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Ferromagnetic Phase Transition at Around 20 K in Neutral Dichloro- and Acetylacetonato-manganese Complexes with Two Diethylthiotetrathiafulvalenyl- Dithiolato Groups

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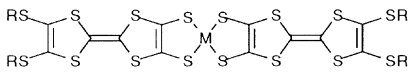
Abstract Neutral dichloro- and acetylacetonato (acac)-manganese complexes with two diethylthiotetrathiafulvalenyldithiolato (DETTTFDT) groups (**1**($MnCl_2$; Et) and **1**(Mn(acac); Et)) were prepared by the reaction of bis(tetraethylammonium) bis(DETTTFDT) zinc complex with $MnCl_2 \cdot 4H_2O$ or $Mn(acac)_2$, followed by the treatment with iodine. For both complexes ferromagnetic phase transition occurred at around 20 K. The saturation magnetizations and coercive forces at 2 K were 2,800 emu mol^{-1} and 650 Oe for **1**($MnCl_2$; Et), and 180 emu mol^{-1} and 35 Oe for **1**(Mn(acac); Et), respectively.

Keywords tetrathiafulvalenyldithiolato ligand; neutral manganese complex; ferromagnetic phase transition

INTRODUCTION

Neutral transition metal complexes with two dialkylthio-tetrathiafulvalenyldithiolato groups (**1**(M; R)) attract much attention, since they can serve as a new type of molecular/organic π/d cooperative system and also as a reliable candidate for producing unprecedented one-component

organic conductors and furthermore organic superconductors. Very recently, the nickel (**1**(Ni; Me, Et, *n*-Bu))[1] and copper complexes (**1**(Cu; Me, Et, -CH_2CH_2-))[2,3] were prepared, which exhibited considerably high room-temperature electrical conductivities (3.7 S cm^{-1} in maximum) on their compressed pellets. The EPR and SQUID measurements showed no presence of spins on the nickel and copper atoms. In contrast to these complexes, room-temperature electrical conductivities of the cobalt complexes (**1**(Co; Me, Et, -CH_2CH_2-)) were very low,[4] and a large amount (70 - 100%) of a Co(II) (S=1/2) spin entity remained on the cobalt atom. The spin interaction was weakly antiferromagnetic and any spin ordering was not observed even at low temperatures. In this paper we wish to report ferromagnetic spin ordering below ca. 20 K for two newly-prepared neutral Mn complexes, **1**($MnCl_2$; Et) and **1**(Mn(acac); Et)).



1 (M; R)

EXPERIMENTAL

Bis(tetraethylammonium) bis(DETTTFDT) zinc complex[5] (148 mg, 0.13 mmol) in DMF (10 ml) was added to $MnCl_2 \cdot 4H_2O$ (27 mg, 0.13 mmol) or $Mn(acac)_2$ (34 mg, 0.13 mmol) in DMF (10 ml) at -40 °C under argon, and stirring was carried out for 12 h. After removing the solvent *in vacuo* a dark brown solid was collected, washed with MeOH and dried *in vacuo*. Reaction of the solid with 1/2 equiv. of I_2 (17 mg, 0.065 mmol) was carried out in DMF (10 ml) at -40 °C under argon, followed by removing the solvent *in vacuo*, washing with MeOH and drying *in vacuo* to afford **1**($MnCl_2$; Et) (58 mg, 0.064 mmol; yield 48%) and **1**(Mn(acac); Et) (72 mg, 0.078 mmol; 58%), respectively. Anal. Calcd. for $C_{20}H_{20}S_{16}MnCl_2$: C, 26.71; H, 2.24; N, 0%. Found: C, 26.82; H, 2.27; N, 0% for **1**($MnCl_2$; Et). Anal. Calcd. for $C_{25}H_{27}O_2S_{16}Mn$: C, 32.38; H, 2.93; N, 0%. Found: C, 32.40; H, 2.77; N, 0% for **1**(Mn(acac); Et). Their single crystals suitable for the X-ray structure

analysis are not yet obtained in spite of a lot of attempts.

RESULTS AND DISCUSSION

The room-temperature electrical conductivities measured on the compressed pellets of **1**($MnCl_2$; Et) and **1**(Mn(acac); Et) were $<10^{-10}$ and 1 $\times$ 10^{-5} S cm^{-1}, respectively, indicating that both complexes are essentially insulators. The solid EPR spectrum of **1**($MnCl_2$; Et) at room temperature showed only a broad symmetrical signal (ΔHpp = 150 Oe) at g = 2.0016, which is close to an average (2.0019) of the g values of Mn(IV) complexes (2.00)[6] and alkylthiosubstituted-TTF radical cation salts (2.0065).[7] In the measurement at 77 K there was no change in the spectral pattern in spite of marked increase in the intensity, suggesting that strong interaction occurs between d spin on the Mn atom and π spins on the DETTTFDT moieties. On the other hand, in the solid EPR spectrum of **1**(Mn(acac); Et) at room temperature a broad symmetrical signal (ΔHpp = 623 Oe) was observed at g = 2.0033. This value is also close to an average (2.0028) of the g values of Mn(III) complexes (2.0025)[6] and TTF radical cation salts.

