

The intercalation of transition metal salen complexes into layered MoS₂

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Received: 3 January 2007 / Accepted: 13 March 2007 / Published online: 29 June 2007
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Abstract Exfoliation-restack method has been employed to synthesize the intercalation compounds based on the cationic complexes $[M(\text{Salen})]^+$ ($M = \text{Mn}^{3+}, \text{Fe}^{3+}, \text{Co}^{3+}$; Salen = *N, N'*-ethylene-bis(salicylaldimine)) into the layered MoS₂. Their conductivity is in the range of 0.04–0.1 S/cm, which is much higher than the pristine MoS₂. Magnetic measurement indicated that the intercalation compounds $[\text{Mn}(\text{Salen})]_{0.18}\text{MoS}_2 \cdot 0.25\text{H}_2\text{O}$ and $[\text{Fe}(\text{Salen})]_{0.12}\text{MoS}_2 \cdot 0.3\text{H}_2\text{O}$ exhibit the temperature-dependent paramagnetism, which obviates from the Curie–Weiss law due to the temperature-independent paramagnetism of the exfoliated MoS₂ slabs, while $[\text{Co}(\text{Salen})]_{0.14}\text{MoS}_2 \cdot 0.5\text{H}_2\text{O}$ exhibits the almost temperature-independent paramagnetism. All three intercalation compounds do not show magnetic spin crossover behavior.

Keywords Layered MoS₂ · Intercalation · Metal salen complex · Magnetic property

Introduction

Recently, much attention has been focused on intercalation chemistry because it provides an effective approach to design functional organic–inorganic hybrid materials [1–4]. By this way some novel layered hybrid nanocomposite materials are obtained, thus opening the possibility to regulate the solid-state physical properties through the appropriate selection of host component and guest species [5–7].

Molybdenum disulfide (MoS₂) is a sandwich-like compound, in which a metal atom is bonded to six sulfur atoms and each layer is linked by weak van der Waals force [8]. During past decades molybdenum disulfide has generated a considerable interest owing to its practical applications such as catalyst for hydrodesulfurization [9], solid lubricant like graphite [10] and cathode in lithium battery [11] etc. Generally, the direct redox-process is only limited to some rich electron-donor species such as alkali or alkaline earth metals and organolithium compounds into layered MoS₂. However, Joensen et al. [12] developed a simple and convenient method, exfoliation and restacking process, for the synthesis of MoS₂ intercalation compounds. After intercalation the electrical conductivity sometimes greatly increased due to the structural transformation from 2H form to 1T form for MoS₂ slab [13].

The research on the transition metal salen complexes has been an interesting subject over past decades due to their catalytic and magnetic properties [14–16]. For example, the thermally induced spin crossover effect for some metal complexes based on salen ligands and its derivatives had been investigated in detail [17–19]. And many factors such as the inorganic anion, the synthetic method or the morphology can greatly influence spin crossover effect [20–24]. Recently, the thermally induced spin crossover behavior had been observed in the layered material $[\text{Fe}(\text{salEen})_2]_{0.28}\text{Cd}_{0.86}\text{PS}_3$

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by Clement et al. [25]. Boillot and coworkers [26] found that the layered material of cationic complex $[\text{Fe}(5\text{-MeO-Sal}_2\text{-rien})]^+$ into MnPS_3 not only showed thermal spin crossover of guest molecule but also exhibited the ferrimagnetic ordering at about 40 K. And we also reported a series of cationic complexes into layered MnPS_3 and studied the magnetic properties [27]. In this paper, we present the synthesis, characterization and solid-state properties of some intercalation compounds based on cationic complexes $[\text{M}(\text{Salen})]^+$ ($\text{M} = \text{Mn}^{3+}, \text{Fe}^{3+}, \text{Co}^{3+}$) into layered MoS_2 .

Experimental

Materials and reagents

MoS_2 (99%) was purchased from Aldrich. n-Butyllithium (2.5 M in n-hexane) was purchased from Fluka. n-Hexane was purchased from China National Pharmaceutical Group and refluxed with sodium before application. Other organic and inorganic reagents were purchased from China National Pharmaceutical Group and used without further purification.

