



Synthesis, Characterization and Magnetic Properties of New Inorganic Supramolecular Complex

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ABSTRACT

In this study, a new inorganic polymer of $[Mn(O)_2Cu(dipic)_2]_n$, that dipic is pyridine-2,6-dicarboxylic acid was prepared and characterized by elemental analysis, Fourier transform infrared spectroscopy (FT-IR), UV-Vis, X-ray powder diffraction (XRD) and vibrating sample magnetometer (VSM). Magnetic studies were conducted on the polymer at room temperature, and showed that this polymer at room temperature has paramagnetic behavior.

Keywords: Synthesize; Polymer; Magnetic behavior; Dipic; Copper

INTRODUCTION

In the previous studies, a number of dimers and polymer complexes with dipic ligand were synthesized by our group [1-3]. Pyridine-2,6-dicarboxylic acid (dipicolinic acid, H_2dipic) is a water-soluble, commercially available, cheap and versatile N,O-chelator possessing diverse coordination modes [4-7]. This stems mainly from its ability to form stable chelates, with various coordination modes such as bidentate, meridian, or bridging. Other interesting properties are its biological activity, its ability to stabilize unusual oxidation states, and its usefulness in analytical chemistry, such as chemical analysis of iron at low concentration, in corrosion inhibition and in decontamination of nuclear reactor [8-16]. The pyridine di-carboxylic acids, with the isomers, -2,3, -2,4, -2,6 etc., have been widely exploited to form 1:1 and 1:2 metal derivatives which exhibit various structures and interesting properties. Among them, 2,6-pyridinedicarboxylic acid is remarkably attractive for its flexible and versatile coordination modes to construct supramolecular architectures, metal-organic frameworks, coordination polymers and 2D-3D networks [17-24].

EXPERIMENTAL SECTION

Materials and physical techniques

All synthetic work was performed at room temperature. $Mn(NO_3)_2 \cdot 4H_2O$, Pyridine 2,6-dicarboxylic acid, sodium hydroxide and $Cu(NO_3)_2 \cdot 3H_2O$ were obtained and used as received from Aldrich Chemical. Atomic absorption spectroscopy on metals was performed via Varian AA50 equipment. FT-IR spectra were recorded as KBr pellets on a FT-IR JASCO-460 spectrophotometer. Phase analysis of the products was evaluated by X-ray diffraction (XRD) using $Cu-K\alpha$ radiation between 0° - 50° (2θ) with step size $0.02^\circ/s$ recorded on a diffractometer model X Pert MPD. Vibrating sample magnetometer (VSM) operating at room temperature with applied magnetic fields up to 10000Oe is used to measure the magnetic properties.

Synthesis of $[Mn(O)_2Cu(dipic)_2]_n$

To prepare this polymer (1mmol) of $Mn(NO_3)_2 \cdot 4H_2O$ and (1mmol) of $Cu(NO_3)_2 \cdot 3H_2O$ were dissolved in 20 mL of water. The amount of 2mmol NaOH which dissolved in 5mL of water was added to this solution. 1mmol of $Fe(NO_3)_3 \cdot 9H_2O$ that dissolved in 10 mL of water was added to the solution. In this reaction, $Fe(NO_3)_3 \cdot 9H_2O$ is the catalyst for the polymerization reaction. This solution was stirred for 3 hours at room temperature. The solution was left for several days at room

temperature. After several days, violet crystals of this polymer were formed. Anal. Cal. for $C_{14} H_6 N_2 Mn Cu O_{10}$: C, 34.9; H, 1.2; N, 5.8 Found: C, 34.7; H, 1.1; N, 5.7.

RESULTS AND DISCUSSION

The FT-IR spectra of $[Mn(O)_2Cu(dipic)_2]_n$ shows broad absorption bands at $3341-3241\text{ cm}^{-1}$ which assigned to the asymmetric and symmetric $\nu(H_2O)$ stretching vibration of lattice water molecules. In asymmetric $\nu_{as}(COO)$ and symmetric $\nu_s(COO)$, the stretching vibrations of the dipicolinate carboxylate groups were observed at $1623, 1541\text{ cm}^{-1}$ for $\nu_{as}(COO)$, and $1454, 1431$ and 1312 cm^{-1} , for $\nu_s(COO)$ respectively. Figure 1, shows the electronic spectra of this polymer in H_2O solvent. The electronic spectrum of this polymer in UV region shows absorption bands at 218 and 272 nm for the polymer attributed to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions, respectively. The absorption band at 800nm is assigned to d-d transition of Cu^{2+} center. Mn^{2+} with the electron configurations d^5 (high spin) do not show any type of d-d electron transfer. Figure 2, shows accumulation polymer. Fig. 3 shows the XRD pattern of the polymer. Magnetic property of this polymer was studied by VSM. Figure 4, shows that copper-manganese polymer at room temperature exhibited paramagnetic behavior.

