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Synthesis, X-Ray crystal structure, photophysical characterization and nonlinear optical properties of the unique manganese complex with picolinate and 1,10 phenantroline: toward the designing of new high NLO response crystal

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ABSTRACT

The first manganese complex of picolinic acid (also known as 2-pyridinecarboxylic acid) and 1,10 phenantroline has been synthesized, and its structure has been fully characterized by means of X-Ray diffraction method as well as FT-IR, Raman and UV–vis spectroscopies. In order to provide a deep understanding about the relation among the nonlinear optical properties, structural, spectroscopic and electronic behaviors, density functional theory (DFT) calculations have been performed by using hybrid B3LYP level. The intensive interactions between the bonding orbitals of donor O/N atoms and antibonding orbitals of Mn(II) lone pairs confirm the X-Ray diffraction results. Each of the conditions such as small energy gap between HOMO and LUMO, high energy second order perturbation interaction, elongation of conjugated π system and high spin Mn(II) ion induce the first static hyperpolarizability (β) parameter of investigated complex. The β parameter for $[Mn(pic)_2(phen)]\cdot H_2O$ complex has been found to be approximately 22 times higher than p-nitroaniline.

1. Introduction

Carboxylic acids are known as the most attractive building blocks for coordination compounds due to their different roles through complexation such as one, two or more dentate coordination, counter-ions, bridging or chelating ligands [1–3]. Picolinic acid is recognized by the versatile binding features owing to the different nature of donor N and O atoms. Pyridine N atom, which is a soft donor, keeps transition metals ions at lower oxidation states, while the carboxylate O atom, which is a hard donor, keeps transition metals in their higher oxidation states. These ligands have special networking abilities due to this dual functionality [4,5].

As for the 1,10 Phenantroline (phen) used as a secondary ligand in the present paper, it is a bidentate chelating ligand for metal ions and has made great contributions to the development of coordination chemistry [2,6,7]. Phen ligand, which have two aromatic nitrogen atom, whose unshared electron pairs are excellently located to act together in binding to metal ions, is known as a good π-acceptor [8,9]. The binding of 1,10-phenantroline ligand characterized by low-energy delocalized π*-orbitals increases the possibility of modification in their optical, physicochemical and electrochemical properties as well as the structural characteristics. Also, the synthesis and construction studies on manganese complexes have gained increasing attention, due to manganese plays an important role in biological systems [10–12].

In recent years, a number of papers have been reported concerning the nonlinear optical properties of organic, inorganic, fullerenes, cluster compounds and semiconductors [13–20]. Although, the organic crystals are known to have very large nonlinear susceptibilities, their low optical transparencies, poor mechanical properties and challenges in the crystal growth restrict their use. Similarly, the inorganic materials are considered with the perfect mechanical and thermal characteristics but have relatively limited optical nonlinearities due to the absence of extended π-electron delocalization. Therefore, the search for new NLO materials is directed to coordination compounds instead of pure organic or inorganic materials because they have potential to combine the structural modifiability and high optical nonlinearity of organic ligands with mechanical characteristics, thermal stability and excellent transmittance of inorganics corresponding [21,22]. Through the possibility to changing of metal ions, binding modes, ligands as well as oxidation state, coordination compounds have

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even greater coordination flexibility than organic ones. Additionally, charge transfers from ligand to metal or vice versa enhances the nonlinearity of the systems.

Considering that the above mentioned conditions, we thought that the synthesis, characterization and investigation of nonlinear optical properties of manganese complexes constructed with the cooperation of picolinic acid and 1,10 phenantroline are very attractive. In our previous studies, Ni and Mn complexes of picolinic acid were synthesized and their structures were characterized by experimental and theoretical methods [1,4,23]. Additionally, it was demonstrated that these complexes exhibit considerable NLO character.

2. Experimental procedure

2.1. Synthesis of $[Mn(pic)_2(phen)]\cdot H_2O$

All chemical reagents were analytical grade commercial products. Solvents were purified by conventional methods. To an ethanol/water (20 mL, ca 1:1 (v/v)) containing picolinic acid (2 mmol), an ethanol/water (20 mL, ca 1:1 (v/v)) containing Mn $(CH_3COO)_2$ (1 mmol) was slowly added with continuous stirring. Then, an ethanol/water (20 mL, ca 1:1 (v/v)) containing 1,10 phenantroline (1 mmol) was slowly added to the latter solution. The resulting solution were refluxed for 4 h and then filtered. The yellowish filtrates were allowed to stand for three days at room temperature, and then the yellowish crystals adequate for X-ray diffraction studies were obtained. The synthesis scheme for $[Mn(pic)_2(phen)]\cdot H_2O$ is given in Fig. 1.