Equipments

X-ray powder diffraction (XRD) patterns were recorded on a Dmaxr A X-ray diffractometer using CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$). Infrared spectra were obtained on a Nicolet SX Fourier transform spectrometer. Elemental analysis of carbon, hydrogen and nitrogen was performed on a Carlorba-1106 microanalyzer, and of metals was measured by ICP-AES on an Atomscan-2000 instrument. Thermo-gravimetric analysis (TGA) was conducted in a Rigaku Thermoflex TG 8110 at a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$. The magnetic property was studied by SQUID-magnetometer (MPMS, Quantum Design).

Synthesis of salen ligand and its metal complexes

N, N'-ethylene-bis(salicylaldehyde) (Salen) and its metal complexes were synthesized as in reference [27]. SalenH_2 ($\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2$), Calcd: C, 71.62%; H, 6.01%; N, 10.44%. Found: C, 71.73%; H, 5.85%; N, 10.25%. $\text{Mn}(\text{Salen})\text{Cl} \cdot \text{H}_2\text{O}$ (a), Calcd: Mn: 14.66%; C, 51.29%; H, 4.30%; N, 7.48%. Found: Mn: 15.17, C, 50.67%; H, 4.42%; N, 7.05%. IR (KBr): 1625, 1597, 1540, 1443, 1389, 1290, 1201, 1035, 771, 634, 467 cm^{-1} . $\text{Fe}(\text{Salen})\text{NO}_3$ (b), Calcd: Fe: 14.53%; C, 50.02%; H, 3.67%; N, 10.94%. Found: Fe: 14.56%, C, 49.38%; H, 3.52%; N, 10.89%. IR (KBr): 1629, 1599, 1545, 1445, 1385, 1299, 1198, 1150, 758, 605, 455 cm^{-1} . $\text{Co}(\text{Salen})\text{NO}_3 \cdot 2\text{H}_2\text{O}$ (c), Calcd: Co: 13.92%; C, 45.40%; H, 4.29%; N, 9.93%. Found: Co: 13.14%; C, 45.54%; H, 4.39%; N, 10.17%. IR (KBr): 1641,

1600, 1531, 1449, 1384, 1302, 1198, 1030, 757, 665, 478 cm^{-1} .

The synthesis of intercalation compounds

Synthesis of Li_xMoS_2 [13]

3.0 g of MoS_2 (powder) was added to a Schlenk flask. After removing the air under nitrogen atmosphere 10 mL of n-butyllithium (2.5 M in hexane) was transferred to the Schlenk and the mixture was stirred at room temperature for about 2 days. The mixture was filtered off and washed with hexane (15 mL \times 3). After drying under vacuum a black powder (Li_xMoS_2 , 3.3 g) was obtained.

Synthesis of intercalation compound A

0.5 g of Li_xMoS_2 was put into a 50 mL conical flask and 20 mL methanol was added. The mixture was dispersed with ultrasonic irradiation for about 30 min. The resulting suspension was transferred to a 250 mL round flask, and 1.5 g $[\text{Mn}(\text{Salen})]\text{Cl} \cdot \text{H}_2\text{O}$ in 25 mL methanol was added. The mixture was stirred for 5 days. After filtration the powder was washed several times with methanol and dried under vacuum. Elemental analysis led to the formula $[\text{Mn}(\text{Salen})]_{0.18}\text{MoS}_2 \cdot 0.25\text{H}_2\text{O}$ (A). Calcd: Mn, 4.45; C, 15.55; H, 1.37; N, 2.27. Found: Mn, 4.45; C, 15.70; H, 1.43; N, 2.23. IR (KBr): 1621, 1597, 1542, 1444, 1388, 1289, 1199, 1033, 765, 636, 468 cm^{-1} .

