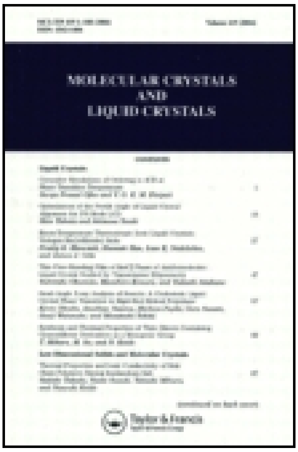

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Study on the Molecular Magnetism in Mixed Valence Iron Complexes, $M[Fe^{II}Fe^{III}(mto)_3]$ ($M=(n\text{-}C_nH_{2n+1})_4N$, mto=monothiooxalato ($C_2O_3S$))

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Study on the Molecular Magnetism in Mixed Valence Iron Complexes, $M[Fe^{II}Fe^{III}(mto)_3](M = (n\text{-}C_nH_{2n+1})_4N$, mto = monothiooxalato $(C_2O_3S))$

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We have synthesized and investigated the physical properties of a new mixed valence iron complex, $(n\text{-}C_3H_7)_4N[Fe^{II}Fe^{III}(mto)_3]$ (mto=C_2O_3S). This complex behaves as a ferrimagnet with T_N=38 K and θ=–117 K. From the analysis of the Mössbauer spectrum of $(n\text{-}C_3H_7)_4N[Fe^{II}Fe^{III}(mto)_3]$ at 298 K, the spin state of Fe^{II} was determined to be the high spin state (S=2), but it was difficult to determine the spin state of Fe^{III}. So that, in order to elucidate the spin state of Fe^{III}, we have investigated ESR spectra, and confirmed the coexistence of high spin state (S=5/2) and low spin state (S=1/2) for the Fe^{III} sites. Moreover, we have synthesized $(n\text{-}C_4H_9)_4N[Fe^{II}Fe^{III}(mto)_3]$. This complex shows the ferrimagnetic phase transition at 41 K, and Weiss constant is –76 K. In our previous paper, we have reported that mixed-valence complex $(n\text{-}C_3H_7)_4N[Fe^{II}Fe^{III}(dto)_3]$ (dto=$C_2O_2S_2$) shows a new type of phase transition connected with charge transfer phase transition and spin-crossover transition around 120 K. In the title complexes, the charge transfer phase transition was not observed.

Keywords: mixed valence complex; charge transfer phase transition; monothiooxalato

INTRODUCTION

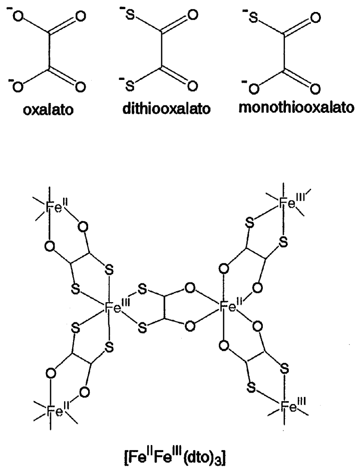

FIGURE 1 Bridging ligands and the network structure of $[Fe^{II}Fe^{III}(dto)_3]$ complexes.

Polynuclear oxalato-bridge complexes are attracting much interest from the viewpoint of molecular magnetism. The magnetic properties of oxalato bridged two-dimensional network complexes $(n\text{-}C_nH_{2n+1})_4N[M^{II}M'^{III}(ox)_3]$ (M=Mn, Fe, etc.; M'=Cr, Fe; ox=C_2O_4) have been well investigated[1-5]. $(n\text{-}C_nH_{2n+1})_4N[M^{II}M'^{III}(dto)_3]$ (M=Mn, Fe, etc.) are also considered to form dto bridged two-dimensional network system[6].

Recently, we have reported that mixed-valence complex $(n\text{-}C_3H_7)_4N[Fe^{II}Fe^{III}(dto)_3]$ shows a new type of phase transition connected with charge transfer phase transition and spin-crossover transition around 120 K, and shows a ferromagnetic phase transition at 6.5 K[7]. This complex has a two dimensional network structure with an alternating array of Fe^{II} and Fe^{III} ions through dto bridges, which is estimated by the single-crystal X-ray analysis of $(n\text{-}C_3H_7)_4N[Co^{II}Fe^{III}(dto)_3]$[8]. Figure 1 shows the bridging ligand, dto, and its derivatives and the network structure of $[Fe^{II}Fe^{III}(dto)_3]$ complexes.

