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Design of Metal–Complex Magnets. Syntheses and Magnetic Properties of Mixed-Metal Assemblies $\{NBu_4[MCr(ox)_3]\}_x$ (NBu_4^+ = Tetra(*n*-butyl)ammonium Ion; ox^{2-} = Oxalate Ion; M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+})

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Abstract: The reaction of $K_3[Cr(ox)_3]\cdot 3H_2O$, a metal(II) salt, and tetra(*n*-butyl)ammonium bromide in the molar ratio of 1:1:1.5 in water at room temperature afforded a series of mixed-metal assemblies with the formula $\{NBu_4[MCr(ox)_3]\}_x$ (M = Mn^{2+} (**1**), Fe^{2+} (**2**), Co^{2+} (**3**), Ni^{2+} (**4**), Cu^{2+} (**5**), Zn^{2+} (**6**)). These compounds are designed so as to assume a three-dimensional structure consisting of alternately arrayed Cr(III) and M(II) ions due to the D_3 symmetry of the building block $[Cr(ox)_3]^{3-}$. The magnetic susceptibility data of **1**–**5** above ca. 20 K obey the Curie–Weiss law with positive Weiss constants, and upon lowering the temperature, the effective magnetic moments increase gradually in the 300–20 K range and abruptly below ca. 20 K. The temperature dependences of magnetizations studied under a weak applied field (1 G) showed a magnetic phase transition at T_c = 6, 12, 10, 14, and 7 K for **1**, **2**, **3**, **4**, and **5**, respectively. Field dependences of the magnetization up to 7.5 T have been studied at 4.2 K using a pulsed magnet and the saturation magnetization values per formula M_S were compatible with $M_S = Ng\beta(S_{Cr} + S_M)$ ($M_S/N\beta$ = 7.74, 6.71, 5.94, 4.94, 3.83, and 2.79 for **1**, **2**, **3**, **4**, **5**, and **6**, respectively). Hysteresis loops have been obtained at 5 K, where the remnant magnetizations are 1500, 4100, 3000, 1200, and 1500 $cm^3\ mol^{-1}$ G and the coercive fields are 20, 320, 80, 160, and 30 G for **1**, **2**, **3**, **4**, and **5**, respectively.

Introduction

The design of molecular-based ferromagnets is one of the stimulating challenges for chemists. Two synthetic strategies to obtain pure organic ferromagnets (through-bond approach and through-space approach) have been proposed,[2] and attempts to obtain molecular-based organic magnets have been extensively carried out. Recently, three types of molecular-based systems exhibiting a spontaneous magnetization have been fully characterized from both structural and magnetic viewpoints: (1) one-dimensional charge-transfer complex $[Fe(Me_5Cp)_2]^+[TCNE]^-$ (Me_5Cp = pentamethylcyclopentadienyl, TCNE = tetracyanoethylene) by Miller et al.,[3] (2) one-dimensional oximato-bridged Mn(II)–Cu(II) complex $\{MnCu(pbaOH)(H_2O)_3\}_n$ ($pbaOH^{4-}$ = 2-hydroxy-1,3-propylenebis(oximato) anion) by Kahn et al.,[4] and (3) one-dimensional Mn(II)–radical complex $\{Mn(hfa)_2(NITR)\}_n$ ($hfac^-$ = hexafluoroacetylacetonato ion and NITR = 2-R-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxy 3-oxide (R = C_2H_5, *n*-C_3H_7, *i*-C_3H_7) by Gatteschi et al.[5]

The molecular-based ferromagnets reported so far are based on one-dimensional chains as the constituents in which the magnetic vectors are assembled by ferromagnetic intrachain interaction (ferromagnetic chain) or by antiferromagnetic interaction in an alternately arrayed S_A and S_B ($|S_A - S_B| \neq 0$) (ferrimagnetic chain) orientation. The crucial step to realize ferromagnets based on the one-dimensional chains is how to achieve the three-dimensional ferromagnetic ordering by controlling interchain interaction between such ferromagnetic or ferrimagnetic chains. If the interchain interaction is antiferromagnetic, the spins of the chains are cancelled in the lattice to produce an antiferromagnetic ordering.[6] The principle to controlling the interchain (intermolecular) interaction so as to achieve a three-dimensional ferromagnetic ordering has not been established, though several attempts have been reported to be successfully accomplished.[7,8] Further, even if the interchain magnetic interaction is achieved to induce three-dimensional magnetic ordering, the magnitude of the interchain interaction is in general very weak and as a result the critical temperature, T_c, is limited to low temperature. In order to achieve a higher T_c, Kahn et al.[7] and Gatteschi et al.[8] have directed their efforts in their recent works to solve the problem of dimensionality.

If the molecular design of ferromagnets based on a three-dimensional structure is developed, the essential problems associated with a one-dimensional system are solved. From this viewpoint, we report here such ferromagnets having a series of mixed-metal assemblies $\{NBu_4[MCr(ox)_3]\}_x$ (M = Mn^{2+} (**1**), Fe^{2+} (**2**), Co^{2+} (**3**), Ni^{2+} (**4**), Cu^{2+} (**5**), Zn^{2+} (**6**)). The compounds are designed as follows: (1) the intermetal linkage M–L–M′ (M′ = Cr(III),

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(2) (a) Iwamura, H.; Izuoka, A. *Nippon Kagaku Kaishi* **1987**, 595. (b) Inoue, K.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1991**, *113*, 9803. (c) Sugawara, T.; Bandou, S.; Kimura, K.; Iwamura, H.; Itoh, K. *J. Am. Chem. Soc.* **1986**, *108*, 368. (d) Izuoka, A.; Murata, S.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1987**, *109*, 2631. (e) Fukutome, H.; Takahashi, A.; Ozaki, M. *Chem. Phys. Lett.* **1987**, *133*, 34. (f) LePage, T. J.; Breslow, R. *J. Am. Chem. Soc.* **1987**, *109*, 6412. (g) Torrance, J. B.; Oostra, S.; Nazzal, *Synth. Met.* **1987**, *19*, 708. (h) Korshak, Y. V.; Medvedeva, T. V.; Ovchinnikov, A. A.; Spector, V. N. *Nature* **1987**, *326*, 370.

(3) (a) Miller, J. S.; Calabrese, J. C.; Rommelmann, H.; Chittipeddi, S. R.; Zhang, J. H.; Reiff, W. M.; Epstein, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 769. (b) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Chem. Rev.* **1988**, *88*, 201. (c) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Science* **1988**, *240*, 40. (d) Miller, J. S.; Calabrese, J. C.; Harlow, R. L.; Dixon, D. A.; Zhang, J. H.; Reiff, W. M.; Chittipeddi, S.; Selover, M. A.; Esptein, A. J. *J. Am. Chem. Soc.* **1990**, *112*, 5496.