Synthesis of intercalation compounds B and C

The synthetic process for intercalation compounds B and C was as that of $[\text{Mn}(\text{Salen})]_{0.18}\text{MoS}_2 \cdot 0.25\text{H}_2\text{O}$ (A). Elemental analysis led to the formula $[\text{Fe}(\text{Salen})]_{0.12}\text{MoS}_2 \cdot 0.3\text{H}_2\text{O}$ (B) or $[\text{Co}(\text{Salen})]_{0.14}\text{MoS}_2 \cdot 0.5\text{H}_2\text{O}$ (C), respectively. Anal. Calcd for $[\text{Fe}(\text{Salen})]_{0.12}\text{MoS}_2 \cdot 0.3\text{H}_2\text{O}$ (B): Fe, 3.28%; C, 11.30%; H, 1.13%; N, 1.65%. Found: Fe, 3.46%; C, 10.29%; H, 1.16%; N, 1.69%. IR (KBr): 1625, 1598, 1546, 1443, 1387, 1295, 1198, 1149, 759, 609, 458 cm^{-1} . Anal. Calcd for $[\text{Co}(\text{Salen})]_{0.14}\text{MoS}_2 \cdot 0.5\text{H}_2\text{O}$ (C): Co, 3.84%; C, 12.54%; H, 1.39%; N, 1.83%. Found: Co, 3.66%; C, 13.38%; H, 1.40%; N, 2.08%. IR (KBr): 1636, 1598, 1533, 1446, 1386, 1301, 1200, 1029, 759, 666, 479 cm^{-1} .

Results and discussion

Thermo-gravimetric analysis (TGA)

Thermo-gravimetric analysis (TGA) of all three intercalation compounds showed a two-step weight loss. As an

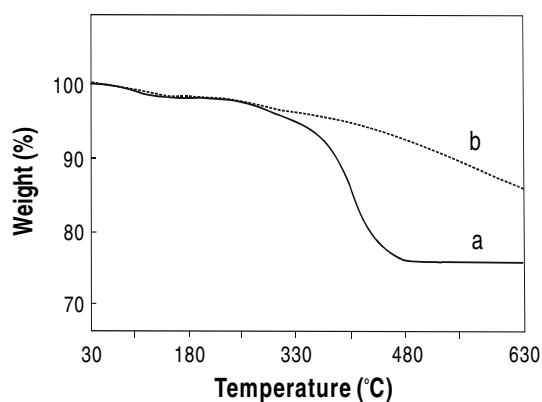


Fig. 1 The TGA curve of $[\text{Mn}(\text{Salen})]_{0.18}\text{MoS}_2 \cdot 0.25\text{H}_2\text{O}$ (A) (a, air; b, nitrogen)

example, Fig. 1 shows the TGA curve of $[\text{Mn}(\text{Salen})]_{0.18}\text{MoS}_2 \cdot 0.25\text{H}_2\text{O}$ (A). The step from 50 to 200 °C under air (curve a) coincides with the curve under nitrogen (curve b). As can be seen in Fig. 1 (curve a), the first step is below 200 °C, where the weight loss is about 2.16% indicating that water was removed. Another step is from 200 to 500 °C, in which the weight loss is about 22.21% indicating the decomposition of organic components. The total weight loss is well in agreement with the results of elemental analysis. The other two intercalation compounds (B and C) showed similar TGA results to intercalation compound A (in Table 1).

X-ray powder diffraction

Three new intercalation compounds based on the cationic complexes $[\text{M}(\text{Salen})]^+$ ($\text{M} = \text{Mn}^{3+}, \text{Fe}^{3+}, \text{Co}^{3+}$) into the layered MoS_2 were synthesized with exfoliation-restack method [12]. The occurrence of full intercalation was ascertained by X-ray powder diffraction (XRD). From Fig. 2 it is found that the XRD reflections of the pre-intercalation compound Li_xMoS_2 are totally disappeared. Instead, a new series of reflection peaks is appeared, which is also different from those of pristine MoS_2 . For $[\text{Mn}(\text{Salen})]_{0.18}\text{MoS}_2 \cdot 0.25\text{H}_2\text{O}$ (A) and $[\text{Fe}(\text{Salen})]_{0.12}\text{MoS}_2 \cdot 0.3\text{H}_2\text{O}$ (B) the lattice spacing increases to about 15.6 and 15.9 Å, respectively, expanding by 9.5 Å (for A) and 9.8 Å (for B) compared with the pristine MoS_2 with the lattice spacing of 6.1 Å. This indicates that the guest is

