Review

Molecular cubes with high-spin ground states

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Abstract

Reactions of Schiff bases with copper(II), nickel(II), iron(II) and manganese(II) sources yielded tetranuclear complexes of [Cu₄(Hhsae)₄]₂H₂O₄CH₃CN (1), [Ni₄(sae)₄(MeOH)₄] (2), [Fe₄(Hsapd)₄]₂H₂O·4MeOH (3) and [Mn₄(sap)₄(MeOH)₄]·H₂O (4), (H₃hsae=2-(4-hydroxysalicylideneamino)-1-ethanol, H₂sae=2-salicylideneamino-1-ethanol, H₃sapd=2-salicylideneaminopropane-2-methyl-1,3-propandiol, and H₂sap=3-salicylideneamino-1-propanol), respectively. Complexes 1–4 have cubane core structures, in which four metal ions are bridged by alkoxides. Magnetic susceptibility measurements revealed that 1–3 have high-spin ground states of S=2, 4 and 8, respectively, while 4 has a diamagnetic ground state.

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Keywords: High-spin molecule; Copper; Nickel; Iron; Manganese; Crystal structure; Magnetic property

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1. Introduction

Multinuclear metal complexes with high-spin ground states have attached an intense interest due to their superparamagnetic behavior. Such molecules show slow magnetic relaxation of the spin reorientation along the magnetic anisotropy axis [1] and quantum tunneling of magnetization [2–6], and they are called single-molecule magnets (SMMs) [7–9]. Single molecule magnets need to have relatively high-spin ground states with an uniaxial magnetic anisotropy. Transition metal complexes with a cubane structure (M₄L₄) are a very important class of compounds [10,11], where four metal ions are linked by...
hydroxo, alkoxo, azido, sulfido, or iminato bridges [12–14]. In cubes, magnetic orbitals of metal ions are accidentally orthogonal to each other and this leads to molecules having high-spin ground states [15–19]. Recently, we found that Schiff base ligands bridge four metal ions to construct cubane core structures [20–24]. Here, we review structures and magnetic properties of metal cubanes composed of copper(II), nickel(II), iron(II) and manganese(II) ions.

2. Experiment

Preparations of 1 and 2 were conducted in air, while those of 3 and 4 were carried out under nitrogen atmosphere. Schiff base ligands (Scheme 1), H2L (H2sae and H2sap) and H3L (H3hsae and H3sapd) were synthesized by condensation reactions of corresponding aldehyde and aminoalkylalcohol in methanol [20–24] and were used for syntheses of complexes without isolation. Reactions of H2Lo or H3L with metal sources yielded tetranuclear metal cubes of M4L4 (1 w 4). [Cu4(Hhsae)4]$^2H2O$·4CH3CN (1) and [Ni4(sae)4(MeOH)4]$^2H2O$ (2) were recrystallized from acetonitrile and acetone/methanol, respectively. The fine crystals of [Fe4(Hsapd)4]$^2H2O$·4MeOH (3) and [Mn4(sap)4(MeOH)4]$^2H2O$ (4) were obtained by standing reaction mixture for several days.

3. Results and discussion

Several mono and dinuclear complexes have been prepared, but their spin-multiplicities were not high enough for observing superparamagnetism above 1.0 K [25–27], we therefore, tried to prepare larger metal complexes, such as metal cubes. Combination of four ligands and four metal ions give 16 different cubes. We discuss here syntheses, structures, and magnetic properties of four metal cubes among the all combinations.

3.1. Crystal structures

All complexes have tetranuclear cubane core consisting of μ3-alkoxo bridged four metal ions (Fig. 1). In 1, copper ion is a square pyramid, while metal ions in 2–4 have pseudo octahedral coordination geometry.

3.1.1. [Cu4(Hhsae)4]$^2H2O$·4CH3CN (1)

The structure of 1 contains a tetranuclear cubane core (Fig. 1a), which locates on crystallographic two-fold axis passing through the middle of Cu1-Cu1’ and Cu2-Cu2’ vectors, the asymmetric unit, thus, consists of the half of the tetramer. The cubane core consists of alkoxo bridged four copper atoms, giving an approximately cubic array of alternating copper and oxygen atoms. Intracluster metal–metal separations of Cu1–Cu2, Cu1-Cu1’, Cu1-Cu2’, and Cu2-Cu2’ pairs are 3.108(1), 3.443(1), 3.134(1), and 3.6154(9), respectively. Coordination geometry about each copper ion is a square pyramid with one nitrogen and two oxygen atoms from the ligand and two oxygen atoms from the next unit of the cubane. According to the coordination bond lengths, basal planes for Cu1 and Cu2 are defined as O1–N1–O2–O5 and O4–N2–O5–O2 planes, respectively.

