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Research Article

Synthesis, Structure, and Catalytic Activity of A New Mn(II) Complex with 1,4-Phenylenediacetic Acid and 1,10-Phenanthroline

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Abstract

A new Mn(II) complex material has been synthesized by one-pot reaction of $Mn(CH_3COO)_2 \cdot 4H_2O$, 1,4-phenylenediacetic (H_2L), 1,10-phenanthroline (phen), and NaOH in water/ethanol (v:v = 1:1) solution. The structure of Mn(II) complex was determined by elemental analysis, FTIR, and X-ray single-crystal diffraction analysis. The results reveal that Mn(II) complex was constructed by a monodentate 1,4-phenylenediacetate ligand, two phen ligands, a coordinated water molecule, 0.5 uncoordinated 1,4-phenylenediacetate ligand and six uncoordinated water molecules. The complex molecules form 1D chain structure by the π-π interaction of phen molecules. The catalytic activity of Mn(II) complex for coupling of benzaldehyde, phenylacetylene and piperidine in 1,4-dioxane has also been investigated and the maximum yield of propargylamine is up to 72.2 % after 12 h at 120 °C.

Keywords: Mn(II) complex; Phenanthroline; Catalytic activity; Mn(II) complex

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1. Introduction

Studies on the design, synthesis and property of metal complex materials have been one of the most important research topics for chemists and materials scientists, because they exhibit not only novel topological structures [1-5], but also many potential applications in catalysis [6,7], luminescence [8,9], magnetic [10], antibacterial and antitumor [11-13], and gas storage [14]. It should be noted that the carboxylate ligands have often been used to synthesize functional metal complexes, because the oxygen atoms of carboxylates are easy to coordinate with metal ions. Meanwhile, they may adopt monodentate coordination mode and bidentate coordination mode [15-18]. The 1,10-phenanthroline is also used as secondary ligand to prevent the coordination of water molecules with metal ions [19-21]. Meanwhile, the complex catalysts show environmentally friendly and economical to synthesis of propargylamines comparing with conventional catalysts [22]. Based on the above reasons, in this work, we report a new Mn(II) complex, $\{[MnL(phen)_2(H_2O)]0.5L.6H_2O\}$, which has been synthesized by one-pot reaction of

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$Mn(CH_3COO)_2 \cdot 4H_2O$, 1,4-phenylenediacetic (H_2L), 1,10-phenanthroline (phen), and NaOH in water/ethanol (v:v = 1:1) solution. The catalytic activity of Mn(II) complex for coupling of benzaldehyde, phenylacetylene, and piperidine in 1,4-dioxane has also been investigated.

2. Materials and Methods

2.1 Materials and measurements

The following chemical reagents used are analytical grade: 1,4-phenylenediacetic acid, 1,10-phenanthroline, $Mn(CH_3COO)_2 \cdot 4H_2O$, NaOH, piperidine, benzaldehyde, phenylacetylene, and 1, 4-dioxane.

Elemental analyses (C, H, and N) were measured on an Elementar Vario III EL Elemental Analyzer. IR spectra were measured on a Nicolet AVATAR 360 infrared spectrometer in the 4000-400 cm^{-1} region. The crystal data of $\{[MnL(phen)_2(H_2O)]0.5L.6H_2O\}$ were collected by a Bruker Smart CCD diffractometer.

2.2. Synthesis of $\{[MnL(phen)_2(H_2O)] \cdot 0.5L \cdot 6H_2O\}$

The 1.0 mmol (0.192 g) 1,4-phenylenediacetic, 1.0 mmol (0.180 g) 1,10-phenanthroline, 2.0 mmol (0.080 g) sodium hydroxide, and 1.0 mmol (0.245 g) $Mn(CH_3COO)_2 \cdot 4H_2O$ were added to the 15 mL of CH_3CH_2OH/H_2O (v:v=1:1) solution. The mixture was continuously stirred for 6 h at refluxing temperature, then the mixture was cooled to room temperature, and was collected by filtration. The single crystal suitable for X-ray determination was obtained from filtrate after 30 days by evaporation at room temperature.

2.3 Crystal data and structure determination

The yellow block crystal of $\{[MnL(phen)_2(H_2O)] \cdot 0.5L \cdot 6H_2O\}$ (0.28 mm × 0.24 mm × 0.22 mm) was mounted on a Bruker Amart CCD diffractometer equipped with a graphite-monochromatic Mo*Ka* (λ = 0.71073 Å) for the collection of intensity data. In the range of $3.32<\theta<25.01$, a total of 15510 reflections were collected and 6947 were independent with R_{int} = 0.0473, of which 4859 were observed with $I>2\sigma(I)$. The structure was solved by direct methods with SHELXS-97 [23] and refined by full-matrix least-squares techniques on F^2 with SHELXL-97 [24].

