Polynuclear Molybdenum(VI)–Molybdenum(V) Complex: A Precursor of the Catalyst for Dinitrogen Reduction

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Crystal structure was determined of the complex $\{[Mg_2Mo_8O_{22}(MeO)_6(MeOH)_4]^{2-}\ [Mg(MeOH)_6]^{2+}\}\cdot 6MeOH$ (**1**), isolated from methanolic solution containing Mo^V, Mo^{VI}, and Mg^{II} compounds; when reduced to the Mo^{III} state the complex forms an active catalyst for N_2 reduction in methanol at ambient temperature and pressure.

Chemical or electrochemical reduction of Mo^V in methanol solution containing NaOH, $MoCl_5$, and $MgCl_2$ produces an active catalyst for dinitrogen reduction by sodium amalgam at room temperature and atmospheric pressure.[1] To understand the nature of the catalyst, which was postulated to be a polynuclear complex of Mo^{III}, its precursor was isolated. The initial solution was prepared by dissolving molybdenum pentachloride (containing about 30% of Mo^{VI}) in methanol after the addition of dry magnesium dichloride ([Mg] : [Mo] ≈0.6). The solution was then neutralized with methanolic NaOH. Following evaporation to one-tenth of the initial volume, hexane (25 vol%) was added, NaCl filtered off, and ether added to the filtrate. The orange precipitate was washed several times with methanol–ether and then crystallized slowly from methanolic solution. Crystals of the product (**1**) suitable for *X*-ray analysis were unstable out of contact with the solution, easily decomposing into powder. The single crystal used was therefore quickly transferred in flowing cold nitrogen gas to the diffractometer, and kept at 163 K during the data collection, thus preventing the crystal decomposition. The *X*-ray analysis was consistent with (**1**) having the formula $[Mg_2Mo_8O_{22}(MeO)_6(MeOH)_4]^{2-}[Mg(MeOH)_6]^{2+}\cdot$-6MeOH.†

Presumably it is the presence of a large number of solvate methanol molecules which causes the instability of the

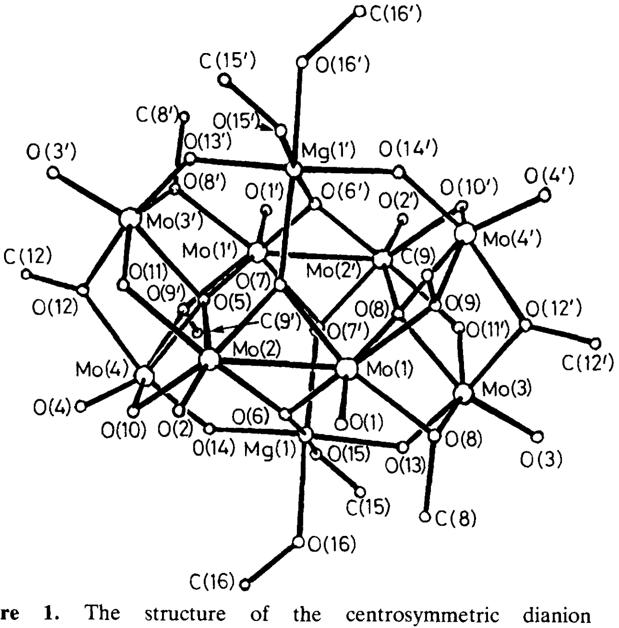

Figure 1. The structure of the centrosymmetric dianion $[Mg_2Mo_8O_{22}(MeO)_6 4MeOH]^{2-}$. Selected bond lengths: Mo(1)–Mo(2) 2.587(1), Mo(1)–O(1) 1.695(1), Mo(2)–O(2) 1.698(5), Mo(3)–O(3) 1.690(6), Mo(4)–O(4) 1.710(5), Mo(4)–O(14) 1.746(5), Mo(1—4)–O(5) 2.110(5)—2.207(5), Mo(1,2)–O(6,7) 1.961(5)—1.970(5), Mo(3)–O(11) 2.120(5), Mo(2)–O(10) 2.115(5), Mo(1,3,4)–O(8,9,12) 2.082(5)—2.152(5), Mg(1)–O(13,14) 1.982(6), 2.005(6), Mg(1)–O(6,7) 2.189(6), 2.212(7), Mg(1)–O(15,16) 2.097(6), 2.091(7) Å. Bond angles at Mo correspond to distorted octahedral, bond angles at Mg(1) are close to ideal octahedral; ∠Mo(1)O(5)Mo(2) 146.0(3)°; other bond angles at μ_4-atom O(5) are 95.7(3)—106.9(3)°; ∠Mo(1)O(6)Mo(2) 82.3(2), Mo(1)O(7)Mo(2) 87.3(2), Mo(2)O(11)Mo(3) 109.3(2)°; ∠MoOMo at μ_2-atoms O(8,9,12) 107.3(2)—111.9(2)°.

