms and only a little below the plane of the metal atoms are the coordinated water molecules. Each metal atom is thus surrounded by a distorted octahedral set of six ligand atoms, and the three octahedra are joined at a common vertex (the μ_3 -CH₃C group) and share edges radiating from that common joint to the three μ_2 -Br atoms. The structure is clearly of the general M₃X₁₃ type depicted in Figure 1.

In its ideal form, such a structure should have C_{3v} symmetry. The present example comes very close to doing so. We have already noted the essential equality of the Mo-Mo distances. The Mo-Mo-Mo angles are all within less than 0.04° of 60°. The Mo-C distances (to the capping atom) are equal within one

standard deviation at 2.01 [1] Å, and the Mo-C-C angles, while a bit more scattered, have very similar values which average to 132.0 [7]°. The six Mo-Br distances range from 2.583 (1) to 2.603 (1) Å with a mean value of 2.595 [4] Å. Considering the absence of any crystallographically imposed symmetry, the structure of the cation approximates very satisfactorily to C_{3v}.

The ClO₄⁻ ions are disordered, as is so commonly the case. A model that refined well, provided the oxygen atoms were assigned isotropic thermal parameters, employed two sets of four oxygen atoms, each with half-occupancy. The Cl-O distances range from 1.36 (2) to 1.56 (5) Å; the average value, 1.45 [2] Å, is in satisfactory agreement with the typical distance in ClO₄⁻ ions of 1.43 ± 0.02 Å. The O-Cl-O angles in one of the half-occupied ClO₄ units range from 105° to 114°, while in the other one the range is from 74° to 132°. No attempt was made to further improve this model, however.

The crystal packing entails an intricate pattern of hydrogen bonds, in which the coordinated water molecules, the lattice water molecules, and the perchlorate ions all participate. The various hydrogen-bonded O...O contacts range from 2.7 to 2.9 Å.

Spectra. The electronic absorption spectrum cannot be assigned, but it serves as a useful means of identifying this cation. It is rather different from any previously reported spectrum of a trinuclear molybdenum cluster. It may be noted that the green color is also unprecedented in this general class of compounds.

The proton NMR spectrum is consistent with the crystal structure provided due allowance is made for the presence of an impurity that presumably arises by hydrolysis in solution. The details have been fully discussed in the Experimental Section.

Discussion

The compound reported here is of unusual interest and importance for three reasons:

(1) It is the first example of the occurrence of a capping alkylidyne group in a M₃X₁₃ type of trimolybdenum (or tungsten) cluster species.

(2) It is the first example of a M₃X₁₃-type discrete cluster cation in which the μ_2 -X atoms are bromine atoms.

(3) It is only the second documented example of a discrete M₃X₁₃ type cluster with an eight-electron configuration in the M₃ core, the other being the Mo₃(μ_3 -O)(μ_2 -Cl)₃ case which has been found in three different chemical compounds.^{16,17,20} Each of these points will now be discussed in more detail.

Capping Alkylidyne Group. The presence of a capping alkylidyne group in this (or any other) metal cluster compound means that we are dealing with an organometallic compound. Just as in the case of the bicapped trimolybdenum species,¹⁹ this is remarkable in view of the fact that the compound is stable in acidic, aqueous solution. In the case of the [Mo₃(μ_3 -CCH₃)₂(O₂CR)₆(H₂O)₃]ⁿ⁺ and [Mo₃(μ_3 -CCH₃)(μ_2 -O)(O₂CCH₃)₆(H₂O)₃]ⁿ⁺ species, the stability of the Mo-C bonds was attributed mainly to their coordinately and electronically saturated nature, since each metal atom is nine-coordinate (counting Mo-Mo bonds) and lacks both orbitals and electrons for the formation of any intermediate resulting from nucleophilic attack by H₂O (or OH⁻) on the metal atoms.

