In Situ Ligand Synthesis for a Novel 1-D Mn Coordination Polymer

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A novel manganiferous coordination polymer, $[Mn(II)(HL)_2]_n$ (H_2L = 4-hydroxynicotinic acid) (**1**) was hydrothermally synthesized. Interestingly, an in situ ligand synthesis for HL from 3,4-pyridinedicarboxylic acid precursor was observed. Structure analysis indicates **1** is built up from building blocks of Mn(II)-centered octahedron and HL ligand. The μ_3-HL ligand plays dual roles for the formation of 1-D framework: chelate and bridge.

Recently, a series of interesting coordination polymers are reported,[1] which are characteristic of reconstruction of covalent bonds of ligands simultaneously occurring during crystallization, such as hydroxylation,[1a] acylate,[1b] decarboxylation,[1c] and dehydrogenation.[1d] The simultaneous organic reaction named as in situ ligand synthesis is of interest, because it may not only produce novel crystal structures,[1] but also provide evidence for some organic reaction mechanisms.[2] However, systematic designs on coordination polymers involving in situ ligand syntheses are quite few,[1,2] compared to those with ligands maintaining integrity.

It has been reported that under hydrothermal conditions, metal ions, especially transition metals with high oxidation state, can be reduced in the presence of organic structural directing agent or ligand.[3] Recently, we investigated hydrothermal reaction systems containing pyridinedicarboxylic derivatives and MnO_2. Interestingly, redox reaction of Mn(IV), as well as the decarboxylation and substitution reactions of 2,3-pyridinedicarboxylic acid was observed, and a novel Mn(II) coordination polymer $[(NA)(ONA)Mn(II)]_n$ (HNA = nicotinic acid; H_2ONA = 2-hydroxylnicotinic acid) (**2**) was isolated.[4] Gillard and Hall suggest that the 2- (or 4-) position of pyridine becomes polarized upon coordination to metal ions and so chemically active.[5] On one hand, as an electron withdrawing group, carboxyl may reduce the density of electron cloud of pyridyl group. On the other hand, the highly polarized 2-(or 4-) position may probably attract an H_2O or OH^-, and other oxygen-containing Lewis bases within reacting distance, leading to a nucleophilic substitution reaction that produces ONA.

According to the above suggestions, we investigated the probability of in situ ligand synthesis of 3,4-pyridinedicarboxylic acid (3,4-pdc) with the presence of MnO_2 in hydrothermal environment. Interestingly, substitution and decarboxylation reactions occurred on the 4-position of 3,4-pdc were observed, and a novel 1-D coordination polymer $[Mn(II)(HL)_2]_n$ (H_2L = 4-hydroxynicotinic acid) (**1**) was isolated. In this paper, we report the synthesis and structural characterization of **1**. **1** and **2** may provide a method for preparing novel coordination polymers through in situ ligand synthesis.

A mixture of MnO_2, 3,4-pdc, 1,10-phenanthroline, H_2O with molar ratio of 1.00:1.61:1.13:88.7 was sealed in a 20-mL Teflon-lined autoclave and was heated at 413 K for 69 h. The resulting mm-sized yellow single crystals were recovered by filtration, and dried in ambient conditions.[6] **1** can be synthesized without using 1,10-phenanthroline, however, the crystal of poor quality was produced.

Figure 1 shows that Mn is coordinated by six O atoms from four HL ligands in the asymmetric unit[7] The Mn–O bond lengths in the range of 2.111(2)–2.319(2) Å; and O–Mn–O bond angles ranging from 83.82(8) to 180.0 degree show that Mn is located in a distorted octahedral coordination environment. X-ray photoelectron spectrum (XPS) indicated N1s binding energy (BE) of 400.5 eV, and $Mn2p_{3/2}$ BE of 641.1 eV for **1**. This former BE value is significantly larger than the N1s BE of 398.8 eV for pyridine,[8a] and lies within the N1s BE range of about 400.4–403.2 eV for amine salts;[8b] the latter BE value is in agreement with the $Mn2p_{3/2}$ BE of about 641.0–641.2 eV for MnO.[8a,8c] The XPS results, crystal structure, and bond valance sum calculation[9] are self-consistent based on the requirement of charge balance for molecular formula.

