Inorg. Chem. **2004**, *43*, 849–851

Inorganic Chemistry
Communication

Slow Magnetic Relaxation in a Mixed-Valence Mn(II/III) Complex: $[Mn^{II}_2(bispicen)_2(\mu_3\text{-}Cl)_2Mn^{III}(Cl_4Cat)_2Mn^{III}(Cl_4Cat)_2(H_2O)_2]_\infty$

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Received September 10, 2003

A layered mixed-valence manganese complex, $[Mn^{II}_2(bispicen)_2(\mu_3\text{-}Cl)_2Mn^{III}(Cl_4Cat)_2Mn^{III}(Cl_4Cat)_2(H_2O)_2]_\infty$, is synthesized and characterized structurally. It displays a slow magnetic relaxation and hysteresis effect.

Cooperative magnetic phenomena or bulk magnetic behaviors are regarded as properties of some extended solid-state compounds normally whereas paramagnetic behavior is often noted in molecular compounds. Moving a step beyond, a related question may arise whether a single molecule or single chain would show characteristics of a magnet. In the past few years, some molecular clusters such as Mn_{12} and Fe_8, which behave like superparamagnets (“single-molecule magnets”[1]), have been reported to exhibit unusual magnetic hysteresis. This is caused by the macroscopic quantum tunneling of magnetization, and the features refer to the slow magnetic relaxation of molecular origin. A similar magnetic relaxation is also present in one-dimensional (1D) Ising systems, predicted in 1963 by Glauber.[2] The first experimental confirmation was, however, made by Gatteschi *et al.*[3] in 2001. Subsequently it was also found in $Mn^{III}-Mn^{III}-Ni^{II}$, Co^{II}, and $Co^{II}-Fe^{III}$ chains,[4−5] which were named as “single-chain magnets”. In this Communication, we report a novel mixed-valence complex $[Mn^{II}_2(bispicen)_2(\mu_3\text{-}Cl)_2Mn^{III}(Cl_4Cat)_2Mn^{III}(Cl_4Cat)_2(H_2O)_2]_\infty$ (**1**) (bispicen = *N*,*N*′-bis(2-pyridylmethyl)-1,2-ethanediamine and Cl_4Cat = tetrachlorocatecholate dianion) also showing a slow magnetic relaxation.

The reaction of $[Mn^{II}(bispicen)Cl_2]$[6] with tetrachlorocatechol (Cl_4CatH_2) in a 1:1 ratio in an acetonitrile−water mixture leads to light green platelike crystals of complex **1**[7] which crystallizes in orthorhombic system with space group *I*222. The molecular structure is shown in Figure 1a.[8] The structural unit consists of a layered mixed-valence manganese complex in the *ab* plane (Figure 1b).

Along the *a*-axis, two manganese atoms in the dimeric $[Mn_2^{II}(bispicen)_2]$ moiety are bridged by a pair of chloride ions forming a $Mn^{II}_2Cl_2$ diamond-like core. The separation between the manganese centers of the core is 3.5178(1) Å. The two Mn(II)−Cl bridging bond lengths are equal [2.5398(1) Å] and comparable to similar systems.[9] Four nitrogen atoms of the bispicen ligand coordinate each manganese atom of

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(7) Synthesis: Complex **1** is obtained as light green plate like crystals by reacting $[Mn^{II}(bispicen)Cl_2]$ (0.37 g, 1 mmol) and tetrachlorocatechol (0.27 g, 1 mmol) in air in an acetonitrile−water (5:1 v/v) mixture. Elemental analysis (%) calcd for $C_{52}H_{40}Cl_{18}Mn_4N_8O_{10}$: C, 34.76; H, 2.22; N, 6.24. Found: C, 35.01; H, 2.39; N, 6.21.

(8) Crystal data for **1**: $C_{52}H_{40}Cl_{18}Mn_4N_8O_{10}$, $M_r = 1794.78$, orthorhombic, *I*222 (No. 23), $a = 9.3480(2)$ Å, $b = 12.6540(2)$ Å, $c = 28.5250(5)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 3374.21(11)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.766$ g cm^{-3}, Mo Kα, $\lambda = 0.71070$ Å. The intensity data were collected by the ω-scan method in the 2θ range 3.2−27.5° on an Enraf-Nonius CAD4 diffractometer at 293 K. Unique data = 3874, number of data included in the refinement = 3685 [$I > 2\sigma(I)$], and R (wR) = 0.032 (0.088).

