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NOTE

Hydrothermal Synthesis and Crystal Stucture of a Mn(II) Coordination Polymer Containing Pyridine-carboxylic Ligand

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By hydrothermal method, a polymer compound, $Mn(nia)_2(H_2O)_2$ was synthe-sized and its structure was characterized with elemental analysis and X-ray diffractometer. The Mn(II) centers adopt a distorted bipyramidal geometry which is surrounded by six coordination atoms from nicotinate and water molecular and the metal centers coordinates to the pyridyl and carboxylate groups to form 2-D framework along bc plane.

Key Words: Mn(II), Coordination polymer.

Great attentions have been paid in recent years to supramolecular chemistry reflecting the intense contemporary interest in the rational design of functional materials with extended architectures[1,2]. The most useful strategy is to employ appropriate multidentate bridging ligands capable to bind metal ions either by strong covalent interactions or supramolecular contacts as hydrogen bonding or staking forces which can be obtained the higher dimensional complex[3-6].

A mixture of nicotinate (0.166 g, 1 mmol), NaOH (0.8 g, 1 mmol), $MnCl_2 \cdot 4H_2O$ (0.1979, 1 mmol) and distillated water (18 mL) was heated in a 25 mL stainless-steel reactor with a Teflon liner 160 ºC for 96 h, followed by slow cooling to room temperature. Colourless crystals of the complex formed. Yield 70 % (based on Mn). Anal. Calcd. (%) for: C, 43.00; H, 3.58; N, 8.36. Found (%): C,42.13; H, 3.60; N, 8.21.

Physical measurements: Elemental analysis was carried out on a Carlo Erba 1106 full-automatic trace organic elemental analyzer.

Structure determination: A suitable white block crystal with dimensions of 0.25 mm × 0.20 mm × 0.15 mm was mounted on a glass fiber and the data were collected on a Bruker Smart 1000 CCD diffractometer with a MoK_α radiation (λ = 0.71073 Å) at 293(2) K by using an ω scan mode in the range of $3.09 < \theta < 24.99°$. The hydrogen atoms bound to carbon were located by geometrically calculations and their positions and thermal parameters were fixed during the structure refinement. All non-hydrogen atoms were refined by full-matrix least-squares techniques. All calculations were performed by the SHELXTL 97 program[7]. Crystallographic data and experimental details for structural analyses are summarized in Table-1.

TABLE-1
CRYSTALLOGRAPHIC DATA AND STRUCTURE REFINEMENT SUMMARY FOR Mn(II) COORDINATION POLYMER COMPLEX

Empirical formula	$C_{12}H_{12}N_2O_6Mn$
Formula weight	335.18
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions (Å)	a = 8.7617(18)
	b = 10.223(2)
	c = 7.1518(14)
Volume ($Å^3$)	630.8(2)
Z, Calculated density (mg/m^3)	2, 1.765
Absorption coefficient	1.078
F(000)	342
Reflections collected/unique	5293 / 1109 [R_{int} = 0.0322]
Data/restraints/parameters	1109 / 0 / 97
Goodness-of-fit on F^2	1.151
Final *R* indices [I > 2sigma(I)]	R_1 = 0.0457, wR_2 = 0.1160
R indices (all data)	R_1 = 0.0465, wR_2 = 0.1168
Largest diff. peak and hole ($e/Å^3$)	2.645 and -0.331

The local coordination geometry of polymer$[Mn(nia)_2]_n$ with numbering scheme is depicted in Fig. 1. It is shown that Mn(II) is coordinated two O_{COO^-} (Mn-O = 2.166 Å), two N atoms (Mn-N = 2.294 Å) and two water moleculars (Mn-O_w = 2.190 Å). The bond angles of O(N)-Mn-O(N) are from 85.47-180.00º. O1, O1A, N1C and N1B form the equatorial plane(the equation of plane is 0.702x + 0.659-0.271 = 5.034) and two O_w occupy the axial sites. The ligands have one coordination mode: μ_2- N, O which acts as a diconnetctor to link two Mn(II) centres. The SBUs$[MnN_2O_4]$ are interconneted through different nia-, thereby generating a 2D network which is composed of four-connected nodes (Fig. 2).

