

## Synthesis of $\text{Na}_2[\text{Fe}_6(\text{OCH}_2\text{CH}_2\text{OCH}_3)_{18}(\mu_6\text{-O})]$ : Its Sol-Gel Application to $\text{Sr}_2\text{FeMoO}_6$

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An air-stable iron cluster alkoxide complex  $\text{Na}_2[\text{Fe}_6(\text{OCH}_2\text{CH}_2\text{OCH}_3)_{18}(\mu_6\text{-O})]$  was prepared from the reaction of iron(III) chloride and sodium 2-methoxyethoxide. The complex was used to prepare  $\text{Sr}_2\text{FeMoO}_6$ , which spin-coated film shows a very high positive magnetoresistance of 25% with a magnetic field of 0.8 T at 300 K.

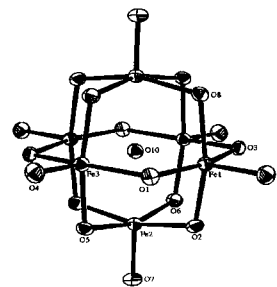
Recent interest in polynuclear iron alkoxide complexes has been attracted by a variety of fields, ranging from biology<sup>1</sup> to materials science.<sup>2</sup> Several interesting hexairon(III) alkoxide complexes have been reported, including  $\text{Na}_2\text{Fe}_6\text{O}(\text{OCH}_3)_{18}\cdot 6\text{CH}_3\text{OH}$ ,<sup>3a</sup>  $[\text{NaFe}_6(\text{OCH}_3)_{12}(\text{dbm})]$  (Hdbm = dibenzoylmethane),<sup>3b</sup> and  $[\text{LiFe}_6(\text{OCH}_3)_{12}(\text{dbm})_6]\text{PF}_6$ .<sup>3c</sup> None of them, however, have been applied to sol-gel process for magnetic materials, even though magnetic properties of some polyiron alkoxides have been observed.<sup>4</sup>

The colossal magnetoresistance (CMR) in doped perovskite manganates has attracted great attention.<sup>5</sup> 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 or at temperatures as low as 5 K. Recently, polycrystalline samples of  $\text{Sr}_2\text{FeMoO}_6$  exhibit a low-field MR at room temperature (RT).<sup>6</sup> But they were prepared by the solid-state reaction and showed only few % MR in high field at RT. Here, we demonstrate the preparation and characterization of a stable hexairon(III) alkoxide precursor, and its application to low-field, RT, high MR magnetic films of  $\text{Sr}_2\text{FeMoO}_6$  by sol-gel process.

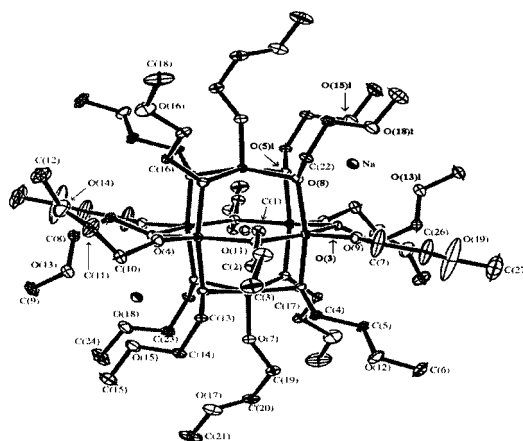
$\text{Na}_2[\text{Fe}_6(\mu_1\text{-}\eta^1\text{-OCH}_2\text{CH}_2\text{OCH}_3)_6(\mu_2\text{-}\eta^1\text{-OCH}_2\text{CH}_2\text{OCH}_3)_6(\mu_2\text{-}\eta^2\text{-OCH}_2\text{CH}_2\text{OCH}_3)_6(\mu_6\text{-O})]$  (**1**) was prepared from addition of  $\text{NaOCH}_2\text{CH}_2\text{OCH}_3$  (0.8537 g, 37.13 mmol) to  $\text{FeCl}_3$  (2.0070 g, 12.3 mmol) in THF (20 mL) at room temperature for 1 h with stirring. The solvent was removed under vacuum to give dark brown solids, which were extracted with ether. Dark brown solids were obtained after removing ether in vacuo and crystallized from benzene/hexane to give grayish green crystals of **1**.

