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Synthesis, Crystal Structure of a Novel Two-Dimensional Complex of Manganese(II) with 2-Phenoxypropionic Acid and 4,4'-Bipyridine

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A novel two-dimensional coordination polymer $[Mn(POPA)_2(bipy)]_n$ (POPA = 2-phenoxypropionic acid; bipy = 4,4'-bipyridine) has been synthesized by hydrothermal reaction and characterized by elemental analysis, IR spectroscopy, TGA and X-ray diffraction. Yellow crystals crystallized in monoclinic system, space group C2/c with a = 2.36748(14) nm, b = 1.16289(7) nm, c = 9.6440(6) nm, β = 96.353(4)°, V = 2.6388(3) nm^3, Z = 4. In the complex, the manganese atom is six-coordinated with four carboxylic oxygen atoms from four 2-phenoxypropionic acid and two nitrogen atoms of two 4,4-bipyridine ligands, giving a octahedral geometry. CCDC:769183.

Key Words: Manganese(II) complex, Hydrothermal synthesis, 2-Phenoxypropionic acid, Crystal structure.

INTRODUCTION

The development of supramolecular and coordination polymer complexes has recently attracted considerable attention due to the fundamental interest in self-assembly processes of transition-mental complexes, supramolecular chemistry and crystal engineering[1-5]. Carboxylic acid is a conventional coordination ligand, so for a number of transition and rare earth coordination polymers with carboxylic acids have been reported[6-8]. There has been extensive interest in manganese coordination polymers containing carboxylate ligands due to the richness in structural chemistry and potential applications in catalysis[9-13], for example, some highly efficient manganese catalysis *mimics*[14,15]. Furthermore, 4,4′-bipyridine is an excellent bridging ligand and so far a number of 1-, 2- and 3-dimensional infinite metal-4,4′-bipyridine frameworks have already been generated[16,17]. However, of the above-mentioned frameworks, most are generated directly by coordination bonds or one-dimensional coordination chains are generated first and then further extend into higher dimensional networks by hydrogen-bonding interactions[18]. Only a few are formed by self- assembly of carboxylate ligands and 4,4′-bipyridine metal ion building blocks[19]. Herein, we choose HPOPA (2-phenoxypropionic acid) as build block for structure coordination polymers because its possible various coordination modes and high reactivity with *d* and *f* elements. The structure of manganese with 2-phenoxypropionic acid is shown in Fig. 1. The hydrothermal technique is well suited to the preparation of crystals of synthetic minerals, new inorganic materials and organometal coordination polymers[20]. In the paper, we report synthesis and structure of a novel 2 dimensional manganese coordination polymer with 2-phenoxypropionic acid and 4,4'-bipyridine ligands, together with IR spectral and thermal studies.

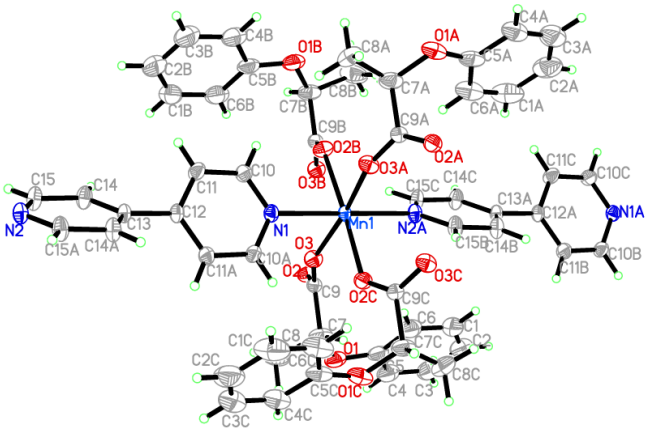

Fig. 1. Molecular structure of the Mn(II) complex. Displacement ellipsoids are drawn at the 30 % probability level

EXPERIMENTAL

2-Phenoxypropionic acid was purchased from Aldrich, the other reagents were of analytical grade from commercial source and were without further purification. Elemental analyses were carried out on Elementar Vario EL III elemental analyzer. The FTIR spectra were obtained from KBr pellets in the range

4000-400 cm^{-1} with a Nicolet NEXUS 670 FTIR spectrometer. Thermal analyses were carried out using Mettler-Toludo TGA/SDTA 851^e thermal analyzer at a heating rate of 10 ºC min^{-1} from 30 to 800 ºC in air atmosphere.

Synthesis of the complex: 2-Phenoxyproionic acid (0.499 g, 3 mmol), 4,4'-bipyridine (0.156 g, 1 mmol) were mixed in distilled water (30 mL), NaOH (1 M) was added dropwise to the solution to adjust pH for 5-6, then $MnCl_2·4H_2O$ (0.198 g, 1 mmol) were sealed in a 50 mL stainless steel reactor and kept 433 K for 3 d. Then, the reactor was cooled to room temperature at a speed of 5º/h. Lots of yellow single crystals were filtered out of the mixture at high yield (80 %). Anal. calcd.(%) for $C_{28}H_{27}N_2O_6Mn$: C, 61.99; H, 5.14; N, 5.16; Found (%): C, 62.47; H, 4.83; N, 5.08.