(4) (a) Kahn, O.; Pei, Y.; Verdaguer, M.; Renard, J. P.; Sletten, J. *J. Am. Chem. Soc.* **1988**, *110*, 782. (b) Kahn, O. In *Organic and Inorganic Low-Dimensional Crystalline Materials*; Delhaes, P., Drillon, M., Eds.; NATO ASI Series 168; Plenum: New York, 1987; p 93.

(5) (a) Caneschi, A.; Gatteschi, D.; Sessoli, R. *Acc. Chem. Res.* **1989**, *22*, 392. (b) Caneschi, A.; Gatteschi, D.; Renard, J. P.; Rey, P.; Sessoli, R. *Inorg. Chem.* **1989**, *28*, 1976. (c) Caneschi, A.; Gatteschi, D.; Renard, J. P.; Rey, P.; Sessoli, R. *Inorg. Chem.* **1989**, *28*, 3314.

(6) (a) Gleizes, A.; Verdaguer, M. *J. Am. Chem. Soc.* **1984**, *106*, 3727. (b) Pei, Y.; Verdaguer, M.; Kahn, O.; Sletten, J.; Renard, J.-P. *Inorg. Chem.* **1987**, *26*, 138. (c) Sapina, F.; Coronado, E.; Beltran, D.; Burriel, R. *J. Am. Chem. Soc.* **1991**, *113*, 7940.

(7) (a) Lloret, F.; Nakatani, K.; Journaux, Y.; Kahn, O.; Pei, Y.; Renard, J. P. *J. Chem. Soc., Chem. Commun.* **1988**, 642. (b) Nakatani, K.; Carriat, J. Y.; Journaux, Y.; Kahn, O.; Lloret, F.; Renard, J. P.; Pei, Y.; Sletten, J.; Verdaguer, M. *J. Am. Chem. Soc.* **1989**, *111*, 5739. (c) Pei, Y.; Kahn, O.; Nakatani, K.; Codjovi, E.; Mathoniere, C.; Sletten, J. *J. Am. Chem. Soc.* **1991**, *113*, 6558.

(8) (a) Caneschi, A.; Gatteschi, D.; Renard, J. P.; Rey, P. *J. Am. Chem. Soc.* **1989**, *111*, 785. (b) Caneschi, A.; Gatteschi, D.; Melandri, M. C.; Rey, P.; Sessoli, R. *Inorg. Chem.* **1990**, *29*, 4228. (c) Caneschi, A.; Gatteschi, D.; Rey, P.; Sessoli, R. *Inorg. Chem.* **1991**, *30*, 3936.

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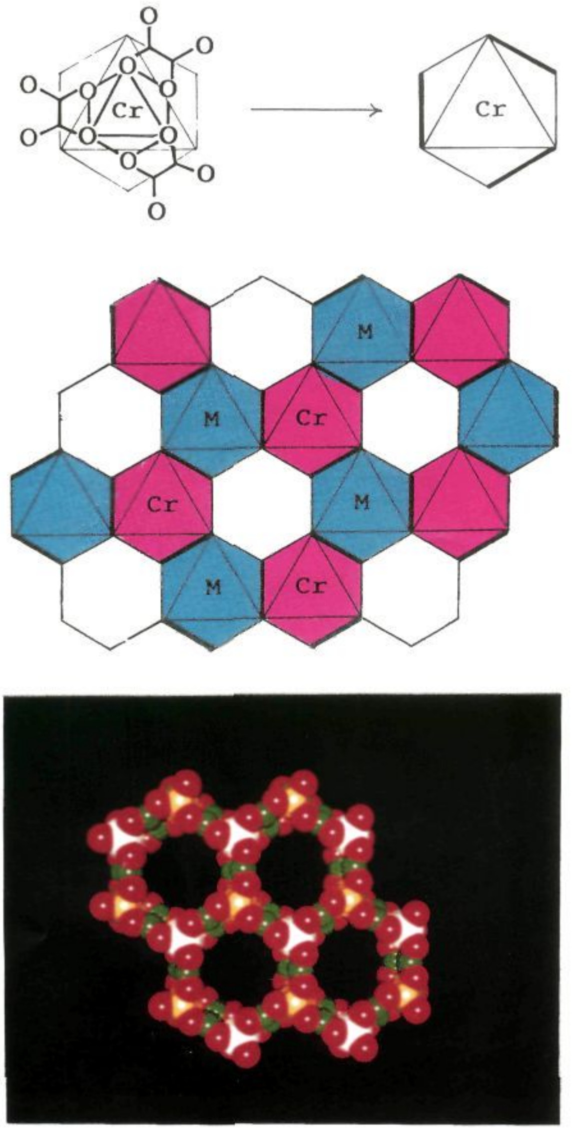

Figure 1. Schematic structure of a two-dimensional structure for $\{NBu_4[MCr(ox)_3]\}_x$ and the figure drawn by computer graphics using the space-filling model, where NBu_4^+ is eliminated for clarity. The structure is a view projected on the plane perpendicular to D_3 axis. The color balls represent carbon (green), oxygen (red), chromium (yellow), and other metal (white).

$L = ox^{2-}$ ion) extends three-dimensionally to the crystal lattice, because the molecular model consideration indicated that the reaction of the η^3-complex with D_3 symmetry $[Cr(ox)_3]^{3-}$, metal(II) ion, and NBu_4^+ ion in 1:1:1 stoichiometry produces an isotropic three-dimensional structure of mixed-metal assemblies, (2) the magnetic vectors are assembled over the lattice reflecting by either ferro- or antiferromagnetic interaction between the neighboring M and M′ ions, (3) the magnetic characteristics of the resulting ferromagnets or ferrimagnets can be varied by the choice of the "building block complex" and the additive metal ion, and (4) the synthesis is undertaken as a one-pot reaction. Here we will report the synthetic strategy, synthesis, characterization, and magnetic properties of a new family of ferromagnets, $\{NBu_4[MCr(ox)_3]\}_x$ ($M = Mn^{2+}$ (**1**), Fe^{2+} (**2**), Co^{2+} (**3**), Ni^{2+} (**4**), Cu^{2+} (**5**), Zn^{2+} (**6**)).[9]