The χ_pT vs. T plots in the temperature range of 5 to 300 K are shown in Figure 1 for both complexes. The χ_pT of **1**($MnCl_2$; Et) at 300 K is ca. 1.5

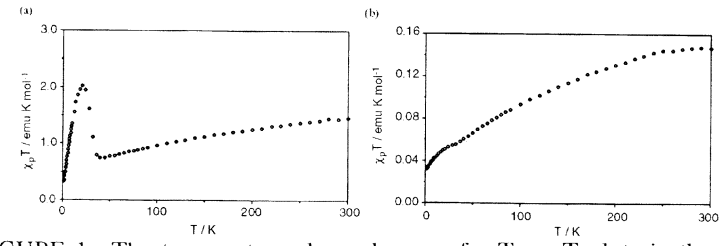


FIGURE 1 The temperature dependences of χ_pT vs. T plots in the temperature range of 5 to 300 K for (a) **1**($MnCl_2$; Et) and (b) **1**(Mn(acac); Et).

emu K mol^{-1}, which is smaller than the value (2.65 emu K mol^{-1}) for non-interacting one Mn(IV) (S = 3/2) d spin and two DETTTFDT π spins per one **1**($MnCl_2$; Et) molecule, but is much larger than the value (0.378 emu K mol^{-1})

for strong antiferromagnetic interaction between the three spins. For **1**(Mn(acac); Et) the χ_pT is ca. 0.15 emu K mol^{-1} at 300 K, which corresponds to only ca. 9% of the value (1.76 emu K mol^{-1}) for non-interacting one Mn(III) (S = 1) d spin and two DETTTFDT radical π spins per one **1**(Mn(acac); Et) molecule. By lowering the temperature from 300 K the χ_pT gradually decreased, suggesting intra- and/or inter-molecular antiferromagnetic interaction between the spins involved in the complexes, and the tendency continued till ca. 30 K. However, for **1**($MnCl_2$; Et) abrupt increase in χ_pT occurred near 30 K, and by lowering the temperature from 30 to 20 K χ_pT sharply increased, but below 20 K again decreased. The similar behavior was also observed for **1**(Mn(acac); Et), but the degree of increase in χ_pT was very small compared to that in **1**($MnCl_2$; Et). This χ_pT vs. T behavior below ca. 20 K suggests occurrence of ferromagnetic spin ordering for both complexes. Indeed, this was confirmed by three different temperature dependences of magnetization, i.e., field-cooled (FCM), zero-field-cooled (ZFCM) and remnant magnetizations (RM), as shown in Figure 2 for **1**($MnCl_2$; Et). The onset temperature of ferromagnetic phase transition was determined to be 22 K from the ZFCM and RM experiments. The similar temperature dependences of magnetization were also performed for **1**(Mn(acac); Et), and there was only slight increase of magnetization near 20 K in the RM experiment because of very small magnetization values in this case.

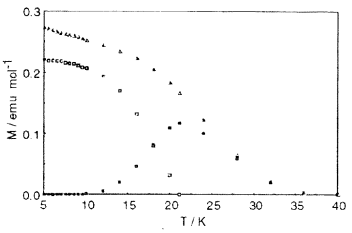


FIGURE 2 The temperature dependences of magnetization for **1**($MnCl_2$; Et): (△) FCM, (○) ZFCM and (□) RM.

Figure 3 shows the field dependences of magnetization in the field range of ±50 kOe at 2 K for both complexes. The magnetizations at 50 kOe were ca. 2,800 and ca. 180 emu mol^{-1} for **1**($MnCl_2$; Et) and **1**(Mn(acac); Et), respectively.

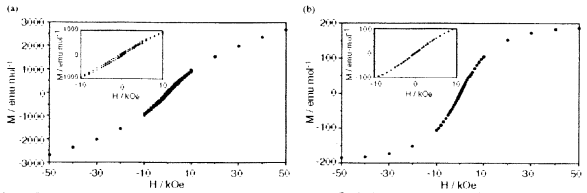


FIGURE 3 The magnetization curves at 2 K in the field range of ±50 kOe and ±10 kOe (an inset) for (a) **1**($MnCl_2$; Et) and in the field range of ±50 kOe and ± 600 Oe (an inset) for **1**(Mn(acac); Et).

A saturation in magnetization seems to be already completed for **1**(Mn(acac); Et), while further increasing tendency in magnetization by increasing the field from ±50 kOe can be observed for **1**($MnCl_2$; Et). The computational simulation suggests that the saturation occurs at the field of ca. ±300 kOe and the magnetization becomes ca. ±5,500 emu mol^{-1}, being close to the value obtained by one S = 1/2 spin entity. The field dependences of magnetization exhibited a hysteresis with coercive forces of 650 and 35 Oe for **1**($MnCl_2$; Et) and **1**(Mn(acac); Et), respectively (see inserts in Figure 3).

There are so far known a number of dianionic, monoanionic and neutral organic transition metal complexes with ethylenedithiolato,[8] ethylenediselenolato,[9] benzenedithiolato,[10] isotrithionedithiolato[11] or tetrathiafulvalenyldithiolato groups, which exhibited high to low electrical conductivities and furthermore superconductivity. However, it is a first case that their derivatives, **1**($MnCl_2$; Et) and **1**(Mn(acac); Et) became ferromagnets at comparatively high temperature of ca. 20 K. It is most conceivable that below 20 K the three spins involved in each molecules are subject to strong intra-/inter-molecular antiferromagnetic interaction, giving rise to ferromagnetic spin ordering. Eventually, ferromagnetic spin ordering due to one S = 1/2 spin entity is achieved for **1**($MnCl_2$; Et). On the other hand, for **1**(Mn(acac); Et) the whole spin cancellation occurs, so that formally the magnetization should become zero. However, very small magnetization remains as a result of different g values between the Mn(III) d spin and DETTTFDT radical π spin. Nevertheless, the details on the magnetism and spin interaction in these Mn complexes remain to be still open, till their single

crystals are successfully obtained and the X-ray structure analysis as well as the magnetic measurement are performed.

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