Inorg. Chem. **2003**, *42*, 5486–5488

Inorganic Chemistry
Communication

A Three-Dimensional Manganese(II) Complex Exhibiting Ferrimagnetic and Metamagnetic Behaviors

Ruihu Wang,[†] Enqing Gao,[‡,§] Maochun Hong,[*,†] Song Gao,[§] Junhua Luo,[†] Zhenzhong Lin,[†] Lei Han,[†] and Rong Cao[†]

State Key Laboratory of Structural Chemistry, Fujian Institute of the Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China, Department of Chemistry, Qufu Normal University, Shandong 273165, China, and State Key Laboratory of Rare Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

Received May 22, 2003

A three-dimensional complex, [Mn$_3$(4-aba)$_6$]$_n$ (**1**) (4-Haba = 4-aminobenzoic acid), consisting of manganese(II) chains and 4-aba bridging ligands, has been synthesized and characterized. Magnetic studies show that the compound behaves as a three-dimensional metamagnet built of homometallic ferrimagnetic chains. The required noncompensation in spin moments is achieved by alternating interactions in an AF–AF–F sequence (AF = antiferromagnetic; F = ferromagnetic) by considering intrachain magnetic interactions.

Metal−organic hybrid materials of paramagnetic metal ions exhibiting extended structures are currently of great interest in the field of molecular magnetism and materials chemistry due to their fascinating structural diversities and potential application as functional materials.[1−6] A commonly used strategy in the construction of such extended architectures is to employ appropriate bridging ligands, which can transmit magnetic interaction as well as bind several metal centers of specific coordination geometry. But there are few examples of three-dimensional homometallic complexes with ferrimagnetic behaviors reported because the conditions for the noncompensation of the individual spin moments are difficult to achieve in these systems.[4−6] Thus, the rational design and synthesis of three-dimensional homometallic molecular ferrimagnets is still an intellectual challenge, and a great deal of work is required to understand the structural and chemical factors that govern the exchange coupling between paramagnetic centers. Lloret[4] and Livage[5] have recently employed fumarate ligands with π-delocalization to link chains of edge-sharing Ni(II) octahedra, and they obtained a three-dimensional homometallic ferrimagnet. Gao and Chen[6] have reported a Mn(II) three-dimensional coordination polymer using the mixed ligands of azide and nicotinate, which affords a ferrimagnetic-like ordering.

The multifunctional organic ligands containing a carboxylate group, such as nicotinate and isonicotinate, have been frequently used in the preparation of the ferromagnetic, antiferromagnetic, and metamagnetic materials.[6,7] The different coordination modes adopted by the carboxylate group perform the transmission of the magnetic coupling in different degrees; the heteroatomic coordination in the ligands may result in the extension of frameworks through the linkers or spacers. In our course of ongoing studies on transitional metal complexes of 4-aminobenzoic acid (4-Haba),[8] a Mn(II)−aba complex reported by Amiraslanov[9] has drawn our interest. If the 4-aba ligand acts as a multifunctional bridge and links Mn(II) centers, the extended structure with corner-sharing octahedra of Mn(II) centers may be produced, and

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* To whom correspondence should be addressed. E-mail: hmc@ms.fjirsm.ac.cn. Fax: +86-591-3714946.

[†] The Chinese Academy of Sciences.

[‡] Qufu Normal University.

[§] Peking University.

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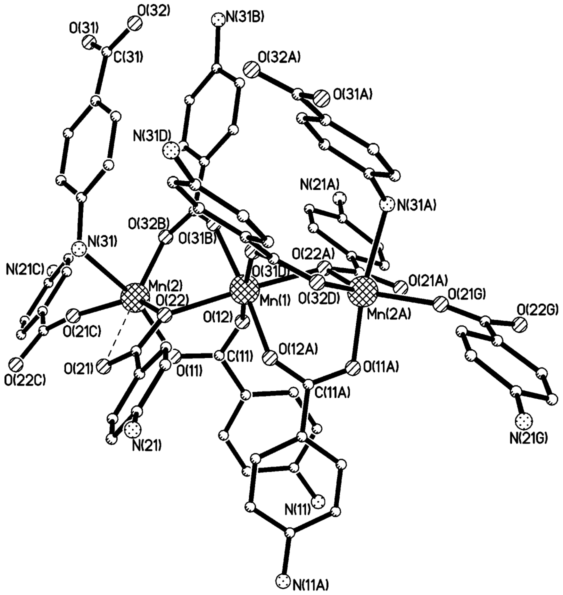


Figure 1. View of trinuclear manganese(II) with atomic numbering scheme in **1**.