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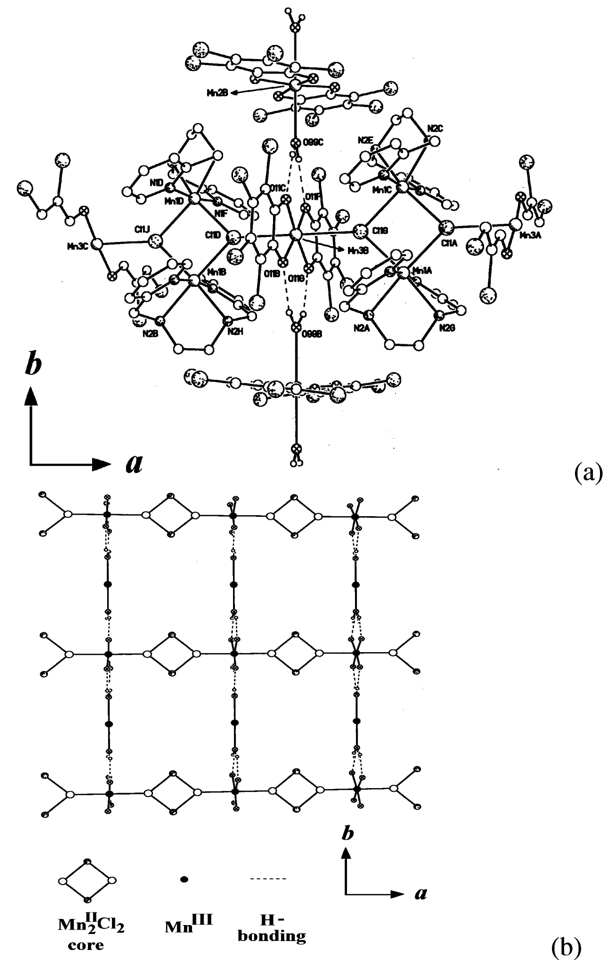

Figure 1. (a) Molecular structure of complex **1**. Hydrogen atoms are omitted for clarity. (b) Skeletal representation of **1** in the *ab* plane.

this moiety in a folded manner, resulting in a distorted octahedral environment. The Mn(II)$-$N$_{amine}$ and Mn(II)$-$N$_{pyridine}$ bond distances are 2.285(2) and 2.252(2) Å, respectively, which agree well with the previously reported Mn(II)$-$N bond distances.[9a,10] The bridged chloride ions coordinate the Mn(III) ion of the [Mn^{III}(Cl$_4$Cat)$_2$] unit axially along the *a*-axis with a Mn(III)$-$Cl bond length of 2.8418(1) Å. This is significantly larger than the Mn(II)$-$Cl bond distance in the dimeric unit, caused by the Jahn$-$Teller distortion of the high-spin Mn(III) ion in the octahedral environment.[11] Each Mn(III)$-$O$_{Cat}$ bond length of the Mn^{III}(Cl$_4$Cat)$_2$ unit in the chain is 1.8917(16) Å, consistent with those observed in structurally characterized Mn(III)$-$catecholate complexes.[12] The catecholate C$-$O and C$-$C (bearing the $-$OH groups) bond lengths are 1.3445(19) Å and 1.413(3) Å, respectively. These data indicate that the ligands are chelated in the fully reduced catecholate form.[13]

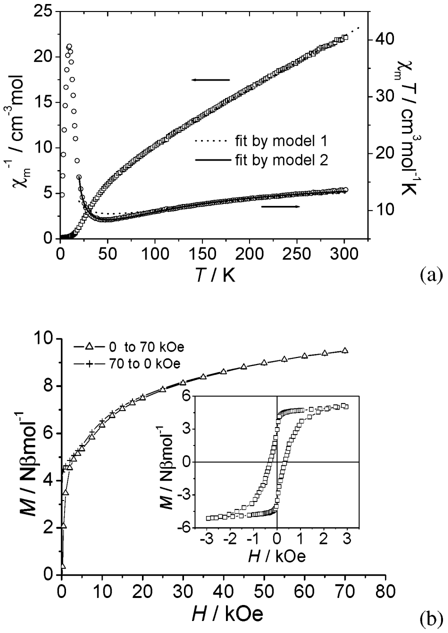

Figure 2. (a) Temperature dependence of χ_m^{-1} and $\chi_m T$ at 5 kOe of **1**. The dotted lines correspond to the best fits obtained with the Curie$-$Weiss law and a Fisher 1D-chain ($S = 2$) model combining a dimer Mn$^{II}_2$ ($S = {}^5/_2$) model; the solid line is the best fit using an alternating chain model (see text). (b) Field dependence of magnetization at 1.8 K. The lines are guides.

