Inorg. Chem. **2009**, *48*, 792−794

Inorganic Chemistry Communication

Ferromagnetic Disklike $Mn^{IV}Mn^{II}_3Na^{I}_3$ Heptanuclear Complex with a $S = 9$ Ground State

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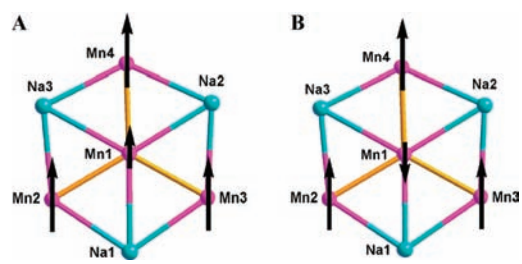
Received September 27, 2008

The wheel-shaped heptanuclear cluster complex {[Mn_4Na_3(thmp)$_2$(acac)$_6$(H_2O)$_6$]CH_3COO}·4H_2O is the first heterometallic mixed-valent disklike compound with apical alkali-metal ions. The weak ferromagnetic interaction between the central Mn^{4+} ion and the peripheral Mn^{2+} ones leads to a high-spin ground state ($S = 9$).

The construction of polynuclear complexes showing not only nanoscopic size but also magnetic or optical properties is a powerful approach to new molecule-based materials. In particular, a considerable ongoing research has been directed toward such molecules because they were discovered to be able to exhibit the behavior of a single-molecule magnet, which generally requires a high-spin ground state.[1] With pleasing structural aesthetics and interesting physical properties, the wheel-shaped complexes occupy an important position among polynuclear compounds.[2] They can be approximately analyzed and categorized as two classes: one lacks the metal center, forming a ring-like structure,[3] while the other consists of a metal axis and several peripheral metal ions, showing a disklike structure.[4]

Thus far, most of reported wheel-shaped polynuclear complexes are homometallic. Nevertheless, the alkali-metal ion plays a special role in the assembly of heterometallic disklike cluster complexes because it is an ideal guest for hexanuclear metallacrown hosts.[5] In such host−guest systems, the alkali-metal ion is apt to situate at the center position as an axis. Herein we report a novel disklike heptanuclear cluster complex with apical Na^+ ions, {[Mn_4Na_3(thmp)$_2$(acac)$_6$(H_2O)$_6$]CH_3COO}·4H_2O [**1**; H_3thmp = 1,1,1-tris-(hydroxylmethyl)propane, Hacac = acetylacetone], where a Mn^{4+} ion serves as the axis to connect with three Mn^{2+} and three Na^+ ions at the periphery. Interestingly, for the spin topology structure of **1**, the ferromagnetic interaction between the central Mn^{4+} ion and the apical Mn^{2+} ones would lead to an $S = 9$ ground state (Scheme 1A),

Scheme 1



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10.1021/ic8018474 CCC: $40.75

Published on Web 12/23/2008

while the antiferromagnetic interaction would result in an $S = 6$ ground state (Scheme 1B).

Complex **1** was obtained with the following procedure. A mixture of H_3thmp (0.5 mmol), $Mn(acac)_2$ (0.5 mmol), NaN_3 (1.0 mmol), and NaOEt (1.0 mmol) in 33 mL of ethanol−water solvent (10:1 volume ratio) was stirred for 6 h. The resulting red solution was air-oxidized and filtered. The filtrate was then evaporated for 3 weeks to produce dark-red rhombus crystals of **1** (yield 36% based on Mn).[6] The balance acetate anion was generated through the decomposition of the $acac^-$ ligand; such a retro-Claisen condensation reaction of β-diketones in the presence of strong bases was known before.[7] Although the azido anion is not incorporated into the structure of **1**, it plays an important role in the formation of **1**. The absence of sodium azide in the reaction mixture could not yield any crystalline products (the reason is not yet clear). The air oxidation of manganese(II) salts is an effective approach to the assembly of disklike high-valent manganese clusters, but the trivalent Mn^{3+} ion was generally obtained before.[4c,d,f,h,5f] It is surprising that the tetravalent Mn^{4+} ion could be generated in **1**. As far as we are aware, **1** is the first example of a disklike heptanuclear cluster complex containing the central Mn^{4+} ion though the peripheral Mn^{4+} ions were observed in a $Mn^{IV}{}_6Ce^{IV}$ disk complex recently.[4i]

