Unusual binuclear alkoxomolybdenum(V) complex free of oxo groups: synthesis, structure and IR spectra

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The interaction of $MoCl_5$ with NaOMe in methanol led to the formation of a new neutral binuclear molybdenum(V) alkoxo complex with Cl ligands, *trans*-$[Cl(OMe)_3Mo(\mu\text{-}OMe)_2Mo(OMe)_3Cl]$; the complex was characterised by X-ray analysis, IR spectroscopy and DFT quantum-chemical calculations.

Unique catalytic systems based on Mo complexes capable of reducing dinitrogen to hydrazine and ammonia in protic media as effectively as the nitrogenase enzyme were found.[1] Both homogeneous[1] and heterogeneous[2] Mo-containing systems were produced by the interaction of molybdenum pentachloride with bases (OH^- or MeO^-). It was suggested that the active sites of such systems include di- or polynuclear Mo^{III} complexes,[3] although neither their structure nor the mechanism of N_2 reduction catalysed by these complexes were adequately explored. We studied the interaction products of $MoCl_5$ and bases with their further reduction in methanol solution. Here we report on the structure and physico-chemical characteristics of initial products formed by $MoCl_5$ and NaOMe.

Complex *trans*-$[Cl(OMe)_3Mo(\mu\text{-}OMe)_2Mo(OMe)_3Cl]$ **1**† was obtained by the reaction between $MoCl_5$ and NaOMe in methanol under argon at the molar ratio $MeO^-/Mo \sim 3$ and –15 °C as dark green (almost black) crystals. These crystals have slight solubility in methanol, water and diethyl ether. They are stable in air, while the mother liquor is highly sensitive to oxygen and moisture. The fast colour change from brown red through blue to colourless indicates the oxidation of Mo^V to Mo^{VI}. Such a behaviour is apparently common to all of Mo^V alkoxy complexes.[4]

The molecular structure of **1** is presented in Figure 1.‡ The presence of oxo groups is typical of oxygen-containing Mo^V compounds. The lack of oxo groups in **1** is of great interest. As far as we know, there are only few compounds of this type, which can be obtained by the replacement of halogen atoms with alkoxy groups in MoX_5 (X = Cl, Br) to give $Mo(OR)_nX_{5-n}$, and their anions.[5] The other unexpected feature is the Mo:Cl = 1:1 in **1**, while the reaction ratio MeO^-/Mo requires the former to be 1:2. To reveal the reasons for the formation of Cl-deficient complex **1**, the DFT calculations of its molecular structure and properties have been carried out. The geometry optimization of all the structures was done using the PBE functional and SBK pseudopotential[6] and expanded basis set implemented in the PRIRODA program package.[7] The effects of solvation were treated at the level of the polarized continuum model (PCM) using the B3LYP functional and SDD basis set augmented by polarization functions implemented in the GAUSSIAN 98 program package.[8] Both PBE and B3LYP methods have a similar average accuracy of ~0.03 Å and 1.5° for bond lengths