Table 1. Crystal data of $\{[MnL(phen)_2(H_2O)] \cdot 0.5L \cdot 6H_2O\}$

Empirical formula	$C_{39}H_{42}MnN_4O_{13}$
Formula weight	829.71
Temperature/K	293(2)
Crystal system	triclinic
Space group	*P*-1
a/Å	10.703(2)
b/Å	12.287(3)
c/Å	16.900(3)
α/°	69.25(3)
β/°	72.47(3)
γ/°	86.72(3)
Volume/Å^3	1978.7(7)
Z	2
ρ_{calc}mg/mm^3	1.393
μ/mm^{-1}	0.404
S	1.057
F(000)	866
Index ranges	$-12 \le h \le 12$, $-14 \le k \le 14$, $-20 \le l \le 18$
Reflections collected	15510
Independent reflections	6947 [*R*(int) = 0.0473]
Data/restraints/parameters	6947/0/514
Goodness-of-fit on F^2	1.057
Final *R* indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0785, wR_2 = 0.2140
Final *R* indexes [all data]	R_1 = 0.0992, wR_2 = 0.2460

3. Results and Discussion

3.1 Data of elemental analysis and IR spectrum

The results of elemental analyses show that the C, H, and N are 56.41, 5.06, 6.75 (calc.) and 56.65, 5.42, 6.53 (found), respectively. The characteristic IR bands of Mn(II) complex appears in 1635 cm^{-1} (C=O) and 3423 cm^{-1} (H2O).

3.2 Structural description of {[MnL(phen)$_2$(H$_2$O)]·0.5L·6H$_2$O}

The crystal data of {[MnL(phen)$_2$(H$_2$O)]·0.5L·6H$_2$O} are given in Table 1. One-pot reaction of $Mn(CH_3COO)_2 \cdot 4H_2O$, 1,4-phenylenediacetic (H_2L), 1,10-phenanthroline (phen), and NaOH in water/ethanol (v:v = 1:1) solution afforded colorless block crystals of Mn(II) complex. Single crystal analysis shows that the Mn(II) complex crystallizes in the triclinic space group *P*-1. The asymmetric unit contains a monodentate 1,4-phenylenediacetate ligand, two phen ligands, a coordinated water molecule, 0.5 uncoordinated 1,4-phenylenediacetate ligand, and six uncoordinated water molecules (Figure 1).

It can be seen that the Mn(II) ion is six-coordinated by four N atoms from two different phen ligands, one O atom from carboxylate group of 1,4-phenylenediacetate ligand, and one O atom from coordinated water molecule, resulting in a distorted octahedral geometry. The Mn–O distances are 2.099(3) Å and 2.147(3) Å, respectively, and the Mn–N distances range from 2.259(3) Å to 2.301(3) Å. All of which are consistent with those reported in the other Mn(II)-containing compound [25-28]. The important bond parameters of {[MnL(phen)$_2$(H$_2$O)]·0.5L·6H$_2$O} are listed in Table 2.

In addition, the Mn(II) complex molecules form 1D chain structure though the π-π interaction of phen ligands (Figure 2). As shown in Figure 2, the main chain is constructed by the phen ligands, the monodentate 1,4-phenylenediacetate ligands are on both sides of chain. The 1D chains are connected by hydrogen bonds to form 3D network structure (Figure 3).

3.3 Catalytic studies

The catalytic activity of Mn(II) complex was tested for the preparation of propargylamine in the A^3 coupling reaction. The coupling of benzaldehyde, piperidine and phenylacetylene with 1,4-dioxane as solvent was selected as a model reaction (Figure 3). The results are summarized in Table 3. It can be seen that Mn(II) complex has a good catalytic activity for the A^3 coupling reaction of benzaldehyde, phenylacetylene, and piperidine with 1,4-dioxane as solvent at 120 °C. Benzaldehyde conversion is 72.7 % within 12 h at 120 °C over Mn(II) complex. And the catalyst feature 100 % selectivity to the product of propargylamine for the A^3 coupling reaction without any byproduct. The catalytic activity of Mn(II) complex for the A^3

