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Synthesis and Characterizations of 1-D Double-Chain Manganese Coordination Polymer $[Mn(ncpo)(H_2O)_3]_n$

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A 1-D double-chain manganese coordination polymer constructed by 2-nitro-4-carboxylphenoxy acetic acid has been synthesized by phase diffuse method. The crystal structure has been determined by X-ray diffraction. The crystal is monoclinic, space group C_c with a = 9.647(10), b = 25.46(3), c = 6.560(7) Å, β = 131.741(11)°, $MnC_9H_{11}NO_{10}$. M_r = 348.13, V = 1202(2) $Å^3$, D_c = 1.923 g/cm^3, F(000) = 708, μ = 1.156 cm^{-1} and Z = 4. The final refinement gave R = 0.0695 and wR = 0.1755 for 1307 reflections with $I > 2\sigma(I)$. The coordination polymer demonstrates 1-D double-chain structure along a axis and it is connected to 3-D supramolecular network by hydrogen bonds. Except for hydrogen bonds, there exist π-π stacking interactions among benzene rings. The complex begins to lose water molecules at 433 K and when it is heated to 693 K, it will lose nitro group and oxyacetate radical.

Key Words: Manganese, 2-Nitro-4-carboxylphenoxyacetic acid, Crystal structure, Thermal analysis.

INTRODUCTION

Crystal engineering and the design of solid-state architectures have recently become areas of increasing interest due to various applications, such as magnetism, catalysis, electrical conductivity, optical materials, host-guest chemistry and biomimetic chemistry[1-3]. Aromatic di- or multi-carboxylic ligands are good candidates for assembling metal-organic supramolecular architectures. During the past decade, many novel and fantastic frameworks have been synthesized and characterized using rigid multicarboxylate ligands such as 1,4-benzenedicarboxylate, 1,3,5-benzene tricarboxylate, 1,2,4,5-benzene tetracarboxylate, 1,2,4-benzene tricarboxylate[4,5]. But the flexible multicarboxylate ligands have been less studied[6,7], possibly due to the difficulties in predicting the resulted framework structures.

As a building block, 2-nitro-4-carboxylphenoxy acetic acid (H_2ncpo) is a multidentate flexible ligand with versatile coordination modes, which can be regarded as an excellent candidate for the construction of supramolecular complexes. To the best of our knowledge, there are few reported coordination polymers containing H_2ncpo ligand. In order to synthesize coordination polymers with novel functional properties, 2-nitro-4-carboxylphenoxy acetic acid (H_2ncpo) is used as ligand to generate a new 1-D coordination polymer $[Mn(ncpo)(H_2O)_3]_n$, which was structurally determined by X-ray diffraction and further characterized with spectrum and thermal analysis in this paper.

EXPERIMENTAL

2-Nitro-4-carboxylphenoxy acetic acid was prepared by the nitration of 4-carboxyphenoxy acetic acid, which was synthesized by the reaction of chloroacetic acid with *p*-hydroxybenzoic acid in a molar ratio of 1:1 at 373 K. All other chemicals are of analytical reagent grade and used without further purification. The coordination complex was synthesized by phase diffuse method. In a 25 mL comparison tubes, underlayer is the solution of 0.3 mmol H_2ncpo and 0.6 mmol NaOH, middle phase is DMF, the superstratum is the DMF solution of 0.3 mmol $MnCl_2·4H_2O$. After 2 months yellow crystals were obtained at the wall of the tube in 24 % yield (based on Mn). Anal. calcd (%) for $C_9H_{11}NO_{10}Mn$: C, 31.08; H, 3.18; N, 4.02. Found (%): C, 31.21; H, 3.09; N, 4.11. IR (KBr, cm^{-1}): ν(O-H), 3380 br; ν_{as}(O-C-O), 1612 s; ν_{as}(O-N-O), 1531 s; ν_s(O-C-O), 1425 s; ν_s(O-N-O), 1388 m; ν_{as}(C-O-C), 1263 w; ν_s(C-O-C), 1037 w.

Elemental analysis was carried out on a Carlo Erba 1106 full-automatic trace organic elemental analyzer. FT-IR spectra were recorded with a Bruker Equinox 55 FT-IR spectrometer in dry KBr pellets in the range of 4000-400 cm^{-1}. A Perkin-Elmer Pyris1 differential scanning calorimeter (DSC) (sample mass: about 1.0 mg; atmosphere, flowing dry, oxygen-free nitrogen; heating rate, 10 K/min) was used for DSC measurement. A Perkin-Elmer Pyris1 thermogravimetry (TG-DTG) analyzer (sample mass: about 1.0 mg; atmosphere, flowing dry, oxygen-free nitrogen; heating rate, 10 K/min) was used for thermogravimetric analysis.

