Synthesis and X-Ray Crystal Structure of a Unique Puckered Six-Membered Metallacycle in $Mo_6O_6Cl_6(\mu_3\text{-}O)_2(\mu_2\text{-}EtO)_6(\mu_2\text{-}Cl)_2$

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The cluster $Mo_6O_6Cl_6(\mu_3\text{-}O)_2(\mu_2\text{-}EtO)_6(\mu_2\text{-}Cl)_2$ exhibits a unique chair configuration of metal atoms incorporating 3 Mo–Mo single bonds and two highly distorted planar $Mo_3(\mu_3\text{-}O)$ bridges, an arrangement derived from the adoption of preferred coordination about the metal centres.

Although molybdenum-oxo complexes are used extensively as industrial catalysts, *e.g.* in the oxidation of propene to acrolein [eqn. (1)], there is comparatively little information on the mechanisms governing their activity.[1] There is evidence that eqn. (1) proceeds *via* the conversion of molybdenum-bound

$$H_2C{=}CHMe + O_2 \xrightarrow[Bi_2O_3,\ MoO_3\ \text{solid catalyst}]{350^\circ C,\ 2\ \text{atm pressure}} H_2C{=}CHCHO + H_2O \quad (1)$$

propene to allyl by hydrogen elimination, and recent research in this laboratory has been directed towards the preparation of allyl complexes to serve as models for these species. The complex $Cl_2OMo(\mu\text{-}EtO)_2(\mu\text{-}EtOH)MoOCl_2$ constitutes a potentially useful starting material,[2] and we now report its reaction with $Me_3Si(CH_2CH{=}CH_2)$ to form not the anticipated allyl-oxo-molybdenum product, but propene and the novel complex $Mo_6O_6Cl_6(\mu_3\text{-}O)_2(\mu_2\text{-}EtO)_6(\mu_2\text{-}Cl)_2$ **1**,† which contains a unique puckered six-membered molybdenum homocycle [eqn. (2)]. Interest in **1** is aroused not only by its unusual structure, but also because it can be viewed as a metal-oxide core surrounded by organic ligands, which confer solubility in common solvents like toluene and chloroform, so that **1** may serve as a soluble model for surface-bound intermediates on solid molybdenum oxide catalysts.

$$Cl_2OMo(\mu\text{-}EtO)_2(\mu\text{-}EtOH)MoOCl_2 \xrightarrow{\text{Excess } Me_3SiC_3H_5} \underset{\mathbf{1}}{Mo_6O_6Cl_6(\mu_3\text{-}O)_2(\mu_2\text{-}EtO)_6(\mu_2\text{-}Cl)_2} + H_2C{=}CHMe \quad (2)$$

In the solid state **1** consists of a cyclic array of six (Cl–Mo=O) units in a chair configuration (Fig. 1). Four sets of adjacent Mo atoms are singly bridged by μ_2-OEt units, one is doubly bridged by two such units, and one is asymmetrically bridged by two μ_2-Cl atoms (Fig. 2). The average oxidation state of the molybdenum is +5 and six electrons are used in the formation of three Mo–Mo bonds between Mo(1)–Mo(2)[2.6722(6) Å], Mo(3)–Mo(4)[2.7413(6) Å] and Mo(5)–Mo(6) [2.6653(7) Å], in keeping with the diamagnetism of the compound. Other Mo···Mo distances are beyond the commonly accepted non-bonding distance between metal atoms bridged by alkoxide ligands (3.3 Å).[7] Each metal atom participates in one of two planar $Mo_3(\mu_3\text{-}O)$ interactions in which μ_3-O bridges span one Mo–Mo single bond. The geometry about the triply bridging oxygen atoms is highly distorted with three significantly different Mo–O bond lengths [*e.g.* O(123)–Mo(1,2,3) 2.001(3), 1.935(3) and 2.194(3) Å, respectively] and Mo–O–Mo angles [*e.g.* 85.5(1), 107.2(1) and 164.2(2)° about O(123)]. The smallest angle and shortest bridges are associated with singly bonded Mo–Mo interactions [Mo(1)–Mo(2) and Mo(5)–Mo(6)], while the longest bridging bonds [O(123)–Mo(3) and O(456)–Mo(4)] are formed *trans* to terminal Mo=O bonds, consistent with the *trans* influence of such bonds. Overall, the complex exhibits approximate (non-crystallographic) C_2 symmetry.

