Crystal Structures and Magnetic Properties of Isonicotinate- and Dicyanometallate-bridged Manganese(II) Complexes

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Two novel 3D network coordination polymers $[Mn(H_2O)(ina)\{M(CN)_2\}]\cdot H_2O$ (ina = isonicotinato, M = Ag (**1**) or Au (**2**)) have been synthesized and characterized crystallographically and magnetically. In both complexes, the coordination geometries of the Mn^{II} atoms have MnN_3O_3 octahedral coordination built up by one tridentate ina ligand, one H_2O molecule, and two μ-$[M(CN)_2]^-$ units. SQUID data show weak antiferromagnetic interactions among the Mn atoms bridged by the ina ligands in **1** and **2**.

Cyano-bridged coordination polymers, prepared from self-assembling polycyanometallates and transition-metal complexes as building blocks, have been shown to exhibit fascinating structures with interesting magnetic, optical, electrochemical, magneto-optical, and zeolitic properities.[1] Among the successful synthetic strategies of cyano-bridged coordination polymers, linear dicyanometallates $[M^I(CN)_2]^-$ (M = Ag and Au) have been used as building blocks because they can bridge coordination centers through the nitrogen atoms of the cyano groups. Another interesting feature of some of these silver and gold compounds is the metallophilic interactions.[1,2] The metallophilicity is closed-shell intermolecular interactions between silver(I) or gold(I) atoms. The interactions are comparable to hydrogen bonds.

Manganese(II)–carboxylate systems have been also used to design coordination polymers with unique structures and interesting magnetic behavior.[3,4] And, isonicotinate anion contains both a pyridyl group and a carboxylate group in the opposite position of an aromatic ring. It can connect metal ions with one nitrogen donor and one or two oxygen donors. Several intriguing high-dimensional structures have been obtained by introducing the isonicotinato ligand.[4,5]

In this work, we report the synthesis, crystal structures,[6] and magnetic properties of novel bimetallic 3D coordination polymers with the formula $[Mn(H_2O)(ina)\{M(CN_2)\}]\cdot H_2O$ (ina = isonicotinato, M = Ag (**1**) or Au (**2**)) (See Supporting Information).[7]

In complex **1**, the Mn(1) exhibits a MnN_3O_3 octahedral coordination geometry (Figure 1). One N(3) atom from the pyridyl of the ina ligand and one O(3) atom from the H_2O molecule occupy the Mn(1) axial positions whereas two nitrogen atoms (N(1) and N(2)) from the two μ-$[Ag(CN)_2]^-$ ions and two oxygen atoms (O(1) and O(2)) from the two μ-carboxylate groups of the ina ligands are situated in the equatorial plane. The O(4) atom is an uncoordinated water molecule and is connected to O(2) atom and O(3) atom by hydrogen bonds (O(2)···O(4) = 3.017(7) Å; O(3)···O(4)′ = 2.718(7), O(3)···O(4)″ = 3.147(9), and O(3)···O(4)‴ = 3.225(9) Å). Each ina ligand is coordinated to three Mn^{II} ions via the nitrogen atom and the two oxygen atoms. Two μ-carboxylate groups of the two ina ligands bridge two Mn(1) atoms in a syn–anti fashion, resulting in double μ-OCO bridges and a bridging eight-membered ring. The bond distance of Mn(1)–O_{syn} (=O(1)) is shorter than Mn(1)–O_{anti} (=O(2)). The Mn···Mn distance through the Mn–$(OCO)_2$–Mn edge is 4.711 Å, similar to Mn···Mn distances found in analogous complexes in which carboxylate groups also bridge in a syn–anti manner.[3] The Mn···Mn distances through the Mn(1)–pyridyl–C(8)–O_{syn}–Mn(1) edge and Mn(1)–pyridyl–C(8)–O_{anti} edge are 9.438 and 7.890 Å, respectively (Figure S2).[7] The $[Mn(H_2O)(ina)]$ moiety shows a stair-like structure (Figure 2). The closest approach between pyridine rings of ina ligands corresponds to π–π stacking in the $[Mn(H_2O)(ina)]$ stair. The Ag^I atoms lie across the *yz* plane. Each $[Ag(CN)_2]^-$ group connects two manganese atoms defining the edge of a $[Mn\{Ag(CN)_2\}]$ helical chain. Three helical $[Mn\{Ag(CN)_2\}]$ chains construct a triple helix formation along the *c* axis (Figure 2). The closest approach between the helical chains corresponds to argentophilic Ag(1)···Ag(2) interactions, which zigzag chain Ag arrangements along *c* axis. The Mn···Mn distances through the Mn–NC–Ag(1)–CN–Mn edge and Mn–NC–Ag(2)–CN–Mn edge are 10.631 and 10.659 Å, respectively. The C(1)–Ag(1)–C(1)′ angle is slightly bent, in contrast, the C(2)–Ag(2)–C(2)′ angle is linear. This might be due to metallophilic interactions.

