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Octakis(trimethylsilylmethyl)dioxotetramolybdenum. A novel tetranuclear compound with two localized metal–metal triple bonds

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Dedicated to Professor Sheldon Shore (Super Sheldon), alias the Red Boron, on the occasion of his 70th birthday.

Abstract

1,2-$Mo_2Br_2(CH_2SiMe_3)_4$ reacts with water (two equivalents) in hexane solution in the presence of $HNPr^i_2$ (four equivalents) to give the dark red crystalline compound $Mo_4O_2(CH_2SiMe_3)_8$ which has been characterized by single crystal X-ray crystallography in the solid-state and by NMR spectroscopy in solution. Two ethane-like $OC_2Mo{\equiv}MoC_2O$ units are held together by the agency of a pair of oxo bridges: Mo–Mo = 2.20(1) Å (ave), Mo–O = 1.89(1) Å (ave), Mo–C = 2.11(2) Å (ave), Mo–Mo–C = 101(1)° (ave), Mo–Mo–O = 105(1)° (ave) and Mo–O–Mo = 133(1)° (ave). © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Octakis(trimethylsilylmethyl)dioxotetramolybdenum; Metal–metal triple bonds; Oxo bridges: Mo–Mo

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1. Introduction

Tetranuclear compounds formed from the coupling of dinuclear compounds having M–M multiple bonds have two limiting bonding descriptions. 1) the M–M multiple bonds remain discrete and are merely brought in to close proximity through the agency of bridging ligands. 2) the M–M bonding is delocalized over the M_4 unit which is now best described as a cluster. Compounds of the formula $Mo_4X_8L_4$, where X = a halide and L = tertiary phosphine, are formed from M–M quadruply bonded complexes $Mo_2X_4L_2(MeOH)_2$ by the elimination of MeOH [1]. They have a common rectangular M_4 unit but when X = I the M–M quadruple bonds are retained whereas for X = Cl there is electron delocalization and the M_4 unit is well described as a metallocyclobutadiyne. Similarly, for tetranuclear compounds of formula $Mo_4X_4(OR)_8$ which are formed from the M–M triply bonded complexes $Mo_2(OR)_6$ by the replacement of OR by X, where X = halogen, the structures are dependent on the nature of R and X [2]. For R = ^{t}Bu and X = F there is a bisphenoidal Mo_4 unit with two localized Mo–Mo triple bonds and four non-bonding Mo-to-Mo distances of 3.5 Å [3]. The two $(Mo{\equiv}Mo)^{6+}$ units are brought together through the agency of fluoride bridges. However, in the structures of $Mo_4X_4(O^iPr)_8$ we find terminal halide bonds and bridging alkoxides. In $Mo_4Cl_4(O^iPr)_8$ there is a square of molybdenum atoms but for $Mo_4Br_4(O^iPr)_8$ there is a Mo_4-butterfly or opened-tetrahedron. Both the chloride and bromide complexes are 12-electron clusters. The compound $Mo_4(O^iPr)_{10}(OMe)_2$, which is formed upon partial alcoholysis of $Mo_2(O^iPr)_6$ with MeOH [4], adopts a rectangular structure akin to that of $Mo_4I_8L_4$ but with localized Mo–Mo triple bonds, $[Mo_2(O^iPr)_4(\mu\text{-}O^iPr)(\mu\text{-}OMe)]_2$ whereas $W_2(O^iPr)_6$ dimerizes reversibly to give $W_4(O^iPr)_{12}$ which has a diamond structure with alternating short, 2.5 Å, and long, 2.70 Å, W–W distances [5]. Related compounds of formula $M_4(OR)_{12}$, where M = Mo and W and R is less sterically demanding, e.g. R = CH_2^tBu, adopt yet a different type of structure based on an Mo_4-butterfly but with a rather

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asymmetric disposition of ligands [6]. One of the wing-tip metal atoms becomes six-coordinate with respect to oxygen ligation and the others remain only four coordinate. The structural motifs of these Mo_4 units are summarized by the line drawings shown in Fig. 1. They are the square, the rectangle, the diamond, the parallelogram, the bisphenoid and the butterfly or opened tetrahedron. We describe here our discovery of an interesting variation on this theme in the preparation and structural characterization of $Mo_4O_2(CH_2SiMe_3)_8$ wherein the metal atoms are only coordinated to three ligand atoms.

