Ultra Chemistry Vol. 8(1), 117-124 (2012).

Synthesis and Spectral studies of new Iron (III) metal complexes With some monodentate Nitrogen based Ligands

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(Acceptance Date 4th April, 2012)

Abstract

A number of iron complexes of type $[FeL_4\ (H_2O)_2](NO_3)_3$ (Where, L=hetero cyclic nitrogen donor ligands, such as imidazole, pyridine, piperidine, piperazine, indole, benzimidazole, benzotriazole, triazole, quinoline, iso-quinoline, carbazole) have been synthesized and characterized. These complexes are soluble in ordinary organic solvents. The conductivity data show that these complexes are 1:3 electrolytes in nature. The IR spectra reveal the coordination of ligand to the central iron atom through nitrogen. The mass spectra show a distinct molecular ion peak and the base peak .The thermal decomposition studies indicate the presence of water molecules which are ligated to the central metal ion. The loss of water molecule and the decomposition of nitrate ion occur at 140^oC. The successive removal of imidazole molecules from the complex begins after 100^oC, finally leaving Fe_3O_4 as the end product.

Key word: Iron, complexes, ligands, indole, benzimidazole, UV spectra, IR spectra, mass spectra.

Introduction

The heterocyclic nitrogen based compounds drew much attention because of their use as model of biological systems[1-5]. Although literature survey reveals quite a large number of work done on the bivalent transitional metal complexes with these ligands, a very few, however, have been reported on trivalent transitional metals. Hence, it was considered of interest to synthesize Iron (III) metal complexes with nitrogen based donor ligands like imidazole,pyridine,piperidine, piperazine, indole, benzimidazole, benzotriazole, triazpole,quinoline,iso-quinoline, and carbazole. Above metal complexes were synthesized, isolated, and characterized by various physico-chemical methods.

Material and Methods

Fe $(NO_3)_3.9H_2O$, indole, pyridine are BDH reagents, while iso-quinoline and carbazole are from Merk (Germany).The benzimidazole and triazole are procured from SD-fine chemicals and the quinoline and piperazine are from Loba. All the chemicals are of analytical grade and used as received.

Analytical Measurements :

Iron was determined by reported methods[6]. Elemental analyses were carried out using an **Erba** instrument. Molecular conductances of these complexes were measured on a direct reading **Systronic 304** model conductivity meter using 10^{-3}M solution in methanol. The UV spectra (λ=200 to 800 nm) were taken using **Hitachi-320 Perkin Elmer Lambda-15** instrument in MeOH solution and IR spectra in the region (υ=400 to 4000 cm^{-1}) were recorded by **Perkin Elmer 783** spectrophotometer employing KBr pellet technique. The mass spectral data are recorded by **Q-Tof micro™ spectroscope.** The thermal decomposition pattern of the complexes was studied using **NETZSCH-garatebau GmbH** thermal analyzer. The measurements were carried out between 25°C to 1000°C in an atmosphere of nitrogen using sample weight 100mg. The rate of temperature increase of 10°C min^{-1} was chosen for all the measurements. The instrument records TG, DST, and DTA simultaneously.

Synthesis of Metal Complexes-$[FeL_4 (H_2O)_2] (NO_3)_3$

An aqueous methanolic solution containing Fe $(NO)_3$. $9H_2O$ (0.25 m mol) and ligand (1 m mol) in methanol were taken separately. Metal ligand ratio was 1:4. Two solutions (metal solution and ligand solution) were warmed separately. The ligand solution was added to the metal solution while on warming. The solution was stirred vigorously under nitrogen atmosphere for three hours. The solution was then cooled and kept undisturbed for 8 hours. Green crystals separated out slowly, which were collected by filtration, washed several times with small volume of cold water, then with MeOH and finally by Et_2O. It was dried in vacuo over $CaCl_2$. All these complexes are prepared by following identical procedure and the yield varied from 50 % to 60 %.

Results and Discussion

All the synthesized nitrate complexes produce satisfactory analytical results, consistent with expected values. These results are presented in (Table 1) along with melting point and conductance values. The molar conductivity data (30-39 Ω^{-1} $cm^{-2}mol^{-1}$) suggest that the complexes are (1:3) electrolyte in nature. The magnetic moments of these complexes are around 6.15 BM corresponding to five unpaired electrons. The electronic spectra display three bands at around 380- 390 nm, 440- 450 nm and at 630 - 670 nm. The lower band corresponds to $n \rightarrow \pi^*$ transition, the second band[7] to $\pi \rightarrow \pi^*$ transition of the ligand and the third band is probably due to *d* (*Fe*) $\rightarrow \pi^*$ transition[8].

IR Spectra :

The IR spectra of free ligands are compared with metal complexes (Fig. 1). It is

found that most of the peaks are identical. A band appearing at around 3372 cm^{-1} indicates the coordination of water molecules[9] to the central metal ion. The absence of a band at around 3200 cm^{-1} implies that there is no hydrogen bonding present in the complex, which amply suggests that the two water molecules are *trans* to each other. The bands for υ(C=N) and υ (N=N) appear at 1580—1600 cm^{-1} and 1380-1390 cm^{-1} in Fe (III) complexes. These bands are shifted to lower frequency by 20-30 cm^{-1} compared to free ligand[10] values. This is in support of the π- acidic character of the azoimine group, which receives electron from Fe (III) through π back donation.