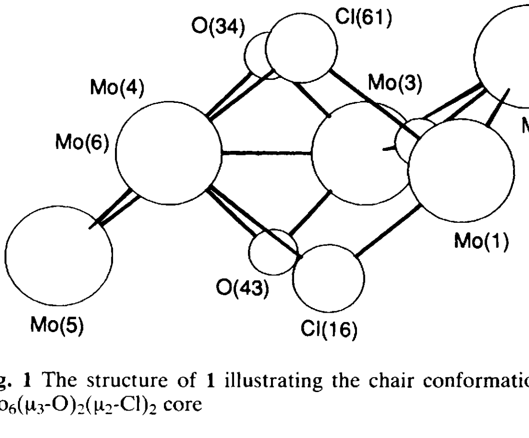

Fig. 1 The structure of **1** illustrating the chair conformation of the $Mo_6(\mu_3\text{-}O)_2(\mu_2\text{-}Cl)_2$ core

Hexametallic clusters and complexes are reasonably common, and exhibit a range of structural motifs, including octahedra, trigonal prisms, bridged squares and planar hexagons.[8] The only puckered structures appear in the complexes $M_6(O_2CCH_2R)_{12}$, where R = SPh or PPh_2, and M = Co, Cu or Ni. Metal–metal bonding is absent in these complexes, and **1** therefore represents a hitherto unknown structural type for transition-metal M_6 clusters. Aggregation of metal centres *via* μ_2-OR or μ_3-OR bridges can be regarded as involving the minimum of oligomerisation consistent with the preferred coordination geometry of the metal, as exemplified by $[Ti(OEt)_4]_4$, with its planar array of metal atoms incorporating two μ_3-O bridges.[7] Molybdenum analogues of this compound are formed in the clusters $Mo_4O_4(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OPr^i)_2(OPr^i)_2(py)_4$ (py = pyridine)[7] and $Mo_4O_4Cl_4(\mu_3\text{-}O)_2(\mu_2\text{-}OPr^n)_4(OPr^n)_2$,[9] which both exhibit two Mo–Mo singly-bonded interactions [lengths 2.600(1) and 2.669(2) Å, respectively] and pyramidal μ_3-OMo_3 bridges, with the only major structural differences arising from the number of electrons available for metal–metal bonding. The related hexatitanium complex $Ti_6(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OEt)_2(\mu\text{-}OAc)_8(OEt)_6$ **2** also contains a near-planar arrangement of metal atoms with no M–M bonding, although in this case the

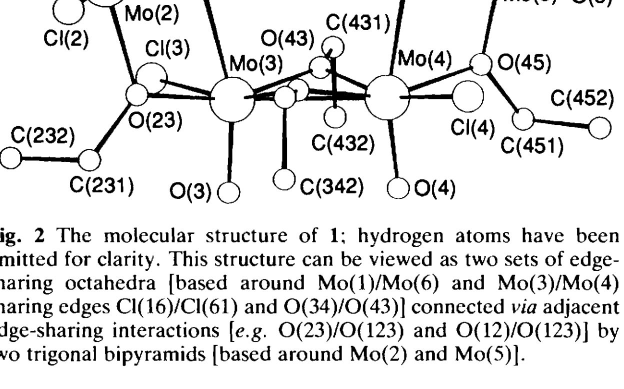

Fig. 2 The molecular structure of **1**; hydrogen atoms have been omitted for clarity. This structure can be viewed as two sets of edge-sharing octahedra [based around Mo(1)/Mo(6) and Mo(3)/Mo(4) sharing edges Cl(16)/Cl(61) and O(34)/O(43)] connected *via* adjacent edge-sharing interactions [*e.g.* O(23)/O(123) and O(12)/O(123)] by two trigonal bipyramids [based around Mo(2) and Mo(5)].

μ_3-O bridges are planar.[10] The structures of the (μ_3-O)M_3 moieties in **1** and **2** are therefore closely related, and the only major difference is the extreme distortion of the Mo–O–Mo bond angles in **1** (see above) imposed by the metal–metal bonds.