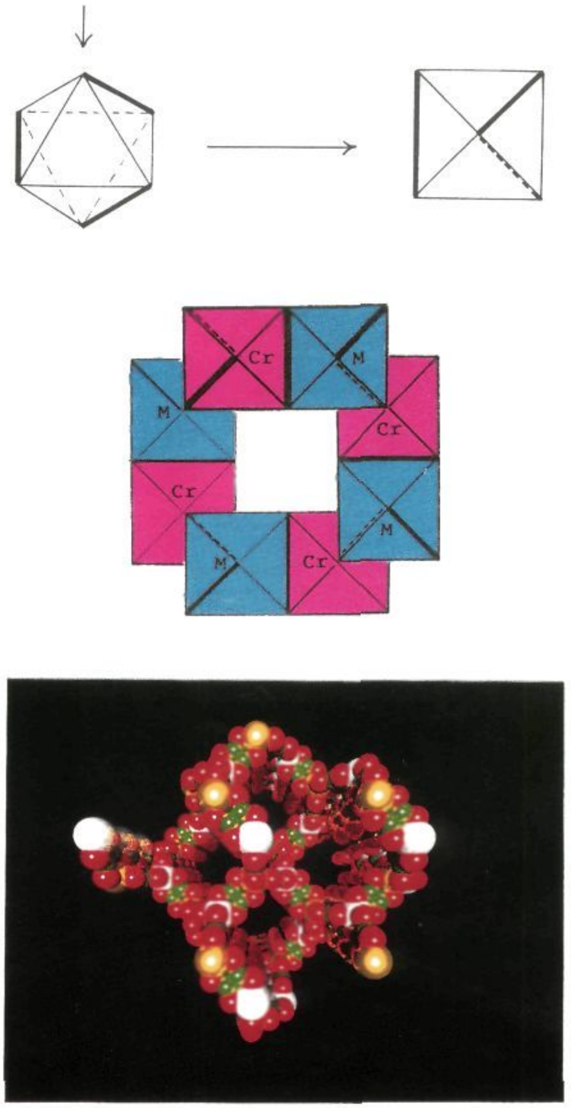

Figure 2. Schematic structure of a three-dimensional structure for $\{NBu_4[MCr(ox)_3]\}_x$ and the figure drawn by computer graphics using the space filling model, where NBu_4^+ is eliminated for clarity. The structure is a view projected along the 4-fold screw axis. The color balls represent carbon (green), oxygen (red), chromium (yellow), and other metal (white).

Results and Discussion

Synthetic Strategy. Ferromagnets can be described as having magnetic vectors of constituting paramagnetic centers that are aligned parallel over the three-dimensional lattice.[10] When we attempt to obtain synthetic ferromagnets, the molecular design of ferromagnets should have the answers to the questions (i) how to achieve a ferromagnetic interaction between the nearest neighboring magnetic spins and (ii) how to extend parallel alignment of the magnetic spin vectors over the three-dimensional lattice. Day et al. have found that compounds with the formula $A_2[CrCl_4]$ ($A = NH_3CH_3$, $NH_3C_2H_5$, ...) satisfied the above two conditions, since the compounds with a two-dimensional layer structure assume ferromagnetic (i) intra- and (ii) interlayer interactions.[11] We can find the most definite answer to the questions for a mixed-metal assembly. The mixed-metal system whose magnetic orbitals are strictly orthogonal to each other can give the ferromagnetic interaction between the mixed-metal ions.[12] For particular pairs of mixed-metal ions such as Cr(III)–Cu(II),

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(9) Preliminary data of one of the compounds, $\{NBu_4[CuCr(ox)_3]\}_x$, has been reported. Zhong, Z. J.; Matsumoto, N.; Ōkawa, H.; Kida, S. *Chem. Lett.* **1990**, 87.

(10) (a) Carlin, R. L. In *Magnetochemistry*; Springer-Verlag: Berlin, 1986; pp 112–162. (b) Kittel, C. In *Introduction to Solid State Physics*, 3rd ed.; John Wiley & Sons: New York, 1966; pp 455–498.

(11) Bellitto, C.; Day, P.; Wood, T. E. *J. Chem. Soc., Dalton Trans.* **1986**, 847.

Cr(III)–Ni(II), Cu(II)–V(IV)O, low-spin Fe(III)–Cu(II), and Ru(III)–Cu(II), a ferromagnetic spin-exchange has been experimentally confirmed by the magnetic investigations of their discrete binuclear and oligonuclear mixed-metal complexes.[13] In order to achieve the parallel alignment of spins over the three-dimensional lattice in addition to the ferromagnetic spin-coupling between the nearest neighboring mixed-metal ions, a three-dimensional polymeric structure in which the strictly orthogonal mixed-metal ions are alternately arrayed should be constructed. Trioxalatochromate(III), $[Cr(ox)_3]^{3-}$, a D_3 symmetric η^3-complex, can be such a building block since this complex anion functions as a "ligand" capable of binding three metal ions through its ox groups, and the resulting Cr–ox–M linkage can be extended three-dimensionally due to the D_3 symmetry. Further, it is known that the $[Cr(ox)_3]^{3-}$ ion is significantly inert toward ligand substitution and the oxalate bridge is a good mediator in both antiferromagnetic and ferromagnetic interactions between similar and dissimilar metal ions.[12,14] Indeed, the reaction of $K_3[Cr(ox)_3]\cdot 3H_2O$ and a metal(II) nitrate in water, followed by the addition of tetra(*n*-butyl)ammonium bromide, NBu_4Br, resulted in the immediate precipitation of green microcrystals with the formula $\{NBu_4[MCr(ox)_3]\}_x$ (M = Mn^{2+} (**1**), Fe^{2+} (**2**), Co^{2+} (**3**), Ni^{2+} (**4**), Cu^{2+} (**5**), Zn^{2+} (**6**)). On the basis of molecular model considerations it is suggested that compounds $\{NBu_4[MCr(ox)_3]\}_x$ form either a two-dimensional or a three-dimensional network structure extended by the Cr(III)–ox–M(II) bridges. Figures 1 and 2 show these two- and three-dimensional structures drawn by a computer graphics program,[15] where the positive cation is eliminated for clarity. The large-sized positive cation tetra(*n*-butyl)ammonium ion is positioned in the cavity to neutralize the charge. If the compounds assume a three-dimensional structure, in view of the concept of the strict orthogonality of magnetic orbitals, the complexes **4** and **5** can be ferromagnets, because the ferromagnetic interaction of Cr(III)–Cu(II) and Cr(III)–Ni(II) would be extended over the three-dimensional lattice. To the best of our knowledge, with respect to the magnetic character between the metal ion pairs Cr(III)–Mn(II), Cr(III)–Fe(II), and Cr(III)–Co(II), it has not been confirmed whether the magnetic interaction is antiferromagnetic or ferromagnetic. When the magnetic interaction is ferromagnetic, the compounds would be ferromagnets. Even if the magnetic interaction is antiferromagnetic in these metal ion pairs, magnetic vectors are assembled by the difference in the neighboring magnetic spin vectors per one unit ($|S_{Cr} - S_M| \neq 0$) to afford a ferrimagnet except for $\{NBu_4[CoCr(ox)_3]\}_x$ (**3**) ($S_{Cr} = S_{Co} = 3/2$, $|S_{Cr} - S_{Co}| = 0$).[16] If the compounds assume a two-dimensional sheet structure, the magnetic properties depend on the nature of the inter-sheet magnetic interaction.