X-ray structural analysis[8] revealed that **1** is composed of a discrete $[Mn_4Na_3(thmp)_2(acac)_6(H_2O)_6]^+$ cation, an acetate anion, and solvent water molecules. The manganese oxidation states were established by bond-valence-sum (BVS) calculations.[9] The core of the $[Mn_4Na_3(thmp)_2(acac)_6(H_2O)_6]^+$ cation has a virtual C_3 symmetry; it can be described as an almost planar Mn_4Na_3 heptanuclear disk that is constructed from a centered Mn^{4+} ion and a six-membered ring of three Mn^{2+} and three Na^+ ions arranged alternatively (Figure 1). The core is linked by six μ^3-alkoxide O atoms from two $tripod^{3-}$ ligands, whereas chelating $acac^-$ anions and water molecules are observed on the remaining coordination sites for the apical Mn^{2+} and Na^+ ions. The topology of the core is reminiscent of those in other homoheptanuclear[4a−d,h] or heteroheptanuclear[4i,5,10] disklike complexes. However, the angles of the Mn_3Na_3 hexagon deviate from 120° for a regular one (the mean Mn−Na−Mn and Na−Mn−Na angles are 111.57° and 128.35°, respectively).

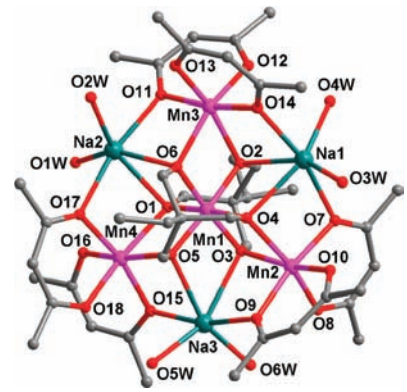

Figure 1. Heptanuclear cluster structure of **1** with coordination atom labeling.

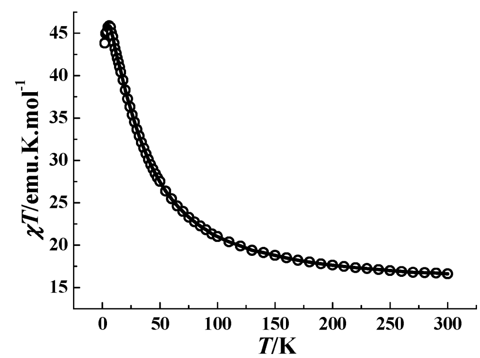

Figure 2. Plot of χT as a function of T for **1**. The solid line represents the best fit of the data to the theoretical model.

The central Mn^{4+} ion is coordinated by six alkoxide O atoms from two $tripod^{3-}$ ligands to display a distorted octahedral configuration. The distorted octahedral coordination sphere of the peripheral Mn^{2+} ion is composed of four O atoms from two $acac^-$ anions and two alkoxide O atoms from two $tripod^{3-}$ ligands. The Na^+ ion is also six-coordinated, with two alkoxide O atoms from two $tripod^{3-}$ ligands, two O atoms from two $acac^-$ anions, and two hydrate molecules. Each alkoxide O atom of the $tripod^{3-}$ ligand connects with one central Mn^{4+} ion, one peripheral Mn^{2+} ion, and one peripheral Na^+ ion, adopting the μ^3-bridging mode, whereas one $acac^-$ O atom acts as a μ^2 bridge to link to one peripheral Mn^{2+} ion and one peripheral Na^+ ion.