2. Results and discussion

2.1. Preparation

The new compound was discovered serendipitously in the reaction of the chiral amine (S) HN(Me)CH(Me)Ph with $1,2\text{-}Mo_2Br_2(CH_2SiMe_3)_4$. Interest in this reaction arose from the fact that the reaction between $1,2\text{-}Mo_2Br_2(CH_2SiMe_3)_4$ and $HNMe_2$ proceeds to give $1,1'\text{-}Mo_2Br(NMe_2)(CH_2SiMe_3)_4$ where one Mo center is chiral. The reaction of a chiral amine should lead to a compound of formula $1,1'\text{-}Mo_2Br(NR^*R)(CH_2SiMe_3)_4$ for which chirality at one Mo center could manifest in NMR spectroscopy. Two optically active species would be present Mo(*R*)-amine(*S*) and Mo(*S*)-amine(*S*) and the mechanism of amide-for-bromide replacement in a reaction employing the chiral (*S*)-amine might well be expected to favor one over the other. Since the two are diastereomers a subsequent crystallization could yield access to a pure compound with a resolved stereochemistry at Mo. The studies of the reaction between $1,2\text{-}Mo_2Br_2(CH_2SiMe_3)_4$ and (*S*) HN(Me)CH(Me)Ph in hexane failed to yield the desired product but instead gave a dark red crystalline compound, $Mo_4O_2(CH_2SiMe_3)_8$. Reasoning that the commercially supplied chiral amine was wet we felt a suitable synthesis of the compound might involve the reaction between $1,2\text{-}Mo_2Br_2(CH_2SiMe_3)_4$ and water in the presence of a bulky base which would act as a trap for the HBr and a hydrogen bonding medium for the water in a solvent such as hexane. Indeed, the reaction shown in Eq. (1) yields the title compound in greater than 50% yield after crystallization.

$$2[1,2\text{-}Mo_2Br_2(CHSiMe_3)_4] + 2H_2O + 4{}^iPr_2NH \rightarrow Mo_4O_2(CH_2SiMe_3)_8 + 4[{}^iPr_2NH_2Br] \quad (1)$$

2.2. Characterization data for $Mo_4O_2(CH_2SiMe_3)_8$

The ^1H- and $^{13}C\{^1H\}$-NMR spectra of $Mo_4O_2(CH_2SiMe_3)_8$ are temperature independent and reveal only one type of CH_2SiMe_3 ligand. The methyl-

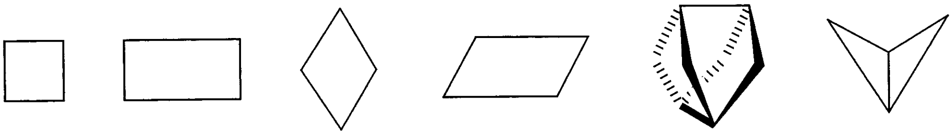

Fig. 1. Structural motifs of the M_4 units showing from left to right the square, rectangle, diamond, parallelogram, bisphenoid, and the butterfly-structure or opened-tetrahedron.

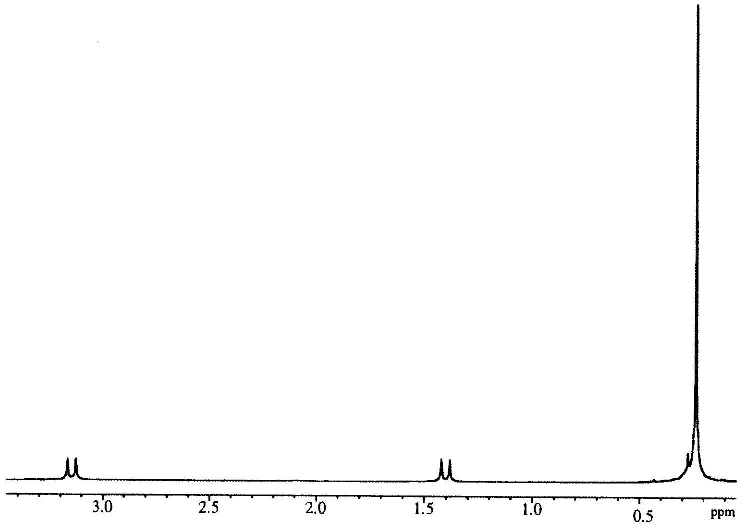

Fig. 2. ^1H-NMR of $Mo_4O_2(CH_2SiMe_3)_8$ at 20°C, 300 MHz in toluene-d_8.