Synthesis and Characterization. A series of compounds, $\{NBu_4[MCr(ox)_3]\}_x$ (M^{2+} = Mn^{2+} (**1**), Fe^{2+} (**2**), Co^{2+} (**3**), Ni^{2+} (**4**), Cu^{2+} (**5**), Zn^{2+} (**6**)), were synthesized in a one-pot reaction by mixing aqueous solutions of $K_3[Cr(ox)_3]\cdot 3H_2O$, metal(II) salt, and NBu_4Br with the mole ratio of 1:1:1.5 at room temperature. The compounds were obtained as green microcrystals. Microanalyses of the compounds (C, H, N, Cr, and M elements) are all consistent with the general formula of $\{NBu_4[MCr(ox)_3]\}_x$. Attempts to grow single crystals suitable for single-crystal X-ray diffraction analysis so far have been unsuccessful. The X-ray powder diffractions showed an isomorphous pattern to each other and the observed densities (1.46–1.52 g cm^{-3}) are similar, indicating that the series of compounds all have similar crystal structures. When the compounds assume the three-dimensional structure depicted in Figure 2, the densities can be evaluated by the crystal cell volumes. The Cr–M distance of 5.0 Å gives the calculated density of 1.48 g cm^{-3} that is in good agreement with the observed values. The Cr–M distance of 5.0 Å is compatible with the values reported for the oxalate-bridged binuclear complexes.[14]

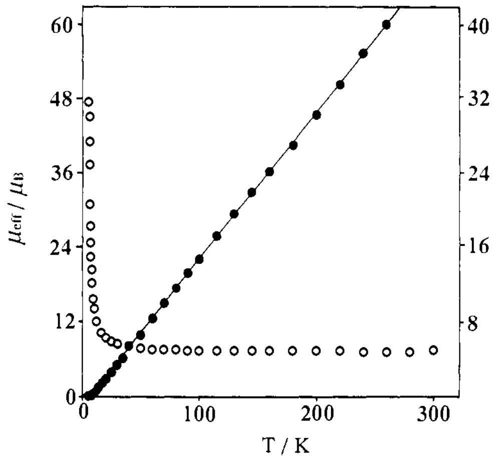

Figure 3. Plot of the temperature dependences of the reciprocal magnetic susceptibilities (●) and the magnetic moment (○) per CrM for $\{NBu_4[MnCr(ox)_3]\}_x$ (**1**).

The powder reflectance spectra of compounds **1**–**6** and their parent complex $K_3[Cr(ox)_3]\cdot 3H_2O$ have been measured. Three d–d bands characteristic of $[Cr(ox)_3]^{3-}$ (420, 580, and 698 nm)[17] are all observed in compounds **1**–**6**, indicating that the inert chromium(III) ion retains the original six-coordinate environment with three oxalate groups. Compounds **2**–**4** should show spin-allowed d–d transition bands due to the Fe(II), Co(II), and Ni(II) ion, but the d–d bands of these ions ($[MO_6]$ chromosphere) are very weak ($\epsilon < 3$) and probably concealed by the more intense d–d bands of the chromium(III) ($\epsilon > 10$). Compound **5** shows an additional band near 840 nm which can be attributed to a d–d component of an axially distorted $[CuO_6]$ chromosphere. Chelated oxalate groups generally show an antisymmetric ν(CO) vibration at ca. 1700 cm^{-1} and a δ(CO) vibration at ca. 800 cm^{-1}. In the IR spectra of **1**–**6** the vibrations due to oxalate group appear at 1652 and 810 cm^{-1}, indicating that all the oxalate groups function as bridging groups.[18]

Magnetic Susceptibilities. The temperature dependences of the magnetic susceptibilities were measured in the temperature range 4.2–300 K. The magnetic behavior of **1** is shown in Figure 3, in the form of $1/\chi_M$ vs T and μ_{eff} vs T plots, where χ_M is the magnetic susceptibility per MCr unit and μ_{eff} is the effective magnetic moment calculated by the equation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$. The magnetic behavior of **2**–**6** are reported as supplementary material (Figure S1–S5). The magnetic behaviors of **1**–**5** are essentially similar. The effective magnetic moments per MCr at room temperature of **1**–**5** are slightly larger than the spin-only value expected for magnetically dilute Cr(III)–M(II) systems ($S_{Cr} = 3/2$, $S_{Mn} = 5/2$, $S_{Fe} = 2$, $S_{Co} = 3/2$, $S_{Ni} = 1$, $S_{Cu} = 1/2$). The

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(12) (a) Kahn, O. *Struct. Bonding (Berlin)* **1987**, *68*, 89. (b) Kahn, O. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 834. (c) Cairns, C. J.; Busch, D. H. *Coord. Chem. Rev.* **1986**, *69*, 1.

(13) (a) Pei, Y.; Journaux, Y.; Kahn, O. *Inorg. Chem.* **1989**, *28*, 100. (b) Journaux, Y.; Kahn, O.; Zarembowitch, J.; Galy, J.; Jaud, J. *J. Am. Chem. Soc.* **1983**, *105*, 7585. (c) Kahn, O.; Galy, J.; Journaux, Y.; Jaud, J.; M-Badarau, I. *J. Am. Chem. Soc.* **1982**, *104*, 2165. (d) Matsumoto, N.; Inoue, K.; Ōkawa, H.; Kida, S. *Chem. Lett.* **1989**, 1251. (e) Zhong, Z. J.; Matsumoto, N.; Ōkawa, H.; Kida *Inorg. Chem.* **1991**, *30*, 436. (f) Zhong, Z. J.; Ōkawa, H.; Matsumoto, N.; Sakiyama, H.; Kida, S. *J. Chem. Soc., Dalton Trans.* **1991**, 497. (g) Matsumoto, N.; Tamaki, H.; Inoue, K.; Ōkawa, H.; Kida, S. *Chem. Lett.* **1991**, 1393. (h) Gupta, G. P.; Lang, G.; Koch, C. A.; Wang, B.; Scheidt, W. R.; Reed, C. A. *Inorg. Chem.* **1990**, *29*, 4234.