In the present case, the metal atoms are only eight-coordinate, and, in fact, the ethylidyne species is less inert than in the bicapped compounds. On standing in 0.3 M HClO₄ at room temperature for several hours, the [Mo₃(CCH₃)Br₃(O₂CCH₃)₃(H₂O)₃]⁺ ion decomposes appreciably to give a blue precipitate, which we presume lacks the alkylidyne group. Under comparable conditions, the alkylidyne-containing bicapped species are far more stable. The relative stabilities of the two kinds of alkylidyne-containing cluster species are evidently in qualitative accord with their expected openness to solvolysis, but it is, perhaps, surprising that the [Mo₃(μ_3 -CCH₃)Br₃(O₂CCH₃)₃(H₂O)₃]⁺ ion is stable enough to be isolated.

While the Mo-C bonding in this case is probably similar to that in the previously reported μ_3 -CCH₃ clusters, there are some

Table III. Important Bond Lengths and Angles

A. Bond Lengths, Å			
Mo(1)–Mo(2)	2.594 (1)	Mo(3)–CCa(1)	2.02 (1)
Mo(1)–Mo(3)	2.593 (1)	O(11)–C(11)	1.30 (1)
Mo(1)–Br(1)	2.603 (1)	O(12)–C(11)	1.26 (1)
Mo(1)–Br(3)	2.592 (1)	C(11)–C(12)	1.50 (2)
Mo(1)–O(11)	2.082 (8)	O(21)–C(21)	1.27 (1)
Mo(1)–O(32)	2.079 (8)	O(22)–C(21)	1.29 (1)
Mo(1)–OW(1)	2.218 (8)	C(21)–C(22)	1.48 (1)
Mo(1)–CCa(1)	2.01 (1)	O(31)–C(31)	1.31 (1)
Mo(2)–Mo(3)	2.595 (1)	O(32)–C(31)	1.28 (1)
Mo(2)–Br(1)	2.583 (1)	C(31)–C(32)	1.48 (1)
Mo(2)–Br(2)	2.603 (1)	CCa(1)–CCa(2)	1.51 (1)
Mo(2)–O(12)	2.082 (9)	Cl–OCl(1)	1.46 (1)
Mo(2)–O(21)	2.097 (8)	Cl–OCl(2)	1.43 (2)
Mo(2)–OW(2)	2.231 (9)	Cl–OCl(3)	1.43 (1)
Mo(2)–CCa(1)	2.01 (1)	Cl–OCl(4)	1.36 (2)
Mo(3)–Br(2)	2.600 (1)	Cl–OCl(5)	1.56 (5)
Mo(3)–Br(3)	2.590 (1)	Cl–OCl(6)	1.50 (5)
Mo(3)–O(22)	2.110 (8)	Cl–OCl(7)	1.45 (7)
Mo(3)–O(31)	2.082 (8)	Cl–OCl(8)	1.41 (5)
Mo(3)–OW(3)	2.184 (8)		
B. Bond Angles, deg			
Mo(2)–Mo(1)–Mo(3)	60.04 (3)	Mo(1)–Mo(3)–Mo(2)	59.98 (3)
Mo(2)–Mo(1)–Br(1)	59.62 (4)	Mo(1)–Mo(3)–Br(2)	101.88 (4)
Mo(2)–Mo(1)–Br(3)	101.39 (4)	Mo(1)–Mo(3)–Br(3)	60.01 (4)
Mo(2)–Mo(1)–O(11)	85.0 (2)	Mo(1)–Mo(3)–O(22)	130.1 (2)
Mo(2)–Mo(1)–O(32)	130.8 (2)	Mo(1)–Mo(3)–O(31)	85.1 (2)
Mo(2)–Mo(1)–OW(1)	145.0 (2)	Mo(1)–Mo(3)–OW(3)	147.2 (2)
Mo(2)–Mo(1)–CCa(1)	49.7 (2)	Mo(1)–Mo(3)–CCa(1)	49.8 (3)
Mo(3)–Mo(1)–Br(1)	101.34 (4)	Mo(2)–Mo(3)–Br(2)	60.13 (4)
Mo(3)–Mo(1)–Br(3)	59.92 (4)	Mo(2)–Mo(3)–Br(3)	101.41 (5)
Mo(3)–Mo(1)–O(11)	130.7 (2)	Mo(2)–Mo(3)–O(22)	84.7 (2)
Mo(3)–Mo(1)–O(32)	85.5 (2)	Mo(2)–Mo(3)–O(31)	130.0 (2)