Table 1 The data of thermo-gravimetric analysis for intercalation compound A, B and C

Sample no	The first step weight loss		The second step weight loss	
	Found	(Calcd.)	Found	(Calcd.)
A	2.16	(2.02)	22.21	(21.62)
B	2.53	(2.65)	14.64	(15.65)
C	4.33	(4.20)	16.92	(17.37)

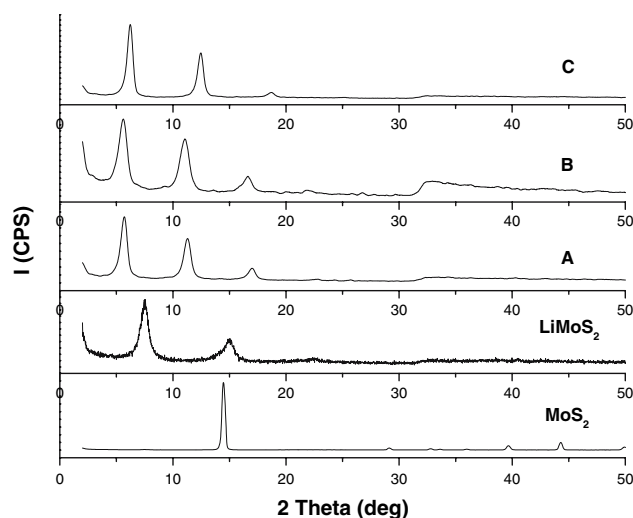


Fig. 2 The XRD of pristine MoS_2 , Li_xMoS_2 , intercalation compounds A, B and C

arranged with the long molecular axis tilted to the host layer (Fig. 3). However, the lamellar distance for the intercalation compound $[\text{Co}(\text{Salen})]_{0.14}\text{MoS}_2 \cdot 0.5\text{H}_2\text{O}$ (C) is only 14.2 Å and the lattice expansion is about 8.1 Å. This suggests that the guest in the interlayered region of layered MoS_2 is arranged with the long molecular axis parallel to host layer (Fig. 3).

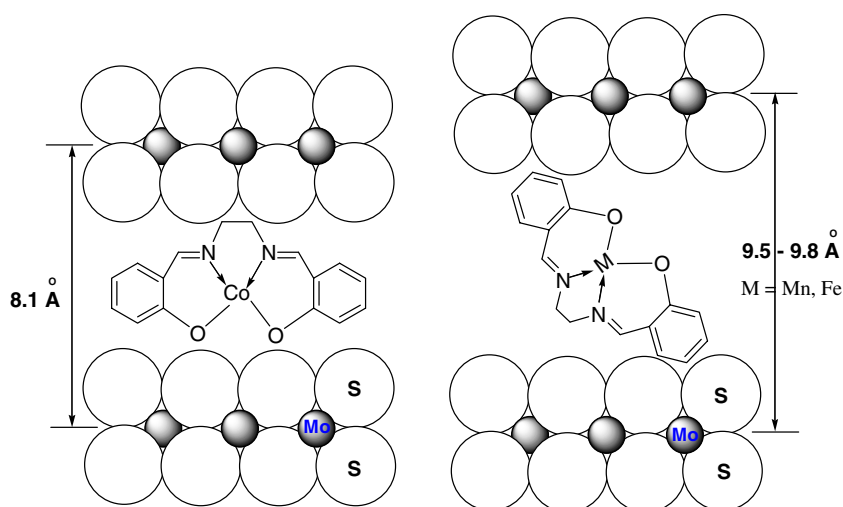
From Fig. 2 it is also found that all three intercalation compounds exhibit sharp $00l$ ($l = 1, 2, \text{ and } 3$) reflection patterns, indicative of the good crystallinity and the well-maintained layer structure after intercalation.