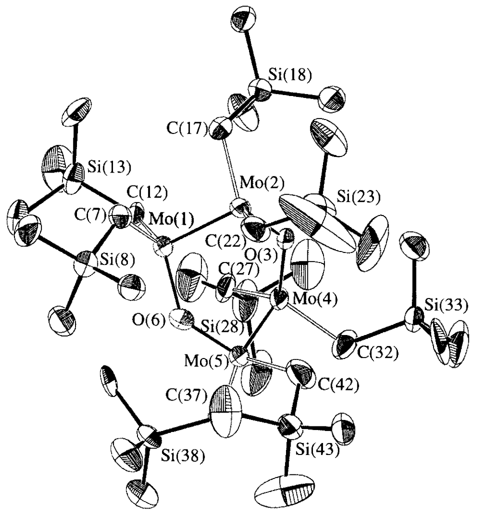

Fig. 3. Molecular structure of the molecule $Mo_4O_2(CH_2SiMe_3)_8$.

ene protons are, however, diastereotopic as shown in Fig. 2. The NMR data, though entirely reconcilable with the X-ray structure (vide infra), are not uniquely informative with regard to the structure present in solution.

2.3. Solid-state and molecular structure

An ORTEP drawing of the molecular structure found in the solid state is given in Fig. 3. This drawing also shows the atom numbering scheme and selected bond distances and angles are given in Table 1. Another view of the molecule is given in Fig. 4.

The Mo_4 unit, though not planar, is approaching that of a rectangular unit with two short Mo–Mo distances, 2.20(1) Å (ave) and four long non-bonding distances all greater than 3.5 Å. Clearly, there are two localized Mo≡Mo bonds which are linked by a single pair of oxo bridges. The Mo–O distances span a small range 1.88(1)–1.90(1) Å and are typical of Mo–OR distances in compounds such as $Mo_2(OCH_2{}^tBu)_6$ [7]. The Mo–O–Mo angles are 133(1)° which, together with the short Mo–O distances, are similar to Mo–O–C angles in M–OR groups that have both σ and π metal bonding. The local $OC_2Mo{\equiv}MoC_2O$ unit is a near eclipsed ethane-like geometry with Mo–Mo–C=101(1) (ave) and Mo–Mo–O=105(1)° (ave). The distances and angles are as might have been expected for a $Mo_2(CH_2SiMe_3)_4(OR)_2$ compound based on our knowledge of the structures of $Mo_2(CH_2SiMe_3)_6$ [8], $Mo_2(OCH_2{}^tBu)_6$ and $W_2({}^nBu)_2(O^iPr)_4$ [9].

3. Concluding remarks

The synthesis and molecular structure of $Mo_4O_2(CH_2SiMe_3)_8$ provides a new structural type for linked dimers of dimers derived from compounds with metal–metal triple bonds. The two localized Mo–Mo triple bonds are brought together through the agency of a single pair of bridging ligands in contrast to the use of two pairs of bridges as in the structures of $Mo_4(\mu\text{-}F)_4(O^tBu)_8$ and $Mo_4(\mu\text{-}OMe)(\mu\text{-}O^iPr)_2(O^iPr)_8$ which have bisphenoid and rectangular Mo_4 units, respectively. The present findings bear further testimony to fact that in the coupling of Mo≡Mo bonds to give tetranuclear complexes — two and two make four in more ways than one. One can still but speculate upon the structures of compounds of formula $Mo_4E_2(CH_2SiMe_3)_8$, where E=S, Se and Te, for example, which could be related to the present oxo compound or could be quite different.

4. Experimental

All manipulations were carried out under an inert atmosphere of oxygen-free UHP-grade argon using standard Schlenk techniques or under a dry and oxygen-free atmosphere of nitrogen in a Vacuum Atmospheres Co. Dry Lab System. Hexane was degassed and distilled from sodium benzophenone ketyl under nitro-