(14) (a) Julve, M.; Faus, J.; Verdaguer, M.; Gleizes, A. *J. Am. Chem. Soc.* **1984**, *106*, 8306. (b) Felthouse, T. R.; Laskowski, E. J.; Hendrickson, D. N. *Inorg. Chem.* **1977**, *16*, 1077. (c) Curtis, N. F.; McCormick, I. R. N.; Waters, T. N. *J. Chem. Soc., Dalton Trans.* **1973**, 1537.

(15) Whitted, T. An Improved Illumination Model for Shaded Display. *Commun. ACM* **1980**, *23*, 343.

(16) Unpublished result. In fact, we have obtained a ferrimagnet with the formula of $\{NBu_4[Ni^{2+}Fe^{3+}(ox)_3]\}_x$. The $1/\chi_M$ vs T curve of the complex obeys the Curie–Weiss law with negative Weiss constant and the μ_{eff} vs T curve shows a round minimum. The Neel temperature is determined to be 28 K by the magnetization measurement under a weak magnetic field of 1 G. In $\{NBu_4[NiFe(ox)_3]\}_x$, Fe^{3+} and Ni^{2+} ions are antiferromagnetically coupled.

(17) Erisken, J.; Monsted, O. *Acta Chem. Scand.* **1983**, *A37*, 579.

(18) Nakamoto, K. In *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd ed.; Wiley-Interscience: New York, 1970; p 244.

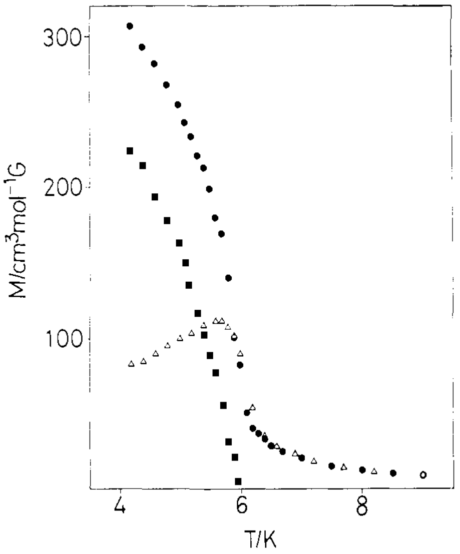

Figure 4. Plot of the temperature dependences of the magnetization *M* for $\{NBu_4[MnCr(ox)_3]\}_x$ (**1**): (●) field-cooled magnetization (FCM) (1 G), (■) remnant magnetization, (△) zero-field-cooled magnetization (ZFCM).

plots of $1/\chi_M$ vs T of **1**–**5** are linear in the range of ca. 20–300 K but deviate significantly from the line below 20 K. The Weiss constant determined from the plots in the 20–300 K range based on the equation $1/\chi_M = C(T - \theta)$ are all positive (θ = 7.2 (**1**), 18.2 (**2**), 15.1 (**3**), 19.0 (**4**), 18.0 K (**5**)), suggesting the operation of a ferromagnetic interaction between Cr(III) and M(II) ions. Upon cooling from room temperature, the effective magnetic moment of each complex increases gradually until ca. 20 K and sharply below 20 K, suggesting the onset of ferromagnetism. The maximum magnetic moment is very large compared with the corresponding spin-only value expected for the highest total spin of a discrete binuclear Cr(III)–M(II) system ($S_T = S_{Cr} + S_M$). For example, the maximum magnetic moment of **1** is 47.45 μ_B at 4.7 K, which is very large compared with 8.94 μ_B, the spin-only value of $S_T = 4$ expected for the largest total spin of a Cr(III)–Mn(II) system. Compound **3** with the spin-system $S_{Cr} = 3/2$ and $S_{Co} = 3/2$ showed an increase in magnetic moment with the lowering of temperature. This fact demonstrates that the magnetic vectors on Cr(III) and Co(II) ions are ferromagnetically coupled in the lattice. It should also be noted that in the μ_{eff} vs T curves of **1**–**5**, there is no round minimum which has been observed for Kahn's ferrimagnets.[4,8] On the other hand, complex **6** showed a practically constant magnetic moment (3.75 μ_B per CrZn) in the temperature range studied. This value is slightly smaller than the spin-only value of 3.87 μ_B for $S = 3/2$ and is compatible with the values observed for magnetically isolated Cr(III) complexes.[19] The plots of $1/\chi_M$ vs T obey the Curie law. The Curie behavior of **6** is in contrast to the other compounds **1**–**5**, demonstrating that the structure is comprised of alternating Cr(III) and Zn(II) ions arrayed in a three-dimensional lattice.

Magnetization Studies. To confirm the ferromagnetic phase transition, the temperature dependences of the magnetization under a weak magnetic field (1 G) and the remnant magnetization were measured. The field-cooled magnetization (FCM), remnant magnetization, and zero-field-cooled magnetization (ZFCM) curves of $\{NBu_4[MnCr(ox)_3]\}_x$ (**1**) are shown in Figure 4 as an example. The behaviors of **2**, **3**, **4**, and **5** are similar and are reported as supplementary material (Figure S6–S9). As shown in Figure 4, the field-cooled magnetization (FCM) obtained by cooling the sample under 1 G shows a rapid increase in magnetization when the temperature is lowered below 6.5 K and a break in the curve around T_c = 6 K. When the field was switched off, a remnant magnetization was observed which varnished at T_c upon warming. The zero-field-cooled magnetization (cooling in zero field and warming under 1 G) shows a maximum at T_c, as expected for a polycrystalline ferromagnet.[4] The ferromagnetic phase transition temperatures (T_c) determined by similar measurements are 12, 10, 14, and 7 K for **2**, **3**, **4**, and **5**, respectively.

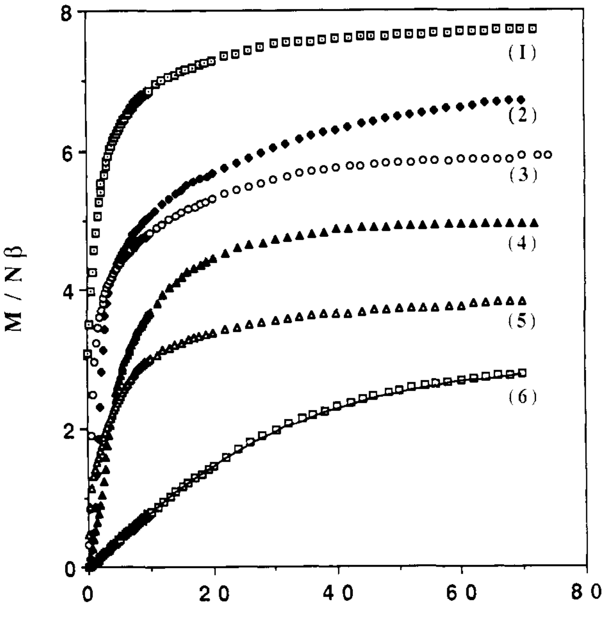

Figure 5. Plot of the field dependences of the magnetization (*M*) for $\{NBu_4[MCr(ox)_3]\}_x$ (M = Mn (**1**), Fe (**2**), Co (**3**), Ni (**4**), Cu (**5**), Zn (**6**)) at 4.2 K in the form of $M/N\beta$ vs H. The solid line of **6** represents the theoretical curve of $M = g\beta SNB_S(x)$ with $S = 3/2$, where $B_S(x)$ is Brillouin function, $x = g\beta H/kT$, and T = 4.2 K.