Mo(3)–Mo(1)–OW(1)	147.8 (2)	Mo(2)–Mo(3)–OW(3)	146.6 (2)
Mo(3)–Mo(1)–CCa(1)	50.2 (2)	Mo(12)–Mo(3)–CCa(1)	49.6 (2)
Br(1)–Mo(1)–Br(3)	88.86 (4)	Br(2)–Mo(3)–Br(3)	89.01 (5)
Br(1)–Mo(1)–O(11)	86.8 (2)	Br(2)–Mo(3)–O(22)	87.0 (2)
Br(1)–Mo(1)–O(32)	169.5 (2)	Br(2)–Mo(3)–O(31)	169.8 (2)
Br(1)–Mo(1)–OW(1)	87.9 (2)	Br(2)–Mo(3)–OW(3)	89.0 (2)
Br(1)–Mo(1)–CCa(1)	108.9 (2)	Br(2)–Mo(3)–CCa(1)	109.4 (2)
Br(3)–Mo(1)–O(11)	169.2 (2)	Br(3)–Mo(3)–O(22)	169.7 (2)
Br(3)–Mo(1)–O(32)	87.8 (2)	Br(3)–Mo(3)–O(31)	88.1 (2)
Br(3)–Mo(1)–OW(1)	89.8 (2)	Br(3)–Mo(3)–OW(3)	89.7 (2)
Br(3)–Mo(1)–CCa(1)	109.8 (2)	Br(3)–Mo(3)–CCa(1)	109.5 (3)
O(11)–Mo(1)–O(32)	94.7 (3)	O(22)–Mo(3)–O(31)	94.2 (3)
O(11)–Mo(1)–OW(1)	80.1 (3)	O(22)–Mo(3)–OW(3)	80.8 (3)
O(11)–Mo(1)–CCa(1)	80.9 (3)	O(22)–Mo(3)–CCa(1)	80.8 (3)
O(32)–Mo(1)–OW(1)	82.2 (3)	O(31)–Mo(3)–OW(3)	81.2 (2)
O(32)–Mo(1)–CCa(1)	81.5 (3)	O(31)–Mo(3)–CCa(1)	80.8 (3)
OW(1)–Mo(1)–CCa(1)	153.8 (3)	OW(3)–Mo(3)–CCa(1)	153.1 (3)
Mo(1)–Mo(2)–Mo(3)	59.98 (3)	Mo(1)–CCa(1)–Mo(2)	80.4 (3)
Mo(1)–Mo(2)–Br(1)	60.36 (4)	Mo(1)–CCa(1)–Mo(3)	80.0 (4)
Mo(1)–Mo(2)–Br(2)	101.80 (5)	Mo(1)–CCa(1)–CCa(2)	130.7 (8)
Mo(1)–Mo(2)–O(12)	85.1 (2)	Mo(2)–CCa(1)–Mo(3)	80.1 (3)
Mo(1)–Mo(2)–O(21)	130.6 (2)	Mo(2)–CCa(1)–CCa(2)	132.3 (8)
Mo(1)–Mo(2)–OW(2)	144.5 (2)	Mo(3)–CCa(1)–CCa(2)	132.9 (8)
Mo(1)–Mo(2)–CCa(1)	49.9 (3)	O(11)–C(11)–O(12)	122 (1)
Mo(3)–Mo(2)–Br(1)	101.82 (5)	O(11)–C(11)–C(12)	118 (1)
Mo(3)–Mo(2)–Br(2)	60.03 (4)	O(12)–C(11)–C(12)	120 (1)
Mo(3)–Mo(2)–O(12)	130.8 (2)	O(21)–C(21)–O(22)	121 (1)
Mo(3)–Mo(2)–O(21)	85.5 (2)	O(21)–C(21)–O(22)	120 (1)
Mo(3)–Mo(2)–OW(2)	147.1 (2)	O(22)–C(21)–C(22)	119 (1)
Mo(3)–Mo(2)–CCa(1)	50.2 (2)	O(31)–C(31)–O(32)	121 (1)
Br(1)–Mo(2)–Br(2)	89.18 (5)	O(31)–C(31)–C(32)	119 (1)
Br(1)–Mo(2)–O(12)	87.0 (2)	O(32)–C(31)–C(32)	120 (1)
Br(1)–Mo(2)–O(21)	169.0 (2)	OCl(1)–Cl–OCl(2)	108 (1)
Br(1)–Mo(2)–OW(2)	86.3 (2)	OCl(1)–Cl–OCl(3)	110 (1)
Br(1)–Mo(2)–CCa(1)	109.8 (3)	OCl(1)–Cl–OCl(4)	105 (1)
Br(2)–Mo(2)–C(12)	169.1 (2)	OCl(2)–Cl–OCl(3)	109 (1)
Br(2)–Mo(2)–O(21)	87.4 (2)	OCl(2)–Cl–OCl(4)	110 (1)
Br(2)–Mo(2)–OW(2)	88.6 (2)	OCl(3)–Cl–OCl(4)	114 (1)
Br(2)–Mo(2)–CCa(1)	109.9 (2)	OCl(5)–Cl–OCl(6)	106 (2)
O(12)–Mo(2)–O(21)	94.5 (3)	OCl(5)–Cl–OCl(7)	131 (3)
O(12)–Mo(2)–OW(2)	81.0 (3)	OCl(5)–Cl–OCl(8)	132 (3)
O(12)–Mo(2)–CCa(1)	81.0 (3)	OCl(6)–Cl–OCl(7)	74 (3)
O(21)–Mo(2)–OW(2)	83.1 (3)	OCl(6)–Cl–OCl(8)	98 (3)
O(21)–Mo(2)–CCa(1)	81.2 (3)	OCl(7)–Cl–OCl(8)	94 (3)
OW(2)–Mo(2)–CCa(1)	155.0 (3)		