X-Ray Structure Determination: The diffraction data are collected on a Bruker SMART APEX IICCD area detector employing graphite monochromated MoK_α raditoion (λ = 0.071073 nm) with ψ and ω scan modes. The sample selected for investigation had dimensions of 0.46 × 0.20 × 0.10 mm^3. Collecting the diffraction data between appointed 2θ (1.7°≤ θ ≤ 27.5º) angle and an empirical absorption correction was applied with SADABS. The structure was solved by direct methods and refined by the least squares in the isotropic approximation for hydrogen atoms and anisotropic approximation for other atoms. The final cycle of refinement finally converged to $R_1 = 0.0349$, $wR_2 = 0.1227$. All hydrogen atoms are theoretic hydrogenation, all calculations were carried out using the SHEXTL-97 program[21]. Crystal data are listed in Table-1. Selected bond lengths and angles are given in Table-2.

TABLE-1
CRYSTALLOGRAPHIC DATA FOR **1**

Formula	$C_{28}H_{27}N_2O_6Mn$
Formula weight	541.45
Temperature (K)	296(2)
Wavelength (nm)	0.071073
Crystal system,	Monoclinic
Space group	P21/c
a/nm	2.36748(14)
b/nm	1.16289(7)
c/nm	0.96440(6)
β/º	96.353(4)
Volume (nm^3)	2.6388(3)
Z	4
Calculated density (g/cm^3)	1.363
Absorption coefficient (mm^{-1})	0.545
F(000)	1124
Crystal size (mm)	0.48 × 0.20 × 0.10
Theta range for data collection (º)	1.7 to 27.5
Limiting indices	-30 <= h <= 30, -15 <= k <= 15, -12 <= l <= 12
Reflections collected / unique	10670
Independent reflections	3040
Reflections observed	2530
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	0.908
Final R indices [I>2σ(I)]	$R_1 = 0.0349$, $wR_2 = 0.1125$
R indices (all data)	$R_1 = 0.0437$, $wR_2 = 0.1227$
Largest diff. peak and hole (e nm^{-3})	271 and -362

TABLE-2
SELECTED BOND LENGTHS (nm) AND ANGLES (º)

Bond	Dist.
$Mn1–O3^i$	0.21149(12)
Mn1–O3	0.21150(12)
$Mn1–O2^{ii}$	0.21943(12)
$Mn1–O2^{iii}$	0.21943(12)
Mn1–N1	0.22828(19)
$Mn1–N2^{iv}$	0.2288(12)
Angle	(°)
$O3^i$–Mn1–O3	172.23(7)
$O3^i$–Mn1–$O2^{ii}$	83.76(5)
O3–Mn1–$O2^{ii}$	96.01(5)
$O3^i$–Mn1–$O2^{iii}$	96.01(5)
$O2^{ii}$–Mn1–N1	88.30(3)
$O3^i$–Mn1–$N2^{iv}$	93.88(4)
$O2^{ii}$–Mn1–$N2^{iv}$	91.70(3)
N1–Mn1–$N2^{iv}$	180.000(1)
O3–Mn1–$O2^{iii}$	83.76(5)
$O2^{ii}$–Mn1–$O2^{iii}$	176.59(7)
$O3^i$–Mn1–N1	86.12(4)
O3–Mn1–N1	86.12(4)
$O2^{iii}$–Mn1–N1	88.30(3)
O3–Mn1–$N2^{iv}$	93.88(4)
$O2^{iii}$–Mn1–$N2^{iv}$	91.70(3)

Symmetry codes: (i) $–x + 1, y, –z + 3/2$; (ii) $–x + 1, –y + 1, –z + 2$; (iii) $x, –y + 1, z–1/2$; (iv) $x, y–1, z$; (v) $x, y + 1, z$

RESULTS AND DISCUSSION

FTIR spectra: The IR spectrum of the title complex displays characteristic strong bands at 1584 cm^{-1} and 1417 cm^{-1}, indication of the presence of ν_{as}(-COO^-) and ν_s(-COO^-) for the carboxylic group, respectively, which are finally confirmed by X-ray diffraction analysis. The band at 748 cm^{-1} and 690 cm^{-1}, typical for benzene. The stretching bands in the ligand spectrum at 1447 cm^{-1} was assigned to the methyl. A sharp peak at 529 cm^{-1} was attributed to the ν(Mn-O) stretching vibration.

