Synthesis, Crystal, Molecular and Electronic Structure of a Novel Heterobinuclear Alkoxide Cluster [(MeO)$_2$ReO(μ-OMe)$_3$MoO(OMe)$_2$]

Vadim G. Kessler,*[a] Gulaim A. Seisenbaeva,[b] Andrei V. Shevelkov[a] and Gennady V. Khvorykh[a]

[a] *M.V. Lomonosov Moscow State University, Department of Chemistry, Vorobjovy Gory, 119899 Moscow, Russia*
[b] *M.V. Lomonsov Moscow State Academy of Fine Chemical Technologies, Pr. Vernadskogo 86, 117571 Moscow, Russia*

The new heterobimetallic methoxide [ReMoO$_2$(OMe)$_7$] **1** is obtained in 62% yield by hexane extraction from the electrolyte prepared by anodic oxidation of Re metal in a methanolic solution of [MoO(OMe)$_4$] in the presence of LiCl as electrolyte; the molecule of **1** consists of two [MO(OMe)$_5$] octahedra with three shared μ-OMe groups; while **1** shows high volatility and under such conditions remains intact, mass spectrometry indicates complete dissociation into homometallic species in the gas phase.

Despite considerable interest in the study of heterometallic alkoxides,[1] there have only been a few publications concerning controlled formation of heterometallic cluster compounds *via* homometallic precursors. Such studies have mainly concerned addition of a higher oxidation state derivative to an M–M multiply bonded species,[2] for instance as in eqn. (1) (R = Pr^i or Bu^t).

$$[WO(OR)_4] + [Mo_2(OR)_6] \rightarrow [Mo_2WO(OR)_{10}] \qquad (1)$$

The present paper reports the successful preparation of a heterometallic binuclear alkoxide cluster *via* addition of a higher oxidation state derivative of one metal to a lower oxidation state derivative of a second metal formed *in situ*. Molybdenum(VI) methoxide[3] was thus reacted with a rhenium species generated by anodic oxidation of rhenium metal in methanol. It has been established previously that the dissolution of a rhenium anode in alcohols leads to formation of rhenium(V) oxoalkoxide derivatives and in methanol formation of moisture insensitive but poorly soluble, diamagnetic [Re$_4$O$_2$(OMe)$_{16}$] took place.[4] Since [Re$_4$O$_2$(OMe)$_{16}$] was presumably formed *via* soluble oxoalkoxide intermediates this provided an approach to an attractive lower oxidation state (d^2) component in the synthesis of a heterometallic binuclear alkoxide.

A light yellow methanolic solution (50 ml) of [MoO(OMe)$_4$] (*ca.* 1 g) and LiCl (as electrolyte additive) was placed into an electrochemical cell. Electrosynthesis was performed for *ca.* 10 h at 25 °C (water cooling) using a potential of 110 V and a high purity rhenium rod (4 × 4 × 35 mm) as anode (A 20 cm^2 platinum plate was the cathode). The process was periodically interrupted to determine the Mo : Re ratio in solution by measuring the weight loss of the anode and was stopped finally when the ratio reached 1 : 1 and an emerald green electrolyte was obtained. On evaporation of the solvent *in vacuo* the residue was reddish purple. This residue was extraced twice with hexane (2 × 20 ml) and the volume of the extract was reduced to 15 ml *in vacuo*. A crop of dark purple platelet crystals precipitated on cooling to 0 °C. These analysed for [ReMoO$_2$(OMe)$_7$] **1** {62% yield, based on [MoO(OMe)$_4$], found: Re 35.2; Mo 18.2; C 15.36; H, 3.84. Calc. for [ReMoO$_2$(OMe)$_7$]: Re 35.03; Mo 18.08; C 15.82; H 3.95%}. The crystal and molecular structure of **1** was determined by X-ray crystallography.†

