Structure of Hexakis(trimethylsilylmethyl)dimolybdenum: The First Compound Reported to have a Mo≡Mo Bond

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The crystal and molecular structures of hexakis(trimethylsilyl-methyl)dimolybdenum, $Mo_2(CH_2SiMe_3)_6$, were determined from three-dimensional X-ray diffraction data about 33 years ago using the facilities available at Imperial College, London, U.K. The crystals are monoclinic with unit-cell dimensions: a = 31.20 Å, b = 12.457 Å, c = 23.415 Å, β = 112.17°, space group Pc and Z = 8. The complex is dimeric and there are four crystallographically independent dimers, all having the same structure. In each dimer the two molybdenum atoms are joined by a short Mo≡Mo bond (2.168 Å) and each molybdenum atom has a distorted tetrahedral coordination, with Mo—C bonds of 2.124 Å. The configuration of the methylene groups in the dimer, which has approximately $32(D_3)$ symmetry is staggered. The Mo—Mo triple bond is considered to be made up of d_{Z^2} orbitals forming the σ-bond and the overlap of two sets of d_{xz} and d_{yz} orbitals of both metal atoms forming the two π-bonds.

Key Words: Molybdenum, Triple bond, Silylmethyl, Monoclinic.

INTRODUCTION

Compounds with multiple bonds between atoms represent an important class in non-directional coordination chemistry[1]. The study of transition-metal complexes, multiple metal-metal bonds including structures, bonding and spectroscopies has been the subject of considerable interest during the past few decades[2]. Many compounds have been prepared in which metal atoms are united by bonds of order greater than one, including those of order 4. Among the transition elements, molybdenum is the most prolific former of metal-metal triple bonds[3], characterized by metal-metal distances of 2.2–2.4 Å and an M_2X_6 coordination geometry in which the ligands assume an ethane-like staggered conformation. Hexakis(trimethylsilylmethyl)dimolybdenum was the first compound reported to have a molybdenum-molybdenum triple bond. The structure of the compound was determined over thirty years ago by single crystal X-ray diffractometry. Because the complex is dimeric and there are four crystallographically independent dimers, all with the same structure, solution of the structure proved to be

difficult. This paper describes the solution of the structure of hexakis(trimethyl-silylmethyl)dimolybdenum as it was carried out in the Department of Chemistry, Imperial College, London in the year 1971[4].

EXPERIMENTAL

Hexakis(trimethylsilylmethyl)dimolybdenum, prepared from metathetic reaction involving molybdenum halide and organolithium reagent involving β-hydrogen[4] stabilized by Me_3SiCH_2 ligand, crystallizes from light petroleum as yellow plates. The crystals are air-sensitive and decompose in air within a few minutes.

Crystal data

$C_{24}H_{66}Si_6Mo_2$, M = 715.2 g mol^{-1}, monoclinic, space group, Pc, with unit-cell dimensions: a = 31.20 Å, b = 12.457 Å, c = 23.415 Å, β = 112.17°, U = 8427 Å^3, Z = 8, d_c = 1.13 g cm^{-3}, F(000) = 3024, μ(Cu-K_α) = 67.3 cm^{-1}. The structure of the compound was solved using the facilities at Imperial College, London. Preliminary Weissenberg photographs of crystals sealed under nitrogen in a Lindemann tube showed that the systematic absences were: $h0l : l = 2n + 1$ and $0k0 + k = 2n + 1$. These are consistent with the space group $P2_1/c$. The successful solution and refinement of the structure, however, showed that the space group was actually Pc, that the three-dimensional arrangement of the molecules was not consistent with the space group $P2_1/c$ and $0k0$ absences arose from the special arrangement of the molecules in terms of y.

A crystal of approximate size $0.9 \times 0.8 \times 0.3$ mm was selected, sealed in a Lindemann tube and intensity was measured on a Siemens off-line automatic diffractometer. CuK_α radiation at a take-off angle of 4.5°, an Niβ filter and a Na(tl)I scintillation counter were used. The θ–2θ scan technique was used, with a five-point measuring procedure[5]. A total of 3475 independent reflections were measured (to θ = 35°) of which 539 were judged to be unobserved. The 402 reflection was used as a reference every 25 reflections. There was no significant change in the net count for the reflection during the data collection (approximately 12 d).

