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Dithiooxalato(dto)-Bridged Bimetallic Assemblies $\{NPr_4[MCr(dto)_3]\}_x$ (M=Fe, Co, Ni, Zn; NPr_4=Tetrapropylammonium Ion): New Complex-Based Ferromagnets

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The reaction of potassium calcium tris(dithiooxalato)chromate(III) hexahydrate $KCa[Cr(dto)_3]\cdot 6H_2O$, a metal(II) salt and a tetrapropylammonium bromide (NPr_4Br) in aqueous methanol forms bimetallic assemblies $\{NPr_4[MCr(dto)_3]\}_x$ (M=Fe (**1**), Co (**2**), Ni (**3**), Zn (**4**)), where the dto group bridges Cr(III) and M(II) ions through the sulfur atoms to Cr(III) and through the oxygen atoms to M(II) to provide an alternate array of Cr(III) and M(II) ions. The magnetic susceptibility data for **1**—**3** in the temperature range 5—300 K obey the Curie Weiss law ($\chi_M^{-1}=(T-\theta)/C$) with a positive Weiss constant (+18 K for **1**, +24 K for **2**, and +41 K for **3**), and the effective magnetic moments increase with decreasing temperature. The megnetization studies (field-cooled magnetization, remnant magnetization, and zero-field cooled magnetization) reveal the ferromagnetic phase transition at T_C=8, 16, and 23 K for **1**, **2**, and **3**, respectively. The assembly **4** shows paramagnetic behavior in the temperature range of 5—300 K.

In the past few years, there has been increasing interest in the design of molecular-based magnetic materials using paramagnetic matal complexes as the constituents.[1,2] In pioneering studies, three types of molecular-based systems exhibiting spontaneous magnetization have been reported: one-dimensional charge-transfer complexes by Miller et al.,[3] bimetallic chain complexes by Kahn et al.,[4] and radical-bridged chain complexes by Caneschi et al.[5] In those magnets based on one-dimensional chains the magnetic phase-transition temperature (T_C or T_N) is governed by both intra- and interchain magnetic interactions[6] and remains low because interchain interaction is generally weak. Therefore, recent efforts have been devoted to two- or three-dimensional network structures of bimetallic assemblies,[7—11] with the hope of obtaining high T_C or T_N ferromagnets.

Recently we have reported a new synthetic strategy for complex-based ferromagnets using a three-bridging, D_3-symmetric complex as the building block to provide a two- or three-dimensional network structure of bimetallic assemblies in a one-pot reaction.[7] In our previous study tris(oxalato)chromate(III) $[Cr(ox)_3]^{3-}$ was adopted as such a building block to give a series of bimetallic assemblies $\{NBu_4[MCr(ox)_3]\}_x$ (NBu_4= tetrabutylammonium ion; M(II)=Mn, Fe, Co, Ni, Cu, Zn). They are presumed to have a two-[12] or three-dimensional[13] network structure with an alternating array of Cr(III) and M(II) ions through ox bridges. The assemblies except for that of M=Zn show the ferromagnetic phase-transition at T_c=6—14 K. Our subsequent magnetic studies on heterodinuclear Cr(III)-ox-M(II) (M=Mn, Fe, Co, Ni, Cu) complexes as the nearest unit of $\{NBu_4[MCr(ox)_3]\}_x$ have proved that the T_C of those ferromagnets is governed by the exchange integral J between the nearest neighbors.[14] Further, a series of bimetallic assemblies $\{NBu_4[MFe(ox)_3]\}_x$ (M=Mn, Fe, Ni, Zn)[15] have been obtained using tris(oxalato)ferrate(III) $[Fe(ox)_3]^{3-}$ as the building block, and $\{NBu_4[FeFe(ox)_3]\}_x$ and $\{NBu_4[NiFe(ox)_3]\}_x$ have been found to be ferrimagnets of T_N=+43 and +28 K, respectively.