Infrared spectra (IR)

The IR data of the metal salen complexes and the related intercalation compounds are given in the experimental section. By comparison, intercalation compound exhibits the analogous characteristic IR absorptions to the related metal salen complexes in the range of 700–2,000 cm^{-1} [28–30].

For example, the IR spectra of intercalation compound B and the related guest molecule $\text{Fe}(\text{Salen})\text{NO}_3$ are shown in Fig. 3. The absorptions at about 1626, 1599, 1542, 1445, 1389, 1298, and 760 cm^{-1} are the characteristic vibrations of $[\text{Fe}(\text{salen})]^+$ cation similar to the IR data in the previous literatures [31–33]. The small shift of some characteristic vibrations observed between guest molecule and related intercalation compound can be attributed to the interlayered region environment of the host, which exerts a small influence on the vibration of the guest molecule. The absorption around 450–480 cm^{-1} is the stretch vibration of M–O band of the metal complexes [28–33]. Similar results were observed for the other intercalation compounds (A and C). Therefore, the IR spectra also provide the evidence

Fig. 3 The possible arrangement of the guest in the interlayered space of layered MoS₂ in intercalation compounds A, B and C



to support the intercalation of guest species into layered MoS₂.

Electrical conductivity

The conductivity of three intercalation compounds (as compressed pellets) at room temperature was measured with the two-probe method. [Mn(Salen)]_{0.18}MoS₂ · 0.25H₂O (A), [Fe(Salen)]_{0.12}MoS₂ · 0.3H₂O (B), and [Co(Salen)]_{0.14}MoS₂ · 0.5H₂O (C) have electrical conductivity of 4.0×10^{-2} , 6.0×10^{-2} and 1.0×10^{-1} S/cm, respectively. They show at least 1,000 times higher conductivity than pristine MoS₂ with the room-temperature electrical conductivity of $\sim 10^{-5}$ S/cm. This can be attributed to the structural transformation of MoS₂ during the intercalation as reported in references [13, 34, 35].

Magnetic properties

The curves of magnetic susceptibility (χ) and of the reciprocal of the susceptibility ($1/\chi$) versus temperature as well as the relationship of magnetization (M) with applied magnetic field (H) at 1.85 K are shown in Figs. 4–6, respectively. From the χ –T curves (Fig. 4), it is found that the intercalation compounds A and B clearly show temperature-dependent paramagnetism. However, intercalation compound C exhibits the almost temperature-independent paramagnetism.

As can be seen from Fig. 6 (curve A), the $1/\chi$ –T curve of intercalation compound A slightly deviates from the Curie–Weiss law, but it can not be attributed to the spin crossover of Mn³⁺ ion. Generally, if the thermal-induced magnetic crossover exists from high spin state to low spin state, the $1/\chi$ versus T curve must obviously deviate from the Curie–Weiss law due to an abrupt magnetic spin-transition. Colub et al. [36] had reported that the exfoliated MoS₂ slabs showed the almost temperature-independent paramagnetism

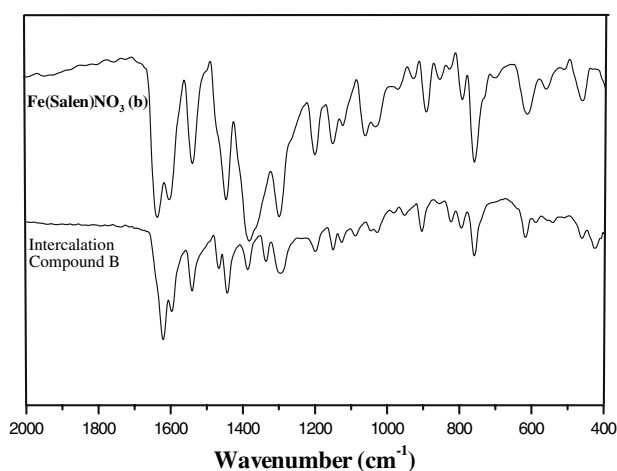


Fig. 4 The IR spectra of [Fe(Salen)]NO₃ (b) and the related intercalation compound [Fe(Salen)]_{0.12}MoS₂ · 0.3H₂O (B)