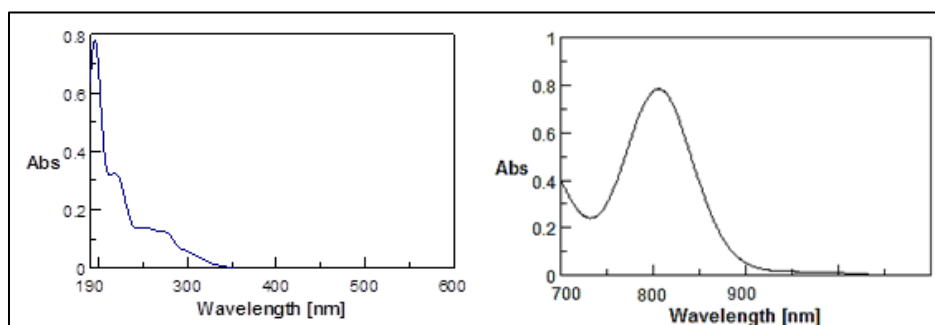


Figure 1: Electronic spectra of $[Mn(O)_2Cu(dipic)_2]_n$ in H_2O

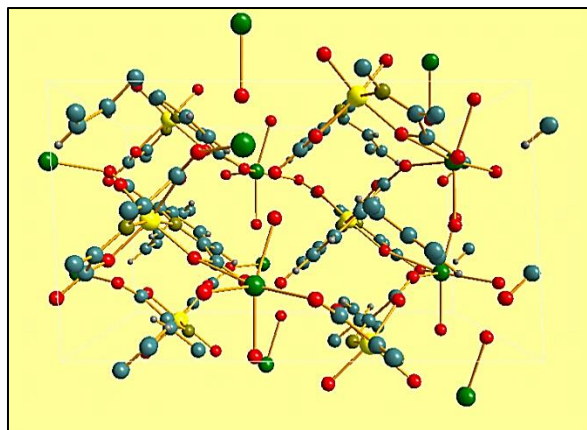


Figure 2: The packing of $[Mn(O)_2Cu(dipic)_2]_n$ viewed approximately along c

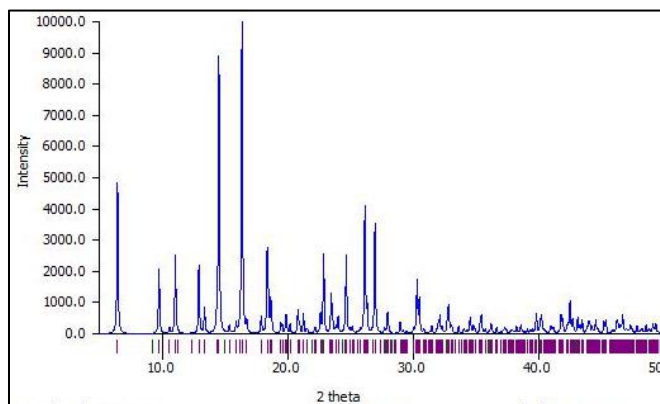


Figure 3: XRD pattern for $[Mn(O)_2Cu(dipic)_2]_n$.

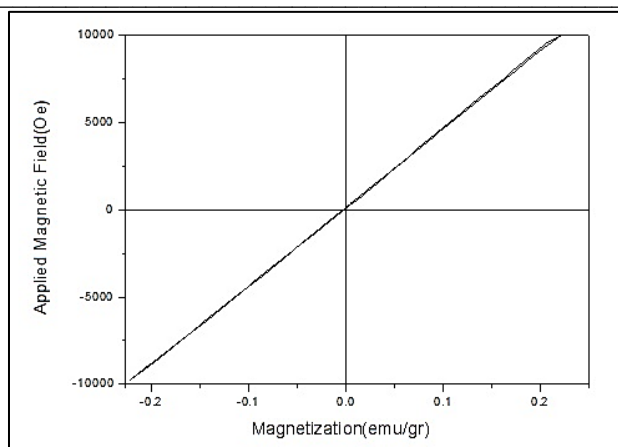


Figure 4: Hysteresis loop of $[\text{Mn}(\text{O})_2\text{Cu}(\text{dipic})_2]_n$ at room temperature

CONCLUSION

A new inorganic polymer of $[\text{Mn}(\text{O})_2\text{Cu}(\text{dipic})_2]_n$ was synthesis and characterized by various technique such as, FT-IR, UV-Vis, elemental analysis and XRD. The magnetic behavior of this polymer was studied by VSM. The results show that the interaction between metal centers of Cu^{2+} and Mn^{2+} is paramagnetic.

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