The Mn(II) ion of the dimeric unit is apart from the Mn(III) ion of the Mn^{III}(Cl$_4$Cat)$_2$ unit in the chain by 4.994(10) Å. As a whole, a μ_3-Cl bridged infinite 1D chain with alternate Mn(II) dimers and Mn(III) ions is generated along the *a*-axis.

The previously described [Mn^{III}(Cl$_4$Cat)$_2$] unit is connected with another [Mn^{III}(Cl$_4$Cat)$_2$(H$_2$O)$_2$] unit through hydrogen bonds (Figure 1), forming a chain which is along the *b*-axis. The geometry of the Mn(III) ion of the [Mn^{III}(Cl$_4$Cat)$_2$(H$_2$O)$_2$] moiety is a distorted octahedron. The in-plane positions are occupied by four oxygen atoms from two tetrachlorocatecholate ions with Mn(III)$-$O$_{Cat}$ and catecholate C$-$O bond lengths of 1.8972(17) and 1.340(3) Å, respectively, comparable to the previously described unit. The two H$_2$O molecules occupy the axial positions of the Mn(III) center with a considerably long Mn(III)$-$O$_{water}$ bond length [2.462(3) Å] due to the Jahn$-$Teller distortion.[11] These are involved in a strong hydrogen-bonding interaction [O$_{water}$ H$\cdots$O$_{Cat}$ = 2.918(3) Å] with the adjacent catecholato oxygen atoms of the Mn^{III}(Cl$_4$Cat)$_2$ moiety. The distance between the adjacent Mn(III) ions in the chain along the *b*-axis is 6.3270(1) Å. The two perpendicularly crossed chains form a layer in the *ac* plane. The interlayer distance is *c*/2 (14.26 Å). It is worth mentioning that the Mn(III)$-$Mn(III) separations between the chains along the *a*-axis are significantly large [a = 9.349 and 15.00 Å].

Magnetic susceptibility measurements are performed on a collection of small crystals of **1** at 5 kOe in the temperature range 2$-$300 K (Figure 2a). The magnetic susceptibility χ_m in the temperature range 130$-$300 K obeys the Curie$-$Weiss

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law ($\chi_m = C/(T - \theta)$) with $C = 17.17(2)$ cm^3 mol^{-1} K and $\theta = -83.3(5)$ K. The negative Weiss constant suggests a dominant antiferromagnetic exchange between the magnetic centers. The $\chi_m T$ value decreases upon cooling to a minimum of 8.33 cm^3 mol^{-1} K at 48 K, and then increases to a maximum of 38.86 cm^3 mol^{-1} K at 10 K. This is a characteristic of ferrimagnetic behavior. In the absence of a suitable model for such a complicated 2D layer, the $\chi_m T$ data above 20 K was fitted first into a Fisher 1D-chain (along the *b*-axis Mn^{III} chain, $S = 2$) model involving a dimer Mn$^{II}_2$ ($S = {}^5/_2$) model ($H = -2J_b\Sigma S_iS_j - 2J_dS_1S_2$ with intrachain Mn^{III}−Mn^{III} coupling J_b, intradimer coupling J_d), giving $J_d = -13(2)$ cm^{-1}, $J_b = 0.96(8)$ cm^{-1}, $g = 2.08(4)$, and $R = 3.1 \times 10^{-3}$ ($R = \sum[(\chi_mT)_{obs} - (\chi_mT)_{calcd}]^2/\sum[(\chi_mT)_{obs}]^2$). Alternatively, the 2D layer may be regarded as an alternating chain containing Mn$^{II}_2$ dimers and Mn^{III} ions along the *a*-axis involving interchain interaction with intradimeric, intrachain, and interchain exchange constants J_d, J_a, and zJ' respectively ($H = -2J_a\Sigma S_{Mn(III)}S_d$, S_d being the effective spin of the Mn$^{II}_2$).[14] The best fitting gives $J_d = -4.32(5)$ cm^{-1}, $J_a = -12.7(1)$ cm^{-1}, $zJ' = 0.93(2)$ cm^{-1}, $g = 2.00$, $g_{Mn(III)} = 2.30$, and $R = 6.5 \times 10^{-5}$. Two models give similar results: the two Cl-bridged Mn^{II} ions are antiferromagnetically coupled (J_d),[15] and the interaction between the neighboring Mn^{III} ions ($S = 2$) along the *b*-axis ($J_b \approx zJ'$) could be ferromagnetic (F). The latter model suggests a strong antiferromagnetic (AF) coupling (J_a) between Mn$^{II}_2$ dimers and Mn^{III} ions along the *a*-axis. Overall, the coexistence of AF and F interactions leads to such a ferrimagnetic-like behavior.