Structure description: Fig. 1 displays the coordination environment of the manganese atom and gives the atomic labeling scheme. In the crystal structure of $[Mn(POPA)_2(bipy)]_n$, the $POPA^-$ ligand exhibit bridging coordination mode. The Mn^{2+} ion is six-coordinated with four carboxylate oxygen atoms from four 2-$POPA^-$ ligands and two nitrogen atoms of two bipy ligands, giving a regular octahedral geometry. The average (Mn-N) bond length of 0.22828-0.2288 nm is adjacent to the value (0.2307 nm) found in the previous complex, $[Mn(L)_2(bipy)]_n$ [22] (HL = 3,5-dimethylbenzoic acid). The distance between Mn1 and Mn1B is 0.48596 nm. The Mn-O bond length is in the range of 0.21149-0.21943 nm, which is similar to that of $[Mn (L)_2(bipy)]_n$ (0.2146-0.2171 nm).

The two-dimensional chain of the present manganese(II) complex can be viewed as constructed from $[Mn(POPA)_2(bipy)]$ building blocks. The center ion bridging four oxygen atoms from four carboxylic group, every $POPA^-$ ligand bridging two Mn^{2+} ions by two carboxylic group oxygen atoms. Simultaneously the center ion bridging two nitrogen atoms from two bipy ligands. A novel two-dimensional chain structure is formed through this coordination mode of the bridging $POPA^-$ and bipy ligands (Fig. 2). In addition, there are no classical

hydrogen bonds in the crystal structure, because good hydrogen bond donors are absent. Nevertheless, there are infinite parallel pyridine rings in the two-dimensional chain, the distance between two adjacent rings is 0.96440 nm. Hence there is weak π-π stacking interaction[23] between the adjacent bipy rings, which strengthen the stability of coordination compound.

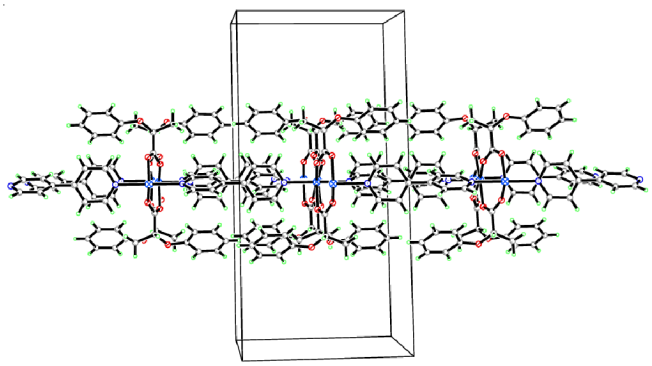

Fig. 2. 2D sheet-like structure linked by π-π stacking attraction

Thermal decomposition: The TG-DTG curves of the present Mn(II) complex are shown in Fig. 3. The thermal behaviour of $[Mn(POPA)_2(bipy)]_n$ was studied from 30 ºC to 800 ºC. It experiences two steps of weight loss. The first step from 220 ºC to 312 ºC with a mass loss of 38.71 %, it corresponds to the loss of half of bipy and one $POPA^-$, but two oxygen atoms of the carboxyl are retained (the calculated value is 38.96 %). The second step in the range 312 ºC - 395 ºC with a mass loss of 45.10 % corresponds to the release of one $POPA^-$ and another half of bipy (the calculated value is 44.99 %). Finally, the remaining mass of 16.19 %, seems likely to correspond to MnO_2 (calcd. 16.06 %).

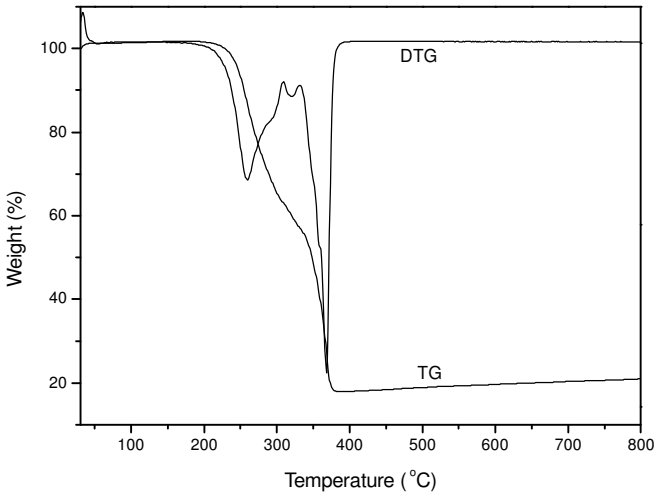

Fig. 3. TG-DTG curves of the Mn(II) complex

The decomposition equation may be as follows:

$$Mn(POPA)_2(bipy) \xrightarrow[220\ ^{\circ}C\text{-}312\ ^{\circ}C]{1/2\ bipy,\ phenoxy,\ propyl} MnC_{13}O_5$$

$$\xrightarrow[312\ ^{\circ}C\text{-}395\ ^{\circ}C]{-POPA^-,\ 1/2bipy} MnO_2$$

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