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Synthesis of spherical Fe_3O_4 nanoparticles from the thermal decomposition of iron (III) nano-structure complex: DFT studies and evaluation of the biological activity

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ABSTRACT

A novel Fe(III) Schiff base complex of the $[FeL_2(NO_3)_2]NO_3$ type where L = 2-((pyridin-4-yl)methyleneamino)-3-aminomaleonitrile was synthesized using the reflux and sonochemical methods and their antibacterial and antifungal activity were evaluated. The nanoparticles of iron oxide (Fe_2O_3) were obtained from the iron nano-structure complex as a precursor after calcination at 600 °C for 3 h. All the synthesized compounds were characterized by various spectroscopic techniques. The results of SEM showed that the morphology of iron nano-structure complex was rod-like while the morphology of the Fe_2O_3 nano powder was spherical. The results of the biological studies indicated that the iron nano-structure complex showed a stronger antibacterial and antifungal efficiency than its bulk complex. Finally, the empirical geometrical parameters of complexes revealed a good agreement with calculated ones at DFT-B3LYP level.

1. Introduction

Schiff base ligands and its metal complexes have attracted a considerable attention and are investigated from both the experimental and theoretical perspectives. They have been used in several zones such as the bioinorganic chemistry, industrial, and catalysis. These compounds have been synthesized by Schiff for the first time [1]. Due to their unique features and structural diversity, Schiff bases are the most varied and studied ligands in the coordination chemistry [2,3]. In addition to their broad spectrum of biological activities such as antibacterial, antifungal, antiviral, antitumor, anti-HIV, and anticancer [4,5], Schiff bases are reported to have several metal chelating that inhibit the tumor growth [6].

Recently, many biological, catalytical, analytical and industrial applications have been reported for the Schiff bases metal complexes [7]. Diaminomaleonitrile (DAMN) and its derivatives have received substantial attention in recent years and have been widely used in the synthesis of many other imine compounds and amino-functionalized macrocycles [8–15]. DAMN is one of the most excellent reagents in the organic chemistry, used as a precursor for synthesizing a broad range of heterocyclic compounds [16–18]. Only a few synthesized complexes of DAMN-based ligands are known. Recently, the synthesis of the compounds in nano size has been expanded because, in comparison to their bulk form, the particles' size reduction to a nanometer scale cause some of their properties like the magnetic, electronic, physical and biological properties to be modified [19].

Today, many researchers are working on the synthesis of metal complexes, especially transition metals on the nanometer scale. The overriding purpose of this study was to investigate the synthesis of the iron Schiff base complex, $[FeL_2(NO_3)_2]NO_3$ in nano scale in the absence of any surfactant and toxic solvent using the sonochemical method. The synthetic process is a green method. In comparison to other methods, the sonochemical methods are low-cost, fast, facile, safe, and suitable for the industrial production. The nano powders were described using X-ray diffraction (XRD), scanning electron microscopy (SEM), and Atomic Force Microscope (AFM).

On the other hand, the computational chemistry methods have become increasingly important as a supplement, if not a substitute, for the empirical methods in almost all areas of chemistry. Therefore, the theoretical interaction of bi-dentate Schiff base ligand with iron metal ion as a host–guest model was investigated. Then, the interaction energies, HOMO-LUMO energies and the molecular electrostatic potential (MEP) for the iron complexes was studied. Not only the cavity of the host Schiff base molecule, but also its shape and dimensions are important for the ligand's interactions with the guest metal ion [20–23]. Molecular computational chemistry has become widely identified as a

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useful protocol for the design of new molecular ligands.

2. Experimental section

2.1. Material

2,3-diaminomaleonitrile, 4-pyridine carboxaldehyde and Fe $(NO_3)_3{\cdot}9H_2O$ salt were purchased from Merck or Fluka Chemical Company. All reagents and solvents for the synthesis and analysis were used without further purification.

2.2. Physical characterizations

Fourier-transform infrared spectra were recorded on Shimadzu FT-IR 8400S (Japan) with resolution of 4 cm^{-1} in the scan range of 400–4000 cm^{-1} using KBr pellet. UV–Vis spectra were recorded on a Carry 100 Conc Varian spectrophotometer. Melting points were measured with Electrothermal 9300 apparatus. The isolation, measurement, and identification of compounds by the gas chromatography unit (GC-Mass) of the GC-17A Shimadzu model equipped with a mass spectrometer detector being model MS-QP5050 were carried out. SEM images were obtained from MIRA3 TESCAN Field Emission Scanning Electron Microscope equipped with a link Energy-Dispersive X-ray (EDX) analyzer. AFM images were obtained from Ara-AFM (Iran), model full plus, method non-contact. A multiwave ultrasonic generator (Bandeline GM 2200) equipped with a converter/transducer and titanium oscillator operating at 20 kHz with a maximum power output of 200 W was used for the ultrasonic irradiation.