Single-crystal X-ray diffraction analyses of the complex **1** was carried out.<sup>7</sup> Crystal data: Crystal dimensions  $0.16 \times 0.14 \times 0.10$  mm, Formula  $\text{Na}_2\text{Fe}_6\text{O}_{37}\text{C}_{54}\text{H}_{126}$ , Fw 1748.65, triclinic, space group  $P\bar{1}$ ,  $a = 12.962(2)$  Å,  $b = 13.905(4)$  Å,  $c = 14.198(3)$  Å,  $\alpha = 118.34(2)^\circ$ ,  $\beta = 92.65(2)^\circ$ ,  $\gamma = 112.77(2)^\circ$ , and  $V = 1991.6(7)$  Å<sup>3</sup>,  $T = 180(1)$  K,  $Z = 2$ ,  $R(wR) = 0.0331(0.0176)$  for 8398 reflections with  $F_o > 2\sigma(F_o)$ . The crystallographic analyses revealed the presence of a neutral complex in which six  $\text{Fe}(\mu_1\text{-}\eta^1\text{-OCH}_2\text{CH}_2\text{OCH}_3)(\mu_2\text{-}\eta^1\text{-OCH}_2\text{CH}_2\text{OCH}_3)(\mu_2\text{-}\eta^2\text{-OCH}_2\text{CH}_2\text{OCH}_3)$  are bound to a central oxygen atom ( $\mu_6\text{-O}^{2-}$ ). In the core of  $\text{Fe}_6\text{O}_{19}^{2-}$  moiety of **1**, the coordination around the

central oxygen ion has crystallographically imposed  $\bar{1}$  symmetry but shows approximately  $\bar{3}m$  molecular symmetry (see Figure 1). The iron atoms are connected to each other by 12 bridging oxygens of  $\mu_2\text{-OCH}_2\text{CH}_2\text{OCH}_3$  ligands. A distorted octahedral coordination sphere of the Fe(III) ions is completed by one terminal and four bridging 2-methoxyethoxide ligands, and a central oxygen atom. The  $\text{Fe}_6\text{O}_{19}^{2-}$  core is surrounded by all of 2-methoxyethoxide ligands, generating a hydrophobic surface and making the compound soluble in nonpolar solvents. Each of the two  $\text{Na}^+$  ions is coordinated in the slightly distorted trigonal prism of near-by oxygen atoms of 2-methoxyethoxides, all of



**Figure 1.** The scheme of  $\text{Fe}_6\text{O}_{19}^{2-}$  core of **1** with vibrational ellipsoids at 50% probability level.

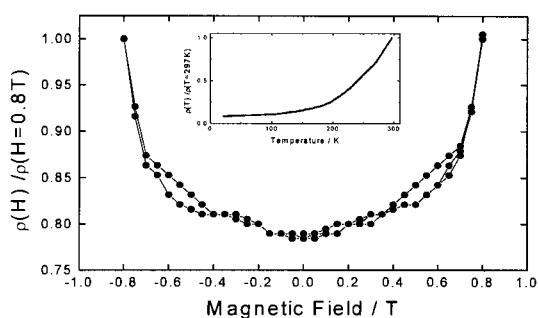


**Figure 2.** The molecular structure of **1**. Selected bond lengths(Å) and angles( $^\circ$ ): Na-O(3) 2.371(2), Na-O(5)i 2.364(2), Na-O(8) 2.387(2), Na-O(13)i 2.324(2), Na-O(15)i 2.340(2), Na-O(18)i 2.383(2), O(3)-Na-O(18)i 128.11(7), O(8)-Na-O(13)i 129.41(7), O(3)-Na-O(8) 70.30(6). i represents imposed symmetry (-x+1, -y+2, -z+1).

which are ligated via van der Waals interaction ( $2.324(2) \leq d_{\text{Na-O}} \leq 0.387(2) \text{ \AA}$ ) (see Figure 2). Six methanol molecules, however, in  $\text{Na}_2\text{Fe}_6(\text{O})(\text{OCH}_3)_{18} \cdot 6\text{CH}_3\text{OH}$  (**2**) are directly solvated to Na atoms with slightly longer bond lengths ( $2.30 \leq d_{\text{Na-O}} \leq 2.48 \text{ \AA}$ ).<sup>3a</sup> This feature suggests why **1** is more resistant to hydrolysis and robust in the air for several days compared with **2**. Thus, **1** could be a better candidate for the precursor of iron-based clusters or oxides than **2**. The complex **1** was also characterized by paramagnetic  $^1\text{H}$  NMR and FT-IR spectroscopy.<sup>8</sup> These results are well consistent with the solid-state structure.