The structure of **1** is of the well-known bioctahedral M$_2$X$_9$ type. It can be considered as [(OMe)$_2$ORe(μ-OMe)$_3$MoO(OMe)$_2$] (Fig. 1) although statistical disorder is present in the crystal structure with one metal site occupied preferentially by Re [0.71(1) Re + 0.29(1) Mo] and the other by Mo [0.29(1) Re + 0.73(1) Mo] atoms; the total occupancies being unity within the accuracy of the experiment. The observed M–O distances fall into the limits usually observed for both molybdenum[3] and rhenium[6,7] alkoxo compounds. The symmetry of **1** is C_1, since although it does not contain any elements of symmetry it would contain a plane, were the metal sites equivalent. The structure of **1** is very similar to that of [Re$_2$O$_3$(OMe)$_6$][6] where one of μ-OMe groups is replaced by a μ-O atom to conserve the average number of electrons per cluster unit equal to two, and the idealized symmetry of [Re$_2$O$_3$(OMe)$_6$] is very close to C_S. This observation prompted a comparative investigation of the electronic structures of [ReMoO$_2$(OH)$_7$] and [Re$_2$O$_3$(OH)$_6$] models using the extended Hückel method, applying the program package CACAO.[8–10]

The MO calculations of the model molecules [MoReO$_2$(OH)$_7$] and [Re$_2$O$_3$(OH)$_6$)] led to the molecular orbital diagram shown in Fig. 2. The HOMO arises from σ-type bonding combinations of d$_{z^2}$ AOs in both [MoReO$_2$(OH)$_7$] (37a) and [Re$_2$O$_3$(OH)$_6$] (22a′). Since only these MOs are filled and the corresponding antibonding orbitals, 40a and 18a″, respectively are empty, a single metal–metal bond is predicted. For [MoReO$_2$(OH)$_7$], the Mo–Re bond is strongly polarized owing to the more electronegative Re atom, and leads to an increase of bond length from 2.559(1) (Re–Re) to 2.658(2) Å (Mo–Re) and seems to explain the dissociation observed in the gas phase by mass spectrometry (see below) of [MoReO$_2$(OMe)$_7$] preferentially into MoO(OMe)$_4$ and ReO(OMe)$_3$.

The other MOs of [Re$_2$O$_3$(OH)$_6$] shown in Fig. 2 are two π/δ and two π*/δ* orbitals, possessing noticeable differences from those observed for a face-sharing bioctahedron (D_{3h}.[11] (i) The reduction of symmetry from D_{3h} to C_s causes the splitting of each e′ (π/δ) and e″ (π*/δ*) orbitals into a′ and a″ orbitals. (ii) The mixed orbitals originate from d_{xy}/d_{xz} and $d_{yz}/d_{x^2-y^2}$ combinations instead of d_{xy}/d_{yz} and $d_{x^2-y^2}/d_{xz}$. (iii) The mixing is not so strong as in the case of an ideal bioctahedron and the orbitals are mainly δ_{xy} and π_{yz} in character with only a slight contribution of, π_{yz} and $\delta_{x^2-y^2}$-components respectively (iv) the δ_{xy} orbital is located above δ_{xy}* due to a strong interaction with the p$_y$ orbital of the oxygen atom of the oxo group leading to the antibonding character of the LUMO.

The δ_{xy} and π_{yz} MOs are also formed in [MoReO$_2$(OH)$_7$], but they are localized on the metal atoms: orbitals 38a and 39a (Re) and 41a, 42a (Mo): possible reason for such localization is the energy gap between the AOs of Mo and Re. As filling of MOs localized on the metal atoms would be expected to lead to

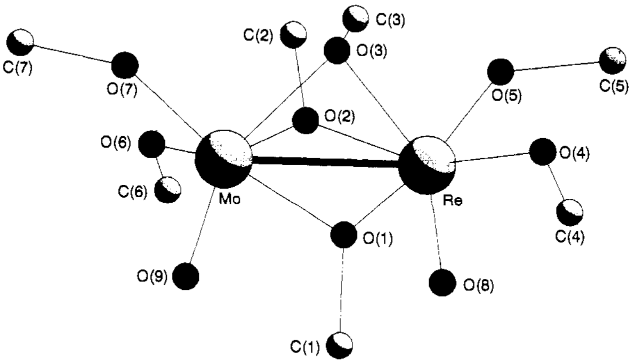

Fig. 1. The molecular structure of [ReMoO$_2$(OMe)$_7$] **1**. Selected bond distances (Å): Re–Mo 2.658(2), Re–O(1) 2.105(6), Re–O(2) 2.036(7), Re–O(3) 2.097(7), Re–O(4) 1.863(8), Re–O(5) 1.879(8), Re–O(8) 1.691(9), Mo–O(1) 2.111(7), Mo–O(2) 2.030(7), Mo–O(3) 2.162(7), Mo–O(6) 1.895(7), Mo–O(7) 1.904(8), Mo–O(9) 1.691(8).

distortion of the molecule, the number of cluster electrons able to be added is likely to be limited to two.