As shown in Figure 2b, the magnetization of **1** at 1.77 K increases very fast at low field, and reaches 9.49 $N\beta$ per Mn$^{II}_2$Mn$^{III}_2$ at 70 kOe, higher than the calculated saturation value 8.32 $N\beta$ for Mn$^{III}_2$ unit ($S_T = 4$, $g = 2.08$) with the assumption of S_{dimer} being zero for the Mn$^{II}_2$ unit. When the magnetic field is large enough to result in some populated spin levels above $S = 0$, one cannot ignore the contribution of the Mn^{II} dimer to the magnetization. A hysteresis loop is observed clearly at 1.75 K (inset of Figure 2b), with a coercive field of 310 Oe and a remnant magnetization of 3.2 $N\beta$.

Is it a long-range ferrimagnetic ordering? Because of the unusually long M−M separations between the layers along the *c*-axis (>12 Å), the dipole−dipole interactions between the adjacent layers should be considerably weak, suggesting a low-dimensional behavior. The alternating-current (*ac*) magnetic susceptibility of **1** measured at different frequencies (shown in Figure 3a) is strongly frequency-dependent below 5−6 K, precluding a three-dimensional ordering. The magnetic relaxation obeys the Arrhenius law ($\tau = \tau_0 \exp(\Delta/k_BT)$), suggesting a thermally activated mechanism. The best Arrhenius fitting gives $\tau_0 = 3.4 \times 10^{-10}$ s and $\Delta/k_B = 50.5(5)$ K. At a fixed temperature 3.76 K around the cusp of out of phase χ'', a semicircle Cole−Cole diagram is obtained (χ'' vs χ'), as shown in Figure 3b. This can be fitted by a generalized Debye model with $\alpha = 0.3$, indicating a distribution of relaxation time. The magnetic relaxation is strongly reminiscent of that observed in single-molecule magnets as well as in molecular magnetic nanowires, where the energy barrier originates from the magnetic anisotropy.[1−5] The Mn$^{III}\cdots$Mn^{III} interaction along the *b*-axis (0.93−0.96 cm^{-1}) and the barrier Δ/k_B (50.5(5) K) in the title complex are comparable to those (0.67−0.7 K and 72 K) of a reported Mn^{III}-containing compound.[4]

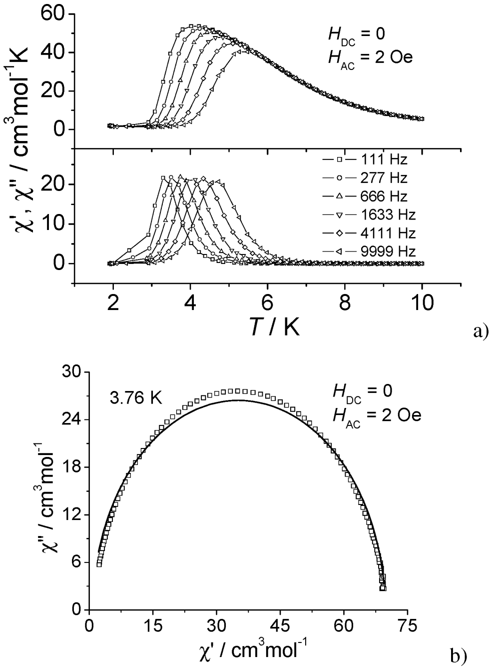

Figure 3. (a) Temperature dependence of the real (top) and imaginary (bottom) components of the *ac* susceptibility in zero applied static field with an oscillating field 2 Oe in frequency of 111−9999 Hz. The lines are guides. (b) Cole−Cole diagram at 3.76 K.

All efforts to get a big single crystal of **1** for magnetic anisotropy measurements have been unsuccessful so far, and the 1D Ising model could not be used for fitting the low-temperature data. However, the elongated octahedral environment of each Mn(III) ion displays a uniaxial (Jahn−Teller) distortion along the *a* or *b* direction, suggesting the contribution of the magnetic anisotropy. The ferromagnetic coupling of Mn^{III} ions ($S = 2$) along the *b*-axis is unique, which might play a key role in the observation of the slow magnetic relaxation in consideration of the nonmagnetic ground state of the Mn^{II} dimer at zero field and low temperature. The ferromagnetic interaction between the Mn^{III} ions is due to the strict orthogonality of the magnetic d_{z^2} orbitals in the *a* and *b* directions alternately.

Acknowledgment. Thanks are due to the Council of Scientific and Industrial Research, New Delhi, for financial support to A.P. and granting a project to P.B. S. Gao thanks the NSFC Fund for Distinguished Young Scholars.

Supporting Information Available: A table of selected bond lengths and angles, synthesis, a view of the crystal structure, IR details, more magnetic data, and an X-ray crystallographic file for **1** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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