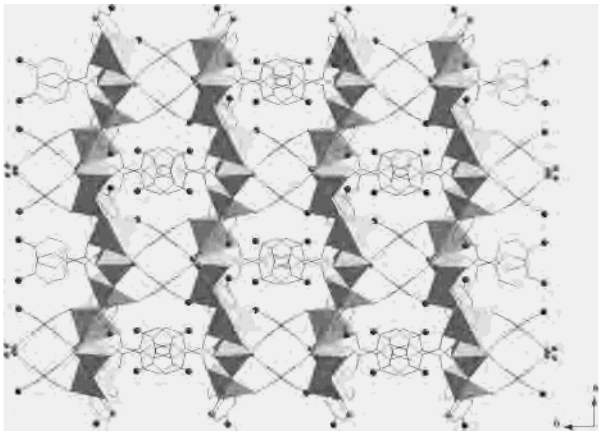
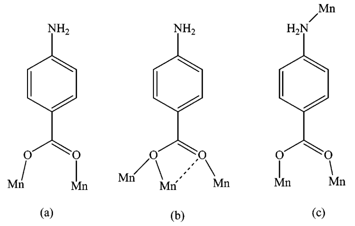


Figure 2. View of packing diagram along *c* axis in **1**.

the complex may favor a strong long-range superexchange coupling. Herein, we wish to report synthesis and characterization of a three-dimensional complex, $[Mn_3(4\text{-aba})_6]_n$ (**1**), consisting of carboxylate-bridged Mn(II) chains and exhibiting ferrimagnetic and metamagnetic behaviors.

Slow evaporation of an ethanol and aqueous solution containing $MnCl_2 \cdot 4H_2O$, 4-Haba, and NaN_3 (ca. 1:1:2) at room temperature produced the light-yellow block crystals of compound **1**.[10] N_3^- is not involved in coordination to Mn(II) and acts as a base to deprotonate 4-Haba. Single-crystal X-ray diffraction analysis[11] reveals that **1** is a three-dimensional coordination network constructed by trinuclear Mn(II) subunits and 4-aba bridges. As shown in Figures 1 and 2, there are two crystallographically independent Mn(II) centers in the trinuclear subunit. The central Mn(1) is located at a crystallographic inversion center and is coordinated by six *trans*-related carboxylate oxygen atoms from different 4-aba species in a distorted octahedral geometry. However, each of two terminal Mn(II) adopts a highly distorted octahedral geometry and is coordinated by an amino nitrogen atom, three carboxylate oxygen atoms, and one semi-chelating carboxylate group from different 4-aba [Mn(2)−O(21) = 2.556 Å] species. The 4-aba has three types of distinctly different bridging modes: one behaves in a μ_2,η^2-carboxylate bridging mode (Scheme 1a); the second acts as a μ_3-carboxylate bridge (Scheme 1b); the third adopts an *exo*-tridentate bridging mode through an amino nitrogen atom and μ_2,η^2-carboxylate group (Scheme 1c). Thus, the central Mn(II) is linked to each terminal Mn(II) by two *syn*−*syn* μ-carboxylate bridges (Scheme 1a,c) and one μ-O atom in the μ_3-carboxylate group (Scheme 1b) from three different types of 4-aba, respectively, which forms a trinuclear Mn(II) subunit with the Mn−O−Mn angle of 100.73(6)°. The Mn−Mn distance of 3.425 Å is significantly shorter that those in carboxylate-bridged trinuclear Mn(II) complexes.[6,12] The other μ-O atom in the μ_3-carboxylate bridge (Scheme 1b) links the trinuclear Mn(II) subunits into a one-dimensional chain structure. The shortest intercluster Mn−Mn distance within the chain is 3.527 Å, which is slightly longer than that in the corner-sharing trinuclear Mn(II) subunit. In each trinuclear Mn(II) subunit, there are two pairs of *exo*-tridentate 4-aba ligands (Scheme 1c) with the dihedral angles between them being 72.5°. The adjacent chains are further cross-linked by *exo*-tridentate 4-aba into a three-dimensional coordination network. The shortest interchain Mn−Mn distance across 4-aba is 9.266 Å.