TABLE-2
BOND LENGTHS (Å) AND ANGLES (º) FOR THE COMPOUND

Bond	Distance	Bond	Distance
Mn(1)-O(1)	2.166(19)	Mn(1)-O(1)#1	2.166(19)
Mn(1)-O(1W)#1	2.190(19)	Mn(1)-O(1W)	2.190(19)
Mn(1)-N(1)#2	2.294(2)	Mn(1)-N(1)#3	2.294(2)
Angle	(º)	Angle	(º)
O(1)-Mn(1)-O(1)#1	180.00(10)	O(1)-Mn(1)-O(1W)#1	88.36(8)
O(1)#1-Mn(1)-O(1W)#1	91.64(8)	O(1)-Mn(1)-O(1W)	91.64(8)
O(1)#1-Mn(1)-O(1W)	88.36(8)	O(1W)#1-Mn(1)-O(1W)	180.00(10)
O(1)-Mn(1)-N(1)#2	91.58(8)	O(1)#1-Mn(1)-N(1)#2	88.42(8)
O(1W)#1-Mn(1)-N(1)#2	85.47(8)	O(1W)-Mn(1)-N(1)#2	94.53(8)
O(1)-Mn(1)-N(1)#3	88.42(8)	O(1)#1-Mn(1)-N(1)#3	91.58(8)
O(1W)#1-Mn(1)-N(1)#3	94.53(8)	O(1W)-Mn(1)-N(1)#3	85.47(8)
N(1)#2-Mn(1)-N(1)#3	180.00(7)	–	–

: #1 -x+1,-y,-z; #2 x,-y+1/2,z-1/2; #3 -x+1,y-1/2,-z+1/2;#4 -x+1,y+1/2,-z+1/2

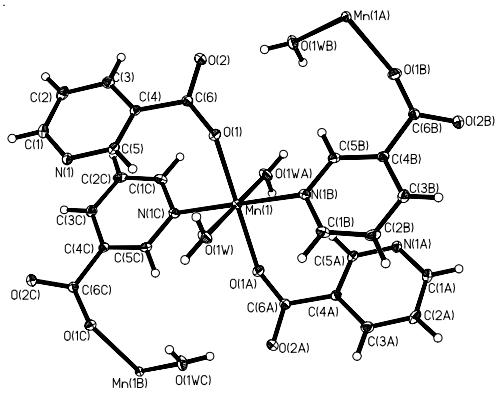

Fig. 1. Local coordination geometry of polymer $Mn(nia)_2(H_2O)_2$ with the atom-numbering scheme

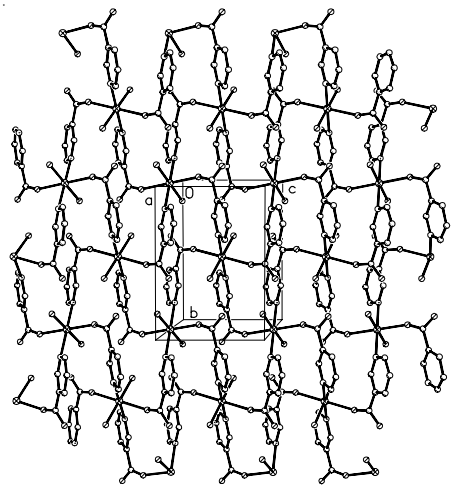

Fig. 2. The (4,4)-network formed along bc plane

In the complex, there exist hydrogen bonds between all water molecules and uncoordinated O-atoms of the carboxylate groups, which interactions contribute to the alignment of the complex in the crystalline state.

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