Synthesis and Molecular Structure of An Octanuclear Oxomolybdem(V) Cluster Compound and Its Sol-Gel Application to Magnetoresistant Oxides

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The colossal magnetoresistance (CMR) in perovskite oxides including doped manganates has attracted great attention. But it is questionable whether these compounds would be useful for most applications, because the high values of magnetoresistance (MR) only occur with magnetic fields as high as 7 T and/or temperatures as low as 5 K. Recently, the ordered double perovskite Sr2 FeMoO 6 has been reported to have a low-field MR at room temperature (RT) and a high Curie temperature over 400 K. The large MR, however, can be obtained only in high magnetic fields of several Tesla at RT. For magnetic recording devices, magnetic materials should have a large MR at low fields and ambient temperatures.

The sol-gel process is one of the candidate methods used to enhance the low field MR of Sr2FeMoO6, because of relatively easy control of particle size with high purity and homogeneous stoichiometry. Even though a limited number of the sol-gel methods are reported for the preparation of mixed-metal perovskite magnetic oxides, the study of the alkoxide or oxoalkoxide precursors to Sr2FeMoO6 remains relatively unexplored. Here, we demonstrate the preparation and structural characterization of an octamolybdenum(V) oxoalkoxide precursor, and its application to low-field, RT, high MR and polycrystalline Sr2FeMoO6 by sol-gel process.

The molybdenum precursor complex was obtained from Mo(O)Cl3 and the potassium salt of triethanolamine in methanol. The synthetic procedure yielded single crystals of [Mo8(O)8(µ3-O)4(µ2-O)4(µ3-OCH3)2(µ2-OCH3)4]Cl2(HOCH3)4·6(CH3OH) (1). X-ray characterization was performed to reveal the solid state structure depicted in Fig. 1. The crystallographic analysis shows the presence of a neutral Mo(V) complex in which four Mo(V)(O)(µ3-O)(µ2-O)(µ2-OCH3) dimers are bound to share edges each other. Each molybdenum atom has one solvated methanol and/or one chlo-

Fig. 1. ORTEP drawing of [Mo8(O)8(µ3-O)4(µ2-O)4(µ3-OCH3)2(µ2-OCH3)4]Cl2(HOCH3)4·6(CH3OH) (1).
ride. In Fig. 2 two chains of four octahedra Mo are fused to form a chain structure, which is similar to chains of MoO3(OH) octahedra in the structure of α-MoO3·H2O. Addition of base to [MoOCl5]2− yields a brown precipitate that is often formulated as [MoO(OH)3] but no structural information is available for this substance or any [Mo2O5] species, even though mixed-valence oxides are well-characterized crystallographically including rhombohedral and monoclinic phases of Mo8O23 (7MoO3·MoO2).1 Thus, 1 may provide useful information about pure “Mo(V) oxide” phases.

In the core of the [Mo4O16]12+ moiety of 1, the coordination around the molybdenum ion has one terminal oxo, one μ2-O, one μ2-OC3H7, three μ3-O and Mo-Mo bond (2.5782 Å average distance) (see Table 1 and Fig. 3). Each molybdenum ion in the structure of [Mo4O10(OMe)6]2− coordinates to one terminal OCH3, one μ2-OCH3, one μ2-O, one μ3-OCH3 and two terminal oxo oxygens. The alkoxy ligands can substitute a number of oxo groups to reduce the charge and stabilize the cluster in alcoholic solvents. This provides the basis for a number of Mo(VI) species including [Mo4O10(OMe)4Cl2]− and [Mo4O8(OEt)2{(OCH2)3CR}2]− whose core structure is isostructural to the tetranuclear core of 1, as shown in Fig. 3. Limberg and coworkers have reported structure and characterization of oxomolybdenum(V) clusters from the reaction between MoCl5 and alcohols.8 Molecular structures of [Mo4O4Cl4(µ2-OEt)4(PMe3)2((µ3-O)2]2− (38b) and [Mo4O4(µ2-O)4(µ2-OH)2](HpzMe2)6−(HpzMe2 = 3,5-dimethylpyrazole) (39) also show Mo4 core clusters similar with that of 1.

As far as we know, the structure of 1 is unique. There are a number of octanuclear molybdate species in polyoxomolybdates,7 based on the β-molybdate(VI), [Mo10O30(SO4)6]18− structure including [Mo10O30(OMe)6]18−, [Mo10O30(HCO3)4]18− and [Mo10O4(sal)18− (sal-salicylideneiminopropyliminato). Relatively few examples of Mo(V) clusters are known;7 [Mo8O28(µ3-O)]16−, [Mo8O26(HCO2)2]16− and [Mo8O8Cl6(µ3-O)4(µ3-OH)2(µ2-OEt)4]3− The first two clusters exhibit the cyclic framework, while the last one shows the cubane-like distorted rutile struct-