2.2. Instrumentation

FT-IR spectra for $[Mn(pic)_2(phen)]\cdot H_2O$ were recorded on a Perkin-Elmer FT-IR spectrophotometer, where samples were measured in KBr at the region of 4000–600 cm^{-1}. Raman spectroscopy analysis of $[Mn(pic)_2(phen)]\cdot H_2O$ was performed by Kaiser RAMANRXN1. The UV–vis absorption spectrum of the $[Mn(pic)_2(phen)]\cdot H_2O$ was examined in the range 1050–200 nm using an Agilent Model 8453 diode array spectrophotometer in ethanol solvent.

2.3. X-ray data collection and structure refinement

The solid-state structure of $[Mn(pic)_2(phen)]\cdot H_2O$ was confirmed by X-ray diffraction analysis. Data were obtained with Bruker APEX II QUAZAR three-circle diffractometer. Indexing was performed using APEX2 [24]. Data integration and reduction were carried out with SAINT [25]. Absorption correction was performed by multi-scan method implemented in SADABS [26]. The Bruker SHELXTL [27] software package was used for structure solution and structure refinement. All non-hydrogen atoms were refined anisotropically using all reflections with $I > 2\sigma(I)$. Aromatic C-bound H atoms were positioned geometrically and refined using a riding mode. H atoms of water molecules were located in a difference Fourier map and the O–H distances restrained to be 0.84 Å from O atom using DFIX command and their positions were constrained to refine on their parent O atoms with $Uiso(H) = 1.5\ Ueq(O)$. Crystallographic data and refinement details of the data collection for $[Mn(pic)_2(phen)]\cdot H_2O$ are given in Table 1. The selected bond lengths and bond angles are given in Table 2. Final geometrical calculations were performed using PLATON software [28]. MERCURY software [29] was used for visualization of the cif file. The important conditions for the data collection and the structure refinement parameters of $[Mn(pic)_2(phen)]\cdot H_2O$ are given in Table 1.

3. Computational procedures

The whole calculations including optimized geometry, vibrational frequencies, electronic absorption spectrum, HOMO and LUMO energies, natural bond orbital (NBO) analysis, molecular surfaces, atomic polar tensor charges and nonlinear optical properties of $[Mn(pic)_2(phen)]\cdot H_2O$ complex have been carried out by using GAUSSIAN 09 Rev: D.01 program [30], and the obtained data have been visualized by means of GaussView 5 program [31]. The B3LYP level (Becke's three parameter hybrid model using the Lee-Yang Parr correlation functional) [32,33] which is known as hybrid density functional theory (DFT) method has been used in cooperation with 6-311++G(d,p) [34] basis set for C, H, N and O atoms, LanL2DZ (effective core potential of Hay and Wadt) basis set [35–37] for Mn(II) ion. The time-dependent density functional

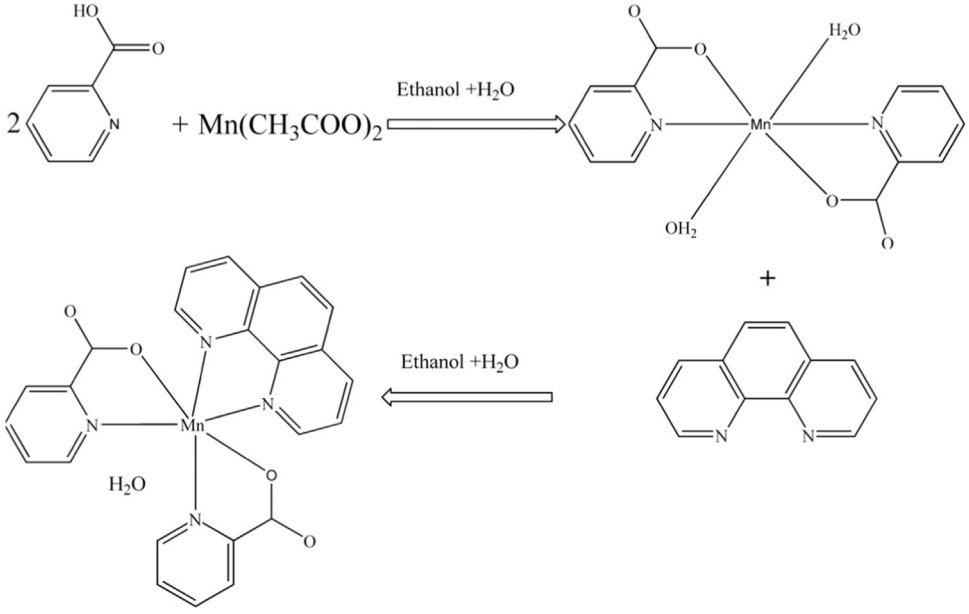

Fig. 1. The synthesis schema for $[Mn(pic)_2(phen)]\cdot H_2O$ complex.