Structure determination: A suitable yellow block crystal with dimensions of 0.24 mm × 0.22 mm × 0.18 mm was mounted on a glass fiber and the data were collected on a Bruker Smart CCD diffractometer with a MoK_α radiation ($\lambda = 0.71073$ Å) at 293(2) K by using an ω scan mode in the range of $2.94 < \theta < 25.01°$. For the title complex, a total of 3070 reflections were collected, of which 1617 were unique with $R_{int} = 0.0342$. All non-hydrogen atoms were refined by full-matrix least-squares techniques for observed 1996 reflections with $I > 2\sigma(I)$ to the final R = 0.0695, wR = 0.1755 ($w = 1/[\sigma^2(F_o)^2 + (0.1P)^2]$, where $P = (F_o^2 + 2F_c^2)/3)$, S = 1.054 and $(\Delta/\sigma)_{max}$ = 0.000. The highest and lowest residual peaks in the final difference Fourier map are 0.703 and -0.842 e/Å^3, respectively. The structure was solved by direct methods using SHELXS-97 program[8] and refined by full-matrix least squares techniques based on F^2 with SHELXTL 97 program package[9].

RESULTS AND DISCUSSION

The complex crystallizes in monoclinic, space group Cc with the asymmetric unit containing one Mn^{2+} cation, one $ncpo^{2-}$ anion, three coordinated water molecules and the coordination environment of the metal atoms is shown in Fig. 1. The Mn(II) atom is hepta-coordinated by seven O atoms, among which (O(1A), O(2A)) from one H_2ncpo, O(1) and O(2) from two different H_2ncpo ligands and the other three O atoms (O(8), O(9) and O(10)) from three coordinated water molecules.

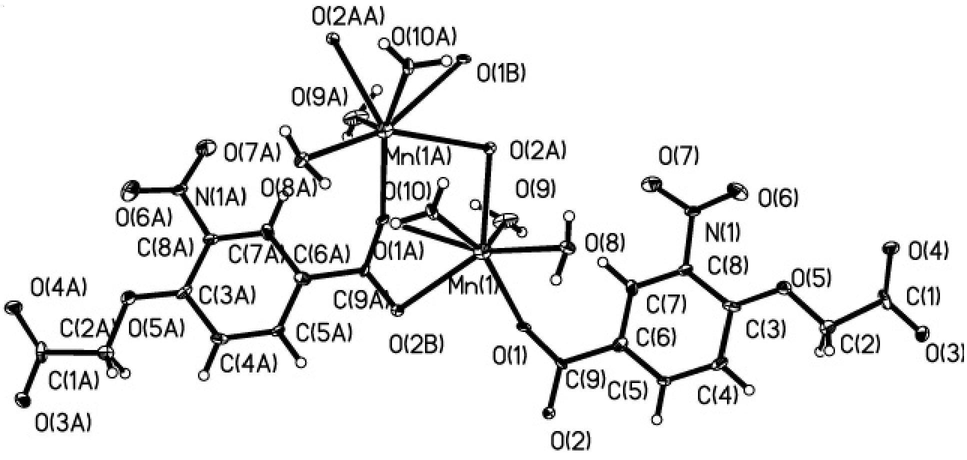

Fig. 1. Coordination environment of the Mn atoms in $[Mn(ncpo)(H_2O)_3]_n$

Selected bond lengths and bond angles are listed in Table-1. The Mn-O distances range from 2.337(7) to 2.505(6) Å, which are comparable with those of $[Mn(3,5\text{-}pdc)_2H_2O]_n$[10] and $\{[Mn_2(cda)_2 4H_2O]4H_2O\}_n$[11]. In the complex, the carboxyl group of oxyacetic acid does not coordinate with Mn ion, only C9-carboxyl group takes part in the coordination with three Mn ions through the coordination mode of μ_3-η^2 : η^2, which form 1-D double-chain structure along a axis (Fig. 2).

