Design and Construction of Coordination Polymers Based on the Topological Property of the Multidentate Ligand

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The crystal structures and magnetic properties of two-dimensional coordination polymers $[M(tdpd)(H_2O)_2]_n$ ($M = Mn^{2+}$ and Co^{2+}) involving the triangular lattice are determined. The magnetic behaviors of **1** and **2** may come from the single-ion behavior and the specific arrangement of the metal ions.

The construction of new coordination polymers, whose structures are governed by the topological properties of the precursor metal ions and ligands, is a rapidly developing area of functional materials. It is hoped that by judicious choice of ligand and metal connectivity,[1] we can control the topology and geometry of the network formed (e.g., square, rectangular and triangular lattice), and possibly the physical properties of the resultant compounds. Such strategy may afford new materials with useful properties such as catalytic activity, microporosity and co-operative magnetic behavior.[2–4]

The recent efforts in the field of crystal engineering of networked materials based on polymeric coordination compounds have been devoted to the use of novel polydentate ligands.[5] In contrast to the more common frameworks based on metal centers and bidentate organic rods, the presence of polyhapto bases also introduces organic centers in addition to the metallic ones, which can give rise to new and varied topological types.[6] Early studies suggest that the polydentate ligands may provide coordination polymers with diverse structures.[7–12] In this concern a potentially hexadentate ligand 1,4,5,6-tetrahydro-5,6-dioxo-2,3-pyrazinedicarbonitrile (H_2tdpd)[13] seems quite suitable for the preparation of the networks with unusual topology. We report here two-dimensional coordination polymers $[M(tdpd)(H_2O)_2]_n$ ($M = Mn^{2+}$ (**1**), Co^{2+} (**2**)) involving a triangular lattice.

An aqueous solution (10 mL) of manganese(II) chloride tetrahydrate (0.2 mmol L^{-1}) was transferred to a glass tube, then an ethanolic solution (10 mL) of H_2tdpd (0.2 mmol L^{-1}) poured into the tube without mixing the two solutions. Yellow plate crystals (**1**) began to form in two weeks. One of these crystals was used for X-ray crystallography. Compound **2** was synthesized from cobalt(II) sulfate heptahydrate by a procedure similar to that employed for **1**. Orange plate crystals began to form in two weeks.[14]

Compounds **1** and **2** are isomorphous, possessing similar cell parameters and identical space group. An ORTEP drawing of **1** is shown in Figure 1.[15] The atom labeling scheme for **2** is the same as that for **1**. The crystal structure of **1** consists of two-dimensional infinite layers formed by metal ions, the $tdpd^{2-}$ dianion and coordinated water molecules. Two water molecules in the *trans* position and two oxygen atoms and two nitrogen atoms of three $tdpd^{2-}$ dianions create an octahedral environment around the metal ion. The mean distance around the metal ion of **1** (2.18 Å) is longer than that of **2** (2.08 Å), because of the larger ionic radius of the manganese(II) ion. The $tdpd^{2-}$ dianion is planar and shows maximum out-of-plane deviations of 0.0036(19) Å in **1** and of 0.0038(17) Å in **2** for N(1). Although the $tdpd^{2-}$ dianion is a potentially hexadentate ligand, it acts as a triconnected ligand, binding to three metal ions through two carbonyl oxygen atoms and each of two cyano nitrogen atoms. From topological point of view, the $tdpd^{2-}$ dianion has a specific trigonal geometry and the two-dimensional framework of $[M(tdpd)(H_2O)_2]_n$ is a triangular lattice, comprised of triconnected metal ions and $tdpd^{2-}$ dianion in the ratio 1:1. The triangular lattice is constructed from D_{3h} ligands so far,[7,8] but $[M(tdpd)(H_2O)_2]_n$ is the first example of the triangular lattice constructed from the C_{2v} $tdpd^{2-}$ ligand. A closer examination reveals that the coordinated water molecules intrude into the triangular voids in the adjacent layers to result in interdigitation of the two-dimensional networks.

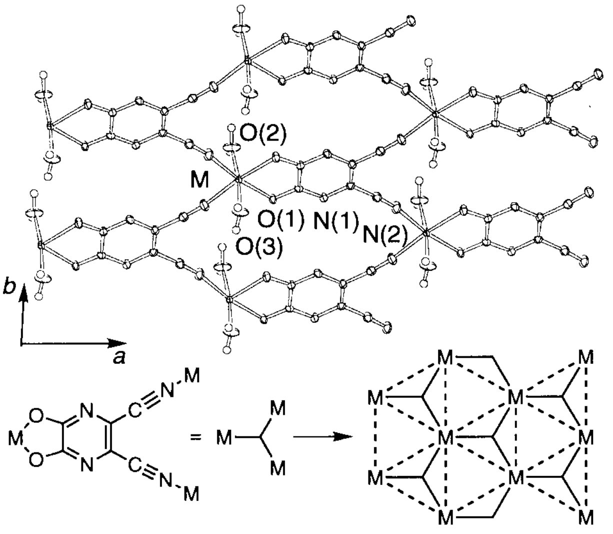

Figure 1. Two-dimensional architecture of the structure of $[M(tdpd)(H_2O)_2]_n$. The bond distances around manganese(II) are: Mn-O(1), 2.164(2) Å; Mn-O(2), 2.126(3) Å; Mn-O(3), 2.144(3) Å and Mn-N(2'), 2.292(3) Å. The bond distances around cobalt(II) are : Co-O(1), 2.079(1) Å; Co-O(2), 2.051(2) Å; Co-O(3), 2.023(2) Å and Co-N(2'), 2.158(2) Å.

