Hydrothermal Synthesis and Structural Characterization of a Manganese(II) Wire Made Up of Octahedral and Square Pyramidal Mn(II) Ions

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Hydrothermal reaction between Mn(II) ion and α-phenylcinnamic acid yields a 1D-chain complex, $[Mn_5L_8(OH)_2]$ ($L = \alpha$-phenylcinnamate). $[Mn_5L_8(OH)_2]$ contains pentanuclear Mn(II) cores, α-phenylcinnamate and hydroxide ions as bridging ligands. The pentanuclear Mn(II) core consists of distorted octahedral $\{MnO_6\}$ and distorted square pyramidal $\{MnO_5\}$ linked through μ-carboxylate and μ_3-hydroxide ligands. The octahedrons and the distorted square pyramids share the edges and vertexes to form 1D-chain structure.

Synthesis and characterization of transition metal aggregates with desired functions and fascinating topological architecture has become an area on increasing interest in recent years.[1] Mn assembled complexes are of interest from variety of viewpoints, including magnetic materials and bioinorganic chemistry.[2] In the former area, it has been found that such compounds often behave as single-molecule magnets or single-chain magnets. In the bioinorganic arena, Mn cluster is an integral component in the photosystem II reaction center of green plants. However, synthesis and structural characterization of Mn cluster-assembled systems are still sparse examples.[3] We have been focused on hydrothermal synthesis and structural characterization of M(II)-carboxylate (M = Co, Ni).[4] During the course of the study, we found π-conjugated monocarboxylic acid, α-phenylcinnamic acid reacts with Co(II) ion to yield Co(II) cluster assemby.[5] To extend our chemistry, we used Mn(II) ion as a metal source. Here we report the hydrothermal synthesis, crystal structure of a 1D-chain Mn(II) compound, $[Mn_5L_8(OH)_2]$, constructed by pentanuclear manganese aggregation of octahedral Mn(II) and square pyramidal Mn(II) ions.

$[Mn_5L_8(OH)_2]$ was synthesized as follow. $Mn(NO_3)_2{\cdot}6H_2O$ (1.8 g) was dissolved in distilled water (ca. 30 mL) and solution of α-phenylcinnamic acid (0.7 g) and NaOH (0.25 g) in distilled water (ca. 30 mL) was added. The mixture was placed in the Teflon lined autoclave, which was then sealed and heated to 150 °C for 3 d then cooled to room temperature in a water bath. The colorless crystals are filtered off and washed with water and acetone. The crystals are allowed to air dry. Uncharacterized byproducts are removed manually under optical microscope by handpicking. Anal. Calcd for $Mn_5C_{120}H_{90}O_{18}$: C, 68.61; H, 4.33%, Found: C, 68.64; H, 4.30%. Yield: 60%.

IR spectrum of the complex displays sharp band at $3616\,cm^{-1}$, which is indicative of presence of bridging hydroxide ions. The X-ray structure analysis of $[Mn_5L_8(OH)_2]$ revealed the formation of a 1D-chain structure (Figure 1).[6] Asymmetric unit of the 1D-chain consists of pentanuclear manganese aggregates made up of two types of Mn ions (octahedral and square pyramidal Mn ions), eight α-phenylcinnamate and bridging hydroxide ions. Based on the charge balance consideration, the oxidation state of the Mn ions is Mn(II) oxidation state. α-Phenylcinnamate shows three bridging modes to afford a pentanuclear core. Mn(1), Mn(3), and Mn(5) exhibit slightly distorted octahedral $\{MnO_6\}$ geometries comprising of oxygen atoms of α-phenylcinnamate and bridging oxygen. Each Mn(1) and Mn(5) has five carboxylate oxygen atoms and a bridging oxygen. Mn(3) has four oxygen atoms of *a*-phenylcinnamate and two bridging hydroxide ions in *trans*-positions to complete its octahedral geometry. Bond distances lie in the range 2.065(4)–2.322(4) Å. On the other hand, Mn(2) and Mn(4) show distorted square pyramidal $\{MnO_5\}$ geometry comprising of four oxygen atoms of α-phenylcinnamate and a hydroxide ion. The distortion from the regular square pyramidal geometry is characterized by not only bond distances (2.075(4)–2.395(4) Å) but also O(5)–Mn(2)–O(6) and O(17*)–Mn(4)–O(18) bond angles of 57°. These an-

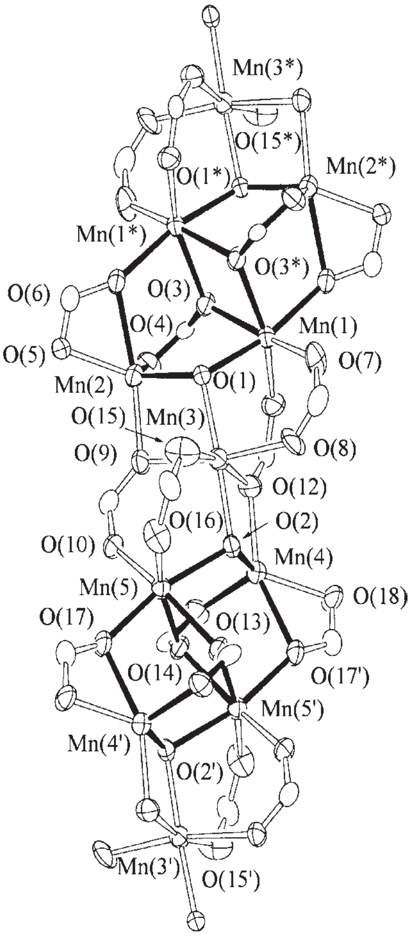

Figure 1. 1D-chain structure of $[Mn_5L_8(OH)_2]$. Stylben groups and hydrogen atoms are omitted for clarity.