Figure 1 and the figure in graphic abstract show that the HL ligands play dual roles for the formation of 1-D framework: as a bridge ligand with O(1) and O(2) linking two adjacent Mn atoms forming an extended linkage of Mn and carboxyl groups; as a chelate ligand with O(2) and O(3) atoms capping one Mn atom resulting in an interrupted framework. The dihedral angle of carboxyl and pyridyl planes is 30.1°, indicating a corrugated 6-membered ring made up of Mn(1), O(2), C(6), C(2), C(3), and O(3) atoms.

Figure 2 shows the 1-D frameworks extending along the *a*-axis. Interestingly, there is no interdigitated structure of aromatic planes, indicating the absence of face to face π–π interaction between adjacent frameworks. The 1-D frameworks of **1** are held

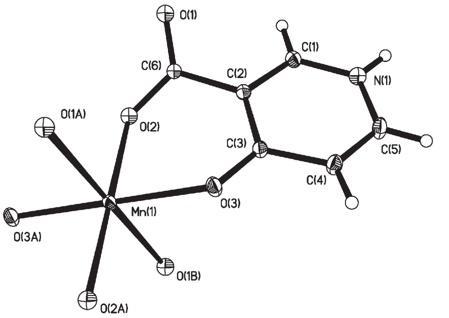

Figure 1. ORTEP drawing for the asymmetric unit of **1** with 30% probability ellipsoids, showing the atomic numbering scheme. Symmetry operation $(-3-x, 1-y, -1-z)$ for O(2A) and O(3A); $(x, 1+y, z)$ for O(1A); $(-4-x, 1-y, -1-z)$ for O(1B).

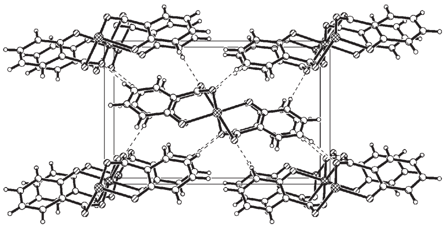

Figure 2. Projection (100) of 1-D chains illustrates the H-bonds between the adjacent chains: weak H-bonds of C–H···O, and H-bonds of N–H···O.

together by H-bond interaction: weak H-bond between aromatic C–H donors and O acceptors; H-bond between the dangling N–H donors and O acceptors.[10]

This reaction system involved MnO_2 precursor, instead of the soluble Mn salts generally reported. On one hand, the reaction systems of **1** and **2** are different from those reported by Hong et al. that "uncharacterized precipitation" and "micro-crystals" unsuitable for single crystal characterization are obtained by directly using carboxylic acid and soluble Mn salt as precursors.[1a] Considering the dynamic feature of phase transition reaction in hydrothermal environment, we adopted chelate ligands and insoluble inorganic reactant for large single crystal products,[4] similarly to the cases for preparing some zeolite or zeolite-like large single crystals using fluoride as a mineralizer and insoluble precursors containing framework elements.[11] On the other hand, MnO_2 functions as an oxidant reagent, which can facilitate the organic reactions under hydrothermal conditions.[4] Different from **2**, decarboxylation product, nicotinic acid (NA), does not incorporate in the crystal product. However, NA with concentration of ca. 2×10^{-3} M in the liquid phase of the final reaction system has been detected using internal standard method on a GC–MS, suggesting the coordination competitions among ligands to Mn ion, or transition reactions among ligands during crystallization. Consequently, it should be noted that the present results can not exclude multiple possibilities on the reaction pathways of the substitution and decarboxylation reactions companied by phase transition. Systematic investigations on dynamics and combinations of ligands and metals will be reported somewhere.

In summary, the hydrothermal reaction of MnO_2 and ligand(s) is a brief but rarely investigated method for preparing large single crystal carboxylato-Mn coordination polymers, and for synthesizing novel structures.

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6 Elemental analyses data: Found C, 43.7; H, 2.9; N, 8.6; Mn 16.9%. Calcd. for C, 43.52; H, 2.44; N, 8.46; Mn, 16.59%.

7 Crystal data for **1**: C6H4NO3Mn0.5, fw = 165.57, monoclinic space group $P2_1/c$ (No. 14) with lattice parameters of $a = 5.1600(10)$, $b = 13.280(3)$, $c = 8.2800(17)$ Å, $\beta = 90.45(3)^\circ$, $V = 567.4(2)$ Å^3, $Z = 4$, $R = 0.0345$, $R_w = 0.0841$. Crystallographic data reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-249072. 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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