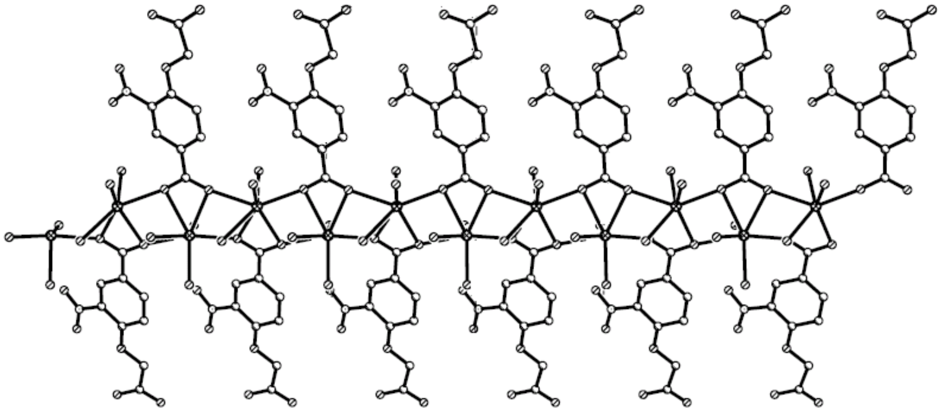

Fig. 2. 1-D double-chain structure of $[Mn(ncpo)(H_2O)_3]_n$

TABLE-1
SELECTED BOND LENGTHS (Å), ANGLES (º)

Bond	Distance	Bond	Distance
Mn(1)-O(1)	2.337(7)	Mn(1)-O(8)	2.356(7)
Mn(1)-O(9)	2.392(7)	Mn(1)-O(2)#1	2.395(7)
Mn(1)-O(1)#2	2.497(6)	Mn(1)-O(10)	2.504(7)
Mn(1)-O(2)#2	2.505(6)	–	–
Angle	**(º)**	**Angle**	**(º)**
O(1)-Mn(1)-O(8)	88.3(2)	O(1)-Mn(1)-O(9)	72.0(3)
O(8)-Mn(1)-O(9)	109.6(3)	O(1)-Mn(1)-O(2)#1	140.3(2)
O(8)-Mn(1)-O(2)#1	82.3(2)	O(9)-Mn(1)-O(2)#1	75.1(2)
O(1)-Mn(1)-O(1)#2	122.4(2)	O(8)-Mn(1)-O(1)#2	148.5(3)
O(9)-Mn(1)-O(1)#2	88.4(3)	O(2)#1-Mn(1)-O(1)#2	77.5(2)
O(1)-Mn(1)-O(10)	148.8(2)	O(8)-Mn(1)-O(10)	82.8(2)
O(9)-Mn(1)-O(10)	139.1(2)	O(2)#1-Mn(1)-O(10)	68.0(2)
O(1)#2-Mn(1)-O(10)	67.3(2)	O(1)-Mn(1)-O(2)#2	78.4(2)
O(8)-Mn(1)-O(2)#2	143.5(2)	O(9)-Mn(1)-O(2)#2	98.4(3)
O(2)#1-Mn(1)-O(2)#2	128.5(2)	O(1)#2-Mn(1)-O(2)#2	51.0(2)
O(10)-Mn(1)-O(2)#2	91.2(2)	C(9)-O(1)-Mn(1)	150.8(6)

Symmetry transformations used to generate equivalent atoms: #1 x, y, z-1; #2 x, -y+1, z-1/2; #3 x, -y+1, z+1/2; #4 x, y, z+1.

Due to the existence of uncoordinated carboxyl group and three coordinated water moleculars, there are rich hydrogen bonds in the crystal and the parameters of hydrogen-bonding interactions are shown in Table-2. 1-D double-chain is connected to 2-D microporous structure along c axis through the hydrogen bond between O10 water molecules and carboxyl groups (Fig. 3). Hydrogen bonds also exist among coordinated water molecules, which leads the 2-D layers to 3-D structure.

