A Homometallic Ferrimagnet Based on Mixed Antiferromagnetic and Ferromagnetic Interactions through Oxamato and Carboxylato Bridges

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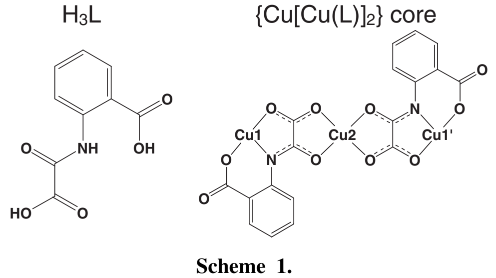
Two novel coordination polymers (CPs), $\{Cu[Cu(L)(H_2O)(py)]_2\}_n$ (**1**) and $\{Cu[Cu(L)(MeOH)]_2 \cdot 2H_2O\}_n$ (**2**), were synthesized using 2-(oxaloamino)benzoic acid (H_3L) providing oxamate and carboxylate groups, and magnetically characterized. Different 2-D layer structures were formed based on oxamato-bridged tricopper units bridging via the carboxylate group. In compound **1**, a simple antiferromagnetic interaction operates through the oxamato bridge in the tricopper core, whereas, **2** showed a tendency for ferrimagnetic ordering at 2 K, resulting from mixed antiferromagnetic and ferromagnetic interactions through oxamato and syn–anti-type carboxylato bridges.

Coordination polymers have attracted much attention in the past decade because of their unique structures and properties. The CPs' frameworks show a rich diversity due to the combination of various components (metal ion, bridging ligand, coligand, etc.), which makes it possible to tune the CPs' frameworks and properties.[1–3] Consequently, CPs are expected to be a platform to deliver multiple functions. From this aspect, it is one of the rational strategies to incorporate physical properties, e.g., magnetic,[2] dielectric properties,[3] etc., in the CPs' frameworks. Here, the design and construction of sensible frameworks providing target properties are the principal significant challenges. To construct a new magnetic framework, we selected a bridging ligand, 2-(oxaloamino)benzoic acid (H_3L; Scheme 1), having oxamate and carboxylate groups. H_3L can form an oxamato-bridged trinuclear complex, $M^{II}[M^{II}(L)]_2$, which contains mononuclear complexes, $[M^{II}(L)]^-$. Furthermore, the trinuclear complex provides coordinatable sites and can form a self-assembled structure because of the terminal carboxylate groups. Because the carboxylate groups bridge the terminal M^{II} ions in a syn–anti style, which mediates a ferromagnetic interaction[4] due to steric demand, the coexistence of oxamato and carboxylato bridges is expected to exhibit a unique magnetic behavior resulting from the mixed antiferromagnetic and ferromagnetic interactions. Here, we report the synthesis, crystal structures, and magnetic properties of new CPs, $\{Cu[Cu(L)(H_2O)(py)]_2\}_n$ (**1**) and $\{Cu[Cu(L)(MeOH)]_2 \cdot 2H_2O\}_n$ (**2**), which consist of a tricopper (Cu_3) core with L^{3-}.



Scheme 1.

H_3L was prepared as the ethyl ester by the reaction of anthranilic acid and excess diethyloxalate upon heating in EtOH. $\{Cu[Cu(L)(H_2O)(py)]_2\}_n$ (**1**) was prepared by the reaction of $Cu(CH_3COO)_2 \cdot H_2O$, H_3L, and pyridine in 3:2:20 mole ratio in H_2O/MeOH (1:1 v/v). Greenish blue crystals of **1** appeared after allowing the reaction mixture to stand at room temperature (rt) for several days. $\{Cu[Cu(L)(MeOH)]_2 \cdot 2H_2O\}_n$ (**2**) was obtained as green crystals by slow reaction of $Cu(CH_3COO)_2 \cdot H_2O$ and H_3L (3:2) in H_2O/MeOH (1:1 v/v). ORTEP drawings of **1** and **2** are shown in Figure 1.[5] In both cases, the ligand L^{3-} coordinates to Cu1 with the tridentate NO_2 site to afford a $[Cu1(L)]^-$ unit, and two $[Cu1(L)]^-$ units coordinate to Cu2 affording an oxamato-bridged Cu_3 core. In the case of **1**, pyridine coordinates to the equatorial position of Cu1 as a terminal ligand; on the other hand, the carboxylate oxygen atom of the nearest Cu_3 unit ($O2^{\#6}$: symmetry operations are listed in Ref. 5) occupies the same position in **2**. The geometry about Cu1 is square pyramidal with the NO_2 site of L^{3-} and nitrogen of pyridine for **1** or carboxylate oxygen for **2** in the equatorial plane, and an axial water for **1** or MeOH for **2**. Cu2 of **1** is located on the inversion center and has an elongated octahedral geometry consisting of two oxamato groups of L^{3-} (O3, O5, $O3^{\#1}$, $O5^{\#1}$) and two axial carboxylate oxygen atoms of the adjacent Cu_3 cores ($O2^{\#2}$ and $O2^{\#3}$) with bond distance of 2.491(4) Å. Cu2 of **2** is in a square planar environment with two oxamate groups (O3, O5, $O3^{\#5}$, $O5^{\#5}$).