Polycrystalline samples of  $\text{Sr}_2\text{FeMoO}_6$  were prepared by sol-gel process. A sol-gel precursor complex was prepared from the reaction of **1** with strontium 2-methoxyethoxide<sup>9</sup> and molybdenum isopropoxide (Alpha Aesar) in a metal-based ratio of 2:1:1 in 2-methoxyethanol. The precursor solution was deposited onto the Si(111) substrate three times by the spin-on coating method using 2500 rpm and 0.1 M solution to obtain its thin layer of final thickness about 250 nm. The film was annealed at 850 °C in a stream of 5%  $\text{H}_2/\text{Ar}$  for 12 h.

Preliminary investigation of the thin film showed that the sample with the nominal composition  $\text{Sr}_2\text{FeMoO}_6$  was polyphasic, with about 5%  $\text{SrMoO}_4$  impurities being apparent in diffraction patterns. It may be explained from the stoichiometry of iron alkoxide,  $\text{Na}_2\text{Fe}_6(\text{O})(\text{OCH}_2\text{CH}_2\text{OCH}_3)_{18}$ , which is not equivalent composition of pure " $\text{Fe}(\text{OR})_3$ " but contains about 3 mol%  $\text{Na}_2\text{O}$ . Thus the deficiency of iron content in the  $\text{Sr}_2\text{FeMoO}_6$  system may give rise to form  $\text{SrMoO}_4$ . But any other impurity phases were not observed. The temperature dependent resistivity  $\rho(T)$  and the isothermal MR at 300 K for the spin-coated film are shown in Figure 3. Its  $\rho(T)$  curve exhibits a metallic behavior due to  $d\rho/dT > 0$  (see Figure 3 inset). The preliminary result also shows that the magnitude of MR increases with the increase of applied field, reaching a value of 25% in a field of 0.8 T at room temperature. The positive MR is unusual and not-fully understandable for ferromagnetic materials. But this positive MR phenomenon was also observed in the metallic  $\text{Sr}_2\text{FeMoO}_{6-y}$  thin film.<sup>10</sup> This low-



**Figure 3.** Isothermal magnetoresistance at 300 K, and temperature dependence of normalized resistivity for  $\text{Sr}_2\text{FeMoO}_6$  thin layer (inset).

field MR value is the highest at this mild condition, as far as we know, because it is much higher than a reported value, 10%, with a field of 7 T at 300 K.<sup>6</sup> Now the study of chemistry from the single molecular precursor of three metal complexes to ceramic magnetic oxides is under way.

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#### References and Notes

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- 7 The data collection was performed with  $\text{MoK}\alpha$  radiation on an MXC3 diffractometer (Mac Science) at 180(1) K. The crystal structure was solved by direct methods. Since one of the side chains associated with the atom O(19) is disordered, as evidenced by large anisotropic displacement of parameters ( $U_{\text{eq}} = 0.181 \text{ \AA}^2$  for data collected at 180(1) K). The distances and angles in this chain are not reliable. All of the calculations were performed by using the SHELXL97 version. Crystallographic details and complete listings were deposited at the Cambridge Crystallographic.
- 8 IR (KBr,  $\text{cm}^{-1}$ ): 2880s, 1651w, 1462w, 1360w, 1196w, 1119s, 1080s, 1040w, 898w, 832w, 480m, and 419w.  $^1\text{H}$  NMR ( $\text{CH}_3\text{CN}-d_3$ , ppm):  $\delta$  55 (br,  $\mu_1\text{-OCH}_2\text{CH}_2\text{OCH}_3$ ,  $T_1 = 0.05$  ms), 18 (br,  $\mu_1\text{-OCH}_2\text{CH}_2\text{OCH}_3$ ,  $T_1 = 0.6$  ms), 6.6 (br,  $\mu_2\text{-OCH}_2\text{CH}_2\text{OCH}_3$ ,  $T_1 = 2.2$  ms), 5.2 (sh,  $\mu_2\text{-OCH}_2\text{CH}_2\text{OCH}_3$ ,  $T_1 = 2.3$  ms) and 3.3 (br,  $\mu_1\text{-and } \mu_2\text{-OCH}_2\text{CH}_2\text{OCH}_3$ ,  $T_1 = 124$  ms). Anal. Calcd for  $\text{C}_{54}\text{H}_{126}\text{O}_{37}\text{Na}_2\text{Fe}_6$ : C, 37.09; H, 7.26; Na, 2.63; Fe, 19.16%. Found C, 36.66; H, 7.15; Na, 2.51; Fe, 18.55%.
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