A Mixed-Valence Mn(II,III) Complex with a 2D Structure: Crystal Structure and Magnetic Property of K[$Mn_2(\mu\text{-}CrO_4)_2(\mu\text{-}OH)_2$]

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Reaction of $MnSO_4{\cdot}4H_2O$ with K_2CrO_4 in water yielded highly crystalline black solids, which was chracterized to a 2D mixed valent Mn(II,III) complex, potassium di-μ-chromato-di-μ-hydroxo-dimanganate (1-) K[$Mn_2(\mu\text{-}CrO_4)_2(\mu\text{-}OH)_2$] (**1**).

Mixed-valent manganese clusters have been extensively studied from solid state chemical view points. Competing magnetic interactions in some μ_3-oxide bridged manganese clusters show frustration in their spin alignment.[1] Large magnetic anisotropy in these giant spin clusters or "superparamagnets" results in magnetic hysteresis[2] and quantum spin tunneling[3] between spin states. Such solid state phenomena are due to the strong intervalent charge transfer interaction between mixed valent manganese ions through the μ-oxo bridges. On the other hand, $[CrO_4]^{2-}$ ions bridge metal ions and mediate a variety of magnetic interactions depending upon bridged metal ions. In copper(II) and nickel(II) complexes, $[\{Cu(acpa)\}_2(\mu\text{-}CrO_4)]$ (acpa = tridentate Schiff base) and *catena*-(μ-CrO_4-O,O')[Ni(cyclam)], ferromagnetic interactions (J = +14.6 and +0.6 cm^{-1}, respectively) were mediated through the chromate ions.[4] Two iron(III) ions in $[LFe^{III}(\mu\text{-}CrO_4)_3Fe^{III}L]$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane), showed a weak antiferromagnetic interaction (J = –7.5 cm^{-1}).[5] On the other hand, charge transfer interactions prompt interatomic or intermolecular electronic interactions and the weak magnetic interactions in the reported chromato bridged complexes are due to the lack of the charge-transfer interactions between paramagnetic centers. This motivates us to prepare a mixed-valent complex with chromato bridges, which is supposed to have the intervalence charge transfer interaction. Here we report synthesis, structure and magnetic properties of a 2D mixed valent Mn(II,III) complex, potassium di-μ-chromato-di-μ-hydroxo-dimanganate (1–) K[$Mn_2(\mu\text{-}CrO_4)_2(\mu\text{-}OH)_2$] (**1**).

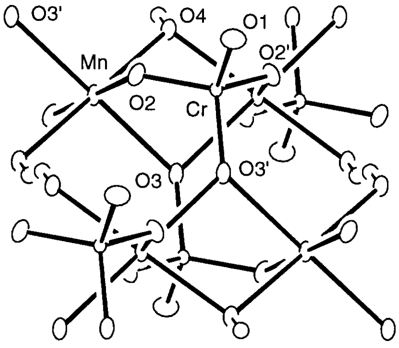

Figure 1. The rectangular core structure in **1**. Selected distances [Å] and angles [°] with standard deviation in parentheses: Mn-O2 2.144(2), Mn-O3 2.229(4), Mn-O4 2.139(3), Cr-O1 1.605(4), Cr-O2 1.650(3), Cr-O3 1.696(5), Mn-Mn 3.274(1), Mn-Cr 3.4224(7), Mn-Cr 3.567(1), O2-Mn-O3 90.7(1), O2-Mn-O4 88.2(1), O2-Mn-O3 89.3(1), O3-Mn-O4 99.0(1), O1-Cr-O2 109.9(1), O1-Cr-O3 108.3(2), O2-Cr-O3 109.9(1), O2-Cr-O2 109.0(2), Mn-O2-Cr 128.4(2), Mn-O3-Cr 130.3(1), Mn-O3-Mn 94.5(2), Cr-O3-Mn 130.3(1), Mn-O4-Mn 99.9(2).