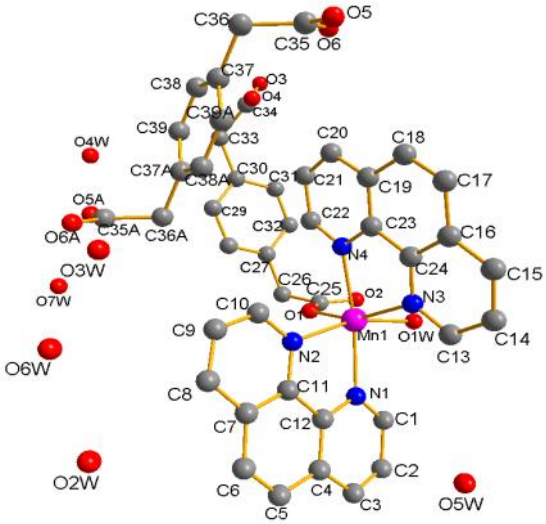

Figure 1. Molecular structure of Mn(II) complex

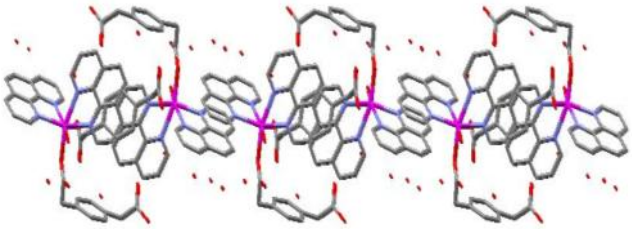

Figure 2. 1D chained structure of Mn(II) complex

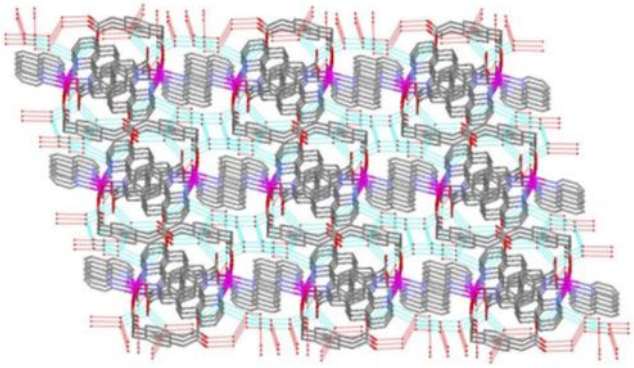

Figure 3. 3D network structure of Mn(II) complex

Table 2. The important bond parameters of {[MnL(phen)$_2$(H_2O)] ·0.5L ·6H_2O}

Bond	Distance(Å)	Angle	(°)
Mn1-O1	2.099(3)	O1W-Mn1-O1	89.51(13)
Mn1-O1W	2.147(3)	O1-Mn1-N4	89.00(13)
Mn1-N4	2.259(3)	O1W-Mn1-N4	106.59(14)
Mn1-N1	2.263(4)	O1-Mn1-N1	100.52(13)
Mn1-N3	2.282(4)	O1W-Mn1-N1	89.89(16)
Mn1-N2	2.301(3)	N1-Mn1-N4	161.13(15)
		N3-Mn1-O1	160.66(13)
		N3-Mn1-O1W	88.37(13)
		N3-Mn1-N4	73.23(13)
		N1-Mn1-N3	98.70(13)
		O1-Mn1-N2	98.86(11)
		O1W-Mn1-N2	162.15(15)
		N2-Mn1-N4	89.39(12)
		N1-Mn1-N2	73.16(14)
		N2-Mn1-N3	88.75(12)

Table 3. Coupling of benzaldehyde, phenylacetylene, and piperidine catalyzed by Mn-complex in 1,4-dioxane [a]

run	Solvent	Temperature (°C)	Time (h)	Conversion(%)[b]
1	1,4-dioxane	120	12	72.2
2	1,4-dioxane	120	12	61.6
3	1,4-dioxane	120	12	52.6
4	1,4-dioxane	120	12	42.6

[a]Reaction conditions: aldehyde (0.13 mmol), amine (0.15 mmol), alkyne (0.17 mmol), Mn-complex (80 mg), dioxane (1.5 g);
[b]The products was determined by GC analysis of the samples (GC-1100, capillary column SE-54) using *n*-nonane as the external standard.

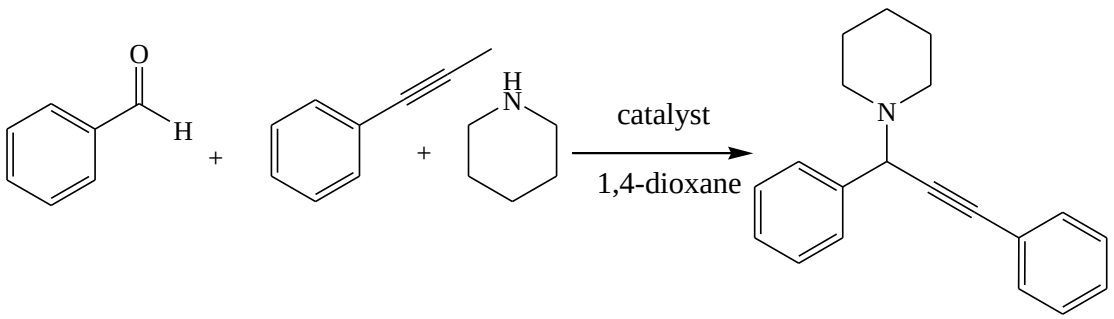

Figure 4. The coupling of benzaldehyde, piperidine, and phenylacetylene with 1,4-dioxane as solvent using Mn(II) complex as a catalyst

coupling reaction of benzaldehyde, phenylacetylene, and piperidine is better than that of Cu(II) complex reported in ref. [7]. To check the reusability, the catalyst of Mn(II) complex was repeatedly filtered out and subjected to a new reaction batch without any further treatment. The catalyst of Mn(II) complex exhibited 61.6%, 52.6 %, and 46.2 % within 12 h at 120 °C in the first, second, and third cycles, respectively. Clearly, the recovered catalyst features a significant deactivation by around 10.6 % for the first run, while further recycling leads to 9.0 % and 6.4 % deactivation.

4. Conclusions

In summary, a new Mn(II) complex has been prepared and its structure has also been determined by elemental analysis, FTIR spectra, and single crystal X-ray diffraction. The Mn(II) complex exhibits good catalytic activity for A^3 coupling reaction of benzaldehyde, piperidine, and phenylacetylene.

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