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† *Crystal data*: $Mg_3Mo_8C_{22}H_{82}O_{44}$, $M = 1891$, 2, triclinic space group $P\bar{1}$, $Z = 1$, Mo-K_α-radiation ($\lambda = 0.71069$ Å). At 163 K: $a = 11.058(2)$, $b = 11.262(6)$, $c = 13.158(6)$ Å, $\alpha = 106.86(4)$, $\beta = 106.07(4)$, $\gamma = 99.26(4)°$, $U = 1454$ Å^3, 4472 independent reflections with $2\theta \leqslant 50°$ were measured on a Syntex P2$_1$ diffractometer at 163 K with $I \geqslant 2\sigma(I)$. The structure was solved by direct methods (MULTAN[2]) and refined with 4056 reflections with $|F| \geqslant 8\sigma(F)$ to $R = 0.045$ and $R_w = 0.055$ (nonhydrogen atoms anisotropic, H atoms isotropic with fixed positions and B_{iso} 4.0 Å^2). The high threshold was chosen because this gave the most self-consistent results. All calculations were performed on an Eclipse S/200 computer using INEXIL programs.[3] Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors. Issue No. 1.

crystalline complex out of contact with its solution. The structure of the centrosymmetric dianion of (**1**) is shown in Figure 1. It is a mixed-valence Mo^V–Mo^{VI} molybdenum–magnesium cluster. Metal atoms are bound by μ_2, μ_3, and μ_4 type oxide bridges, methoxy-μ_2-bridges, and direct $Mo^V(1)$–$Mo^V(2)$ bonds [bond length 2.587(1) Å]. Mo(3) and Mo(4) are formally Mo^{VI}. Each molybdenum is bound to a terminal molybdenyl oxygen atom with bond lengths Mo(3)–O(13) 1.760(5) and Mo(4)–O(14) 1.746(5) Å, which are consistent with double Mo=O bonds. The other terminal Mo–O distances are rather long owing to the co-ordination of O(13) and O(14) with Mg^{2+} ions. All Mo–O distances are normal on the basis of those in the polynuclear molybdenum oxide complexes which have been reported earlier.[4,5] Bridging Mo–O distances increase in the order $\mu_2 < \mu_3 < \mu_4$. For the methoxy-bridges noticeable deviation is observed from the plane of the three closest neighbours by 0.23—0.45 Å. The co-ordination around molybdenum may be described as octahedral with all the O=Mo–O angles different from 180° [156.2(3)—158.1(3)°]. For the μ_4-bridging O(5) atom the Mo(1)–O(5)–Mo(2) angle is 146.0(3)°, considerably larger than a tetrahedral angle. The co-ordination around Mg(1) [2 μ_2–O_2, 2 μ_3–O, and 2 terminal MeOH] is close to ideal octahedral.

All protons of the methanol OH groups participate in a system of hydrogen bonds. Both methanol and molybdenyl O atoms act as proton acceptors in hydrogen bonds. The i.r. spectrum of (**1**) shows absorptions at 627, 735, 780, 865, 890, (bridging Mo–O–Mo), and 935 cm^{-1}, ν(Mo=O). It shows a u.v. maximum at 306 nm, 2.4×10^3 l mol^{-1} cm^{-1}.

When a methanolic solution of the pure complex (**1**) is reduced electrochemically to Mo^{III}, the complex formed is an effective catalyst for N_2 reduction in the system reported in ref. 1.

Gel-chromatographic analysis of (**1**) and the Mo^{III} complex obtained on reduction of (**1**) with Na(Hg) shows that the reduced complex retains the polynuclear structure, confirming the earlier conclusion.[1] Details of the structure of the Mo^{III} complex and the reasons for its catalytic activity remain to be determined.

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References

1 L. P. Didenko, A. B. Gavrilov, A. K. Shilova, V. V. Strelets, V. N. Tsarev, and A. E. Shilov, *Nouv. J. Chim.*, 1986, **10**, 503.

2 G. Germain, P. Main, and M. M. Woolfsen, *Acta Crystallogr., Sect. A.*, 1971, **27**, 368.

3 R. G. Gerr, A. I. Yanovskii, and Yu. T. Struchkov, *Kristallografiya*, 1983, **28**, 1029.

4 E. M. C. McCarron, III, and R. L. Harlow, *J. Am. Chem. Soc.*, 1983, **105**, 6179.

5 T.-C. Hsiech and J. A. Zubieta, *Polyhedron*, 1986, **5**, 305.

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