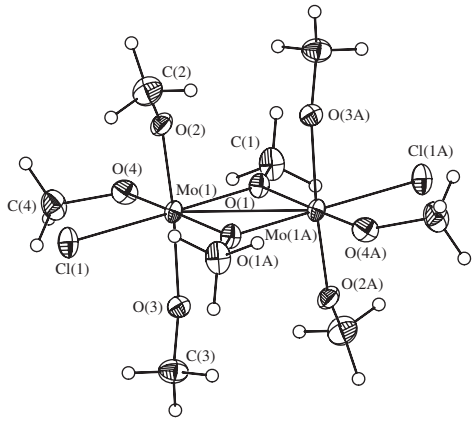

Figure 1 The general view of **1** in the representation of atoms by thermal ellipsoids ($P = 50\%$). Selected bond lengths (Å) (the second and third values in square and round brackets are obtained within the DFT PBE and DFT B3LYP calculations): Mo(1)–O(2) 1.840(2) [1.899] (1.865), Mo(1)–O(3) 1.844(2) [1.898] (1.860), Mo(1)–O(4) 1.913(2) [1.929] (1.902), Mo(1)–O(1) 1.994(2) [2.033] (2.013), Mo(1)–O(1A) 2.099(2) [2.143] (2.129), Mo(1)–Cl(1) 2.4294(6) [2.451] (2.469), Mo(1)–Mo(1A) 2.8077(4) [2.830] (2.819); bond angles (°): O(2)–Mo(1)–O(3) 166.13(8) [166.4] (165.2), O(4)–Mo(1)–O(1) 84.74(7) [82.9] (84.2), O(4)–Mo(1)–Cl(1) 94.50(6) [94.4] (93.5), O(1A)–Mo(1)–Cl(1) 87.35(5) [87.9] (88.3), O(2)–Mo(1)–Mo(1A) 90.52(5) [89.9] (90.6), O(3)–Mo(1)–Mo(1A) 90.30(5) [90.9] (90.6), O(4)–Mo(1)–Mo(1A) 132.97(6) [131.9] (132.9), O(1)–Mo(1)–Mo(1A) 48.27(4) [49.0] (48.8), O(1A)–Mo(1)–Mo(1A) 45.15(4) [45.8] (45.3), Cl(1)–Mo(1)–Mo(1A) 132.50(2) [133.7] (133.6).

† $MoCl_5$ (1.3 g, 4.75 mmol) was transferred to a round bottom Shlenk flask and then methanol (9.5 ml) was distilled onto the substance in a vacuum line at –15 °C with stirring. A bright green solution was obtained. In the same atmosphere, using a syringe, a solution of sodium methoxide (4 ml, 12.84 mmol), which was prepared by dissolving sodium metal in methanol under a stream of dry argon, was added to it. The red brown solution obtained was allowed to warm to +5 °C. The precipitate of NaCl was filtered, and the solution was left in a cool place for crystallization. Approximately 12 h later, $[(MeO)_3Mo(\mu\text{-}OMe)_2Mo(OMe)_3]$ started to form. The crystalline dark green precipitate was separated by decantation and washed twice with cold MeOH (2 ml) and then dried in a vacuum. Yield 0.23 g (9.5%). IR spectra were measured on a Perkin–Elmer Spectrum BX2 spectrometer. IR (Nujol, ν/cm^{-1}): 515 (m), 533 (m), 567 (m), 593 (m), 668 (m), 963 (s), 986 (vs), 1063 (s), 1096 (m), 1152 (m). Found (%): C, 17.24; H, 4.29; Cl, 14.81. Calc. for $C_8H_{24}Cl_2Mo_2O_8$ (%): C, 18.79; H, 4.70; Cl, 13.90.

‡ *Crystallographic data for* **1**. At 120 K crystals of **1** ($C_8H_{24}Cl_2Mo_2O_8$) are triclinic, space group $P\bar{1}$, $a = 7.2542(3)$, $b = 7.6729(4)$ and $c = 8.6297(4)$ Å, $\alpha = 96.2430(50)°$, $\beta = 112.8910(50)°$, $\gamma = 95.9160(50)°$, $V = 434.31(4)$ Å^3, $Z = 1$ ($Z' = 0.5$), $M = 511.05$, $d_{calc} = 1.954$ g cm^{-3}, μ(MoKα) = 17.78 cm^{-1}, $F(000) = 254$. Intensities of 4760 reflections were measured with a Smart 1000 CCD diffractometer at 120 K [λ(MoKα) = = 0.71072 Å, $2\theta < 58°$], and 2266 independent reflections ($R_{int} = 0.0227$) were used in the further refinement. The structure was solved by a direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. The hydrogen atoms were located from the Fourier density synthesis. The refinement converged to $wR_2 = 0.0585$ and GOF = 1.025 for all independent reflections [$R_1 = = 0.0256$ was calculated against F for 2207 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL PLUS 5.0.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 628558. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2006.

and angles, respectively (see Figure 1). Quantum-chemical calculations of other isomers with different arrangements of Cl ligands showed that the experimentally found structure of **1** has a minimal energy.

A short Mo–Mo distance (2.8077 Å) in the complex is due to metal–metal bond formation by pairing free *d* electrons on the Mo centres. In the triplet state, this bond is absent and the Mo–Mo distance is elongated to 3.40 Å. However, the triplet state energy was found to be higher by 9.2 kcal mol^{-1}.