In the lattice, **1** forms a 2-D sheet structure on the *bc* plane through the carboxylato bridges between the equatorial position of the terminal Cu1 and the adjacent axial position of the central Cu2. The 2D sheets are linked through complementary hydrogen bonds between the carboxylate oxygen O2 and the axial water on

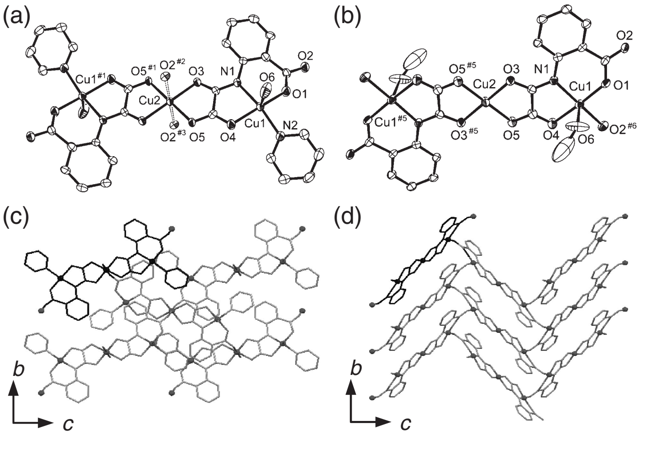


Figure 1. Tricopper core structures of **1** (a) and **2** (b) and projections of the 2D sheet structures of **1** (c) and **2** (d) onto the *bc* plane.

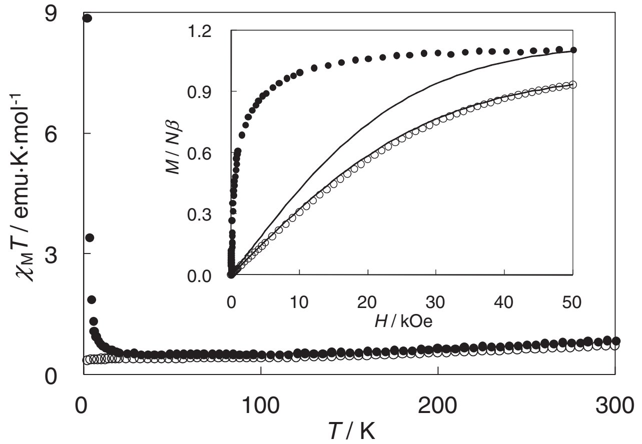


Figure 2. $\chi_M T$ vs. T plots of **1** (○) and **2** (●). Insert: Field dependence of magnetization of **1** (○) and **2** (●) at 2 K. The solid lines are the Brillouin function for $S = 1/2$ with $g = 2.00$ (**1**) and $g = 2.11$ (**2**).

Cu1 (O6$^{\#4}$) with a distance of 2.805 Å, the nearest intersheet Cu···Cu distance being Cu1···Cu1$^{\#4}$ with a value of 5.707 Å. In contrast, compound **2** forms a different 2-D sheet structure from **1** extended on the (101) plane, where the Cu_3 cores are connected to each other by the syn–anti-type carboxylato bridge between terminal Cu1 atoms, complementary hydrogen bonds between oxamate oxygen O5 and the axial MeOH on Cu1 (O6$^{\#8}$), and $\pi\cdots\pi$ contacts (e.g., C8···C6$^{\#9}$ = 3.440 Å, C9···C1$^{\#9}$ = 3.473 Å), and forms a 1-D 2_1 helical arrangement of Cu1 atoms along the b axis. The helical chains are linked by oxamato bridges forming a 2-D sheet structure. The nearest intersheet Cu···Cu distance is Cu1···Cu1$^{\#7}$ with a value of 7.316 Å.

