Self-assembly of a Novel Manganiferous Coordination Polymer with Mixed Ligands

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A novel coordination polymer, $[(NA)(ONA)\,Mn(II)]_n$ (HNA = nicotinic acid; H_2ONA = 2-hydroxynicotinic acid) has been hydrothermally synthesized. Its structure is constructed by mixed-ligands and chains of hexa-coordinated Mn(II) linkers: ONA groups bridge Mn ions to give the right-handed and left-handed helical $[(ONA)Mn]_n$ chains running along (010). The helical chains are further held together by NA groups to form a novel 3-D framework.

Extended networks built up from organic ligand(s) and metal linker(s) attracted considerable interest, because of their intriguing supramolecular structures and potential applications for energy storage and optical materials etc.[1–3] One of the strategies for constructing novel architectures of coordination polymers is to bridge metal ions by carboxylato ligands.[2] Generally, the syntheses of carboxylato–metal coordination polymers could be affected by two factors of carboxylato ligand: stereochemistry and reactivity. From the viewpoint of crystal engineering, the former may be helpful for adjusting microstructures of frameworks, such as carboxylato ligands with diversified relative positions of carboxyl resulting in frameworks with various channels or dimensionalities;[2] While the latter is more related to coordination selectivity between carboxylato ligand and metal, which could lead to different coordination model, coordination number and polyhedra connectivity.[3] Besides these two main factors, the organic reaction during crystallization, namely in situ ligand synthesis is observed dramatically and this is helpful for building novel crystal structures.[2,3] Additionally, redox reactions between transition metal atoms with high oxidation state and organic additives often occurred under hydrothermal conditions.[4]

In the present research of the hydrothermal system of 2,3-pyridinedicarboxylic acid (pdc), 1,10-phenanthroline (phen), with MnO_2, by using the redox reaction between transition metal and organic species, as well as the decarboxylation and substitution reactions of pdc, a novel 3-D framework coordinate polymer $[(NA)(ONA)Mn(II)]_n$ (HNA = nicotinic acid; H_2ONA = 2-hydroxynicotinic acid) was successfully prepared. To our knowledge, there is no reported example of coordination polymer involved in two aromatic ligands, which are from in situ synthesis yet. Here, we report this first manganiferous coordination polymer built up from mixed aromatic ligands originating from in situ ligand synthesis.

All chemicals used in the syntheses are of reagent grade and used as purchased without further purification. A mixture of MnO_2 (0.071 g, 0.793 mmol), 1,10-phenanthroline (0.353 g, 2.12 mmol), 2,3-pyridinedicarboxylic acid (0.562 g, 3.36 mmol) and H_2O (1.5 mL, 83.3 mmol) was hydrothermally treated at 140 °C for 72 h. The resulting yellow single crystals were recovered by filtration, washed with copious distilled water, and dried in ambient condition.[5] The yield was 56%, based on Mn.

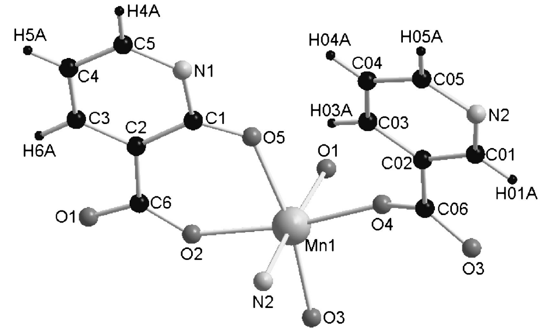

Figure 1. Stick-and-ball representation of the asymmetric unit of the title compound with atoms labeled.

A single crystal of the title compound with dimension of $0.70 \times 0.55 \times 0.38$ mm was examined by X-ray crystallography.[5] The structure of the compound is made up of infinite 1-D chain of $[(ONA)Mn]_n$ and NA bridges.[6] The asymmetric unit is shown in Figure 1. Interestingly, the 1-D chains are chiral. Figure 2a indicates the right-handed and left-handed helical chains running along [010] direction, respectively. The chirality can be clearly shown by the -Mn(1)–O(1)–C(2)–O(6)- bold bonds. Projection along the *b* axis (Figure 2b) shows that the helical chains with the same chirality are located within the *ab* layers. One NA ligand bridges three nearest helical chains located within, above and below an *ab* layer. Thus a 3-D framework of the title compound is formed.