Besides the combination of metal ions, the nature of the bridging group must be an important factor contributing to the phase transition temperature of such bimetallic ferromagnets. In this study, we have adopted the dithiooxalate (dto) group as the bridge of the bimetallic assemblies. The choice of the dto bridge is based on our recent finding that a dto-bridged Cr(III)-Ni(II)$_3$ complex $[Cr(dto)_3\{Ni(tet\ b)\}_3](ClO_4)_3$ (tet b= racemic 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane),[16] having a centrosymmetric triangular core structure with the Cr(III) ion at the center and the Ni(II) ions at the corners, exhibits a strong ferromagnetic interaction (J=+5.9 cm^{-1} based on the spin Hamiltonian $\mathscr{H}=-2J\hat{S}_1\hat{S}_2$) relative to the corresponding ox-bridged Cr(III)Ni(II)$_3$ complex $[Cr(dto)_3\ \{Ni(tet\ b)\}_3](ClO_4)_3$ (J=+2.65 cm^{-1}).[17] In this study a series of dto-bridged bimetallic assemblies $\{NPr_4[MCr(dto)_3]\}_x$ (M(II)=Fe (**1**), Co (**2**), Ni (**3**), Zn (**4**); NPr_4^+= tetrapropylammonium ion) (see Fig. 1) have been prepared and their magnetic properties have been studied.

Experimental

Physical Measurements. Elemental analyses of C, H, and N were obtained from the Service Center of Elemental Analysis, Kyushu University. Analyses of metals were done on a Shimadzu AA-680 Atomic Absorption/Flame Emission Spectrophotometer. Infrared (IR) spectra were measured on KBr disks or Nujol mulls with a JASCO IR-810 spectrometer. Electronic spectra of powdered samples were recorded on a Shimadzu MPS-2000 Multipurpose Spectrophotometer. Magnetic susceptibilities were measured on a HOXAN HSM-D SQUID susceptometer (applied magnetic field: 50 G) in the temperature range of 4.5—100 K and on a Faraday

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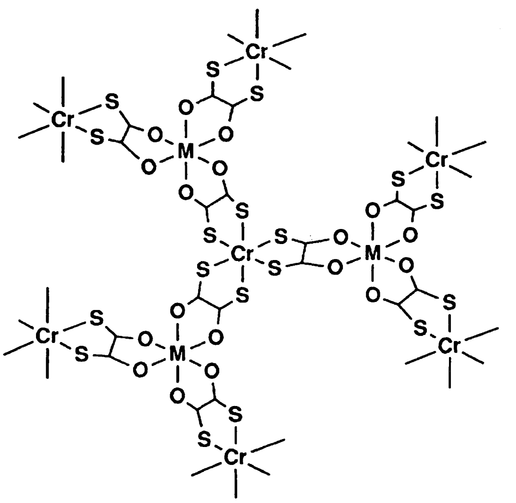

Fig. 1. Schematic representation of the dto-bridged network structure.

balance (applied field: 5000 G) in the range of 80—300 K. Calibrations were made with $(NH_4)_2Mn(SO_4)_2{\cdot}6H_2O$[18] for the SQUID susceptometer and with $[Ni(en)_3]S_2O_3$[19] for the Faraday balance. Diamagnetic corrections for the constituting atoms were made using Pascal's constants.[20] Magnetization studies (field-cooled magnetization, remnant magnetization, and zero-field-cooled magnetization) were carried out on the SQUID susceptometer.

Materials. $KCa[Cr(dto)_3]{\cdot}6H_2O$[21] was prepared by the literature method. Tetrapropylammonium bromide NPr_4Br, $FeCl_2{\cdot}4H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, and $Zn(NO_3)_2{\cdot}6H_2O$ were of reagent grade and used as purchased.

Preparation of $\{NPr_4[MCr(dto)_3]\}_x$. The bimetallic assemblies $\{NPr_4[MCr(dto)_3]\}_x$ (M=Fe (**1**), Co (**2**), Ni (**3**), Zn (**4**)) were obtained in a similar way. The synthesis of **1** is described. A solution of $KCa[Cr(dto)_3]{\cdot}6H_2O$ (300 mg, 0.5 mmol) in a deaerated methanol-water mixture (6 : 4 in volume, 10 cm^3) was stirred at 50 °C. To this was added dropwise a solution of $FeCl_2{\cdot}4H_2O$ (99 mg, 0.5 mmol) and NPr_4Br (260 mg, 0.8 mmol) in a deaerated methanol–water mixture (6 : 4 in volume, 15 cm^3) to result in the precipitation of reddish brown microcrystals. They were separated by suction filtration, washed successively with a methanol–water (1 : 1 in volume) mixture, methanol, and ether, and dried over P_2O_5 in a vacuum dessicator.

The yields and elemental analyses of **1**—**4** are summarized in Table 1.