Table 1. Characteristic Average Bond Distances (Å) in the Mo5 Clusters

<table>
<thead>
<tr>
<th>2</th>
<th>3</th>
<th>4</th>
<th>1</th>
</tr>
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<tbody>
<tr>
<td>Mo-Mo</td>
<td>2.6647</td>
<td>2.568</td>
<td>2.647</td>
</tr>
<tr>
<td>Mo=O</td>
<td>1.664</td>
<td>1.681</td>
<td>1.660</td>
</tr>
<tr>
<td>Mo-O(µ2)</td>
<td>na</td>
<td>2.172</td>
<td>na</td>
</tr>
<tr>
<td>Mo-O(µ3)</td>
<td>1.985</td>
<td>1.977</td>
<td>2.018</td>
</tr>
<tr>
<td>Mo-OR(µ2)</td>
<td>1.989</td>
<td>na</td>
<td>1.991</td>
</tr>
<tr>
<td>Mo-OR(µ3)</td>
<td>na</td>
<td>na</td>
<td>na</td>
</tr>
</tbody>
</table>

na=not available
ture. However, the structure of I shows an one-dimen-
sional extended framework with six µ3-O coordinations,
which is quite different from those of three above com-
plexes. Table 1 shows some characteristic average bond
lengths of tetramers (2 and 3) and octamers (1 and 4).

In addition to crystallographic study, complex I was
also characterized by FT-IR spectroscopy. The spectrum
of I is much more complicated than that of methanol
between 1000 and 430 cm⁻¹. The band at 970 cm⁻¹ is
assigned to the terminal Mo=O bond. 9,11 Bands are also
observed at 717, and 681 cm⁻¹, that can be attributed to
asymmetric Mo-O-Mo and terminal Mo-Cl, respectively.
Bands at 550, 519, and 494 cm⁻¹ can be attributed to M-
O stretching vibration of Mo-CH₃. These results are
well consistent with the solid-state structure.

Polycrystalline samples of Sr₂FeMoO₆ were prepared
by sol-gel process using strontium 2-methoxyethoxide,
iron 2-methoxyethoxide and I in a metal-based ratio of
2 : 1 : 1 in 2-methoxyethanol.12 The hydrolyzed precip-
itate was calcined at 850 °C in air before the powder was
pressed into pellets. Samples A, B, C, and D were sin-
tered at temperatures of 875, 900, 1000, and 1100 in
a stream of 5% H₂/Ar for two hours, respectively. Each
polycrystalline phase was confirmed by X-ray powder
diffraction pattern. The diffraction peaks are indexed
with respect to the cubic symmetry (Fm3m) with a slight
tetragonal distortion.

Preliminary MR investigations of the sample are shown
in Fig. 4. The magnitude of negative MR for sample A
with the magnetic field of 0.8 T at 12 and 300 K is as
large as 33 and 2.5%, respectively.13 In the case of metal-
nic sample D, the magnitude of MR is smaller than that
of semiconducting sample. Since the field dependent
magnetization is almost the same for both metallic and
semiconducting samples, the discrepancy in MR is not
due to a bulk phenomenon. It is a consequence of grain
boundary scattering due to different grain size formed at
different sintering temperature. Individual moments are
aligned by the external magnetic field and the hopping of
the spin-polarized electron between grains is controlled
by the external field. Therefore the large MR observed in
the semiconducting sample is due to the enhanced inter-
grain tunneling by reducing the relative angle of mag-
netization directions at the grain boundaries.

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6. Addition of the mixture of brown MoO3(Cl) (1.00 g,
4.58 mmol) in 100 mL of methanol to the colorless
solution of K₃[(OCH₂CH₂)₃]N (1.20 g, 4.77 mmol) in
50 mL of methanol gave orange crystals of complex
I(2.02 g, 1.26 mmol) with 27.5% yield based on molybdenum. IR (KBr pellet, cm$^{-1}$): 3433(br), 2933(w), 1632(br), 1030(w), 970(s), 717(m), 681(m), 519(m), 494(m), 464(w). Anal. Found: C, 11.76; H, 3.49; Cl, 4.61. Calc. for C$_{16}$H$_{58}$O$_{32}$Cl$_{2}$Mo$_{8}$: C, 12.00; H, 3.66; Cl, 4.43. Pink rod-shape crystals of [Mo$_{8}$ (O)$_{8}$ ($\mu$-O)$_{4}$ ($\mu$-O)$_{4}$ ($\mu$-OCH$_{3}$)$_{2}$ ($\mu$-OCH$_{3}$)$_{4}$ Cl$_{2}$ (HOCH$_{3}$)$_{4}$ · 6 (CH$_{3}$OH)] were analyzed at 208±1 K: triclinic, space group $P$(-1) with $a=7.8373(4)$ Å, $b=10.1107(5)$ Å, $c=15.0384(7)$ Å, $\alpha=92.9500(10)^\circ$, $\beta=98.4170(10)^\circ$, $\gamma=1175.94(10)^\circ$, $V=1175.94(10)^3$ Å$^3$, $Z=1$, $d_{calc}=2.261$ g/cm$^3$, $\mu$ (Mo K$\alpha$)=2.263 mm$^{-1}$, goodness of fit on $F^2=1.000$, $R=0.0351$ and $R_w=0.0884$.


13. The definition of the magnitude of MR: MR=$\Delta$$\rho$/\rho(0)=[\rho(H)-\rho(0)]/\rho(0) where $\rho(0)$ is the zero field resistivity and $\rho(H)$ is the resistivity under magnetic field.