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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[1] 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 Sr_2FeMoO_6 has been reported to have a low-field MR at room temperature (RT) and a high Curie temperature over 400 K.[2] 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 Sr_2FeMoO_6 because of relatively easy control of particle size with high purity and homogeneous stoichiometry.[3] 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 Sr_2FeMoO_6 remains relatively unexplored.[4] 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 Sr_2FeMoO_6 by sol-gel process.

The molybdenum precursor complex was obtained from $Mo(O)Cl_3$[5] and the potassium salt of triethanolamine in methanol. The synthetic procedure yielded single crystals of $[Mo_8(O)_8(\mu_4\text{-}O)_4(\mu_2\text{-}O)_4(\mu_3\text{-}OCH_3)_2(\mu_2\text{-}OCH_3)_4Cl_2(HOCH_3)_4\cdot 6(CH_3OH)]$ (1).[6] 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 $Mo^V(O)(\mu_3\text{-}O)(\mu_2\text{-}O)(\mu_2\text{-}OCH_3)\text{-}Mo^V(O)(\mu_3\text{-}O)(\mu_2\text{-}O)(\mu_2\text{-}OCH_3)$ dimers are bound to share edges each other. Each molybdenum atom has one solvated methanol and or one chlo-

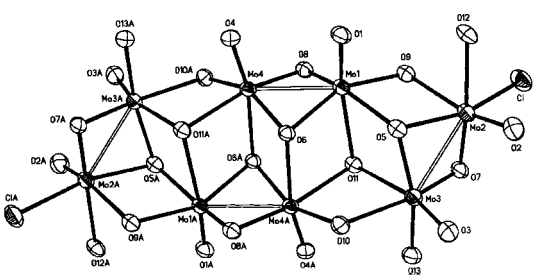

Fig. 1. ORTEP drawing of $[Mo_8(O)_{12}(\mu_3\text{-}O)_6(\mu_2\text{-}O)_6Cl_2]$core of $[Mo_8(O)_8(\mu_4\text{-}O)_4(\mu_2\text{-}O)_4(\mu_3\text{-}OCH_3)_2(\mu_2\text{-}OCH_3)_4Cl_2\ (HOCH_3)_4\cdot 6(CH_3OH)]$ (1).

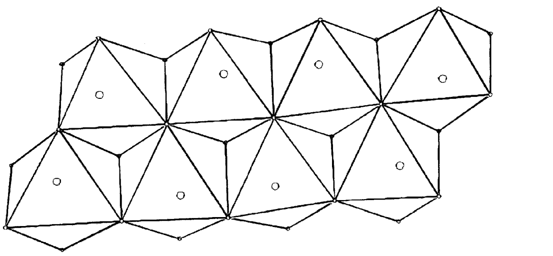

Fig. 2. Polyhedral representation drawing of $[Mo_8(O)_8(\mu_3\text{-}O)_4(\mu_2\text{-}O)_8Cl_2]$core of $[Mo_8(O)_8(\mu_3\text{-}O)_4(\mu_2\text{-}O)_4(\mu_3\text{-}OCH_3)_2(\mu_2\text{-}OCH_3)_4Cl_2(HOCH_3)_4 \cdot 6(CH_3OH)]$ (**1**).

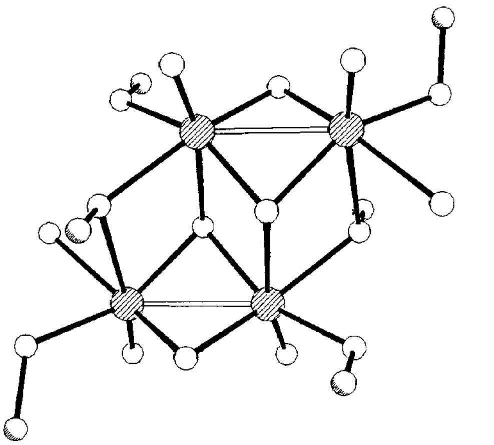

Fig. 3. Ball and stick drawing of $[Mo_4(O)_4(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_3\text{-}OCH_3)_2(OCH_3)_4]$ core of $[Mo_8(O)_8(\mu_3\text{-}O)_4(\mu_2\text{-}O)_4(\mu_3\text{-}OCH_3)_2(\mu_2\text{-}OCH_3)_4Cl_2(HOCH_3)_4 \cdot 6(CH_3OH)]$ (**1**).