Table IV. Bond Lengths and Angles in Ethynyl-Capped Molybdenum Trimers

cluster	M-C _{cap} , Å	M-C-M, deg	Mo-Mo, Å	ref
[Mo ₃ (μ ₃ -CCH ₃) ₂ (O ₂ CCH ₃) ₆ (H ₂ O) ₃] ⁺	2.05 [1]	86.9 [2]	2.815 [7]	19
[Mo ₃ (μ ₃ -CCH ₃) ₂ (O ₂ CCH ₃) ₆ (H ₂ O) ₃] ²⁺	2.079 [6]	88.0 [3]	2.888 [5]	19
[Mo ₃ O(CCH ₃)(O ₂ CCH ₃) ₆ (H ₂ O) ₃] ⁺	2.053 [2]	84.1 [1]	2.751 [1]	18
[Mo ₃ (CCH ₃)(Br) ₃ (O ₂ CCH ₃) ₃ (H ₂ O) ₃] ⁺	2.01 [1]	80.2 [4]	2.594 [1]	this work

Table V. Mo₃X₁₃-Type Clusters: Structural and Electronic Data

cluster	μ ₃ -ligand	μ ₂ -ligand	electron count	Mo-Mo dist	ref
[Mo ₃ (μ ₃ -O)(μ ₂ -Cl) ₃ (OAc) ₃ (H ₂ O) ₃] ²⁺	O	Cl	8	2.550 (2)	17
[Mo ₃ (μ ₃ -O)(μ ₂ -Cl) ₃ (OAc) ₃ Cl] ²⁻	O	Cl	8	2.567 2.585, 2.58 [1] 2.579	16
[Mo ₃ (μ ₃ -O)(μ ₂ -Cl) ₃ (OAc) ₂ Cl] ⁻	O	Cl	8	2.591 (3) 2.616 (1), 2.60 [2] 2.583 (3)	16, 20
[Mo ₃ (μ ₃ -O)(μ ₂ -O) ₃ (C ₂ O ₄) ₃ (H ₂ O) ₃] ²⁻	O	O	6	2.486 (1)	5
[(Mo ₃ (μ ₃ -O)(μ ₂ -O) ₃) ₂ (EDTA) ₃] ⁴⁻	O	O	6	2.51 [1]	6
[Mo ₃ (μ ₃ -CCH ₃)(μ ₂ -Br) ₃ (OAc) ₃ (H ₂ O) ₃] ⁺	CCH ₃	Br	8	2.593 [1]	this work
[Mo ₃ (μ ₃ -S)(μ ₂ -S ₂) ₃ Cl] ³⁻	S	S ₂	6	2.755 (1) 2.755 (1), 2.571 [6] 2.743 (1)	16
[Mo ₃ (μ ₃ -S)(μ ₂ -S ₂) ₃ (S ₂ P(OEt) ₂) ₃ Cl]	S	S ₂	6	2.727 (1) 2.722 (1), 2.725 [3] 2.725 (1)	16
[Mo ₃ (μ ₃ -S)(μ ₂ -S ₂) ₃ (S ₂) ₃] ²⁻	S	S ₂	6	2.722 [5]	9
[Mo ₃ (μ ₃ -S)(μ ₂ -S) ₃ (CN) ₉] ⁵⁻	S	S	6	2.765 (7)	14
[Mo ₃ (μ ₃ -S)(μ ₂ -O) ₃ (Hnta) ₃] ²⁻	S	O	6	2.598 [?]	23

small quantitative differences that arise because of the appreciable differences (0.15–0.30 Å) in the Mo–Mo bond lengths in the two classes of clusters. Comparisons are made in Table IV. Because the Mo₃ triangle is smaller in the present case, the Mo–C–Mo angles are smaller, i.e., 80.2 [4]° compared to the range of 84.1 [1]° to 88.0 [3]° in the bicapped-type clusters. There would have been an even greater contraction in this angle had there not been a decrease in the Mo–C bond lengths, from the range of 2.05–2.08 Å down to 2.01 [1] Å.