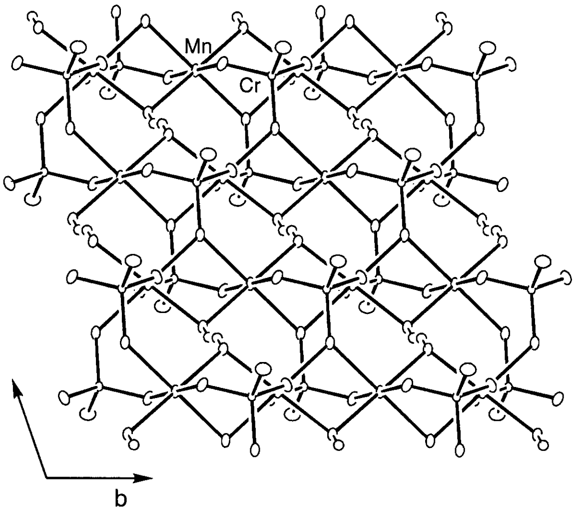

Figure 2. 2D-structure of **1**.

The reaction of $MnSO_4{\cdot}4H_2O$ with K_2CrO_4 in water yielded highly crystalline black **1**. X-ray crystallographic study revealed that **1** has the chemical formula K[$Mn_2(\mu\text{-}CrO_4)_2(\mu\text{-}OH)_2$], which implies that the manganese ions are mixed valent Mn(II,III).[6] Complex **1** crystallizes in the monoclinic space group *C2/m*. In the crystal, manganese ion locates at only one kind of crystallographically independent position. The manganese and potassium ions locate on the crystallographic inversion center and twofold rotation axis, respectively, while the $[CrO_4]^{2-}$ and hydroxide groups locate on the mirror plane. In **1**, the manganese ions are bridged by hydroxide and chromate ions to form an extended 2D structure (Figures 1 and 2). Two oxygen atoms (O4 and O3) from the OH^- and $[CrO_4]^{2-}$ ions together with O2–Cr–O2' unit bridging the manganese ions form a chain like structure along the b-axis. The manganese ions in the chains are doubly linked by O2–Cr–O3' bonds and, as a result, **1** forms a layered structure with layers separation of 7.751(1) Å in the ab-plane (Figure 2). The octahedral coordination sites of the manganese ions are occupied by six oxygen atoms (Mn–O: 2.139(3)–2.229(4) Å). The bridging hydroxide (Mn–O4–Mn) and oxide (Mn–O3–Mn) bond angles of the $[CrO_4]^{2-}$ ions are 99.9(2)° and 94.5(2)°, respectively. The coordination geometry of the chromate ion is tetrahedral with three

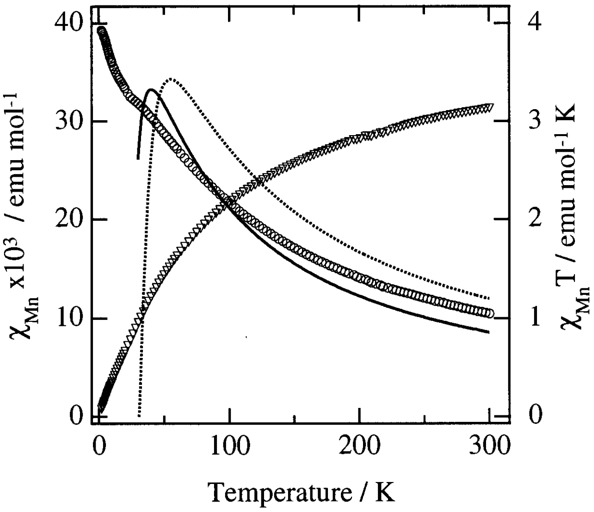

Figure 3. Plots of χ_{Mn} (○) and $\chi_{\mathrm{Mn}}T$ (▽) *vs* T for **1**. Solid and dotted lines correspond to the theoretical curves for antiferromagnetic 2D systems with S = 2 and S= 5/2, respectively. The parameters are given in the text.

oxygen atoms bridging manganese ions. The fourth oxygen atom remains non-coordinated and has the shortest bond length (1.605(4) Å). XPS spectrum was measured to study the mixed valency of **1**, photoelectron-signals characteristic of Mn(II) and Mn(III) were, however, too close in energy to be resolved. It is unclear from the X-ray analysis and physical measurements whether the valence electrons are trapped on certain atoms or delocalized over the entire structure.