Scheme 1. Coordination Modes of 4-aba in **1**



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(10) Synthesis of complex **1**: An ethanol solution (10 mL) of 4-aminobenzoic acid (0.07 g, 0.5 mmol) was added to an aqueous solution (10 mL) of $MnCl_2 \cdot 4H_2O$ (0.10 g, 0.5 mmol) with constant stirring for 30 min. To the resulting mixture was added dropwise an aqueous solution (10 mL) of NaN_3 (0.65 g, 1 mmol) to yield a colorless solution which was filtered, and the filtrate was kept in a $CaCl_2$ desiccator for two weeks. Light-yellow crystals of **1** suitable for X-ray diffraction were obtained. (Yield: 0.07 g, 63.04%.) Anal. Calcd for $C_{21}H_{18}Mn_{1.50}N_3O_6$ (490.79): C, 51.39, H, 3.67, N, 8.56. Found: C, 51.32, H, 3.61, N, 8.59. IR (KBr, cm^{-1}): 3341 (m), 3245 (w), 1631 (m), 1620 (m), 1607 (s), 1588 (m), 1534 (s), 1516 (s), 1497 (s), 1431 (s), 1401 (vs), 1316 (w), 1258 (vw), 1174 (m), 1087 (vw), 849 (vw), 785 (m), 700 (w), 625 (m), 548 (w).

(11) Crystal data: crystal dimensions 0.60 × 0.60 × 0.46 mm^3, $C_{21}H_{18}Mn_{1.50}N_3O_6$, M_r = 490.79, monoclinic, space group *C*2/*c*, a = 14.90090(10) Å, b = 19.0579(4) Å, c = 15.0144(2) Å, β = 102.9450(10)°, V = 4155.42(11) $Å^{-3}$, Z = 8, D_c = 1.569 $g \cdot cm^{-3}$, T = 293(2) K, λ = 0.7107 Å, μ = 0.970 mm^{-1}, 7894 reflections were collected, of which 3671 were unique (R_{int} = 0.0226, $2.43 \le \theta \le 25.05$), R1 = 0.0331, wR2 = 0.0878, GOF = 1.032 for 357 parameters. The intensity data were measured on a Siemens Smart CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 298 K. Empirical absorption corrections were applied by using the SADABS program. All calculations were performed using the SHELXL-97 program package. The structure was solved by direct methods and refined by full-matrix least-squares methods. All non-hydrogen atoms were refined anisotropically, while all hydrogen atoms were located from differential Fourier maps.

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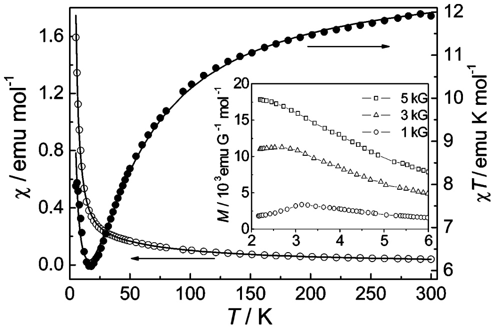
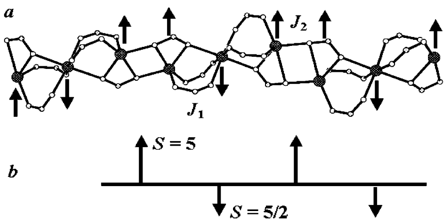


Figure 3. χ and χT vs T plot with the theoretical fit (—). Inset: Field-cooled magnetization at different fields.