Solution and refinement of structure

The solution and refinement of the structure were performed using X-ray '63 system[6]. Calculations were carried out on the Imperial College IBM7094 computer.

The solution of the structure proved to be difficult. A three-dimensional Patterson was initially interpreted in terms of space group $P2_1/c$ and a 'solution' was found. Although the heavier atoms seemed to refine reasonably, the bond lengths were implausible and no sensible structure seemed to develop as apparent atoms were added. Refinement levelled off at R of about 0.25. The Patterson was re-examined and eventually a solution was found which involved eight independent molybdenum atoms in space group Pc, which accounted for all the major peaks in the Patterson map. With only four molybdenum atoms R was 0.397, with four more metal atoms and sixteen silicon atoms refined R dropped to 0.230.

Successive difference Fouriers located a further eight silicon atoms and 96 carbon atoms. With molybdenum atom anisotropic refinement gave R = 0.099. An absorption correction was then applied. The correction was made according to the method of Busing and Levy using an $8 \times 8 \times 8$ grid, with crystal path lengths determined by vector analysis procedure of Coppens et al.[7] Refinement as previously reduced R to 0.071. Because of the large number of atoms refinement was a slow process. The procedure was to refine the maximum allowable number, and include the rest as "fixed contribution". Rotation ensured that all atoms were refined until shifts were acceptably small. A search was made for hydrogen atoms—eventually a total of 261 out of 264 were located with a fair degree of confidence. These hydrogens were included as a fixed contribution with isotropic temperature factors of the parent carbon atoms and were not refined. The R factor dropped by more than 0.02. The silicon atoms were now allowed to refine anisotropically to reduce R to 0.047. Further recycling, application of anomalous dispersion correction for molybdenum and silicon and introduction of a weighting scheme reduced R to a final value of 0.042. The weighting scheme used was that due to Hughes where $w = 1$ for $F < F^*$, $w = F^*/F$ for $F \geq F^*$, with $F^* = 100$. Application of the weighting scheme reduced R fractionally and gave lower standard deviations. The scattering factors used were those tabulated by Cromer and Waber[8] and the real and imaginary parts of the anomalous dispersion correction for molybdenum and silicon were those given by Cromer[9]. Crytallographic data for $Mo_2(CH_2SiMe_3)_6$ have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC 257737.

RESULTS AND DISCUSSION

The complex exists in the form of dimeric units with all four independent dimers having the same structure (Fig. 1). Table-1 lists important bond lengths and bond angles. In each dimer the two molybdenum atoms are joined by a short metal-metal bond of length ranging from 2.157–2.176 Å (mean is 2.168 Å). Each molybdenum has a distorted tetrahedral coordination, with $Mo-CH_2$ bond length of 2.124 Å. The configuration of the methylene groups in the dimer, which has approximate $32(D_3)$ symmetry is staggered. Fig. 2 shows a view of the molecule that illustrates the approximate threefold symmetry.

The Mo—Mo distance of 2.168 Å is considered as a triple bond, which is consistent with the fact the compound is diamagnetic. It consists of a σ-bond and two π-bonds. The σ-bond is formed by the combining of d_{z^2} orbitals and the π-bonds are formed from the overlap of two sets of d_{xz} and d_{yz} orbitals. The triple bond has a cylindrical symmetry that exhibits unrestricted barrier to rotation. This distance falls within the reported range of Mo≡Mo distances from 2.162(1)–2.226(1) Å[1, 10].