Temperature dependent magnetic susceptibilities for **1** have been measured down to 2.0 K. Figure 3 shows both χ_{Mn} and $\chi_{\mathrm{Mn}}T$ values vs T plots. As the temperature is lowered, the $\chi_{\mathrm{Mn}}T$ values decrease and approach zero at 0 K, while the χ_{Mn} values show a gradual increase with a slight undulation at 30 K. The magnetic behavior for **1** suggests that an antiferromagnetic interaction is operative. As stated in the X-ray structural study, the compound **1** has the layered structure, high-temperature series expansions to a two-dimensional Heisenberg system was, therefore, applied to analyze the magnetic data.[7] When the 2D system has antiferromagnetic coupling, temperature dependent susceptibilities show a maximum value at T_{max}. The intra-layer coupling constant J can be estimated by the formula $\tau_{\mathrm{m}} = k_{\mathrm{B}}T_{\mathrm{max}}/\{|J|S(S+1)\}$ (τ_{m} is a constant for different S values) and the molar susceptibility can be expressed as

$$\chi_{\mathrm{Mn}} = \frac{Ng^2\beta^2 S(S+1)}{3kT}\left(1+\sum_{n=1}^{8} a_n K^n\right)$$

where $K = J/kT$ and a_{n} values are taken from the previous work.[8] The χ_{Mn} vs T plot for **1** shows an anomaly at 30 K. If the T_{max} is taken as 30 K, J becomes -1.4 cm^{-1}. Figure 3 depicts theoretical curves for $S = 2$ (solid line) and 5/2 (dotted line) systems with the g and J values of 1.97 and -1.4 cm^{-1}, respectively. The magnetic analysis cannot fully reproduce the experimental data especially below 30 K, and this might be due to paramagnetic impurity or spin frustration within the layer.

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References and Notes

1 M. W. Wemple, H-L. Tsai, S. Wang, J. P. Claude, W. E. Streib, J. C. Huffman, D. N. Hendrickson, and G. Christou, *Inorg. Chem.*, **35**, 6437 (1996); J. K. McCusker, H. G. Jang, S. Wang, G. Christou, and D. N. Hendrickson, *Inorg. Chem.*, **31**, 1987 (1992); E. Libby, J. K. McCusker, E. A. Schmitt, K. Folting, D. N. Hendrickson, and G. Christou, *Inorg. Chem.*, **30**, 3486 (1991).

2 E. M. Chudnovsky, *Science*, **274**, 938 (1996); R. Sessoli, D. Gatteschi, A. Caneschi, and M. A. Novak, *Nature*, **365**, 141 (1993).

3 S. M. J. Aubin, M. W. Wemple, D. M. Adams, H-L. Tsai, G. Christou, and D. N. Hendrickson, *J. Am. Chem. Soc.*, **118**, 7746 (1996); P. C. E. Stamp, *Nature*, **383**, 125 (1996).

4 H. Oshio, T. Kikuchi, and T. Ito, *Inorg. Chem.*, **35**, 4938 (1996); H. Oshio, T. Kikuchi, and T. Ito, *Inorg. Chem.*, **36**, 3201 (1997).

5 P. Chaudhuri, M. Winter, K. Wieghardt, S, Gehring, W. Haase, B. Nuber, and J. Weiss, *Inorg. Chem.*, **27**, 1564 (1988).

6 Crystal data: ($H_2Cr_2KMn_2O_{10}$), Mw = 270.488, monoclinic space group *C2/m* with a = 9.344(1) Å, b = 6.548(2) Å, c = 7.751(1) Å, $ß$ = 115.06(7)°, V = 429.6(2) Å^{-3}, Z = 2, d_{calc} = 3.208 g cm^{-3}, R = 0.035, R_{w} = 0.057, for 500 unique reflections ($I_0 > 3\sigma(I_0)$).

7 "Magnetic Properties of Layered Transition Metal Compounds," ed. by L. J. de Jongh, Kluwer Academic Publishers, London (1990).

8 C. S. Rushbrooke and P. J. Wood, *Proc. Phys. Soc., London*, **68**, 1161 (1956); P. L. Stephenson, K. Pirnie, P. J. Wood, and J. Eve, *Phys. Lett.*, **27A**, 2 (1968).