Results and Discussion

Synthesis and General Characterization. The ox-bridged bimetallic assemblies $\{NBu_4[MCr(ox)_3]\}_x$ were readily obtained by a one-pot reaction of $K_3[Cr(ox)_3]{\cdot}6H_2O$, a metal(II) salt, and NBu_4Br in aqueous solution. A similar reaction using $KCa[Cr(dto)_3]{\cdot}6H_2O$ instead of $K_3[Cr(ox)_3]{\cdot}6H_2O$ in aqueous solution was not available for the preparation of dto-bridged assemblies because of formation of a tarry material. After many efforts, tetrapropylammonium ion proved to be a better counter cation than NBu_4^+ and eventually the dto-bridged bimetallic assemblies **1**—**4** could be obtained by the reaction in aqueous methanol at elevated temperature (see Experimental). By this method $\{NPr_4[MnCr(dto)_3]\}_x$ and $\{NPr_4[CuCr(dto)_3]\}_x$ were also obtained which gave good elemental analytical results. However, our preliminary cryomagnetic studies have proved paramagnetic nature for the two assemblies. Further, these two are significantly soluble in *N*,*N*-dimethylformamide and dimethyl sulfoxide, whereas **1**—**4** are practically insoluble in common solvents. It appears that the network structure with the alternating array of Cr(III) and M(II) ions (see Fig. 1) is not achieved in $\{NPr_4[MnCr(dto)_3]\}_x$ and $\{NPr_4[CuCr(dto)_3]\}_x$ assemblies. Thus, these two assemblies are not included in this study.

The parent complex $KCa[Cr(dto)_3]{\cdot}6H_2O$ has the CrS_6 coordination sphere with an *S*,*S*′-chelation mode of the dto group and shows ν(CO) vibrations at 1620 and 1530 cm^{-1}. The IR spectra of **1**—**4** show a ν(CO) vibration near 1500 cm^{-1}. The shift of the ν(CO) band to lower frequency implies the bridging function of the dto group in **1**—**4**.[22] The electronic spectra of the parent complex and the bimetallic assemblies **1**—**4** were measured by the reflection on powdered samples. The parent complex with the CrS_6 chromophore shows a charge-transfer band at 495 nm and a d–d band at 590 nm.[23] The spectra of **1**—**4** each contain both of the transitions (near 495 and 580 nm), indicating that the Cr(III) retains the *S*,*S*′ chelation mode in these assemblies. It should be emphasized that the tetranuclear $CrNi_3$ complex $[Cr(dto)_3\{Ni(tet\ b)\}_3](ClO_4)_3$, which has the CrS_6 coordination sphere based on X-ray crystallography,[16] also shows the visible bands at 497 and 565 nm. For **1** and **3**, a discernible shoulder is seen at 690 and 770 nm, respectively, which can be assigned to a d–d band of Fe(II) and Ni(II) ion, respectively. In the reflectance spectra of **2**, no d–d band assignable to the Co(II) ion was resolved. Based on these facts we presume that the bimetallic assemblies **1**—**4** have the network structure with the alternate array of Cr(III) and M(II) ions (Fig. 1), bridged by dto group bonding through sulfur atoms to the Cr and through oxygen atoms to the Ni.

Table 1. Ferromagnetic Phase-Transition Temperatures (T_C/K) of Bimetallic Ferromagnets

M	$\{NPr_4[MCr(dto)_3]\}_x$[a)]	$\{NBu_4[MCr(ox)_3]\}_x$[b)]
Fe	(**1**) 8	12
Co	(**2**) 16	10
Ni	(**3**) 23	14

a) This work; b) Ref. 15.

Oue efforts to grow single crystals suitable for X-ray crystallography were all in vain.

Magnetism. The cryomagnetic property of the bimetallic assemblies **1**—**4** was studied in the temperature range of 4.2—300 K. The respective cryomagnetic behavior of **1**—**4** is shown in Figs. 2, 3, 4, and 5 in the forms of $\chi_{\rm M}^{-1}$ vs. T and $\mu_{\rm eff}$ vs. T plots, where $\chi_{\rm M}$ is the magnetic susceptibility per CrM and $\mu_{\rm eff}$ is the effective magnetic moment calculated by the equation $\mu_{\rm eff}=[8\chi_{\rm M}T]^{1/2}$.