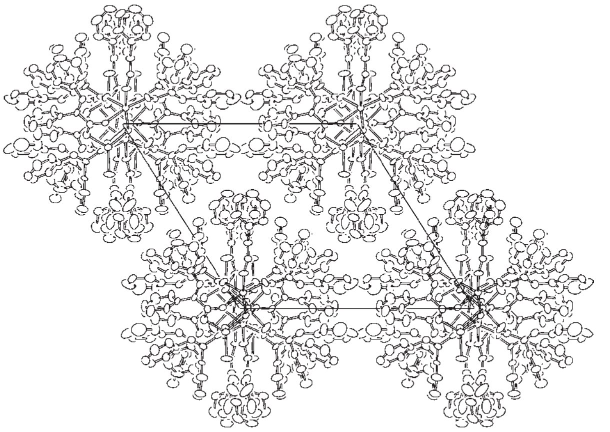

Figure 2. View of 1D-chain along *a*-axis.

gles are imposed by the constraint of the bidentate chelate carboxylate that is rigid with O–C–O angle of 120°. The $[Mn_5(OH)_2]$ core is described as consisting of corners sharing two isostructural $[Mn_3(OH)]$ triangles, [Mn(1)–Mn(2)–Mn(3)] and [Mn(3)–Mn(4)–Mn(5)]. Mn(1) shares corners of Mn(2) and Mn(3) polyhedra and Mn(2) and Mn(3) share edges of their polyhedra. The distances between Mn(II) ions are in the range of 3.36 to 3.56 Å. The angles for Mn(1)–O(1)–Mn(2), Mn(1)–O(1)–Mn(3), and Mn(2)–O(1)–Mn(3) are 112.5(2)°, 111.4(2)°, and 106.1(2)°, respectively. O(1) atom is 0.71 Å away from the least-squares plane defined by three Mn(II) ions. The triangle is connected by three oxygen atoms of α-phenylcinnamate to symmetry related Mn(1*) and Mn(2*) to give $[Mn_4(OH)_2(L)_4]$ incomplete double cubes like motif. One of the important structural differences from well-characterized oxygen bridged tetranuclear complexes is bridging hydroxide ions. These are usually oxo- or alkoxo-bridges.[2,3] Furthermore the double cuboidal motifs are connected through Mn(3) octahedrons to afford a 1D-chains parallel to the *a*-axis. The inorganic moieties are surrounded by π-conjugated α-phenylcinnamate and are well separated each other (Figure 2). Thickness of the chain is nearly 2 nm. No π–π stacking interactions are found between the 1D-chains.

Temperature dependence of magnetic susceptibility was measured on a powder sample in the temperature range 100–300 K. The effective magnetic moment of $[Mn_5L_8(OH)_2]$ at 300 K is 12.2 μ_B which is smaller than the spin-only value. This value decreases with decreasing temperature, indicative of antiferromagnetic interaction.

In conclusion, compound $[Mn_5L_8(OH)_2]$ is a unique example of a structurally characterized 1D coordination polymer comprising of a polynuclear manganese aggregation of octahedral Mn(II) and square pyramidal Mn(II) ions.

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References and Notes

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6 Reflection intensities were measured at room temperature with Mo Kα radiation ($\lambda = 0.71070$ Å); a Lorentz polarization correction and an empirical absorption correction were applied. Crystal data for $[Mn_5L_8(OH)_2]$: triclinic, space group P − 1, $a = 18.336(4)$, $b = 18.817(4)$, $c = 19.086(4)$ Å, $\alpha = 119.535(3)°$, $\beta = 115.848(5)°$, $\gamma = 90.000(5)°$, $V = 4958(1)$ Å^3, for $Z = 2$, $\mu = 35.31\ \mathrm{cm}^{-1}$, $D_{\mathrm{calcd}} = 1.403\ \mathrm{g/cm^3}$, Least-squares refinement based on 16357 reflections with $I > 0.0\sigma(I)$ collected on a Brucker SMART APEX CCD area detector and 1288 parameters on convergence gave a final R of 0.143 and Rw of 0.148 ($R(2\sigma(I)) = 0.053$). The structure was solved and refined using the TEXSAN Ver. 2.0 crystallographic program (Molecular Structure Corporation). Non-hydrogen atoms were refined anisotropically. Hydrogen atoms are located at ideal positions. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC No. 257388. Copies of the data can be obtained free of charge on application to CCDC, 12 union road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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