In order to investigate multi-functional properties coupled with spin, charge and photon, we have synthesized new mixed-valence complexes, $(n\text{-}C_nH_{2n+1})_4N[Fe^{II}Fe^{III}(mto)_3]$ (n=3, 4) and have investigated their magnetic properties. These complexes have the possibility of dielectric response and nonlinear optical effect caused by the lack of inversion-symmetry at the Fe^{III} site.

In contrast to the great number of oxalato-bridged complexes, a few monothiooxalato-bridged complexes[9, 10] are known. In this paper, we report the magnetic properties of $(n\text{-}C_nH_{2n+1})_4N[Fe^{II}Fe^{III}(mto)_3]$ (n=3, 4).

EXPERIMENTAL

Sample Preparation.

$KBa[Fe(mto)_3]\cdot 4H_2O$ was synthesized in a similar way to prepare $KBa[Fe(dto)_3]$[11]. $K_2(mto)$[9] was dissolved in a aqueous solution of $Fe(NO_3)\cdot 9H_2O$, and the precipitate was immediately filtered off to avoid contamination. $BaBr_2\cdot 2H_2O$ was added to the filtrate. In this way, $KBa[Fe(mto)_3]\cdot 4H_2O$ was obtained as orange colored precipitate.

$(n\text{-}C_nH_{2n+1})_4N[Fe^{II}Fe^{III}(mto)_3]$ was synthesized in a similar way to prepare $(n\text{-}C_3H_7)_4N[M^{II}Cr^{III}(dto)_3]$(M=Fe, Co, Ni, Zn)[12]. A solution of $FeCl_2$ and $(n\text{-}C_nH_{2n+4})NBr$ in a methanol-water mixture was stirred. To this, a solution of $KBa[Fe(mto)_3]\cdot 4H_2O$ in a methanol-water mixture was added. In this way, $(n\text{-}C_nH_{2n+1})_4N[Fe^{II}Fe^{III}(mto)_3]$ was obtained as brown colored precipitate.

Magnetic Measurement

The temperature dependence of magnetic susceptibility was measured with Quantum Design MPMS5 SQUID susceptometer. Powdered sample of 40 mg was wrapped in polyethylene film and held in a plastic straw. The applied field was 5000 G. The magnetic susceptibility data were corrected for the core diamagnetism estimated from Pascal's tables and the background of the polyethylene film. The ESR spectra were measured by a JEOL X-band ESR spectrometer equipped with an Air Product LTR-3 cryostat.

RESULTS AND DISCUSSION

$(n\text{-}C_nH_{2n+1})_4N[Fe^{II}Fe^{III}(mto)_3]$ is presumed to have a two-dimensional network structure with an alternating array of Fe^{II} and Fe^{III} ions through dto bridges, which is estimated by the X-ray powder diffraction analogy with $(n\text{-}C_nH_{2n+1})_4N[Fe^{II}Fe^{III}(dto)_3]$.

The inverse magnetic susceptibility and the effective magnetic moment as a function of temperature for $(n\text{-}C_3H_7)_4N$ $[Fe^{II}Fe^{III}(mto)_3]$

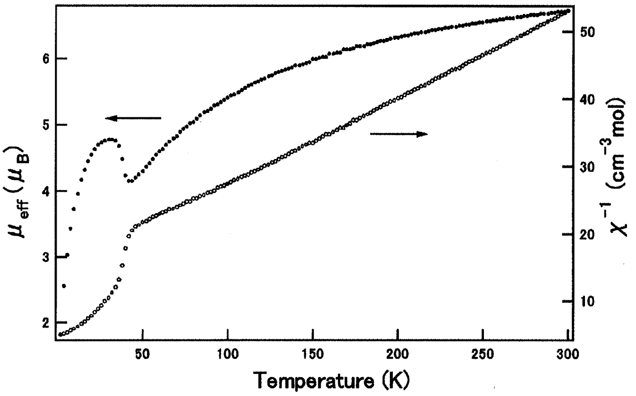

FIGURE 2 Temperature dependence of the inverse magnetic susceptibility and the effective magnetic moment for $(n\text{-}C_3H_7)_4N[Fe^{II}Fe^{III}(mto)_3]$. The applied magnetic field is 5000 G.