Table 1
Selected bond distances (Å) and angles (°) for $Mo_4O_2(CH_2SiMe_3)_8$

Bond distances			
Mo(1)–Mo(2)	2.208(2)	Mo(4)–Mo(5)	2.193(2)
Mo(1)–O(6)	1.890(7)	Mo(4)–O(3)	1.902(7)
Mo(2)–O(3)	1.886(7)	Mo(5)–O(6)	1.893(7)
Mo(1)–C(7)	2.08(1)	Mo(4)–C(32)	2.14(1)
Mo(1)–C(12)	2.11(1)	Mo(4)–C(27)	2.09(1)
C(7)–Si(8)	1.86(1)	C(32)–Si(33)	1.85(1)
C(12)–Si(13)	1.83(1)	C(27)–Si(28)	1.89(1)
Mo(2)–C(17)	2.08(1)	Mo(5)–C(37)	2.13(1)
Mo(2)–C(22)	2.10(1)	Mo(5)–C(42)	2.11(1)
C(17)–Si(18)	1.90(1)	C(37)–Si(38)	1.81(1)
C(22)–Si(23)	1.84(1)	C(42)–Si(43)	1.87(1)
Bond angles			
Mo(1)–Mo(2)–O(3)	104.6(2)	Mo(4)–Mo(5)–O(6)	105.0(2)
Mo(1)–O(6)–Mo(5)	133.0(4)	Mo(2)–O(3)–Mo(4)	133.3(3)
Mo(1)–Mo(2)–C(17)	101.3(3)	Mo(4)–Mo(5)–C(42)	102.0(4)
Mo(1)–Mo(2)–C(22)	101.1(3)	Mo(4)–Mo(5)–C(37)	100.6(4)
Mo(1)–C(12)–Si(13)	118.9(6)	Mo(4)–C(27)–Si(28)	120.5(6)
Mo(1)–C(7)–Si(8)	118.9(6)	Mo(4)–C(32)–Si(33)	121.9(5)
Mo(2)–Mo(1)–O(6)	102.3(2)	Mo(5)–Mo(4)–C(32)	103.8(3)
Mo(2)–Mo(1)–C(12)	104.9(3)	Mo(5)–Mo(4)–C(27)	98.0(4)
Mo(2)–Mo(1)–C(7)	100.8(3)	Mo(5)–Mo(4)–O(3)	102.1(2)
Mo(2)–C(17)–Si(18)	116.5(5)	Mo(5)–C(42)–Si(43)	116.4(6)
Mo(2)–C(22)–Si(23)	118.9(6)	Mo(5)–C(37)–Si(38)	118.1(6)
C(17)–Mo(2)–C(22)	113.7(4)	C(27)–Mo(4)–C(32)	112.1(5)
C(12)–Mo(1)–Si(8)	111.0(4)	C(37)–Mo(5)–C(42)	115.6(5)
O(6)–Mo(1)–C(12)	114.9(9)	O(6)–Mo(5)–C(37)	114.2(5)
O(6)–Mo(1)–C(7)	120.1(4)	O(6)–Mo(5)–C(42)	116.4(4)

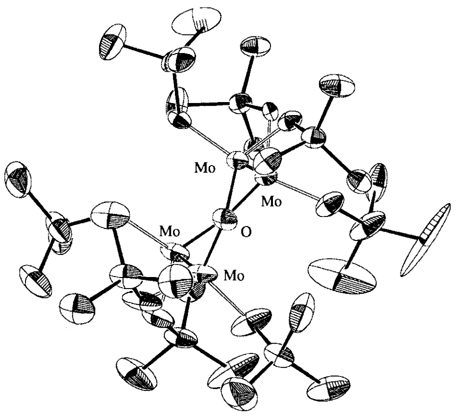

Fig. 4. Alternate view of the molecule $Mo_4O_2(CH_2SiMe_3)_8$, showing the deviation of the Mo atoms from planarity. In this view one oxygen eclipses the other.

Table 2
Summary of crystallographic data for the molecule $Mo_4O_2(CH_2SiMe_3)_8$

Empirical formula	$C_{32}H_{88}Mo_4O_2Si_8$
Formula weight	1113.49
Space group	$P\bar{1}$
a (Å)	21.796(17)
b (Å)	22.909(17)
c (Å)	12.274(10)
γ (°)	96.88(3)
K (°)	102.79(4)
N (°)	72.45(3)
Temperature (K)	108
Z	4
V (Å^3)	5688.96
D_{calc} (g cm^{-1})	1.300
σ (Å)	0.71069
Ω (m^{-1})	10.508
R (F)	0.899
$R_w(F)$	0.0290

gen. Toluene-d_8 was degassed and stored over 4 Å sieves for 24 h prior to use. Diisopropyl amine was purchased from Aldrich, degassed, vacuum transferred and stored over sieves for 24 h prior to use. 1,2-$Mo_2Br_2(CH_2SiMe_3)_4$ was prepared according to a modified literature procedure [10]

NMR spectra were obtained on a 300 MHz Varian Gemini 2000. All ^{1}H-NMR chemical shifts are reported in ppm relative to the ^{1}H impurity in toluene-d_8 at δ 2.09.