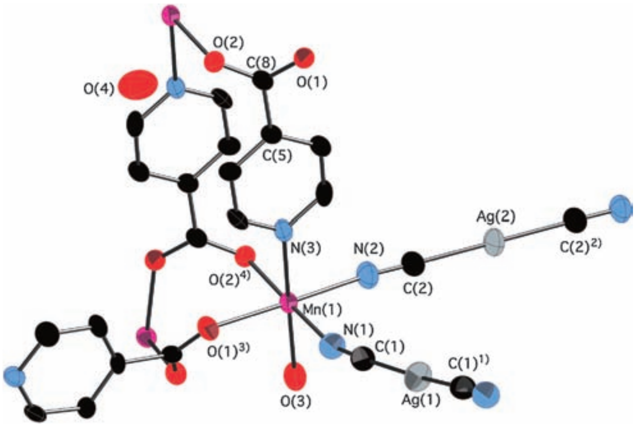

Figure 1. Atomic arrangement scheme around the octahedrally coordinated Mn(1) atom in **1**. Displacement ellipsoids are drawing at the 50% probability level. H atoms are omitted for clarity [symmetry codes: 1) $-x+2$, y, $-z+1/2$, 2) $-x+2$, $-y+2$, $-z+2$, 3) $x-1/2$, $-y+3/2$, $z-1/2$, 4) $-x+3/2$, $-y+3/2$, $-z+2$].

The crystal structure of **2** is an isostructure with **1** (Figure S1).[7] The Au–C_{CN} bond lengths in **2** are slightly shorter than the Ag–C_{CN} bonds in **1**. This is a general tendency in the dicyanometallate systems.[1]

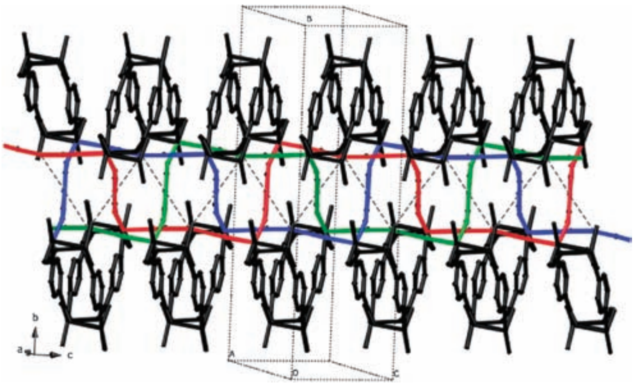

Figure 2. $[Mn(H_2O)(ina)]$ stairs (black sticks), $[Mn\{Ag(CN)_2\}]$ helical chains (red, blue, and green sticks) and argentophilic interactions (dashed line) among the $[Mn\{Ag(CN)_2\}]$ chains in **1**.