There are intracluster hydrogen bonds between the $acac^-$ O atom not working as the μ^2 bridge and the neighboring coordinated water molecule with $O_w \cdots O_{acac}$ distances from 2.775 to 2.831 Å. The other hydrogen bonds exist between the coordinated and solvent water molecules and between the carboxylate anion and the coordinated or solvent water molecule; these weak interactions play important roles in the stabilization of the structure of **1**.

The magnetic susceptibility (χ) of **1** was measured under a 1 kOe applied field in the temperature range of 2−300 K and is plotted as χT vs T in Figure 2. The value of χT at room temperature of 16.61 emu·K·mol^{-1} is a little larger than the 15.00 emu·K·mol^{-1} spin-only value ($g = 2.0$) expected for a $Mn^{IV}Mn^{II}{}_3$ complex with noninteracting metal centers. The χT product increases continuously upon cooling,

(6) Anal. Calcd for $C_{44}H_{87}Mn_4Na_3O_{30}$ (**1**): C, 38.16; H, 6.33. Found: C, 38.32; H, 6.49. IR (KBr, cm^{-1}): 3423(br, s), 2968(w), 2912(w), 2852(w), 1656(w), 1586(s), 1523(s), 1464(m), 1407(s), 1262(w), 1045(w), 1017(w), 926(w), 773(w), 583(m), 541(m), 415(w).

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(8) Crystal data for **1**: $C_{44}H_{87}Mn_4Na_3O_{30}$, $M = 1384.86$ g mol^{-1}, monoclinic, $C2/c$, $a = 39.016(8)$ Å, $b = 13.884(3)$ Å, $c = 23.870(5)$ Å, $\beta = 96.77(3)°$, $V = 12840(5)$ Å^3, $Z = 8$, $T = 173(2)$ K, $D_{calcd} = 1.424$ g cm^{-3}, $\mu = 0.870$ mm^{-1}, GOF = 1.155, R1 = 0.0708, wR2 = 0.1440 [$I \geq 2\sigma(I)$], largest difference peak/hole 0.729 and −0.562 e Å^{-3}. Disorder exists in the solvent water molecules and the carboxylate anion.

(9) Liu, W.; Thorp, H. H. *Inorg. Chem.* **1993**, *32*, 4102. BVS for **1**: Mn1, Mn2, Mn3, and Mn4 are 4.117, 2.094, 2.059, and 2.074, respectively.

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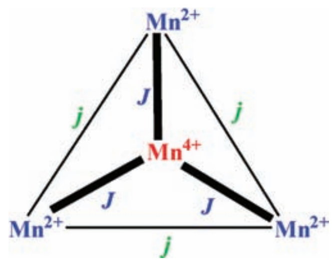
Scheme 2



suggesting intracluster ferromagnetic interactions. A maximum of 45.88 emu·K·mol^{-1} appears at 6 K. After this maximum, χT decreases probably because of zero-field splitting, Zeeman effects, and/or weak intercluster interactions. Above 50 K, the $1/\chi$ vs T plot obeys the Curie–Weiss law with $\theta = 26.27$ K and $C = 15.25$ emu·mol^{-1}·K (Figure S1 in the Supporting Information).

Because the bridging parameters (the Mn–μ^3-O and Mn^{II}–Mn^{IV} distances and the Mn–μ^3O–Mn angles) of **1** exhibit slight differences for the Mn1–Mn2, Mn1–Mn3, and Mn1–Mn4 pairs, only two J parameters are required to describe the magnetic exchange interactions among the four manganese centers in the $[Mn^{IV}Mn^{II}_3Na^I_3]$ core (Scheme 2). The parameter J reflects the magnetic exchange between the central Mn^{4+} ion and the apical Mn^{2+} ones bridged by two μ^3-alkoxide O atoms, whereas j stands for the magnetic coupling interaction between the apical Mn^{2+} ions via the O–Na–O bridge.