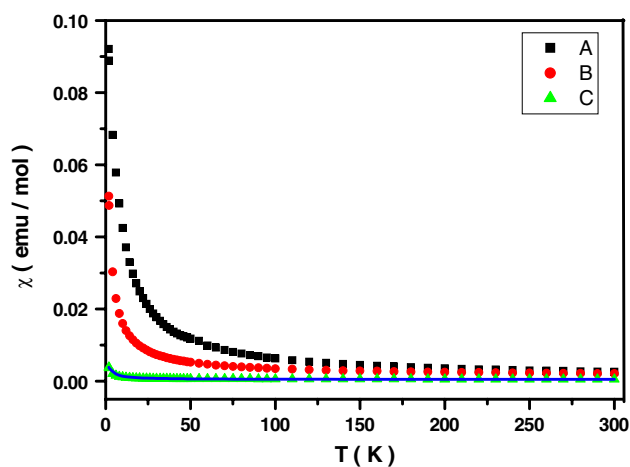


Fig. 5 The χ –T curves for [Mn(Salen)]_{0.18}MoS₂ · 0.25H₂O (A), [Fe(Salen)]_{0.12}MoS₂ · 0.3H₂O (B) and [Co(Salen)]_{0.14}MoS₂ · 0.5H₂O (C) (The solid line shows the best fit to the modified Curie expression of intercalation compound C).

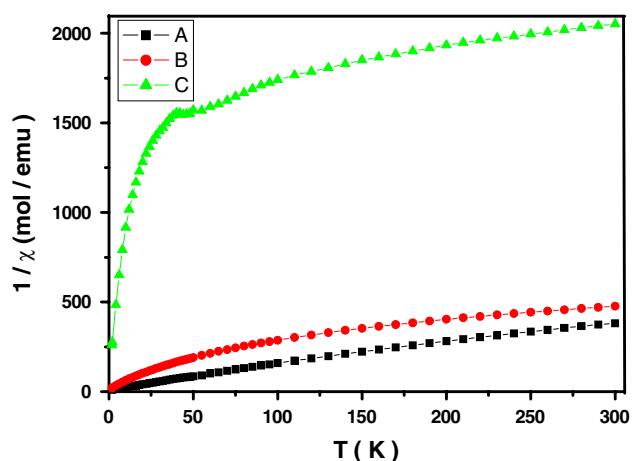


Fig. 6 The $1/\chi$ - T curves for $[\text{Mn}(\text{Salen})]_{0.18}\text{MoS}_2 \cdot 0.25\text{H}_2\text{O}$ (A), $[\text{Fe}(\text{Salen})]_{0.12}\text{MoS}_2 \cdot 0.3\text{H}_2\text{O}$ (B) and $[\text{Co}(\text{Salen})]_{0.14}\text{MoS}_2 \cdot 0.5\text{H}_2\text{O}$ (C)

(TIP), where the magnetic moment came from the defect centers of the exfoliated MoS_2 layer. Therefore, the deviation of $1/\chi$ - T curve from the Curie-Weiss law for intercalation compound A possibly originates from the TIP of the exfoliated MoS_2 slabs. The M - H curve at 1.85 K is shown in Fig. 7 (curve A). It is found that the magnetization (M) is increased with the increment of applied magnetic field (H), and no clear trend for magnetization saturation is shown even at 30,000 Oe. This indicates that intercalation compound A is a paramagnet. Intercalation compound B also shows the deviation from the Curie-Weiss law for its $1/\chi$ - T curve (in Fig. 6, curve B) due to the TIP of the exfoliated MoS_2 slabs. The magnetization (M) is increased with the increment of applied magnetic field (H), and no magnetization saturation is observed till