Scheme 2. Bridging Network and Spin Topology of the Homometallic Ferrimagnetic Chain



The magnetic susceptibility of **1** was measured in the range 5−300 K at 10 kG (Figure 3). The χT value of each Mn_3 unit (12.0 emu K mol^{-1}, 9.80 μ_B) at 300 K is somewhat lower than that (13.1 emu K mol−^{1}, 10.25 μ_B) expected for three magnetically isolated high-spin Mn(II) ions, indicating the presence of a dominant antiferromagnetic interaction. Upon cooling, χT decreases smoothly to a minimum (6.11 emu K mol^{-1}) at 17 K, which is significantly higher than that (12 K) for a three-dimensional complex containing trimanganese units,[6] and then increases rapidly as the temperature decreases. These features are indicative of ferrimagnetic behavior. Since the Mn(II) chains in **1** are well separated by the 4-aba bridges, the ferrimagnetic behavior can be suggested to arise from intrachain magnetic interactions. According to the chain topology, there are two sets of magnetic exchange pathways within the chain: one consists of two *syn*−*syn* μ_2-1,3-carboxylate bridges and a μ_2-O bridge from the μ_3-carboxylate group; the other mainly consists of two μ_2-O bridges from two μ_3-carboxylate groups (Scheme 2a). To achieve noncompensation in spin moments within such a chain, the interaction through the former set of bridges must be antiferromagnetic (AF) and that through the latter set must be ferromagnetic (F). The interactions alternate according to an AF−AF−F repeating sequence to yield the spin topology that corresponds to a (5, $^5/_2$) ferrimagnetic chain (Scheme 2b).

To evaluate the interactions, a least-squares fit of the observed magnetic data based on the theoretical expression proposed by Escuer et al.[13] was made, and a set of satisfactory parameters, $g = 1.99$, $J_1 = -4.5$ cm^{-1}, and $J_2 = 0.38$ cm^{-1}, was obtained. The J_1 value is comparable to those previously reported for trimanganese(II) complexes with similar bridging networks,[12] and the J_2 value confirms that the unprecedented double μ-O bridges from the μ_3-carboxylate groups mediate a ferromagnetic interaction, which may be due to accidental orthogonality between magnetic orbitals around the metal ions.

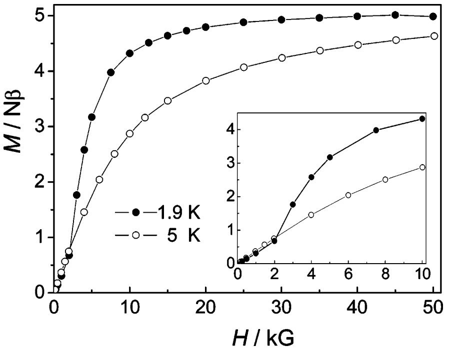


Figure 4. Magnetization curves at 1.9 and 5 K. The inset is a blow-up in the low field region.

The magnetic behaviors of **1** are further characterized by temperature- and field-dependent measurements at low temperature. The field-cooled (FC) magnetization (Figure 3, inset) at 1 kG shows a maximum at about 3.1 K, suggesting the occurrence of three-dimensional antiferromagnetic ordering of the ferrimagnetic chains. The magnetization maximum disappears at or above 3 kG, indicating that the interchain antiferromagnetic interactions are overcome by the external field. These features are characteristic of metamagnetic behaviors, which are confirmed by the field dependence of magnetization (Figure 4). The sigmoidal shape of the $M-H$ curve at 1.9 K indicates clearly the field-induced transition from an antiferromagnetic to a ferromagnetic state. The critical field is 3 kG, at which a maximum $\partial M/\partial H$ value is reached. The saturation magnetization achieved at 50 kG is about 5.0 Nβ, consistent with the $S = {}^5/2$ ground state for a Mn_3 unit. As expected, the sigmoidal feature of the $M-H$ curve disappears at 5 K, which is above the critical temperature. The temperature dependence of the ac magnetic susceptibility is also measured and confirms the occurrence of the antiferromagnetic ordering with $T_N = 3.4$ K, at which both χ' and χ'' reach maximum values (Figure 5, available as Supporting Information). Further measurements revealed **1** is a soft magnet without detectable magnetic hysteresis.

In summary, we have synthesized a three-dimensional manganese(II) complex containing trinuclear Mn(II) subunits from 4-aminobenzoic acid and $MnCl_2 \cdot 4H_2O$ in the presence of NaN_3, and the compound behaves as a three-dimensional metamagnet built of homometallic ferrimagnetic chains. The required noncompensation in spin moments is achieved by alternating interactions in an AF−AF−F sequence. Detailed magnetic investigations on the complex are underway.

Acknowledgment. This work was supported by the grants of National Nature Science Foundation of China, Nature Science Foundation of Fujian Province, and the Key Project of Chinese Academy of Science.

Supporting Information Available: Additional figure. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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