Notably, the ligands of the final compound namely 2-hydroxynicotinic acid and nicotinic acid are organic reaction products from the starting material pdc. Similar decarboxylation reaction of pdc has been reported previously.[3c] According to Gillard and Hall that the 2- (or 4-) position of pyridine becomes polarized upon coordination to metal ions and so chemically active,[7] thus ONA may be the product of nucleophilic substitution reaction between NA and OH^-, like the case found in the hydroxylation of isophthalic acid.[8] However, we cannot exclude the probability that ONA is directly generated from pdc with formic acid as a leaving group. Additionally, redox reaction between Mn(IV) and organic species including formic acid occur simultaneously, which may facilitate the hydroxylation reaction. Bond valence sum (BVS) calculations of the title complex consist with the oxidation state of +2 for all the Mn atoms. However, because hydrothermal reaction system is rather complicated, we cannot give a more definite mechanism at present time.

The Mn–O/N distances ranging from 2.1307(14) to 2.3562(17) Å and the O/N–Mn–O/N bond angles within the range of 80.86(6)–173.29(6)°(indicate that Mn is located in a distorted octahedron. All O atoms of NA and ONA are involved

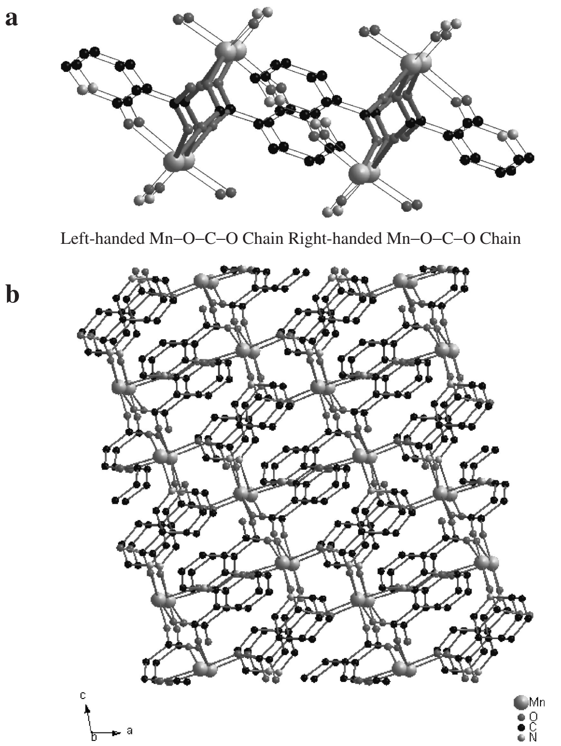

Figure 2. (a) Helical chain of $[(ONA)Mn]_n$ with alternating chiralities (left or right) viewed along *b* axis (clear view of the chiral linkages of carboxylic groups and Mn atoms Mn(1)–O(1)–C(6)–O(2) are shown by thick bonds); (b) 3-D framework structure of the complex showing the $[(ONA)Mn]_n$ chains bridged via NA groups.

in the coordinate with Mn. Interestingly, N of ONA (N(1)) and NA (N(2)) are dangling and coordinating atom, respectively. Thus NA and ONA serving as tridentate ligands result in a six-memebered ring in the structure.

Magnetic susceptibility measurement indicated that the compound is paramagnetic and displays Curie–Weiss behavior in higher temperature range, having Curie constant of $C = 4.59\,\mathrm{emu\,K^{-1}\,mol^{-1}}$ and a Weiss constant of $\theta = -13.8\,\mathrm{K}$, which corresponds to the effective magnetic moments of $\mu_{\mathrm{eff}} = 6.06\,\mathrm{BM}$, and is consistent with the value expected for a system consisting of isolated high-spin Mn^{2+}, $\mu_{\mathrm{cal}} = 5.92\,\mathrm{BM}$.

In summary, based on the in situ ligand synthesis and complicated hydrothermal redox reaction between Mn(IV) and organic species, a novel 3-D framework manganiferous coordinate polymer $[(NA)(ONA)Mn(II)]_n$ has been obtained. The chiral chains of hexa-coordinated Mn(II) linkers formed in the structure made the compound a possible candidate for chiral catalysis and separation.

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5 Elemental analyses data: C, 46.0; H, 2.4; N, 9.0, Mn 17.3%.

6 All measurements were performed on a Rigaku RAXIS RAPID IP diffractometer equipped with Mo Kα radiation ($\lambda = 0.71073$ Å). The data processing was performed using RAPID AUTO program. The structure was solved by the direct method and refined by a full-matrix least-squares technique based on F^2 by use of the SHELXL97 program. Crystal data: monoclinic space group $P2_1/n$ (No. 14) with lattice parameters of $a = 10.388(2)$ Å, $b = 9.5051(19)$ Å, $c = 11.283(2)$ Å, $\beta = 100.50(3)°$, $V = 1095.4(4)$ Å^3, $Z = 4$, $R = 0.030$, $R_w = 0.072$. Crystallographic data reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-230546. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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