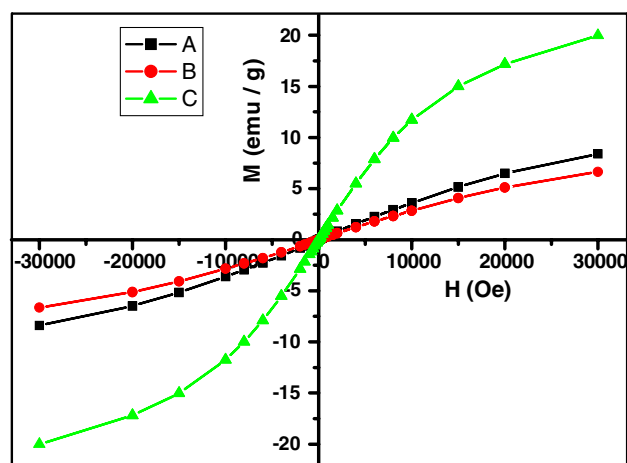


Fig. 7 The M - H curves at 1.85 K for $[\text{Mn}(\text{Salen})]_{0.18}\text{MoS}_2 \cdot 0.25\text{H}_2\text{O}$ (A), $[\text{Fe}(\text{Salen})]_{0.12}\text{MoS}_2 \cdot 0.3\text{H}_2\text{O}$ (B) and $[\text{Co}(\text{Salen})]_{0.14}\text{MoS}_2 \cdot 0.5\text{H}_2\text{O}$ (C)

30,000 Oe (in Fig. 7, curve B), which is similar to the intercalation compound A.

Intercalation compound C exhibited almost temperature-independent paramagnetism (TIP), especially above 50 K (Fig. 5 curve C). The magnetic behavior fits the modified Curie expression $\chi = C/T + \chi_0$ with $C = 8.0 \times 10^{-3} \text{ emu K mol}^{-1}$ and $\chi_0 = 4.75 \times 10^{-4} \text{ emu mol}^{-1}$ (as shown in the solid line of curve C in Fig. 5), which is similar to that of exfoliated MoS_2 slabs, as previously reported by Colub et al. [36]. This suggests that the Co^{3+} ion of $[\text{Co}(\text{Salen})]^+$ is in the low-spin state and magnetic spin crossover does not exist. From the M - H curve (Fig. 7 curve C), it is found that the trend of magnetization saturation is much obvious (at 30,000 Oe) in comparison with intercalation compounds A or B.

Conclusion

Three new intercalation compounds based on the intercalation of the cationic complexes $[\text{M}(\text{Salen})]^+$ ($\text{M} = \text{Mn}^{3+}$, Fe^{3+} , Co^{3+}) into the layered MoS_2 have been synthesized and characterized by XRD, IR, and elemental analysis. The guest arrangement between the host layers is determined by the lattice spacing. All three intercalation compounds show higher electrical conductivity than pristine MoS_2 . Magnetic measurements indicate that both of the intercalation compounds $[\text{Mn}(\text{Salen})]_{0.18}\text{MoS}_2 \cdot 0.25\text{H}_2\text{O}$ and $[\text{Fe}(\text{Salen})]_{0.12}\text{MoS}_2 \cdot 0.3\text{H}_2\text{O}$ exhibit temperature-dependent paramagnetism that obviates from the Curie-Weiss law due to the temperature-independent paramagnetism of the exfoliated MoS_2 slabs. $[\text{Co}(\text{Salen})]_{0.14}\text{MoS}_2 \cdot 0.5\text{H}_2\text{O}$ exhibits the almost temperature-independent paramagnetism especially above 50 K. No magnetic spin cross behavior is observed for all three intercalation compounds.

Acknowledgments We are grateful to the National Natural Science Foundation of China (Nos. 20490215, 90206026) for the financial support.

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