Bridging Bromine Atoms. The presence of bridging (μ₂) bromine atoms is important since it adds further weight to the view that within the M₃(μ₃-X)(μ₂-X')₃ core of the general M₃X₁₃-type cluster, the μ₃ and μ₂ ligands can be varied quite widely indeed. A summary of data for such Mo₃ species is presented in Table V. It is, of course, likely that as these groups are made larger, there might be some stretching of the M–M bonds in order to accommodate them; this could, in an extreme case, destabilize the structure.

It will be noted that in the three species having μ₃-O and μ₂-Cl atoms, Mo₃(μ₃-O)(μ₂-Cl)₃ species, the Mo–Mo bond lengths are 2.55–2.60 Å whereas in the Mo₃O₄ cases this distance is shorter, viz., ca. 2.49 Å. However, the attribution of this increase entirely, or even partly, to the steric requirement of the μ-Cl atoms is rendered uncertain by the fact that the Mo₃O₄ species contain six-electron clusters while the Mo₃OCl₃ species contain eight-electron clusters. As noted when the first Mo₃OCl₃ species was reported,⁵ the additional electrons might occupy an MO that is sufficiently antibonding to be at least partly, or even entirely, responsible for the increased Mo–Mo distances. With the present compound, we can make another (though still imperfect) comparison. In the Mo₃(CCH₃)Br₃ situation, we have the same eight-electron cluster population as in the Mo₃OCl₃ species, but the Mo–Mo bond lengths are within the same range. Thus, the presence of the larger μ₂-Br atoms does not in itself force an increase in the size of the Mo₃ triangle. It could, of course, be that the replacement of μ₃-O by the μ₃-CCH₃ group tends to produce a contraction and that the simultaneous pair of changes, viz., μ₃-O → μ₃-CCH₃ and μ₂-Cl → μ₂-Br, leads to no net effect. It is certainly true that, in general, when μ₂-Cl groups are replaced by μ₂-Br groups, metal–metal separations increase. Clearly, if the blue hydrolysis product discussed earlier really contains the [Mo₃(μ₃-O)Br₃(O₂CCH₃)₃(H₂O)₃]²⁺ cation, as we have hypoth-

esized, it would be possible to get direct information on the effect of replacement of μ₂-Cl groups by μ₃-Br groups by determining its structure. Our efforts to get the blue substance in crystalline form are therefore continuing with this goal in mind.