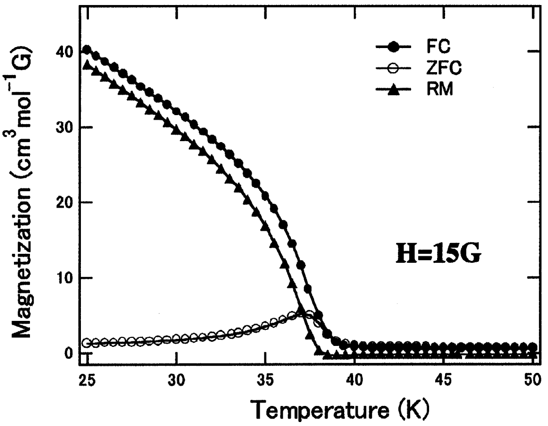

FIGURE 3 Temperature dependence of the magnetization for $(n\text{-}C_3H_7)_4N[Fe^{II}Fe^{III}(mto)_3]$. ● :field-cooled magnetization, ▲ : remnant magnetization, ○ : zero-field cooled magnetization.

are shown Figure 2. The effective magnetic moment, μ_{eff}, decreases with decreasing temperature.

It increases abruptly passing through a maximum of 4.8μ_B at 32 K, and then decreases.

This behavior is typical of ferrimagnetism, where the magnetic

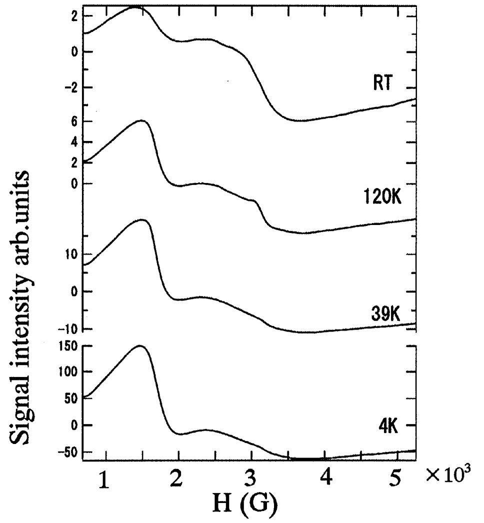

FIGURE 4 X-band ESR signal in $(n\text{-}C_3H_7)_4N[Fe^{II}Fe^{III}(mto)_3]$ at 298 K, 120 K, 39 K, and 4 K.

interaction between Fe^{II} and Fe^{III} are antiferromagnetic. The effective magnetic moment at room temperature is 6.7μ_B which is larger than the spin-only value of 5.19μ_B for Fe^{II}(S=2) and Fe^{III}(S=1/2), while smaller than the spin-only value of 7.68 μ_B for Fe^{II}(S=2) and Fe^{III}(S=5/2). From the analysis of the inverse magnetic susceptibility as a function of temperature, Weiss constant is estimated at −117 K.

In order to confirm the ferrimagnetic phase transition, we investigated the field-cooled magnetization (FCM), the remnant magnetization (RM), and the zero-field-cooled magnetization (ZFCM). As shown in Figure 3, the FCM obtained on cooling in the external magnetic field of 15 G shows a rapid increase below about 38 K. When the magnetic field is switched off at 2 K, the RM remains, and vanishes at about 38 K on heating. The ZFCM curve shows a maximum at 37 K. At any temperature below 38 K, the ZFCM is smaller than the FCM due to the fact that the applied magnetic field of 15 G is too weak to move the magnetic domain walls below the ferrimagnetic temperature. From the analysis of magnetization curves, the ferrimagnetic transition temperature is estimated at 38 K. The magnetic property of this complex is quite similar to that of $(n\text{-}C_3H_7)_4N[Fe^{II}Fe^{III}(ox)_3]$ which shows the ferrimagnetic phase transition at T_c=35 K[2].

From the analysis of the Mössbauer spectrum of (n-C_3H_7)$_4$N[$Fe^{II}Fe^{III}$(mto)$_3$] at 298 K, the spin state of Fe^{II} is considered to be the high spin state (S=2) but it is difficult to determine the spin state of Fe^{III}. So that, in order to elucidate the spin state of Fe^{III}, we have investigated ESR spectra which is shown in Figure 4, and confirmed the coexistence of the signals corresponding to the high spin state (S=5/2) at 300 mT and low spin state (S=1/2) at 150 mT between 4 and 298K. This complex does not show any charge transfer phase transition in contrast with (n-C_3H_7)$_4$N[$Fe^{II}Fe^{III}$(dto)$_3$].

Moreover, we have synthesized (n-C_4H_9)$_4$N[$Fe^{II}Fe^{III}$(mto)$_3$]. This complex shows the ferrimagnetic phase transition at 41 K, and Weiss constant is estimated at –76 K. The μ_{eff} value at room-temperature is $5.7\mu_B$.

Further detailed investigations of the temperature dependence of spin states in (n-C_nH_{2n+1})$_4$N[$Fe^{II}Fe^{III}$(mto)$_3$] are in progress.

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