Table I. Summary of Magnetic Data: Critical Temperature (T_c), Weiss Constant (θ), Saturation Magnetization (M_S), Remnant Magnetization (M_r), and Coercive Field (H_c) for $\{NBu_4[MCr(ox)_3]\}_x$ (M = Mn^{2+} (**1**), Fe^{2+} (**2**), Co^{2+} (**3**), Ni^{2+} (**4**), Cu^{2+} (**5**), Zn^{2+} (**6**))

compd	T_c/K	θ/K	S_{Tol}	M_S/N_β	M_r/cm³ mol⁻¹ G	H_c/G
1	6	7.2	4	7.74	1500	20
2	12	18.2	7/2	6.71	4100	320
3	10	15.1	3	5.94	3000	80
4	14	19.0	5/2	4.94	1200	160
5	7	18.0	2	3.83	1500	30
6		0.1	3/2	2.79		

The field dependences of the magnetization (*M*) were measured on polycrystalline samples under high magnetic field up to 7.5 T at 4.2 K using a pulsed magnet and the curves are shown in Figure 5 in the form of $M/N\beta$ vs H, where M, N, β, and H are magnetization, Avogadro's number, the electron Bohr magneton, and applied magnetic field, respectively. Magnetization curves show saturation up to 7.5 T and the saturation magnetization values, M_s, are summarized in Table I. The saturation magnetization, M_S, is related to the equation $M_S = g\beta NS$, where S is the spin quantum number for a unit formula. By introducing the observed M_S into the equation, gS values corresponding to the number of unpaired electrons per formula of 7.74. 6.71, 5.94, 4.94, 3.83, and 2.79 are obtained for **1**, **2**, **3**, **4**, **5** and **6**, respectively. These values are compatible with $S_T = S_{Cr} + S_M$ ($S_{Cr} = 3/2$, $S_{Mn} = 5/2$, $S_{Fe} = 2$, $S_{Co} = 3/2$, $S_{Ni} = 1$, $S_{Cu} = 1/2$, $S_{Zn} = 0$, $g = 2$). The magnetization curve of $\{NBu_4[ZnCr(ox)_3]\}_x$ (**6**) is well reproduced by the equation $M = g\beta SNB_S(x)$ with $S = 3/2$, where $B_S(x)$ is the Brillouin function and $x = g\beta H/kT$, indicating that the chromium(III) ion in **6** is magnetically isolated. On the other hand, the curves of $M/N\beta$ for **1**–**5** deviate significantly from the equation $M = g\beta SNB_S(x)$ ($S = S_{Cr} + S_M$) and show a rapid saturation. However, the magnetic field necessary to reach the saturation is rather large, probably too large for a genuine fer-

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(19) Earnshaw, A. In *Introduction to Magnetochemistry*; Academic Press: London, 1968.

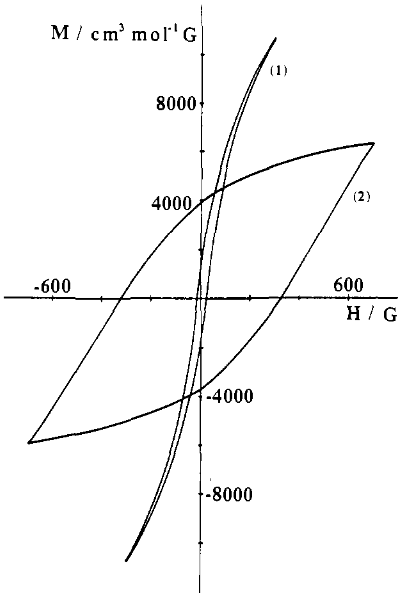

Figure 6. Magnetic hysteresis loop of $\{NBu_4[MnCr(ox)_3]\}_x$ (**1**) and $\{NBu_4[FeCr(ox)_3]\}_x$ (**2**) at 5 K.

romagnet. The shapes of the curves in the low magnetic field suggest a spin decoupling. It seems that in zero field the spins are not rigorously parallel, but canted, and the magnetic field progressively overcomes this canting. Though the spin canting mechanism is unclear at present, a possible origin can be due to the long-range structural disorder.

The magnetic hysteresis loops were measured at 5 K. The hysteresis loops for **1** and **2** are shown in Figure 6 and the loops for **3**–**5** are reported as supplementary material (Figures S10–S12). At 5 K, the remnant magnetizations are 1500, 4100, 3000, 1200, and 1500 cm³ mol⁻¹ G and the coercive fields are 20, 320, 80, 160, and 30 G for **1**, **2**, **3**, **4**, and **5**, respectively.

The magnetic parameters of the compounds (phase-transition temperature, Weiss constant, total spin, saturation magnetization, remnant magnetization, and coercive field) obtained by the magnetic susceptibility, magnetic hysteresis, and magnetization measurements are summarized in Table I.