It is interesting to note in Table V that on changing from Mo₃(μ₃-O)(μ₂-O)₃ to Mo₃(μ₃-S)(μ₂-O)₃, there is a small but significant increase in the Mo–Mo distance, as would be expected, and that on further replacement of the μ₂-O atoms by μ₂-S or μ₂-S₂ groups, there is a further substantial increase. Obviously, it would be interesting to prepare and structurally characterize a species with a Mo₃(μ₃-O)(μ₂-S)₃ core, and this is another goal of our continuing research.

Electronic Structure. As a general rule, trinuclear clusters of this geometric type formed by molybdenum have the metal atoms in the oxidation state of +4, which means that each metal atom has two 4d electrons available for metal–metal bonding. The total of six cluster electrons is exactly sufficient to form three Mo–Mo single bonds. From a delocalized molecular orbital point of view, it can be said that these six electrons occupy bonding orbitals of a₁ and e symmetry to give an (1a₁)²(1e)⁴ configuration.

However, as was first pointed out a long time ago,²¹ there is another a₁ orbital of approximately nonbonding character, 2a₁, lying at only slightly higher energy than the 1e orbital, and it was suggested that this could, in some cases, be occupied by one or two electrons without destabilizing the M₃X₁₃-type structure. In the solid state, Nb₃Cl₈ provided an early example of the situation in which this orbital is singly occupied, giving a (1a₁)²(1e)⁴(2a₁) configuration.

In 1979, the first example of a compound containing a discrete M₃X₁₃-type cluster with a total of eight electrons was reported,¹⁷ and it has been explicitly shown in a theoretical discussion²² that this cation, [Mo₃(μ₃-O)(μ₂-Cl)₃(O₂CCH₃)₃(H₂O)₃]²⁺, may be assigned a (1a₁)²(1e)⁴(2a₁)² electron configuration. Since then, two other examples, both also having the Mo₃(μ₃-O)(μ₂-Cl)₃ central core, have been reported.^{16,20}

The present compound significantly enlarges the scope of these eight-electron compounds since it introduces the new components, μ₃-CCH₃ and μ₂-Br, and shows that there may be a considerable

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variety of the eight-electron systems. The relative stabilities of the six-electron and eight-electron systems are probably influenced more by the nature of the core ligands, i.e., the μ_3 and μ_2 groups or atoms, than by the remaining nine ligand atoms, but we do not yet know what the important factors are. It will be necessary to obtain and study further examples of both the six-electron and eight-electron types before this relationship can be understood.

Acknowledgment. We thank the U. S. National Science

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Foundation and the U. S.-Israeli Binational Science Foundation for support.

Registry No. $[\text{Mo}_3(\text{CCH}_3)(\text{O}_2\text{CMe})_3\text{Br}_3(\text{H}_2\text{O})_3]\text{ClO}_4$, 95344-37-9; $[\text{Mo}_3(\text{CCH}_3)(\text{O}_2\text{CMe})_3\text{Br}_3(\text{H}_2\text{O})_3]\text{ClO}_4 \cdot 4\text{H}_2\text{O}$, 95344-38-0; $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, 14221-06-8; $[\text{Mo}_3(\text{CCH}_3)_2(\text{O}_2\text{CMe})_6(\text{H}_2\text{O})_3]^+$, 95344-39-1; $\text{Mo}(\text{CO})_6$, 13939-06-5.

Supplementary Material Available: Tables of structure factors and anisotropic thermal parameters, details of the X-ray work, and a stereoview of the unit cell contents (23 pages). See any current masthead page for ordering information.