As stated before, the configuration around each molybdenum is staggered as was found to be the case in many Mo_2X_6 complexes, where X can be alkyl, amide, alkoxide, thiolate, selenate and mixtures thereof[11]. The staggered configuration is believed to arise from the need to reduce steric clashing of ligands across the
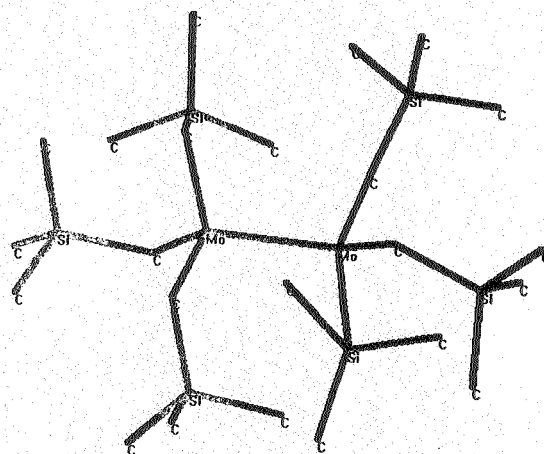
Fig. 1.   Structure of $Mo_2(CH_2SiMe_3)_6$; hydrogen atoms not shown

short $Mo\equiv Mo$ bond[10]. It should be noted that the preparation and characterization of eclipsed Mo_2X_6 and W_2X_6 compounds where X stands for (alkyl-imido)phenylboranes with very short metal-metal triple bond [Mo-Mo: 2.1612(6) and W-W: 2.2351(7) Å] have also been reported recently[10]. In these compounds, the coordination geometry of each metal centre was found to be nearly trigonal bipyramidal unlike that in the compound of the present study where it is nearly tetrahedral. It is suggested that the steric constraints imposed by the three-atom N—B—N bridge may be the determinant factor in the short metal bond lengths.
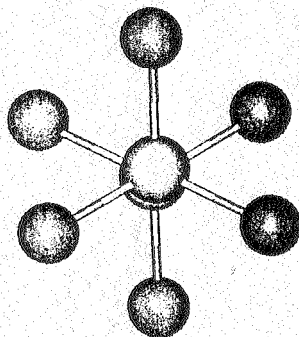

Fig. 2.   A view of the $Mo_2(CH_2SiMe_3)_6$ molecule looking almost down the metal-metal bond and showing the approximate threefold symmetry of the molecule; only molybdenum and methylene carbons bonded to molybdenum are shown

Recently a novel tetranuclear compound namely octakis(trimethylsilyl-methyl)dioxotetramolybdenum that contains two localized $Mo\equiv Mo$ bonds have also been described[12]. In the complex, two ethane-like units are held together by the agency of a pair of oxo bridges.

Density functional calculations were carried out on model compound Mo_2X_6 in which the methyl group replaces the trimethylsilylmethyl group of the compound in the present study using the program HyperChem 7.0.[13] The 2D contour plot of the electrostatic potential in the model compound (Fig. 3) illustrates the symmetry in the electrostatic potential.

TABLE-1
$Mo_2(CH_2SiMe_3)_6$ BOND LENGTHS (Å) AND ANGLES (°) WITH
STANDARD DEVIATION IN PARENTHESES

Bond	Length	Bond	Length
Mo(1)-Mo(2)	2.176(2)	Mo(5)-Mo(6)	2.175(4)
Mo(3)-Mo(4)	2.164(4)	Mo(7)-Mo(8)	2.157(3)
Mean Mo-Mo		2.168	
Mo(1)-C(131)	2.18(2)	Mo(5)-C(531)	2.10(2)
Mo(1)-C(121)	2.23(2)	Mo(5)-C(521)	2.12(2)
Mo(1)-C(111)	2.06(3)	Mo(5)-C(511)	2.13(3)
Mo(2)-C(211)	2.18(3)	Mo(6)-C(611)	2.12(3)
Mo(2)-C(221)	2.13(2)	Mo(6)-C(621)	2.16(3)
Mo(2)-C(231)	2.13(2)	Mo(6)-C(631)	2.17(2)
Mo(3)-C(331)	2.05(2)	Mo(7)-C(731)	2.15(2)
Mo(3)-C(321)	2.14(2)	Mo(7)-C(721)	2.07(3)
Mo(3)-C(311)	2.03(2)	Mo(7)-C(711)	2.14(2)
Mo(4)-C(411)	2.12(3)	Mo(8)-C(811)	2.06(2)
Mo(4)-C(421)	2.11(3)	Mo(8)-C(821)	2.07(3)
Mo(4)-C(431)	2.16(2)	Mo(8)-C(831)	2.19(2)
Mean Mo-CH_2		2.124	
Si-CH_2 (mean of 24)	1.871		
Si-CH_3 (mean of 72)	1.874		
Mo-Mo-CH_2 (mean of 24)	100.7		
CH_2-Mo-CH_2 (mean of 24)	116.6		
Mo-CH_2-Si (mean of 24)	121.4		
CH_2-Si-CH_3 (mean of 72)	110.4		
CH_3-Si-CH_3 (mean of 72)	108.4		