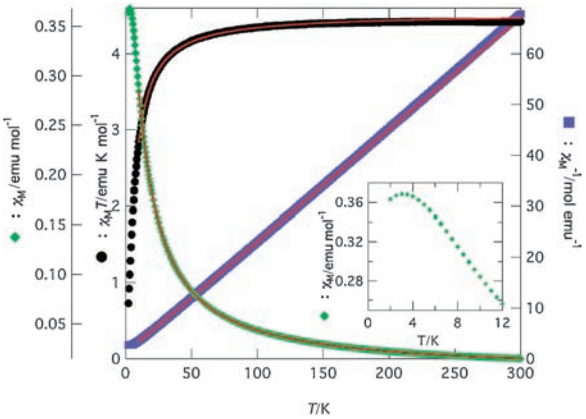

Figure 3. Magnetic property of **1** in 1 kOe. χ_M vs. T, $\chi_M T$ vs. T, and $\chi_M{}^{-1}$ vs. T plot from 0 to 300 K. Red solid lines represent the best fit calculation. Insert: χ_M vs. T plot from 0 to 12 K.

Temperature-dependent magnetic susceptibilities for **1** and **2** were measured in the 2–300 K temperature range. Complexes **1** and **2** have similar magnetic properties. χ_M versus T, $\chi_M T$ versus T, and $\chi_M{}^{-1}$ versus T plots for **1** are shown in Figure 3. The μ_{eff} $(=2.828\sqrt{(\chi_M T)})$ values of **1** and **2** at 300 K are 5.95 and 5.79 μ_B, respectively. The value of **1** is similar to the 5.92 $(=g\sqrt{(S(S+1)})$ that of a pure spin-only system. On the other hand, the value of **2** is slightly smaller than 5.92, whereas the value is similar to the μ_{eff} values of the $[MnL_2\{Ag(CN)_2\}][Mn(H_2O)\{Ag(CN)_2\}]$ (L = 4-cyanopyridine and pyridine-4-aldoxime).[1j] The magnetic values could be fitted with the Curie–Weiss equation $\chi_M{}^{-1} = (T - \theta)/C$ for >10 K, where $C = 4.49$ emu K mol^{-1} and $\theta = -3.89$ K for **1** and $C = 4.2$ emu K mol^{-1} and $\theta = -3.0$ K for **2**. These features are indicative of very weak antiferromagnetic coupling among the manganese(II) ions. Upon cooling for **1**, the $\chi_M T$ values decrease gradually and reach 0.73 emu K mol^{-1} at 2 K, while the χ_M values increase to rounded maximum at about 3 K and then decrease rapidly on further cooling. On the other hand, for **2**, the $\chi_M T$ values decrease gradually and reach 0.72 emu K mol^{-1} at 2 K, while the χ_M values increase to rounded maximum at about 3 K and then decrease gradually on further cooling (Figure S4).[7]

In **1** and **2**, these frameworks are very intricate. However, the magnetic interactions between two Mn^{II} centers separated by >9 Å through the μ-$[M(CN)_2]^-$ and longer μ-ina (Mn(1)–pyridyl–C(8)–O_{syn}–Mn(1)) are expected to be ignored. Thus, the simplified analysis of these coupling system can be accomplished according to an equation for homonuclear alternating chain structure[3d,8] with $S = 5/2$ in the $[Mn(H_2O)(ina)]$ stair (Figure S3).[7] The least-squares fit of the experimental data over the >10 K range led to $g = 2.0347(2)$, $J_1/k = -1.384(3)$ K, $J_2/k = -0.039(6)$ K, and $R = 8.29 \times 10^{-6}$ for **1**, and $g = 1.9844(8)$, $J_1/k = -1.391(6)$ K, $J_2/k = -0.014(9)$ K, and $R = 4.98 \times 10^{-5}$ for **2**. The negative J_1/k and J_2/k values show that the weak antiferromagnetic interactions exist between the Mn^{II} ions through the bridging carboxylate group of the ina ligand and through the extended ina ligand bridge in the $[Mn(H_2O)(ina)]$ stair.

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6 Structure parameters for **1** and **2** are available free of charge via Cambridge Crystallographic Data Centre under deposition numbers CCDC-744886 of **1** and CCDC-744887 of **2**, respectively.

7 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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