Unique Bonding and Geometry in η -Cyclopentadienyltantalum-Diene Complexes. Preparation, X-ray Structural Analyses, and EHMO Calculations

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Abstract: From the 1:1 reactions of tetrachloro(cyclopentadienyl)tantalum or tetrachloro(pentamethylcyclopentadienyl)tantalum (LTaCl_4 , L = Cp, Cp*) with a series of (2-butene-1,4-diyl)magnesiums, six kinds of tantalum-mono(diene) complexes of the formulation $\text{CpTaCl}_2(\text{diene})$ or $\text{Cp}^*\text{TaCl}_2(\text{diene})$ were isolated as air-sensitive purple crystals and characterized by their NMR and mass spectra as well as by X-ray analysis. $\text{CpTaCl}_2(\text{butadiene})$ crystallizes in space group $P2_1/n$ with $a = 6.615$ (1) Å, $b = 10.962$ (1) Å, $c = 14.384$ (2) Å, $\beta = 97.02$ (1)°, and $Z = 4$. Pertinent bond distances are C(1)–C(2) = 1.458 (16), C(2)–C(3) = 1.375 (16) Å, Ta–C(1) = 2.258 (12) Å, and Ta–C(2) = 2.424 (11) Å. The dihedral angle between the C(1)–Ta–C(4) and C(1)–C(2)–C(3)–C(4) planes is 94.9°. These data support the view that the complex assumes the novel bent metallacyclopent-3-ene structure. Six kinds of bis(diene) complexes of the type $\text{LTa}(\text{diene})_2$ (L = Cp, Cp*) including mixed-diene complexes were also prepared in a similar manner and isolated as air-sensitive yellow crystals. $\text{CpTa}(2,3\text{-dimethylbutadiene})_2$ belongs to the orthorhombic space group $Pnma$ with $a = 8.947$ (1) Å, $b = 12.291$ (2) Å, $c = 13.512$ (2) Å, and $Z = 4$. The two diene ligands assume a unique geometrical conformation; one of the dienes lies supine and the other prone looking with the Cp ring upward. $\text{Cp}^*\text{Ta}(2,3\text{-dimethylbutadiene})_2$ crystallizes in space group $P2_1$ with $a = 10.468$ (2) Å, $b = 12.442$ (2) Å, $c = 8.020$ (1) Å, $\beta = 106.68$ (2)°, and $Z = 2$. The plane of one of the dienes is nearly parallel to the Cp* ring, the dihedral angle being 18.5°, while the plane of the other diene makes a dihedral angle of 83.5° with the Cp* ring. Extended-Hückel calculations revealed that the observed orientation of the butadiene ligand in $\text{CpTaCl}_2(\text{C}_4\text{H}_6)$ (lying supine) is 15.7 kcal more stable than the geometrical isomer where the butadiene lying prone is coordinated to metal. Among the three structures considered for $\text{CpTa}(\text{butadiene})_2$, the observed structure is computed to be the most stable, 28.4 kcal more stable than the supine-supine geometry where the two dienes are oriented toward the Cp ring and 23.3 kcal more stable than another isomer (prone-prone) where the CH_2 groups at the diene termini are pointed away from the Cp ring.

In recent years the chemistry of metal-diene complexes has entered a new phase with the advent of highly reactive group 4⁴⁸ metal-diene complexes such as $\text{Cp}_2\text{M}(\text{diene})$ (M = Ti, Zr, Hf) which furnish the synthetically useful selective carbon-carbon bond-forming reactions, reflecting their polar M–C bondings.²⁻⁴

They react not only with alkenes, dienes, and alkynes but also with carbonyl compounds such as aldehydes, ketones, and esters with extremely high regioselectivity. Their structural pattern is also unique and the s-trans coordination of a diene to a mononuclear metal complex has first been found in this field with Zr and Hf complexes.^{5,6} The X-ray and NMR analyses of the s-cis isomers of zirconium-1,3-diene complexes revealed that they have the novel bent metallacyclopent-3-ene structure (1) in which the dihedral angle between the planes defined by C(1), M, C(4) and C(1), C(2), C(3), C(4) atoms are greater than 90° and the C(2)–C(3)

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