The effective magnetic moment of **1** is 6.53 $\mu_{\rm B}$ at room temperature that is slightly larger than the spin-only value of 6.24 $\mu_{\rm B}$ for the magnetically dilute Cr(III)-Fe(II) ($S_{\rm Cr}=3/2$, $S_{\rm Fe}=2$). On decreasing temperature, the moment increases up to a maximum value of 22.0 $\mu_{\rm B}$ at 6.5 K and then decreases below this temperature (see Fig. 2). The magnetic susceptibility of **1** obeys the Curie–Weiss law ($\chi_{\rm M}^{-1}=(T-\theta)/C$) in the range of 70—300 K with a positive Weiss constant of +18 K. The observed magnetic behavior, except for the drop in $\mu_{\rm eff}$ below 6.5 K, suggest the operation of a ferromagnetic interaction within this assembly. The decrease in magnetic moment below 6.5 K may be ascribed to disorder of the network structure.[15]

The magnetic susceptibility data of **2** and **3** (see Figs. 3 and 4, respectively) also obey the Curie–Weiss law in the range of 70—300 K with a positive Weiss constant of +24 and +41 K, respectively. The effective magnetic moment of **2** is 6.45 $\mu_{\rm B}$ at room temperature (spin-only value for Cr(III)Co(II): 5.48 $\mu_{\rm B}$) and increases with decreasing temperature upto 37.5 $\mu_{\rm B}$ at 15.6 K. This moment is the upper limit available in our magnetic measurements under 50 G. The effective magnetic moment of **3** is 5.37 $\mu_{\rm B}$ at room temperature (spin-only value for Cr(III)Ni(II): 4.80 $\mu_{\rm B}$) and increases with decreasing temperature up to 32.9 $\mu_{\rm B}$ at 20.0 K (upper limit available under 50 G). In the case of **4**, the magnetic susceptibility data obey the Curie law, and the effective magnetic moment is practically independent of temperature in the range of 5—300 K (3.87 $\mu_{\rm B}$ per CrZn). This is a good indication that the alternating array of Cr(III) and Zn(II) ions is achieved over the lattice, but no appreciable magnetic interaction occurs within the lattice owing to the presence of diamagnetic Zn(II) ions.

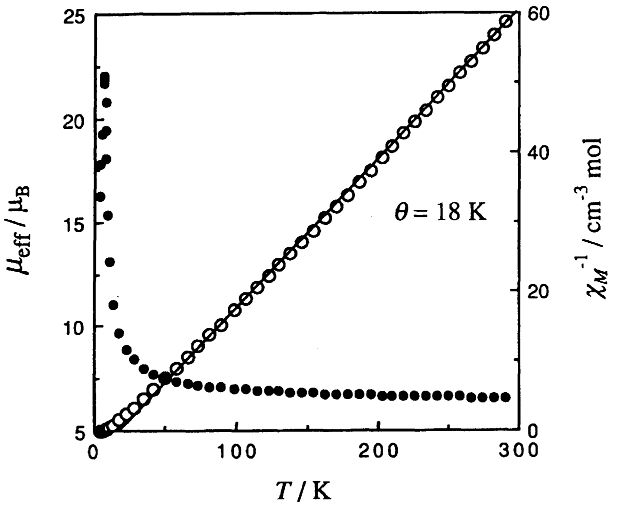

Fig. 2. $\chi_{\rm M}^{-1}$ vs. T (○) and $\mu_{\rm eff}$ vs. T (●) plots of **1**.

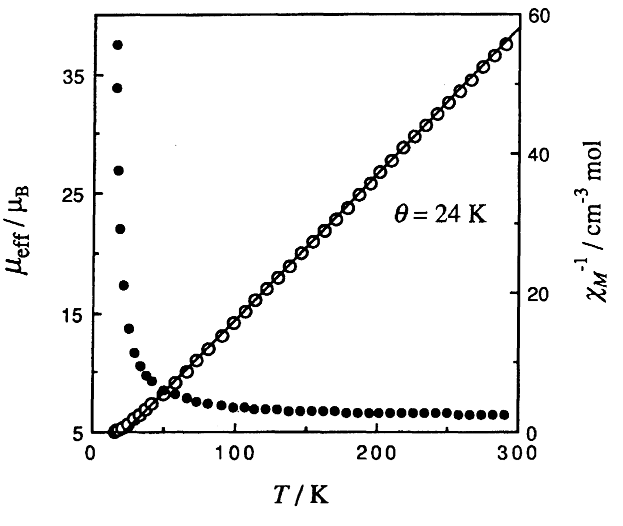

Fig. 3. $\chi_{\rm M}^{-1}$ vs. T (○) and $\mu_{\rm eff}$ vs. T (●) plots of **2**.