ride. In *Fig.* 2 two chains of four octahedra Mo are fused to form a chain structure, which is similar to chains of $MoO_5(OH_2)$ octahedra in the structure of $\alpha\text{-}MoO_3 \cdot H_2O$. Addition of base to $[MoOCl_5]^{2-}$ yields a brown precipitate that is often formulated as $[MoO(OH)_3]$ but no structural information is available for this substance or any $[Mo_2O_5]$ species, even though mixed-valence oxides are well-characterized crystallographically including rhombohedral and monoclinic phases of Mo_8O_{23} ($7MoO_3 \cdot MoO_2$).[7a] Thus, **1** may provide useful information about pure "Mo(V) oxide" phases.

In the core of the $[Mo_4O_{10}]^{12+}$ moiety of **1**, the coordination around the molybdenum ion has one terminal oxo, one μ_2-O, one μ_2-OCH_3, three μ_3-O and Mo-Mo bond (2.5782 Å average distance) (see *Table* 1 and *Fig.* 3). The tetranuclear core cluster is a well-known structural motif in the coordination chemistry of polyoxomolybdates, especially Mo(VI) complexes. The most frequently encountered arrangement is exemplified by the cluster $[Mo_4O_{10}(OMe)_6]^{2-}$, which possesses four edge-sharing octahedra.[7] Each molybdenum ion in the structure of $[Mo_4O_{10}(OMe)_6]^{2-}$ coordinates to one terminal OCH_3, one μ_2-OCH_3, one μ_2-O, one μ_3-OCH_3 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 $[Mo_2O_{10}(OMe)_2Cl_2]^{2-}$, and $[Mo_4O_8(OEt)_2\{(OCH_2)_3CR\}_2]$. The Mo(VI) cluster, $[Mo_4O_{10}(OMe)_2Cl_2]^{2-}$ may be reduced into analogue Mo(V) species, $[Mo_4O_8(OMe)_2(MeOH)_2Cl_4]^{2-}$, 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 $MoCl_5$ and alcohols.[8] Molecular structures of $[Mo_4O_4Cl_4(\mu_2\text{-}OEt)_4(PMe_3)_2((\mu_3\text{-}O)_2]$ (**2**)[8c] and $[Mo_4O_4(\mu_2\text{-}O)_2(\mu_3\text{-}O)_2(\mu_2\text{-}OH)_2](Hpz^{Me2})_6]^{2-}$ (Hpz^{Me2} = 3,5-dimethylpyrazole) (**3**)[9] also show Mo_4 core clusters similar with that of **1**. Sometimes the partial reduction of Mo(VI) to Mo(V) produces mixed-valence Mo(V)/Mo(VI) species including $[Mo_4O_6(OPr)_4(PrOH)_2Cl_2]$.[10]

Table 1. Characteristic Average Bond Distances (Å) in the Mo^V Clusters

	2	3	4	1
Mo-Mo	2.6647	2.568	2.647	2.5782
Mo=O	1.664	1.681	1.660	1.675
Mo-O(μ_2)	na	2.172	na	1.932
Mo-O(μ_3)	1.985	1.977	2.018	2.009
Mo-OR(μ_2)	1.989	na	1.991	2.113
Mo-OR(μ_3) na	na	na	na	2.282