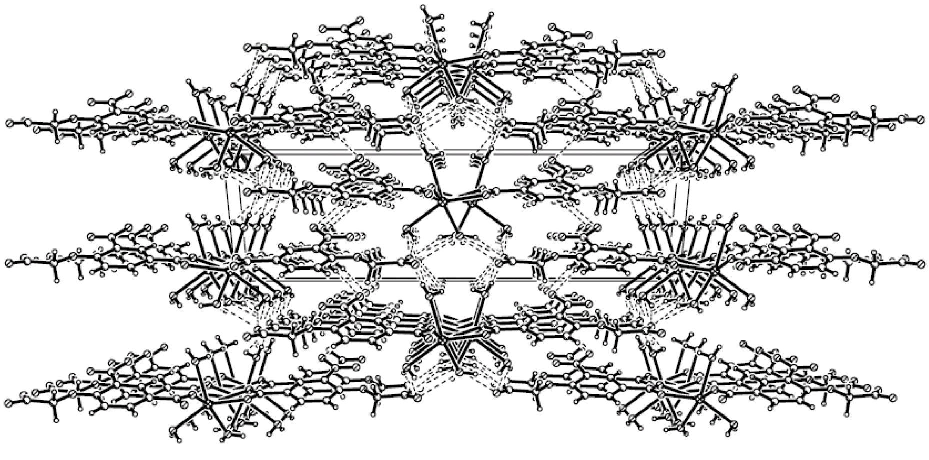

Fig. 3. Packing diagram of $[Mn(ncpo)(H_2O)_3]_n$ along c axis

TABLE-2
PARAMETERS OF HYDROGEN-BONDING INTERACTIONS IN $[Mn(ncpo)(H_2O)_3]_n$

D-H…A	d(D-H)/Å	d(H…A) /Å	d(D…A)/Å	Angle (D-H…A)/°
O8-H8A…O4#5	0.850	2.052	2.776	142.73
O8-H8A…O10#6	0.850	2.460	3.124	135.64
O8-H8B…O3#7	0.850	2.075	2.788	141.04
O9-H9A…O4#8	0.850	2.339	3.169	165.40
O10-H10A…O3#9	0.850	2.125	2.706	125.19
O10-H10B…O4#7	0.850	1.943	2.706	148.86
O10-H10B…O8#10	0.850	2.527	3.124	128.13

Symmetry transformations used to generate equivalent atoms: #5 x+1/2, -y+1/2, z+1/2; #6 x, -y+1, z+1/2; #7 x+1/2, -y+1/2, z-1/2; #8 x-1/2, -y+1/2, z-1/2; #9 x+1/2, y+1/2, z; #10 x, -y+1, z-1/2.

Except for the hydrogen bond interactions, there are π-π stacking interactions among benzene rings along c axis with the face to face distances of 3.286 Å, which is in the range of π-π stacking interactions.

The thermal behaviour of $[Mn(ncpo)(H_2O)_3]_n$ has been studied by DSC and TG-DTG technology, which are shown in Figs. 4 and 5, respectively. In the TG-DTG curves of the coordination polymer, there are three weight loss stages. The first weight loss stage starts at 433 K, reaches its largest rate at 463 K and finishes at 523 K with the weight loss of 14.99 %, which corresponds to the loss of three coordinating water molecules (calc. 15.51 %) and the stage corresponds to the first endothermic process in DSC curve. The second weight loss stage with 33.02 % occurs in the range of 523 to 693 K. The stage may be related to the loss of nitro group and oxyacetate radical ($-OCH_2COO$)[12] (calc. 34.48 %) with a middle intensity exothermic process in the DSC curve. A further decomposition from 694 to 725 K may correspond to the decomposition of the benzene rings with the residual weight 22.62 %.

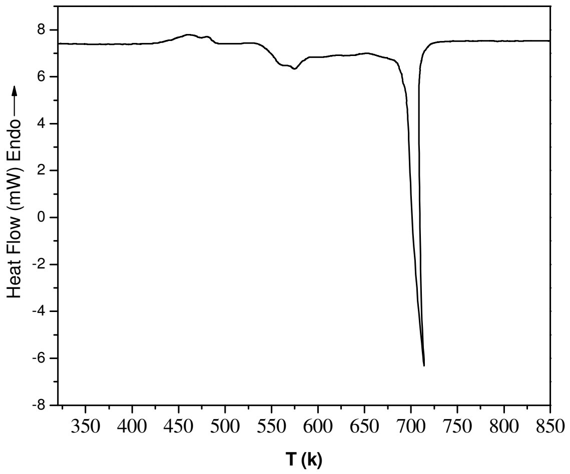

Fig. 4. DSC curve of $[Mn(ncpo)(H_2O)_3]_n$

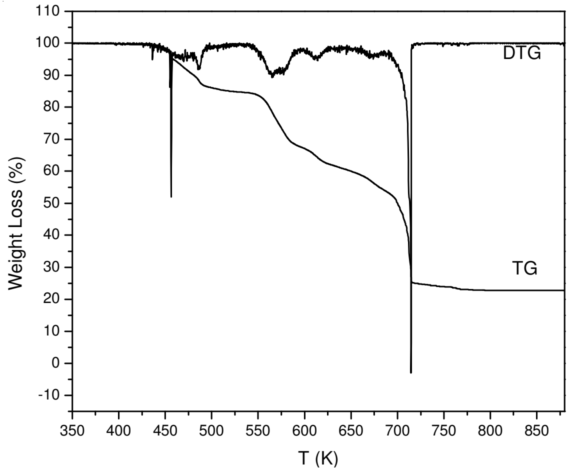

Fig. 5. TG-DTG curve of $[Mn(ncpo)(H_2O)_3]_n$

Conclusion

In summary, 1-D double-chain coordination polymer of Mn^{2+} constructed by 2-nitro-4-carboxylphenoxy acetic acid (H_2ncpo) has been successfully synthesized through phase diffuse method, which is connected to 3-D supramolecular network by hydrogen bonds and π-π stacking interactions. The complex begins to decompose at 433 K and when it is heated to 693 K, it will lose nitro group and oxyacetate radical.

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