The crystal and molecular structure of hexakis(trimethylsilylmethyl)dimolybdenum, $Mo_2(CH_2SiMe_3)_6$, were determined from three-dimensional X-ray diffraction data over thirty three years ago. The crystals are monoclinic with unit-cell dimensions: a = 31.20 Å, b = 12.457 Å, c = 23.415 Å, β = 112.17°, space group Pc and Z = 8. The complex is dimeric and there are four crystallographically independent dimers, all having the same structure. In each dimer the two molybdenum atoms are joined by a short Mo≡Mo bond (2.168 Å) and each molybdenum atom has a distorted tetrahedral coordination, with Mo—C bonds of 2.124 Å. The configuration of the methylene groups in the dimer, which has approximately 32(D_3) symmetry is staggered.
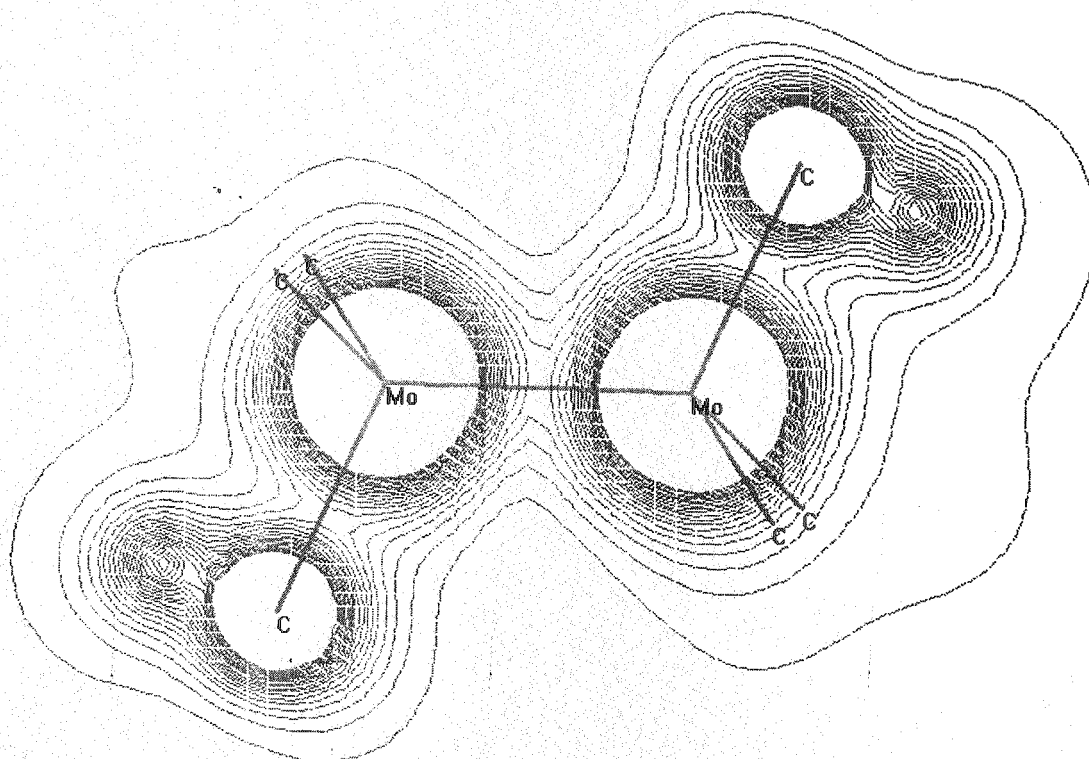
Fig. 3. 2D Contour plots of electrostatic potential around molybdenum atoms and six bonded carbon atoms

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