The Heisenberg spin Hamiltonian corresponding to this exchange scheme is given by

$$H = -2J(S_cS_{a1} + S_cS_{a2} + S_cS_{a3}) - 2j(S_{a1}S_{a2} + S_{a2}S_{a3} + S_{a1}S_{a3})$$

In this Hamiltonian, $S_{a1} = S_{a2} = S_{a3} = {}^5/_2$, $S_c = {}^3/_2$, and the effects of zero-field splitting have not been considered. With these simplifications, the eigenvalues of the spin Hamiltonian may be determined by using the Kambe vector coupling method with the following coupling scheme:

$$S_A = S_{a1} + S_{a2} + S_{a3}, \quad S_T = S_A + S_c$$

The energies of the spin states, which are eigenvalues of the Hamiltonian, are given by

$$E(S, S_A) = -J[S(S+1) - S_A(S_A+1)] - jS_A(S_A+1)$$

Then a theoretical expression for the molar paramagnetic susceptibility (χ) versus temperature (T) was derived by using the van Vleck equation and assuming an isotropic g value (see the Supporting Information).

The least-squares fitting of the experimental χT vs T data above 5 K gives $J = 1.40$ cm^{-1}, $j = 0.50$ cm^{-1}, and $g = 2.03$ with $R = 4.79 \times 10^{-4}$. The positive J value suggests that the interaction between the central Mn^{4+} ion and the apical Mn^{2+} ones is ferromagnetic. The value is larger than that of the centered planar trigonal tetramanganese(II) cluster complex, $[Mn_4L_6](ClO_4)_2$ {HL = 2-[(pyridin-2-yl)methyleneamino]phenol; $J = 0.16$ cm^{-1}},[11] ascribing roughly to the shorter average distance of $Mn_a \cdots Mn_c$ (3.210 Å) with respect to the latter (3.268 Å). The ferromagnetic interaction tends to align one central Mn^{4+} and three apical Mn^{2+} spins in parallel, yielding a ground state with the highest spin ($S = 9$ with $S_A = {}^{15}/_2$; Scheme 1A). The small positive j value indicates a weak ferromagnetic interaction between the terminal Mn^{2+} ions via the O–Na–O bridge. The energy gap between the first excited state ($|S, S_A = 8, {}^{13}/_2\rangle$) and the ground state ($S = 9$) is 11.70 cm^{-1}, quite larger than that of $[Mn_4L_6](ClO_4)_2$ (0.78 cm^{-1}),[11] suggesting that the $S = 9$ ground state is dominating at low temperature. The magnetization increases more rapidly than that of the uncoupled system as the theoretical Brillouin curve indicates (Figure S2 in the Supporting Information), confirming the ferromagnetic interaction. The magnetization per $Mn^{IV}Mn^{II}_3$ at 5T is 17.4 Nβ, closer to the saturation value of 18 Nβ with $S_T = 9$. Furthermore, above 1.8 K, slow paramagnetic relaxation was not observed from alternating current magnetic susceptibility studies under a 2.5 Oe oscillating field at frequencies up to 1488 Hz.

In summary, a disklike heterometallic heptanuclear cluster complex **1** has been synthesized and characterized structurally and magnetically. A central Mn^{4+} ion connects with three peripheral Mn^{2+} ions and three peripheral Na^+ ones through six μ^3-alkoxide O atoms from two tripod^{3-} ligands, generating a planar heptanuclear $[Mn_4Na_3]$ core. A weak ferromagnetic interaction exists between the central Mn^{4+} ion and the apical Mn^{2+} ones, leading to a high-spin ground state ($S = 9$). This work demonstrates that, except as a guest for metallacrown hosts, the alkali-metal ion can incorporate into disklike cluster complexes as an apical component.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (Grants 20671093 and 20473096), the Major State Basic Research Development Program of China (Grant 2006CB932101), and CAS. We thank Dr. Xiang Hao for X-ray crystallography.

Supporting Information Available: Crystallographic information file (CIF), the theoretical expression for the molar paramagnetic susceptibility (χ), and the $1/\chi$–T curve (Figure S1) and the M–H curve (Figure S2) for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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