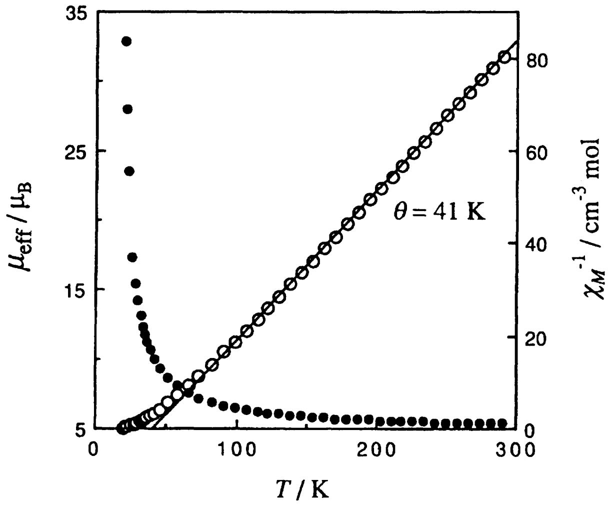

Fig. 4. $\chi_{\rm M}^{-1}$ vs. T (○) and $\mu_{\rm eff}$ vs. T (●) plots of **3**.

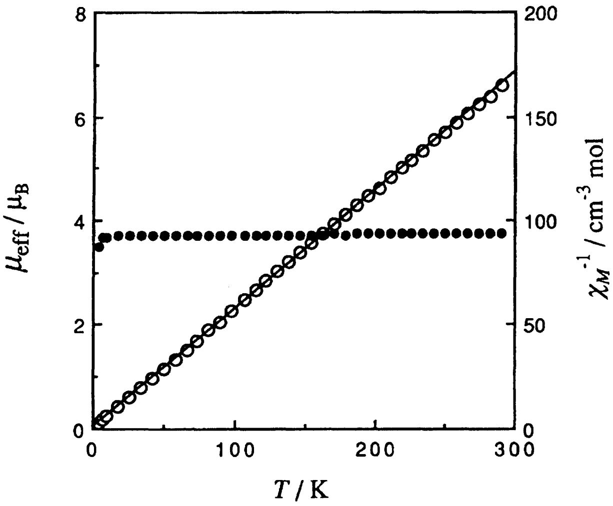

Fig. 5. $\chi_{\rm M}^{-1}$ vs. T (○) and $\mu_{\rm eff}$ vs. T (●) plots of **4**.

The sharp increase in the magnetic moment of **1**—**3** at low temperature is regarded as the onset of long-range magnetic ordering over the lattice. The μ_{CrM} vs. T curves showing a monotonous increase with decreasing temperature are typical of ferromagnets[3,7] but not ferrimagnets.[4,15] In order to confirm the ferromagnetic phase transition in **1**—**3**, field-cooled magnetization (FCM; under applied magnetic field of 3G), remnant magnetization (RM), and zero-field-cooled magnetization (ZFCM; cooling the sample under zero field and warming under 3 G) were measured. The results are given in Figs. 6, 7, and 8.

The FCM curve of **1** showed a rapid increase in molar magnetization below 9 K and a tendency to saturate near 5 K (Fig. 6). When the magnetic field was switched off at 5 K, a RM of 58 cm^3 mol^{-1} G was observed which vanished at 8 K upon warming. The ZFCM curve showed a maximum at 8.3 K. Based on these magnetization studies, the ferromagnetic phase-transition temperature of **1** was determined to be $T_C = 8$ K. At any temperature below 8 K, the ZFCM is smaller than the FCM due to the fact that in this low temperature range the applied field is too weak to move the domain walls.

In the case of **2**, the FCM increased sharply below 16 K and showed a tendency to saturate below 10 K (Fig. 7). The RM at 4.2 K was ca. 200 cm^3 mol^{-1} G which vanished at 16 K on warming. The ZFCM curve showed a maximum at 15.5 K. Based on these studies, the magnetic phase-transition temperature of **2** was determined to be ca. 16 K.