3.1.2. [Ni4(sae)4(MeOH)4]$^2H2O$ (2)

The structure of 2 is comprised of a tetranuclear cubane core with four nickel(II) ions bridged by μ3-alkoxo groups (Fig. 1b). A cubic array of alternating nickel and oxygen atoms give intracluster metal–metal separations of 3.0347(5)–3.1981(5) Å. The coordination geometry about each nickel(II) ion is an axially elongated octahedron in which the equatorial sites are occupied by a tridentate sae2K ligand and an alkoxo oxygen atom from the next unit of the cube. The coordination bond lengths with equatorial atoms are in the range of 1.976(2)–2.052(2) Å, and a tetragonal elongation (2.120(2)–2.191(2) Å) occurs along the trans O–Ni–O vector involving methanol and bridging alkoxide. The bridging angles of the Ni–O–Ni bonds in the cube are in the range of 93.53(8)–100.95(8)°.

3.1.3. [Fe4(Hsapd)4]$^2H2O$·4MeOH (3)

Complex 3 crystallizes in tetragonal space group I41/a and the asymmetric unit constructs quarter of cluster molecules in addition to solvent molecules. A complex molecule has S4 symmetry and consists of a μ3-alkoxo bridged tetranuclear core, giving an approximately cubic array of alternating iron and oxygen atoms (Fig. 1c). Each
iron(II) ion has six coordination sites occupied with one nitrogen and five oxygen atoms from the tetradentate Hsapd$^{2-}$ group, and has Jahn-Teller distortion along O$_2^*$–O$_3^*$ vector. Coordination bond lengths are 1.999(3)–2.183(2) Å for Fe–O and 2.110(3) Å for Fe–N, and the bridging bond angles of Fe–O–Fe are in the range of 97.12(10)–100.79(10)°.

Complex 4 crystallizes in tetragonal space group $I4_1/a$. A complex molecule has $S_4$ symmetry and consists of a $\mu_3$-$\sigma$ alkoxo bridged tetranuclear core, giving an approximately cubic array of alternating manganese and oxygen atoms (Fig. 1d). Coordination geometry about each manganese(II) ion is a pseudo octahedron with one nitrogen and four oxygen atoms from tridentate sap$^{2-}$ group and methanol molecule. Coordination bond lengths are 2.103(2)–2.272(2) Å for Mn–O and 2.209(2) Å for Mn–N, and the bridging bond angles of Mn–O–Mn are in the range of 96.06(6)–102.01(6)°.

3.1.4. [Mn$_4$(sap)$_4$(MeOH)$_4$]·2H$_2$O (4)

Fig. 1. ORTEP diagrams of (a) [Cu$_4$(Hhsae)$_4$], (b) [Ni$_4$(sae)$_4$(MeOH)$_4$], (c) [Fe$_4$(Hsapd)$_4$(MeOH)$_4$], and (d) [Mn$_4$(sap)$_4$(MeOH)$_4$].

Fig. 2. Plots of $\chi_mT$ vs. $T$ for 1 (○) and 2 (□). Solid lines correspond to the fits of the data using parameters described in the text.
3.2. Magnetic properties

Magnetic susceptibility measurements for 1–4 were carried out in the temperature range of 1.8–300 K and results were shown in Figs. 2 and 3. The magnetic susceptibility data for 1 were analyzed by the Heisenberg model with two exchange coupling constants of $J_1$ and $J_2$ (Scheme 2b). Spin Hamiltonian is $H = -2J_1(S_{Cu1} \cdot S_{Cu'1} + S_{Cu2} \cdot S_{Cu'2}) - 2J_2(S_{Cu1} \cdot S_{Cu2} + S_{Cu'1} \cdot S_{Cu'2} + S_{Cu1} \cdot S_{Cu'2} + S_{Cu'1} \cdot S_{Cu2})$, and the derived expression is as follows:

$$\chi_m(T) = \frac{N g^2 \beta^2}{3k(T - \theta)} \times \frac{2 \exp(2J_1/kT) + \exp[(4J_1 - 2J_2)/kT] + 5 \exp[(4J_1 + 2J_2)/kT]}{1 + 6 \exp(2J_1/kT) + 3 \exp[(4J_1 - 2J_2)/kT] + 5 \exp[(4J_1 + 2J_2)/kT] + \exp[(4J_1 - 4J_2)/kT]}$$

in the analysis of the magnetic data, an inter-cluster interaction was included as a mean field correction $\theta$.

The magnetic data for 2–4 were analyzed by using Heisenberg spin Hamiltonian ($H = -2J \sum S_i \cdot S_j$). The Kambe’s vector coupling method [28] gives the eigenvalue expression of $E(S_T) = -JS_T(S_T + 1)(S_T = S_1 + S_2 + S_1 + S_2)$, supposing the identical exchange coupling constants for intra-cube’s magnetic pathways.