The symmetric complex $Cl_2(OMe)_2Mo(\mu\text{-}OMe)_2Mo(OMe)_2Cl_2$ with the ratio Mo:Cl of 1:2, which corresponds to the reaction stoichiometry, was discussed as a hypothetic product. Solvolysis reaction (1) in a gas phase is accompanied by ΔH_{298} = = 11.9 kcal mol^{-1}; however, in a methanol solution, it is close to thermoneutral ΔH_{298} = 1.6 kcal mol^{-1}.

$$[Cl_2(OMe)_2Mo(\mu\text{-}OMe)]_2 + 2MeOH = [Cl(OMe)_3Mo(\mu\text{-}OMe)]_2 + 2HCl \quad (1)$$

This value was found from the calculated solvation energies of initial (–1.39 kcal mol^{-1}) and final (0.29 kcal mol^{-1}) complexes in MeOH, methanol evaporation energy,[9] and the heat of HCl solution in MeOH, which is equal to 13.3 kcal mol^{-1}, as found by the interpolation of available data for HCl solvation energy in EtOH and H_2O.[9] Note that the small value found for complex **1** solvation energy is consistent qualitatively with its insolubility in methanol. The molar ratio [H$^+$]:[Mo] = 1:1 in mother liquor, as well as the existence of a lag period in the crystallization of complex **1** prove that solvolysis reaction (1) is included in the formation mechanism of complex **1**. Indeed, the crystals of complex **1** start to form just after reagent mixing at the molar ratio $MoCl_5$:4NaOMe. As the initial Mo compound is mononuclear, equilibrium (2) of complex **1** decomposition on two mononuclear complexes was considered.

$$Cl(OMe)_3Mo(\mu\text{-}OMe)_2Mo(OMe)_3Cl + 2MeOH = 2Mo(OMe)_4Cl\cdot MeOH \quad (2)$$

Reaction (2) is exothermic both in a gas phase and in methanol; ΔH_{298} = 24.6 and 14.7 kcal mol^{-1}, respectively. Due to the decrease of the particle number in reaction (2), which should cause the entropy decrease, the equilibrium dissociation constant will be negligible. Thus, the quantum-chemical modelling has shown that complex **1** is stable to dissociation and its composition is determined by solvolysis reactions.

The IR spectrum of complex **1** in Nujol is presented in Figure 2 (curve *2*). The theoretically calculated spectra (curves *3* and *4*) were used to identify bands in the experimental IR spectrum. Both the PBE and the B3LYP results are in accordance with experimental data, but the former describes band positions more accurately. The absorption at 492 (515) 523 cm^{-1} (the first values are the PBE calculation data, in parentheses bands of curve *2*) originates from mixed Mo–μO and Mo–O stretching vibrations from apical MeO groups. The Mo–μO bond stretching vibrations have IR bands at 417 (__) 434 and 515 (533) 506 cm^{-1} (the first band has a low intensity and cannot be detected in experimental spectra). IR spectral bands at 558 (567) 576 and 572 (593) 598 cm^{-1} conform to Mo–O bond antisymmetric stretching vibrations from thermal and apical MeO groups, respectively. The absorption bands at 1023 (963) 1076 and 1041 (986) 1076 cm^{-1} correspond to C–O bond mixed stretching vibrations of bridge and termal MeO groups laying in the equatorial plane, and IR spectral bands at 1074 (1063) 1115 and 1093 (1096) 1135 cm^{-1} originate from C–O stretching vibrations from apical MeO groups. These attributions correspond to wavenumber intervals common to the Mo–O and C–O vibrations of alkoxy complexes.[10]

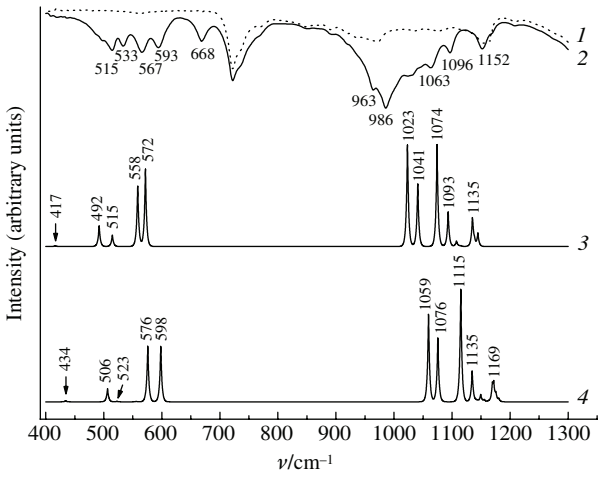

Figure 2 (*1*) IR spectra of Nujol; (*2*) experimental and theoretical [(*3*) DFT PBE, (*4*) DFT B3LYP] IR spectra of complex **1**.

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