Variable temperature magnetic susceptibility measurements were carried out on crystalline samples of **1** and **2** in the temperature range 2–300 K at 0.5 and 3.0 T. In compound **1**, χ_mT reduces with the decrease of the temperature ($\chi_mT = 4.24$

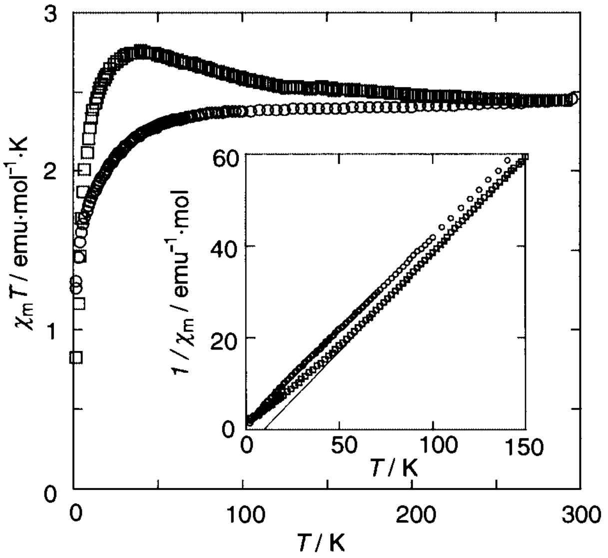

Figure 2. Plots of the temperature dependence of $\chi_m T$ and $1/\chi_m$ for **2** at 0.5 (○) and 3.0 T (□).

emu·mol^{-1}·K). The plots of $1/\chi_m$ vs T follow the Curie–Weiss law with the Weiss constant of –1.4 and –1.7 K at 0.5 and 3.0 T, respectively, indicating a weak antiferromagnetic interaction between the neighboring paramagnetic centers. On the other hand, in compound **2**, $\chi_m T$ decreases at lower temperature at 0.5 T (Figure 2). The plot of $1/\chi_m$ vs T obeys the Curie–Weiss law with a negative Weiss constant of $\theta = -1.8$ K. However, at 3.0 T, with decreasing the temperature, $\chi_m T$ increases up to a maximum value and then decreases. Above 50 K, the data can be fit to the Curie–Weiss expression giving $\theta = +8.0$ K. The magnetic behaviors of **1** and **2** may come from the single-ion behavior and the specific arrangement of the metal ions.

In this study, two metal-assembled complexes governed by the specific topological properties of tdpd^{2-} have been successfully synthesized. Compounds **1** and **2** are two-dimensional metal-assembled complexes with a triangular lattice. In addition, as tdpd^{2-} will have six coordination sites, it can be possible to construct different topologies with various metal ions.

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14 Crystal data for **1**: $C_6H_4MnN_4O_4$, $M_r = 251.06$, monoclinic, $C2/m$ (no. 12), $a = 17.471(2)$, $b = 7.737(2)$, $c = 7.144(2)$ Å, $\beta = 112.62(2)°$, $U = 891.3(3)$ Å^3, $Z = 4$, $F(000) = 500$, $D_c = 1.871$ g cm^{-3}, μ(Mo Kα) = 1.481 mm^{-1}, yellow plate crystal (0.30 × 0.30 × 0.10 mm), 1139 total reflections ($2\theta_{max} = 55°$), 1105 independent reflections ($R_{int} = 0.018$), 1038 observed [$I > 3\sigma(I)$], $R = 0.036$, $R_w = 0.080$, goodness of fit = 1.61.
Crystal data for **2**: $C_6H_4CoN_4O_4$, $M_r = 255.06$, monoclinic, $C2/m$ (no. 12), $a = 17.0438(9)$, $b = 7.634(1)$, $c = 7.077(1)$ Å, $\beta = 112.547(7)°$, $U = 850.4(2)$ Å^3, $Z = 4$, $F(000) = 508$, $D_c = 1.992$ g cm^{-3}, μ(Mo Kα) = 2.019 mm^{-1}, orange plate crystal (0.30 × 0.10 × 0.10 mm), 1090 total reflections ($2\theta_{max} = 55°$), 1056 independent reflections ($R_{int} = 0.005$), 938 observed [$I > 3\sigma(I)$], $R = 0.028$, $R_w = 0.032$, goodness of fit = 1.55.
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