At this stage it is valuable to consider the relation between the critical temperature T_c and the magnetic interaction parameter of the constituting unit J. If the assumption of three-dimensional structures for our compounds is correct, the critical temperature, T_c, might be estimated through a molecular field model (mean-field approximation)[20] $T_c = (nJ/3k)[S_{Cr}(S_{Cr} + 1)S_M(S_M + 1)]^{1/2}$, where T_c is the critical temperature, k denotes the Boltzman constant, and n is the number of neighboring metal ions of Cr(III) with $n = 3$ taken in this case. By introducing the observed T_c and the spin quantum numbers of metal ions ($S_{Cr} = 3/2$, $S_{Mn} = 5/2$, $S_{Fe} = 2$, $S_{Co} = 3/2$, $S_{Ni} = 1$, and $S_{Cu} = 1/2$), the J values of **1**–**5** are evaluated to be +0.73, +1.76, +1.85, +3.55, and +2.90 cm⁻¹, respectively. These J values will be compared with the J values of discrete polynuclear oxalate-bridged Cr(III)–M(II) complexes in order to examine whether or not the assumption is correct. To our knowledge, three Cr(III)–Cu(II) and two Cr(III)–Ni(II) complexes are presently known. Unfortunately, Cr(III)–Co(II), Cr(III)–Mn(II), and Cr(III)–Fe(II) complexes are not known. Three oxalate-bridged binuclear Cr(III)–Cu(II) complexes $[(salen)Cr(ox)Cu(L^1, L^2, \text{or } L^3)]$[21] (**a**, HL^1 = N-salicylidene-N-(2-pyridylethyl)amine; **b**, HL^2 = N-acetylacetonylidene-N-(2-pyridylethyl)amine; **c**, HL^3 = N-salicylidene-N',N'-diethylethylenediamine) have been prepared and the J values based on $H = -2JS_{Cu}S_{Cr}$ are reported to be +2.8, +2.2, and +2.7 cm⁻¹ for **a**, **b**, and **c**, respectively, being very consistent with the J value +2.90 cm⁻¹ for **5**. A tetranuclear Cr(III)–Ni(II) complex, $\{Cr[(ox)Ni(Me_6[14]aneN_4)]_3\}(ClO_4)_3$,[22] and a trinuclear complex, $\{Cr(OH)(H_2O)[(ox)Ni(Me_6[14]aneN_4)]_2\}(ClO_4)$,[22] were synthesized and their interaction parameters based on $H = -2J\sum S_{Ni}S_{Cr}$ have been found to be +2.65 and +4.3 cm⁻¹, respectively, where $Me_6[14]aneN_4$ = *rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane. Its interaction parameters are roughly compatible with the J value of +3.55 cm⁻¹ for **4**. This result suggests that $\{NBu_4[CuCr(ox)_3]\}_x$ assumes a three-dimensional network structure and the critical temperature is determined by the magnitude of the coupling constant of the constituting unit, Cr(III)–ox–Cu(II) or Cr(III)–ox–Ni(II). In other words, the T_c can be linearly improved when the M_A–L–M_B building unit is properly chosen so as to cause a stronger magnetic interaction. This circumstance is of interest when compared with a class of magnetic materials comprised of a one-dimensional structure. In the magnets based on the one-dimensional chains there are two distinct magnetic interactions, i.e. intrachain and interchain interactions. In the mean-field approximation, the critical temperature, T_c, is related to the intrachain J_{intra} and interchain J_{inter} exchange parameters through $kT_c = S^2(|J_{intra}J_{inter}|)^{1/2}$.[23] In general J_{inter} is very small and the resulting T_c is limited to low temperature.

Conclusion

In this paper, we have described the simple and effective synthetic strategy for ferromagnets, using a D_3 symmetric η^3-complex as the "building block". A new family of ferromagnets $\{NBu_4[MCr(ox)_3]\}_x$ (M = Mn^{2+} (**1**), Fe^{2+} (**2**), Co^{2+} (**3**), Ni^{2+} (**4**), Cu^{2+} (**5**)) has been synthesized in a one-pot reaction. They exhibit magnetic features characteristic of ferromagnets: (1) the increase and divergence of the effective magnetic moment at low temperature, (2) the magnetic phase transition evidenced by the measurements of field-cooled magnetization, remnant magnetization, and zero-field-cooled magnetization, (3) magnetic hysteresis loops at 5 K, and (4) the magnetization measurements up to 7.5 T at 4.2 K.

The compounds exhibit several advantages in the molecular design which have not been accomplished so far. The compounds are designed such that the Cr(III) and M(II) ions are alternately arrayed over the three-dimensional lattice through bridging oxalate groups, so that there are no problems associated with ferromagnets and ferrimagnets based on the one-dimensional chains, such as the difficulty to control weak interchain magnetic interaction among ferri- or ferromagnetic chains and the phase matching among ferrimagnetic chains. Further, the critical temperature can be linearly related to the amplitude of the magnetic interaction between Cr(III) and M(II) ions through the oxalate group. Our synthetic principle may be applicable for other magnetic materials exhibiting a higher onset temperature using different types of η^3-complexes with D_3 symmetry as building blocks. The studies along this line are currently in progress in our laboratory.

Experimental Section

Materials. $K_3[Cr(ox)_3]\cdot 3H_2O$ was prepared according to the literature method.[24] Tetra(n-butyl)ammonium bromide, $MnCl_2\cdot 4H_2O$, $Fe(SO_4)\cdot 7H_2O$, $Co(NO_3)_2\cdot 6H_2O$, $Ni(NO_3)_2\cdot 6H_2O$, $Cu(NO_3)_2\cdot 3H_2O$, and $Zn(NO_3)_2\cdot 6H_2O$ were used as purchased.

Syntheses. $\{NBu_4[MnCr(ox)_3]\}_x$ (**1**). Synthetic procedures were carried out under an atmosphere of nitrogen. An aqueous solution (10 cm³) of $K_3[Cr(ox)_3]\cdot 3H_2O$ (974 mg, 2 mmol) and an aqueous solution (10 cm³) of $MnCl_2\cdot 4H_2O$ (395 mg, 2 mmol) were mixed at ambient temperature. To the resulting violet solution was added an aqueous solution (5 cm³) of tetra(n-butyl)ammonium bromide (709 mg, 2.2 mmol) to cause an immediate precipitation of green microcrystals. After the solutions were left to stand at room temperature for 30 minutes, they were collected by filter suction, washed with water, and dried in vacuo over

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(20) (a) Renard, J.-P. In *Organic and Inorganic Low-Dimensional Crystalline Materials*; Delhaes, P., Drillon, M., Eds.; NATO ASI Series 168; Plenum: New York, 1987; p 125.

(21) Ohba, M.; Tamaki, H.; Matsumoto, N.; Ōkawa, H.; Kida, S. *Chem. Lett.* **1991**, 1157.

(22) (a) Pei, Y.; Journaux, Y.; Kahn, O. *Inorg. Chem.* **1989**, *28*, 100. (b) Ohba, M. et al. Unpublished result.

(23) Nakatani, K.; Bergerat, P.; Codjovi, E.; Mathoniere, C.; Pei, Y.; Kahn, O. *Inorg. Chem.* **1991**, *30*, 3978.

(24) Bailar, J. C., Jr.; Jones, E. M. *Inorg. Synth.* **1939**, *1*, 37.

P_2O_5. Yield 75%. $D_{obsd} = 1.46$ g cm^{-3}. Absorption maxima in reflectance spectrum 692, 574, 424 nm. Anal. Calcd for $C_{22}H_{36}NO_{12}CrMn$: C, 43.08; H, 5.92; N, 2.28; Cr, 8.48; Mn, 8.95. Found: C, 43.41, H. 6.00; N. 2.28; Cr, 8.64; Mn, 8.50.