3.2.1. [Cu$_4$(Hhsae)$_4$]·2H$_2$O·4CH$_3$CN (1)

A room temperature $\chi_m T$ value is 1.8 emu mol$^{-1}$ K, which is expected for non-correlated four Cu(II) ions. Upon cooling the $\chi_m T$ values increased until the maximum value of 2.44 emu mol$^{-1}$ K at 14 K, then decreased. This magnetic behavior is indicative of an intracluster ferromagnetic interaction. In 1 the magnetic orbitals (dx$_z$–dy$_z$) of the Cu(II) ions locate on the basal coordination planes, and there are parallel and perpendicular alignments of magnetic orbitals (Scheme 2a). The magnetic orbitals of Cu1 and Cu2 are parallel to those of Cu1’ and Cu2’, respectively, while the other combinations are perpendicular. The parallel alignments ($J_1$) give rise to intra-cluster antiferromagnetic interaction and the perpendicular alignments ($J_2$) are responsible for the occurrence of the intra-cluster ferromagnetic interaction. The propagation of intra-cluster ferromagnetic interactions can be interpreted by accidental orthogonality of magnetic orbitals. The least squares calculation yielded the best fit parameters of g, $J_1$, $J_2$, and $\theta$ values being 2.02(1), $-17.6(1)$, $+36.0(9)$ cm$^{-1}$ and $-1.0(1)$ K, respectively.

3.2.2. [Ni$_4$(sae)$_4$(MeOH)$_4$] (2)

The $\chi_m T$ value for 2 increased as the temperature was lowered, reaching the maximum value of 8.76 emu mol$^{-1}$ K at 8 K. This magnetic behavior is indicative of the occurrence of ferromagnetic interactions among the Ni(II) centers, which predicts an $S=4$ spin ground state for 2. The room temperature $\chi_m T$ value (≈ 4.99 emu mol$^{-1}$ K) corresponds to the value expected for isolated four Ni(II) ions. A sudden decrease of the $\chi_m T$ values below 8 K is due to
an inter-cube antiferromagnetic interaction and/or zero-field splitting. The least squares calculation yielded the best fit parameters of $g$ and $J$ values being 2.171 and $+3.2\text{ cm}^{-1}$, respectively. Ac magnetic susceptibility measurements for poly-crystalline samples were performed in the temperature range of 1.8–4.0 K with a 3 G ac field oscillating at 50–1000 Hz. The out-of-phase ($\chi''_m$) signals for $T_2$ were not observed down to 1.8 K.

### 3.2.3. \([\text{Fe}_4(\text{Hsapd})_4(\text{MeOH})_4]_22\text{H}_2\text{O}4\text{MeOH}(3)\)

The $\chi''_mT$ value (14.49 emu mol$^{-1}$ K) at 300 K is a little bit larger than the value (12.00 emu mol$^{-1}$ K with $g = 2.0$) expected for four non-interacting Fe(II) ions. $\chi''_mT$ values gradually increased as the temperature was lowered, reaching the maximum value (15.63 emu mol$^{-1}$ K) around 10 K, which was followed by sudden decrease. This behavior is characteristic of the occurrence of intramolecular ferromagnetic interactions. The least squares calculation yielded the best fit parameters of $g$ and $J$ values being 2.18(1) and $+0.4(1)\text{ cm}^{-1}$, respectively. It should be noted that the analysis of magnetization data at 1.8 K suggested a positive $D$ value, 3 is not, therefore, a SMM.

### 3.2.4. \([\text{Mn}_4(\text{sap})_4(\text{MeOH})_4]2\text{H}_2\text{O}(4)\)

The $\chi''_mT$ value of 17.57 emu mol$^{-1}$ K at 300 K gradually decreases as the temperature is lowered, reaching to 0.29 emu mol$^{-1}$ K at 1.8 K (Fig. 3). The spin-only value for a unit composed of four non-interacting Mn(II) ions is 17.5 emu mol$^{-1}$ K ($g = 2.0$). The temperature dependence of the $\chi''_mT$ data was fitted to determine the magnitude of the antiferromagnetic coupling constant. The least squares calculation yielded the best fit parameters of $g$ and $J$ values being 2.141(1) and $-1.6(1)\text{ cm}^{-1}$, respectively. A Mn(II) ion has d$^5$ electronic configuration, some of which magnetic orbitals direct to overlap each other. The antiferromagnetic interaction overcomes the ferromagnetic interaction in the Mn(II) cube, which results in the molecule having the diamagnetic spin ground state.

### 4. Conclusion

Schiff base ligands prepared by condensation reactions of aldehyde and aminoalkylalcohol give an opportunity to assemble a variety of four metal ions into cubes. In the metal cubes, orthogonal arrangements for Cu(II), Ni(II) and Fe(II) ions satisfied the condition for the occurrence of ferromagnetic interactions leading to high-spin ground states.

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