Thus, the heteronuclear Mo–Re bond differs from the Re–Re bond and the construction of hetero- and homo-nuclear clusters should differ, provided the electronegativity of the metal atoms differ substantially. It would be of interest to search for other heteronuclear M_2X_9 clusters taking into consideration that the M–M bonding in such clusters might be limited to a single bond.

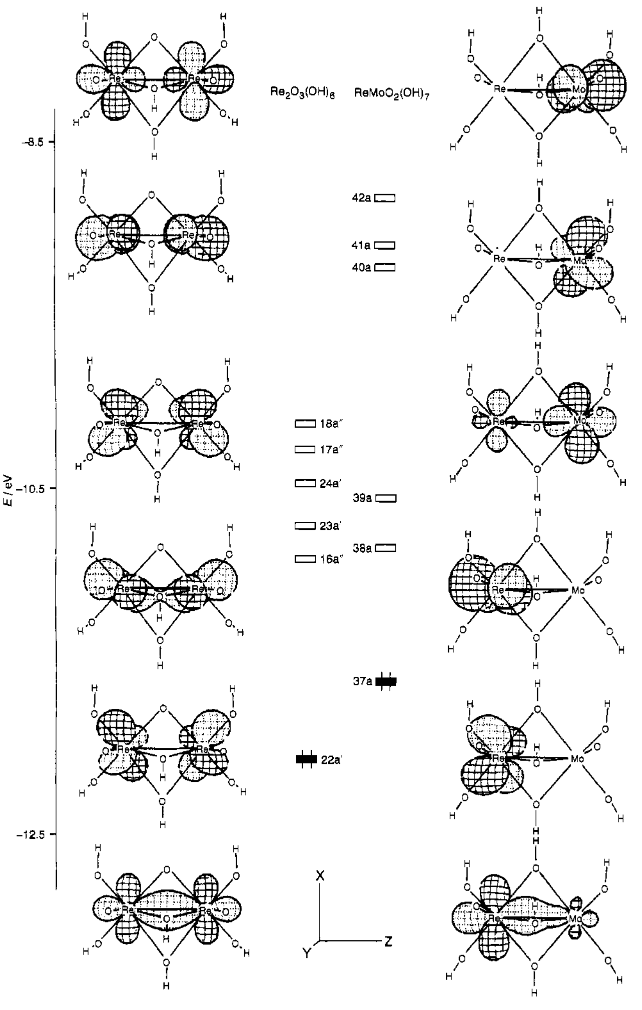

Fig. 2 Results of extended Hückel calculations on $[ReMoO_2(OH)_7]$ (C_1 symmetry) and $[Re_2O_3(OH)_6]$ (C_s symmetry)

By contrast homonuclear clusters are known to possess double or triple metal–metal bonds.

The spectral characteristics of **1** are in good agreement with its geometrical and electronic structure. In the IR spectrum two bands at 430 and 570 cm^{-1}, correspond to M–OMe vibrations, which can be attributed to bridging and terminal OMe groups respectively. Four bands, corresponding to ν(M=O) occur at 905, 920, 940 and 965 cm^{-1} originating apparently from superposition of two different vibration frequencies (for Mo=O and Re=O bonds) in the structure. While compound **1** can be sublimed intact at low temperatures and pressures (60–80 °C, 10^{-2} mmHg) its mass spectrum (MEI-MS 30, 70 eV, direct probe introduction) shows no peaks corresponding to the dinuclear species and the most intense peaks correspond to fragmentation of $MoO(OMe)_4$ and $ReO(OMe)_3$ indicating initial dissociation into these fragments. The presence of $ReO(OMe)_3^+$ ions (*m/z* 294, low intensity) in the mass spectrum indicates that a minor dissociation pathway could include a redox process. This would seem to occur *via* homolytic cleave of the Re-Mo bond [to d′(Mo) and d′(Re)] a less favoured process than heterolytic cleavage [leading to d^0(Mo) and d^2(Re)] as expected on the basis of the electronic structure of **1**.

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