4.1. Preparation of $Mo_4O_2(CH_2SiMe_3)_8$

1,2-$Mo_2Br_2R_4$ (0.100 g, 0.143 mmol) was added to a round-bottomed flask. Hexane (20 ml) was added and the solution was cooled to −50°C. H_2O (0.143 mmol, 2.8 μl) was added to diisopropyl amine (0.286 mmol, 40 μl) in a separate round-bottomed flask containing 5 ml of hexane and this solution was then added to the hexane solution of 1,2-$Mo_2Br_2R_4$ at −50°C. The solution was stirred for 5 h while warming to 20°C. Filtration through a medium frit with a Celite pad and removing the solvent in vacuo gave dark needle crystals suitable for single crystal X-ray diffraction. NMR data were obtained at 20°C in toluene-d_8. ^{1}H: δ 0.24(s, SiMe_3, 72H), 1.40(d, CH_2, $J_{H\text{–}H} = 12$ Hz, 8H), 3.15(d, CH_2, $J_{H\text{–}H} = 12$ Hz, 8H). $^{13}C\{^1H\}$: δ 2.49 (SiMe_3), 62.11 (CH$_2$).

4.2. X-ray crystal structure determination of the molecule $Mo_4O_2(CH_2SiMe_3)_8$

Single crystals of $Mo_4O_2(CH_2SiMe_3)_8$ suitable for X-ray diffraction study were obtained by the slow evaporation of hexane from a saturated hexane solution containing $Mo_4O_2(CH_2SiMe_3)_8$. A nearly equidimensional fragment (0.28 × 0.25 × 0.25 mm) was cleaved from a typical crystal using standard inert atmosphere handling techniques. The sample was then affixed to the glass fiber on a goniometer head using silicone grease and transferred to the goniostat where it was cooled to 108 K for characterization and data collection. Data were collected on a Bruker SMART-6000 sealed-tube system comprising a three-circle platform goniostat, an HOG crystal monochromator, a four kilopixel by four kilopixel single-chip CCD-based detector, a K761 high voltage generator, and a PC interface running Bruker's SMART software. The Bruker SMART autoindexing program was used to determine that the crystal possessed no symmetry or systematic absences, indicating a triclinic space group (Table 2). Subsequent solution and refinement confirmed this choice. The data were collected using the standard hemisphere setting for the SMART-6000. Data were integrated and merged using SAINT, and the structure was solved using direct methods (SHELXTL) and Fourier techniques. A slight disorder is present in one of the CH_2SiMe_3 groups [C(88)–C(92)] with two nearly equal configurations located and refined. In addition the anisotropic thermal parameters indicate that partial disorder may be present in several additional CH_2SiMe_3 groups. The disorder is shown in the ORTEP plot in Fig. 3. A final difference Fourier was featureless, the largest peaks being 1.07e Å^{-3}.

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC 149162. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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References

[1] (a) R.N. McGinnis, T.R. Ryan, R.E.J. McCarley, J. Am. Chem. Soc. 100 1978 7900. (b) T.R. Ryan, R.E. McCarley, Inorg. Chem. 21 1982 2072. (c) F.F. Cotton, M.J. Shang, J. Cluster Sci. 1991 2 121.

[2] M.H. Chisholm, D.L. Clark, J. Errington, K. Folting, J.C. Huffman, Inorg. Chem. 27 (1988) 2701.

[3] M.H. Chisholm, D.L. Clark, J.C. Huffman, Polyhedron 4 (1985) 1203.

[4] M.H. Chisholm, C.E. Hammond, M.J. Hampden-Smith, J.C. Huffman, W.G. Van Der Sluys, Angew. Chem. Int. Ed. Engl. 26 (1987) 904.

[5] M.H. Chisholm, D.L. Clark, M.J. Hampden-Smith, J. Am. Chem. Soc. 111 (1989) 574.

[6] M.H. Chisholm, K. Folting, C.E. Hammond, M.J. Hampden-Smith, K.G. Moodley, J. Am. Chem. Soc. 111 (1989) 5300.

[7] M.H. Chisholm, F.A. Cotton, C.A. Murrillo, W.W. Reichert, Inorg. Chem. 16 (1977) 1801.

[8] F. Huq, W. Mowat, A. Shortland, A.C. Skapski, G. Wilkinson, Chem. Commun. 1971 1079.

[9] M.H. Chisholm, B.W. Eichorn, K. Folting, J.C. Huffman, R.J. Tatz, Organometallics 5 (1986) 1599.

[10] M.H. Chisholm, I.P. Rothwell, K. Folting, J.C. Huffman, Organometallics 1 (1982) 251.