$\{NBu_4[FeCr(ox)_3]\}_x$ (2). This complex was prepared as green microcrystals in a manner similar to the synthesis of **1** except that $Fe(SO_4)\cdot7H_2O$ instead of $MnCl_2\cdot4H_2O$ was used. Yield 35%. $D_{obsd} = 1.48$ g cm^{-3}. Absorption maxima in reflectance spectrum 692, 574, 415 nm. Anal. Calcd for $C_{22}H_{36}NO_{12}CrFe$: C, 43.01; H, 5.91; N, 2.28; Cr, 8.46; Fe, 9.09. Found: C, 43.09; H, 5.99; N, 2.31; Cr, 8.77; Fe, 9.05.

$\{NBu_4[CoCr(ox)_3]\}_x$ (3). This complex was prepared as gray microcrystals in a manner similar to the synthesis of **1** except that $Co(NO_3)_2\cdot6H_2O$ instead of $MnCl_2\cdot4H_2O$ was used. Yield 30%. $D_{obsd} = 1.49$ g cm^{-3}. Absorption maxima in reflectance spectrum 692, 553, 428 nm. Anal. Calcd for $C_{22}H_{36}NO_{12}CrCo$: C, 42.80; H, 5.88; N, 2.27; Cr, 8.42; Co, 9.51. Found: C, 43.01; H, 6.03; N, 2.36; Cr, 8.64; Co, 9.20.

$\{NBu_4[NiCr(ox)_3]\}_x$ (4). This complex was prepared as green microcrystals in a manner similar to the synthesis of **1** except that $Ni(NO_3)_2\cdot6H_2O$ instead of $MnCl_2\cdot4H_2O$ was used and the reaction was carried out in the open atmosphere. Yield 6%. $D_{obsd} = 1.49$ g cm^{-3}. Absorption maxima in reflectance spectrum 748, 692, 580, 425 nm. Anal. Calcd for $C_{22}H_{36}NO_{12}CrNi$: C, 42.81; H, 5.88; N, 2.27; Cr, 8.42; Ni, 9.51. Found: C, 43.20; H, 6.21; N, 2.35; Cr, 8.90; Ni, 9.41.

$\{NBu_4[CuCr(ox)_3]\}_x$ (5). This complex was prepared as green microcrystals in a manner similar to the synthesis of **1** except that $Cu(NO_3)_2\cdot3H_2O$ instead of $MnCl_2\cdot4H_2O$ was used. Yield 99%. $D_{obsd} = 1.52$ g cm^{-3}. Absorption maxima in reflectance spectrum 693, 579, 428 nm. Anal. Calcd for $C_{22}H_{36}NO_{12}CrCu$: C, 42.48; H, 5.83; N, 2.25; Cr, 8.36; Cu, 10.22. Found: C, 42.92; H, 5.94; N, 2.36; Cr, 8.08; Cu, 10.14.

$\{NBu_4[ZnCr(ox)_3]\}_x$ (6). This complex was prepared as green microcrystals in a manner similar to the synthesis of **1** except that $Zn(NO_3)_2\cdot6H_2O$ instead of $MnCl_2\cdot4H_2O$ was used. Yield 98%. $D_{obsd} = 1.49$ g cm^{-3}. Absorption maxima in reflectance spectrum 692, 576, 426 nm. Anal. Calcd for $C_{22}H_{36}NO_{12}CrZn$: C, 42.35; H, 5.82; N, 2.25; Cr, 8.33; Zn, 10.47. Found: C, 42.40; H, 5.92; N, 2.28; Cr, 8.08; Zn, 9.94.

Physical Measurements. Elemental analyses of C, H, and N were carried out at the Service Center of Elemental Analysis, Kyushu University. Metal analyses (Mn, Fe, Co, Ni, Cu, Zn) were made on a Shimadzu AA-680 atomic absorption flame emission spectrophotometer. Infrared spectra were measured on KBr disks with a JASCO IR-810 spectrophotometer. Electronic spectra were recorded by the diffuse reflectance technique on a Shimadzu multipurpose spectrophotometer Model MPS-2000. Densities were measured by a flotation method in benzene/tetrachloromethane solutions. X-ray powder diffraction patterns were obtained using a Toshiba ADG 302 type diffractometer, with Cu Kα and Fe Kα radiations. The scan rate was 1 deg min^{-1}. Space filling models were drawn by the ray tracing method.[14] The computer software and hardware were Cast Co. Ltd. C-TRACE 98 Version 3.1 ray tracing software and NEC PC-9801 RA2 + Intel 80387 (16 MHz) coprocessor. The ratio of atomic radius was C:O:M = 1:1:1.25. Magnetic susceptibilities were measured using a HOXAN HSM-D SQUID susceptometer and a Faraday balance. Magnetic susceptibilities were calibrated by the use of $(NH_4)_2Mn(SO_4)_2\cdot6H_2O$ for the SQUID magnetometer and $[Ni(en)_3]S_2O_3$ for the Faraday balance.[25] Effective magnetic moments were calculated by $\mu_{eff} = 2.828(\chi_M T)^{1/2}$, where χ_M is the molar magnetic susceptibility corrected for diamagnetism of the constituting atoms using Pascal's constants.[26] The field-cooled magnetization (1 G), remnant magnetization, and zero-field-cooled magnetization were measured by the SQUID magnetometer. Field dependence of magnetization was measured using a flux magnetometer in applied fields up to 7.5 T generated by a conventional pulsed technique.[27]

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Supplementary Material Available: Figures showing temperature dependence of the effective magnetic moments per MCr unit for **2**–**6** (Figures S1–S5), temperature dependence of the magnetization *M* in the weak field 1 G for **2**–**5** (Figures S6–S9), and hysteresis loops at 5 K for **3**–**5** (Figures S10–S12) and tables of magnetization vs *H* up to 7.5 T for **1**–**6** (Tables S1–S6) (18 pages). Ordering information is given on any current masthead page.

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(25) Lindoy, L. F.; Katovic, V.; Busch, D. H. *J. Chem. Educ.* **1972**, *49*, 117.

(26) Boudreaux, E. A.; Mulay, L. N. In *Theory and Applications of Molecular Paramagnetism*; John Wiley and Sons: New York, 1976; pp 491–495.

(27) (a) Iwata, N.; Hashimoto, Y.; Kimura, T.; Shigeoka, T. *J. Magn. Magn. Mater.* **1989**, *81*, 354. (b) Hashimoto, Y.; Yamagishi, A.; Takeuchi, T.; Date, M. *J. Magn. Magn. Mater.* **1990**, *90*, 49.