The magnetization behavior of **3** is complicated (Fig. 8). The FCM curve showed a two-step behavior with an increase in magnetization near 23 K and a more abrupt increase near 18 K. The RM observed at 4.2 K was essentially the same as the FCM at this temperature. Upon warming, the RM decreased to a minimum value at 17 K, increased to a maximum value near 18 K, and vanished at 23 K. The ZFCM curve showed a maximum at 15 K and a plateau near 22 K. The same result has been obtained for the separately prepared samples, indicating that the unusual magnetization behavior is inherent in this assembly. The origin for the rate magnetization remains to be studied in the future. The T_C of **3** is taken as the temperature at which the ZFCM vanishes ($T_C = 23$ K).

The magnetic phase-transition temperatures T_C of **1**—**3** are summarized in Table 1, together with those of the corresponding ox-bridged ferromagnets $\{\mathrm{NBu_4[MCr(ox)_3]}\}_x$.

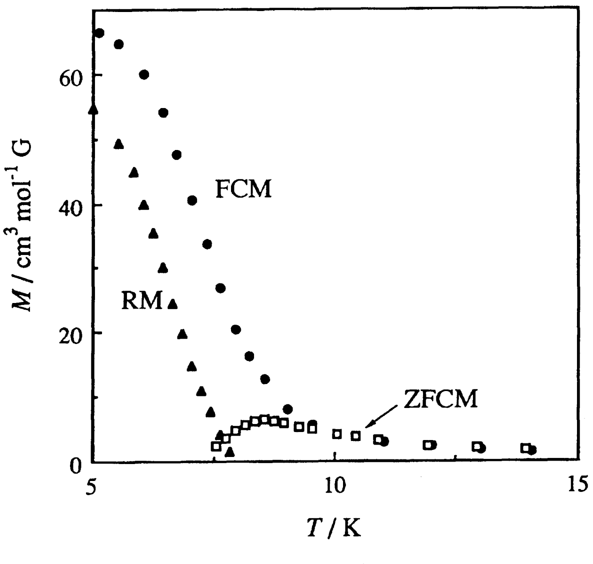

Fig. 6. Field-cooled magnetization (FCM; applied field 3G), remnant magnetization (RM), and zero-field-cooled magnetization (ZFCM) of **1**.

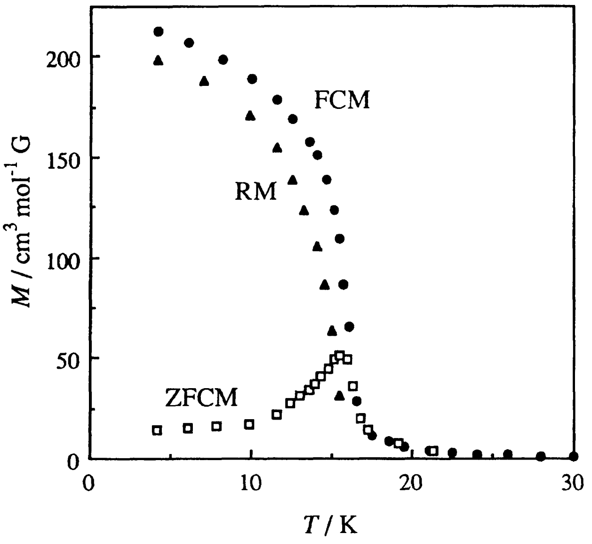

Fig. 7. Field-cooled magnetization (FCM; applied field 3G), remnant magnetization (RM), and zero-field-cooled magnetization (ZFCM) of **2**.

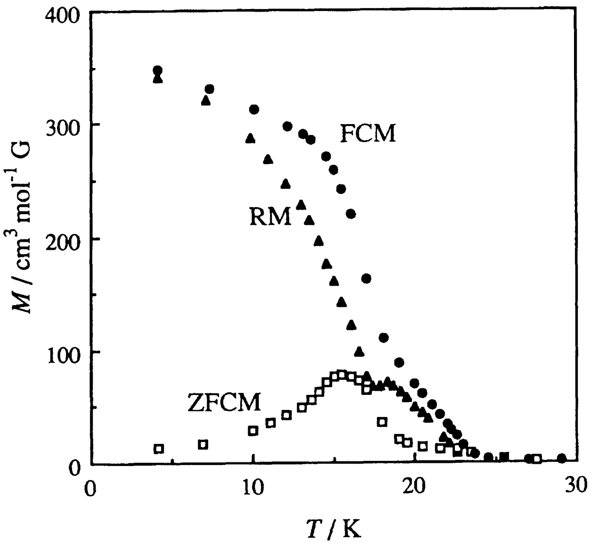

Fig. 8. Field-cooled magnetization (FCM; applied field 3G), remnant magnetization (RM), and zero-field-cooled magnetization (ZFCM) of **3**.