In terms of Green's MLX notation (X = 1-electron ligand, L = 2-electron ligand),[11] the structure of **2** can be correlated with the adoption of the very stable TiX_4L_2 coordination accommodated by two octahedral TiO_6 units sharing adjacent corners with double groups of edge-sharing TiO_6 octahedra, an arrangement which implies a near-planar array of metal atoms. Similarly, the structure of **1** derives from the particular stabilities of MoX_6L_2 and MoX_6L coordinations, and can be viewed (Fig. 2) as two sets of two edge-sharing octahedra [Mo(1), Mo(3), Mo(4) and Mo(6)] linked *via* adjacent edge-sharing interactions by two trigonal bipyramids [Mo(2) and Mo(5)], an arrangement which implies a chair or boat configuration of metal atoms. That the chair configuration is adopted is presumably dictated by the minimisation of steric interactions between the ligands.

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Footnote

† Well-formed red crystals of **1** were obtained in 29% yield by the reaction of $Cl_2OMo(\mu\text{-}EtO)_2(\mu\text{-}EtOH)MoOCl_2$ (4.0 mmol) with $Me_3Si(CH_2CH{=}CH_2)$ (23 mmol) in CH_2Cl_2 (10 cm^3) at 75 °C for 14 h. **1** was characterised by IR, which showed no bands attributable to ν(OH), ^1H NMR [(CD_2Cl_2) δ 1.56 (t, ^3J 6.8 Hz, Me), 1.73 (t, ^3J 6.8 Hz, Me), 2.08 (t, ^3J 7.0 Hz, Me), 4.86 (m, CH_2), 5.57 (m, CH_2), 5.95 (m, CH_2)], and magnetic susceptibility measurements, satisfactory elemental analyses and X-ray crystallography.

Crystal data: $M = 1168.7$, Triclinic, space group $P\bar{1}$, $a = 13.269(1)$, $b = 11.790(1)$, $c = 14.395(1)$ Å, $\alpha = 97.515(8)$, $\beta = 110.236(7)$, $\gamma = 115.911(8)°$, $U = 1791.5(3)$ $Å^3$, $Z = 2$, crystal size 0.30 × 0.45 × 0.15 mm, $\lambda = 0.71069$ Å, $T = 298$ K, $\mu = 24.904$ cm^{-1}, $D_c = 2.20$ g cm^{-3}. The data were reduced to a standard scale and Lorentz and polarisation corrections applied. The positions of all non-hydrogen atoms were located by direct methods (SIR92),[3] and an empirical absorption correction (DIFABS)[4] was applied (max. correction 1.27, min. 0.79). The structure was refined by full-matrix least-squares analysis (CRYSTALS)[5] to give, after weighting (Chebychev three term polynomial),[6] $R = 3.30$, $R_w = 4.04\%$ for 361 parameters and 4792 reflections with $I > 3\sigma(I)$ (6423 measured, 5627 unique), with anisotropic thermal parameters on all atoms. During the final cycles of least-squares refinement hydrogen atoms were placed in chemically reasonable positions on the carbon atoms. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 G. W. Keulks, L. D. Krenzke and T. M. Notermann, *Adv. Catal.*, 1978, **27**, 183; R. K. Grasselli and J. D. Burrington, *Adv. Catal.*, 1981, **30**, 133 and references cited therein.

2 C. Limberg, S. Parsons, A. J. Downs and D. J. Watkin, *J. Chem. Soc., Dalton Trans.*, accepted for publication.

3 A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Cryst.*, 1993, **26**, 343.

4 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

5 D. J. Watkin, J. R. Carruthers and P. W. Betteridge, *CRYSTALS User Guide (Issue 8)*, Chemical Crystallography Laboratory, University of Oxford, 1985.

6 J. R. Carruthers and D. J. Watkin, *Acta Crystallogr., Sect. A*, 1979, **35**, 698.

7 M. H. Chisholm, J. C. Huffman, C. C. Kirkpatrick, J. Leonelli and K. Folting, *J. Am. Chem. Soc.*, 1981, **103**, 6093 and references cited therein.

8 I. G. Dance, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, 1987, vol. 1, p. 135.

9 J. A. Beaver and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 1973, 1376.

10 I. Gautier-Luneau, A. Mosset and J. Galy, *Z. Kristallogr.*, 1987, **180**, 83.

11 M. L. H. Green, in *Molybdenum: An Outline of its Chemistry and Uses*, ed. E. Braithwaite, Elsevier, 1994, in the press. E. A. Seddon and K. R. Seddon, *The Chemistry of Ruthenium*, ed. R. J. H. Clark, Elsevier, 1984, p. 20.