na=not available

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), $[Mo_8O_{26}]^{4-}$ structure including $[Mo_8O_{24}(OMe)_2]^{4-}$, $[Mo_8O_{24}(HCO_2)_2]^{6-}$ and $[Mo_8O_{24}(sal)_2]^{4-}$ (sal=salicylidenepropyliminato). Relatively few examples of Mo(V) clusters are known;[7] $[Mo_8O_{16}(OMe)_8(C_2O_4)]^{4-}$, $[Mo_8O_{16}(OMe)_8(PR_3)]$ and $[Mo_8O_8Cl_4(\mu_3\text{-}O)_4(OH)_2(\mu_2\text{-}OH)_4(\mu_3\text{-}O)_2(\mu_2\text{-}OEt)_4](HOEt)_4]$ (**4**).[8b,c] The first two clusters exhibit the cyclic framework, while the last one shows the cubane-like distorted rutile struc-

ture. However, the structure of **1** shows an one-dimensional extended framework with six μ_3-O coordinations, which is quite different from those of three above complexes. *Table* 1 shows some characteristic average bond lengths of tetramers (**2** and **3**) and octamers (**1** and **4**).

In addition to crystallographic study, complex **1** was also characterized by FT-IR spectroscopy. The spectrum of **1** 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-OCH_3. These results are well consistent with the solid-state structure.

Polycrystalline samples of Sr_2FeMoO_6 were prepared by sol-gel process using strontium 2-methoxyethoxide, iron 2-methoxyethoxide and **1** in a metal-based ratio of 2 : 1 : 1 in 2-methoxyethanol.[12] The hydrolyzed precipitate was calcined at 850 °C in air before the powder was pressed into pellets. Samples A, B, C, and D were sintered at temperatures of 875, 900, 1000, and 1100 in a stream of 5% H_2/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 metallic 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 intergrain tunneling by reducing the relative angle of magnetization directions at the grain boundaries.

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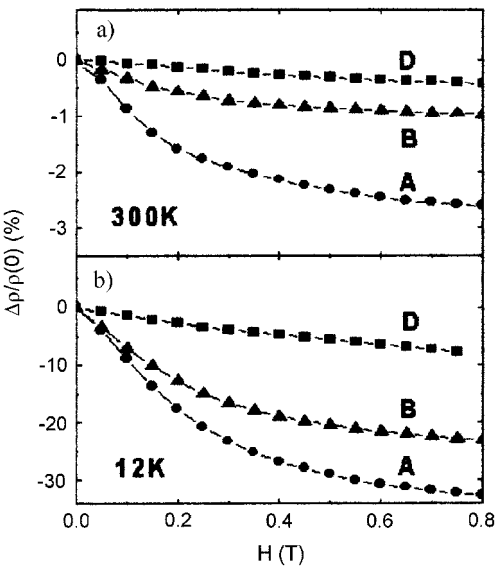

Fig. 4. Magnetoresistance of polycrystalline Sr_2FeMoO_6 samples for different sintering temperatures.

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6. Addition of the mixture of brown $Mo(O)Cl_3$ (1.00 g, 4.58 mmol) in 100 mL of methanol to the colorless solution of $K_3[(OCH_2CH_2)_3N]$ (1.20 g, 4.77 mmol) in 50 mL of methanol gave orange crystals of complex

1(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). 550(m). 519(m). 494(m). 464(w). *Anal.* Found: C. 11.76: H. 3.49: Cl. 4.61. Calc. for $C_{16}H_{58}O_{32}Cl_2Mo_8$: C. 12.00: H. 3.66: Cl. 4.43. Pink rod-shape crystals of $[Mo_8(O)_8(\mu_3\text{-}O)_4(\mu_2\text{-}O)_4(\mu_3\text{-}OCH_3)_2(\mu\text{-}OCH_3)_4Cl_2(HOCH_3)_4 \cdot 6(CH_3OH)]$ were analyzed at 208±1 K: triclinic, space group $P(\text{-}1)$ with $a=7.8373(4)$ Å. $b=10.1107(5)$ Å. $c=15.0384(7)$ Å. $\alpha=92.9500(10)°$, $\beta=98.4170(10)°$. $\gamma=92.2460(10)°$. $V=1175.94(10)$ Å^3. $Z=1$, $d_{calcd}=2.261$ g/cm^3. μ_a (Mo Kα)= 2.263 mm^{-1}, goodness of fit on $F^2=1.000$. $R=0.0351$ and $R_w=0.0884$.

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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.