2.3. Preparation of $FeL_2(NO_3)_3$ complex

Iron nitrate nine hydrate (0.404 g, 1 mmol) in 20 ml of methanol was added to a stirred solution of L (0.396 g, 2 mmol) in 20 ml of hot methanol. The mixture was refluxed for 4–5 h, and then cooled at ambient temperature until an orange precipitate was formed. The product was collected by filtration and washed with cool methanol, and then dried in air. Yield (86%), decompose > 250 °C. IR (KBr, cm^{-1}): 3345–3233, 2200–2216, 1612, 1570–1462 and 447–493 cm^{-1}

2.4. Preparation of $FeL_2(NO_3)_3$ by sonochemical method

10 ml of a 0.1 M solution of $Fe(NO_3)_3{\cdot}9H_2O$ in CH_3OH were positioned in a high-density ultrasonic probe, operating at 20 kHz with a maximum power output of 200 W. To this solution 10 ml of a 0.2 M solution of the ligand L was added dropwise. Two minutes later, after increasing the ligand solution to the metal, an orange precipitate was obtained but in order to complete the process under microwave irradiation, it continued for 10 min (Scheme 1). Thus the obtained precipitate was filtered off, washed with methanol and then dried in air, Yield (85%) decompose > 250 °C. IR (KBr, cm^{-1}): 3348–3244, 2201–2216, 1614, 1546–1497, 496–501 cm^{-1}. UV–Vis [CH_3OH, λ_{max} (nm)]: 219, 241, 290, 392, and 427 nm.

Table 1
Physical characterization, Molar conductance data of iron complexes.

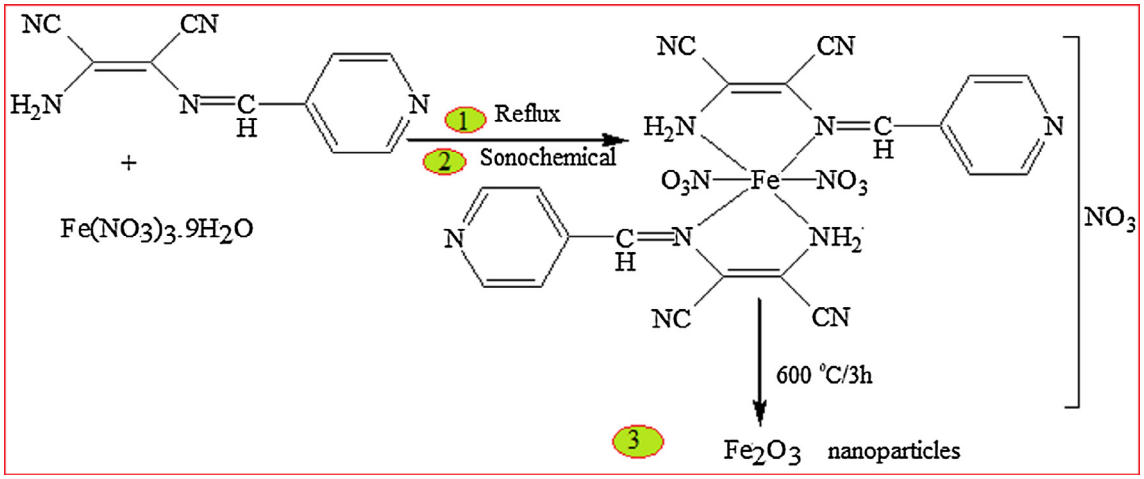
Compound	m.p (°C)	Color	Λ_M (S cm^2 mol^{-1})
Ligand L_1	229–230	Light yellow	13.4 non-electrolyte
1	> 250 (decom.)	Orange	108.1
2	> 250 (decom.)	Orange	104.9
3	–	Dark red	–

2.5. Preparation of Fe_2O_3 nanoparticles

The nano-structure powder of the mononuclear iron (III) Schiff base complex $FeL_2(NO_3)_3$ (about 0.5 g) was loaded into a platinum crucible and then placed in the electrical furnace and heated at a rate of 10 °C min^{-1} in the air up to 600 °C. After 3 h, the resulting nanoparticles of Fe_2O_3 are washed with absolute ethanol, and then dried. IR (KBr, cm^{-1}): 447 and 526 (Fe—O).

2.6. Antibacterial activity

Preliminary test of antimicrobial screening was carried out in vitro for the synthesized compounds against both Gram-positive *Staphylococcus aureus* (ATCC 6538) and *Bacillus cereus* (ATCC 11778) and Gram-negative (*Escherichia coli* (ATCC 8739) and *Klebsiella pneumonia* (ATCC 10031) bacteria using disc diffusion method. The bacteria were cultured for 24 h at 37 °C in nutrient agar medium and then adjusted with sterile saline to a concentration of 2×10^6 cfu/mL. The bacterial suspension in Petri dishes containing sterile Mueller Hinton agar (MHA) was cultured using a sterile cotton swab. 30 µl of the sample (2 mg/mL DMSO) was placed on the inoculated plates. Amikacin (30 µg/disk) was used as a standard antibiotic. After 24 h incubation at 37 °C, the diameter of inhibition zones was measured (mm). The compounds that showed antimicrobial activity were subjected to a minimum inhibitory concentration (MIC) assay using the broth micro dilution method [24]. All the tests were performed in replicating.



Scheme 1. Pathway of synthesis and the proposed structure of the iron complex.