The temperature dependences of $\chi_M T$ per Cu_3 unit for **1** and **2** are shown in Figure 2. In the case of complex **1**, the value of $\chi_M T$ at 300 K was 0.719 emu·K·mol^{-1} (2.40 μ_B), decreased with decreasing temperature and reached a plateau (0.333 emu·K·mol^{-1}; 1.63 μ_B), which is a characteristic behavior of a discrete antiferromagnetically coupled tricopper complex.[6,7] A least-squares fitting of the magnetic behavior based on the equation for $S = 1/2 + 1/2 + 1/2$ system with Heisenberg Hamiltonian ($H = -2J(S_{Cu1} \cdot S_{Cu2} + S_{Cu1'} \cdot S_{Cu2}) - 2J'(S_{Cu1} \cdot S_{Cu1'})$) was performed, where the magnetic interaction between Cu2 and Cu1$^{\#2}$ in the next Cu_3 unit through the carboxylato bridge was treated as an overall intermolecular interaction θ. The best-fit parameters obtained for **1** were $J = -142\,\mathrm{cm}^{-1}$, $J' = 0.00$, $g = 2.00$, and $\theta = -0.56$ K, which suggests that an antiferromagnetic interaction through the oxamato bridge dominantly operated, and the interaction between Cu2 and Cu1$^{\#2}$ was negligible because of a low overlap integral of the magnetic orbitals between the equatorial and axial planes of Cu^{II}.[6] The magnetic behavior of **2** was notably different from that of **1**. The value of $\chi_M T$ gradually decreased with decreasing temperature from 0.839 emu·K·mol^{-1} (2.59 μ_B) at rt to 0.490 emu·K·mol^{-1} (1.98 μ_B) at 44 K. Upon further cooling, the $\chi_M T$ sharply increased to a maximum value of 8.87 emu·K·mol^{-1} (8.42 μ_B) at 2 K, which suggests a tendency to magnetic ordering. The temperature dependences of the ac magnetic susceptibility and weak-field magnetization also support an onset of magnetic ordering.[8]

The M vs. H curve of **2** showed a sharp increase with a value for the saturation magnetization (M_s) of 1.10 $N\beta$ at 50 kOe. The value of M_s means that one spin remains in the Cu_3 core. The observation that saturation occurs faster than the theoretical curve based on the Brillouin function for $S = 1/2$ confirms the magnetic ordering. In the light of these magnetic data of **2**, its magnetic behavior is classified to "ferrimagnetic" based on antiferromagnetic coupling between the syn–anti-type carboxylato-bridged ferromagnetic chain and the central Cu2 through the oxamato bridge. Because cusps were not observed in the ac magnetic response down to 2 K, a complete ferrimagnetic ordering is expected below 2 K.

We have successfully prepared two new CPs using 2-(oxaloamino)benzoic acid as a bridging unit. Compounds **1** and **2** formed different types of 2-D layer structures consisting of oxamato-bridged Cu_3 cores. These structures were derived by the use of the terminal pyridine ligand. In the case of **1**, the central Cu^{II} in the Cu_3 core was linked with the terminal Cu^{II} in the nearest Cu_3 core through carboxylato bridges, whereas, the 2-D layer structure of **2** was constructed by linking the terminal Cu^{II} through syn–anti-type carboxylato bridges. Compound **1** showed a relatively strong antiferromagnetic interaction ($J = -142\,\mathrm{cm}^{-1}$) through the oxamato bridge as a magnetically isolated Cu_3 core. On the other hand, **2** demonstrated a tendency towards ferrimagnetic ordering around 2 K, in which the residual spin in the antiferromagnetically coupled Cu_3 core was aligned by a weak ferromagnetic interaction through the syn–anti-type carboxylato bridge. This is a rare homometallic ferrimagnetic system[9] based on an odd-numbered metal unit with mixed antiferromagnetic and ferromagnetic interactions.

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5 Crystal data for **1**: $C_{28}H_{22}N_4Cu_3O_{10}$, $T = 223$ K, fw 765.14, monoclinic, $C2/c$, $Z = 4$, $a = 19.294(2)$, $b = 10.2228(9)$, $c = 15.446(1)$ Å, $\beta = 112.785(1)°$, $V = 2808.9(5)$ Å^3, $\mu(\mathrm{Mo}\,K\alpha) = 23.28\,\mathrm{cm}^{-1}$, $R_1 = 0.0584$, $wR_2 = 0.133$ (all data, F^2), G.O.F. = 1.145. CCDC 664979; for **2**: $C_{18}H_8N_2Cu_3O_{10}$, $T = 183$ K, fw 602.9, monoclinic, $P2_1/n$, $Z = 2$, $a = 10.8891(7)$, $b = 6.1482(8)$, $c = 17.437(2)$ Å, $\beta = 98.640(2)°$, $V = 1154.1(2)$ Å^3, $\mu(\mathrm{Mo}\,K\alpha) = 27.93\,\mathrm{cm}^{-1}$. $R_1 = 0.0461$, $wR_2 = 0.143$ (all data, F^2), G.O.F. = 1.001. CCDC 664980. Symmetry operations: #1: $-x + 3/2$, $-y + 1/2$, $-z + 1$; #2: x, $-y$, $z - 1/2$; #3: $-x + 3/2$, $y + 1/2$, $-z + 1/2$; #4: $-x + 2$, $-y$, $-z + 2$; #5: $-x$, $-y$, $-z$; #6: $-x - 1/2$, $y - 1/2$, $-z + 1/2$; #7: $-x - 1$, $-y + 1$, $-z$; #8: x, $y - 1$, z; #9: $-x$, $1 - y$, $-z$.

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