It is seen that the T_C of **1** is lowered, whereas the T_Cs of **2** and **3** are heightened relative to the T_C of the respective ox-bridged assembly. We have shown[14)] that the T_C of those ferromagnets is governed by the exchange integral (J) in the nearest neighbors:[24)]

$$T_C = (nJ/3k_B)[S_{Cr}(S_{Cr}+1)S_M(S_M+1)]^{1/2},$$

where n is the number of the nearest M about Cr (vice versa), S_{Cr} and S_M are the spins of the metal ions, k_B is the Bohr magneton. Based on this equation, the J values operating in the dinuclear unit of **1**, **2**, and **3** are evaluated to be +1.2, +3.0, and +5.8 cm^{-1}, respectively. It is emphasized that the J value of **3** agrees with the J value of the dto-bridged tetranuclear complex $[Cr(dto)_3\{Ni(tet\ b)\}_3](ClO_4)_3$ (J=+5.9 cm^{-1}).[16)]

In dinuclear Cr(III)–M(II) complexes, the overall exchange integral J_{CrM} is expressed by the mean of the individual interactions:

$$J_{CrM} = \frac{1}{n_i n_j}\sum_{i,j} J_{ij},$$

where n_i and n_j denote the number of unpaired electrons on Cr(III) and M(II) ions, respectively, and J_{ij} is the exchange integral between a magnetic orbital on the Cr(III) ion and a magnetic orbital on the M(II) ion. It is known that ox bridge can mediate magnetic interactions through both σ- and π-superpathways.[14)] This must also be the case with dto bridge. In a dto-bridged one-dimensional $\{Mn^{2+}\text{–dto–}Cu^{2+}\}_x$ complex,[25)] one unpaired electron on the $d_{x^2-y^2}$(Mn) orbital and one unpaired electron on the $d_{x^2-y^2}$(Cu) orbital (local x and y axes are taken along the donor atoms on the equatorial plane) couple through the dto's HOMO of σ-character and this contribution is dominant, resulting in a negative overall exchange integral J_{MnCu}. In the case of **3**, the J_{CrNi} value of the nearest neighbors, given by (1/6)-$[J_{xy,x^2-y^2}+J_{xz,x^2-y^2}+J_{yz,x^2-y^2}+J_{xy,z^2}+J_{xz,z^2}+J_{yz,z^2}]$, is invariably positive because of the strict orthogonality of magnetic orbitals[26)] in all the J_{ij} components. The J_{CrNi} value of **3** (+5.9 cm^{-1}) is significantly large compared with those of ox-bridged dinuclear and oligonuclear Cr(III)–Ni(II) complexes (J: +2.7—4.6 cm^{-1}).[14)] This may be explained by efficient 3d(M)-3p(S) orbital interaction relative to 3d(M)–2p(O) orbital interaction. Gleizes and Verdaguer[25)] have explained the very strong magnetic interaction in a one-dimensional $\{Mn^{2+}\text{–dto–}Cu^{2+}\}_x$ complex in terms of "diffuseness" of the sulfur p orbitals.

Based on the magnetic studies of a series of the Cr(III)–ox–M(II) (M=Mn, Fe, Co, Ni, Cu) complexes,[14)] we have found that three unpaired electrons on the Cr(III) t_{2g} orbitals and n unpaired electrons on the M(II) t_{2g} orbitals (M=Mn, Fe, Co) couple antiferromagnetically through the dto's occupied MO of π-character. If the ferromagnetic $J[(t_{2g})^3/(e_g)^2]$ contribution in **1** and **2** is assumed to be the same as that of **3** ($J[(t_{2g})^3/(e_g)^2]=6J_{CrNi}=+34.8$ cm^{-1}), the antiferromagnetic contribution $J[(t_{2g})^3/(t_{2g})^n]$ can be evaluated to be -20 cm^{-1} for **1** (n=2) and -8 cm^{-1} for **2** (n=1). The results indicate a significance of the dto's occupied MO of π-character in antiferromagnetic coupling. Thus, it is shown that dto bridge can mediate magnetic spin-exchange through both σ- and π-superpathways, which give rise to a ferromagnetic and an antiferromagnetic contributions, respectively.

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