Mass Spectra :

The mass spectra of $[Fe\ (im)_4(H_2O)_2]\ (NO_3)_3$ compound is in good agreement of calculated values (Fig. 2). The molecular peak appears at 550 cm^{-1} and base peak appears at 137 cm^{-1}. The base peak is due to $[Fe^{++}H_2O]\ NO_3$ fragment, one more prominent peak appears at 279, which is probably due to $Fe\ (NO_3)_3.2H_2O$ fragment[10].

Thermo gravimetric measurement:

All the compounds of this series are thermally stable to some extent. With rise of temperature ligands are detached[11] slowly one after another, giving Fe_2O_3 as the final product. The thermal decomposition data of these complexes are summarized below.

The TG and DTA curves for the compound $[Fe\ (im)_4(H_2O)_2]\ (NO_3)_3$ are shown in Figure 3. The TG curve for this complex indicates that it is considerably stable up to 140°C following which slow decomposition proceeds. The TG curve shows four bendings at 140°C, 220°C, 320°C and 480°C which correspond to four intermediate decomposition products.

$$[Fe\ (im)_4(H_2O)_2](NO_3)_3 \xrightarrow{140\ C} Fe\ (im)_4 + 2\ H_2O + NO_2 + O_2$$

$$Fe\ (im)_4 \xrightarrow{220\ C} Fe\ (im)_3 + im$$

$$Fe\ (im)_3 \xrightarrow{320\ C} Fe\ (im) + 2\ im$$

$$Fe\ (im) \xrightarrow{420\ C} Fe_2O_3 + im$$

The DTA curve of the complex proceeds with three exothermic peaks at 140°C, 220°C and 480°C corresponding to loss of nitrate ion, water molecule and imidazole molecule. The curve shows only one endothermic peak at 320°C corresponding to the loss of two imidazole molecules.

On the basis of the above experimental findings, the three dimensional molecular models of the complexes with pyridine and piperazine ligands are illustrated in the diagram given below (Fig. 4 and Fig. 5).

Table 1. Analytical Data and Other Physical Properties of $[FeL_4(H_2O)_2](NO_3)_3]$
% Found / (calculated)

Sl.	Compound	Mol Wt	Iron	Carbon	Carbon	Nitrogen	Ω	M.P/^{O}C
1	$[Fe(im)_4(H_2O)_2](NO_3)_3$ $FeC_{12}H_{18}N_{11}O_{11}$	550	10.22 (10.18)	26.22 (26.18)	26.22 (26.18)	28.01 (27.99)	32.35	212
2	$[Fe(py)_4(H_2O)_2](NO_3)_3$ $FeC_{20}H_{24}N_7O_{11}$	594	9.45 (9.42)	40.47 (40.41)	40.47 (40.41)	16.51 (16.49)	28.12	193
3	$[Fe(pi)_4(H_2O)_2](NO_3)_3$ $FeC_{20}H_{48}N_7O_{11}$	618	618.5 (618)	38.82 (38.83)	38.82 (38.83)	15.84 (15.85)	35.14	205
4	$[Fe(pip)_4(H_2O)_2](NO_3)_3$ $FeC_{16}H_{44}N_{11}O_{11}$	622	621.9 (622)	30.90 (30.86)	30.90 (30.86)	24.61 (24.75)	34.85	211
5	$[Fe(ind)_4(H_2O)_2](NO_3)_3$ $FeC_{32}H_{32}N_7O_{11}$	746	746.9 (746)	51.42 (51.47)	51.42 (51.47)	13.21 (13.13)	31.65	197
6	$[Fe(bm)_4(H_2O)_2](NO_3)_3$ $FeC_{28}H_{28}N_7O_{11}$	750	750 (750)	44.92 (44.79)	44.92 (44.79)	27.98 (27.99)	29.15	177
7	$[Fe(btz)_4(H_2O)_2](NO_3)_3$ $FeC_{28}H_{24}N_{15}O_{11}$	754	753.8 (754)	44.52 (44.56)	44.52 (44.56)	27.75 (27.85)	30.25	185
8	$[Fe(tri)_4(H_2O)_2](NO_3)_3$ $FeC_8H_{16}N_{15}O_{11}$	554	554.2 (554)	17.27 (17.32)	17.27 (17.32)	37.92 (37.9)	27.65	219
9	$[Fe(qui)_4(H_2O)_2](NO_3)_3$ $FeC_{36}H_{32}N_7O_{11}$	794	794.6 (794)	54.38 (54.4)	54.38 (54.4)	12.34 (12.34)	35.15	215
10	$[Fe(iqui)_4(H_2O)_2](NO_3)_3$ $FeC_{36}H_{32}N_7O_{11}$	794	794.4 (794)	54.42 (54.4)	54.42 (54.4)	12.32 (12.34)	34.95	214
11	$[Fe(car)_4(H_2O)_2](NO_3)_3$ $FeC_{48}H_{40}N_4O_{11}$	946	946.3 (946)	57.09 (57.08)	57.09 (57.08)	10.32 (10.35)	29.35	222

Im = imidazole , Py = pyridine, pi = piperidine, pip = piperazine,
ind = indole, bm = benzimidazole, btz = benzotriazole, tri = trizole
qui = quinoline, i-qui = iso-quinoline, car = carbazole,
Calculated values in parenthesis, conductance values in
ohm^{-1} cm^2mol^{-1} at room temperature

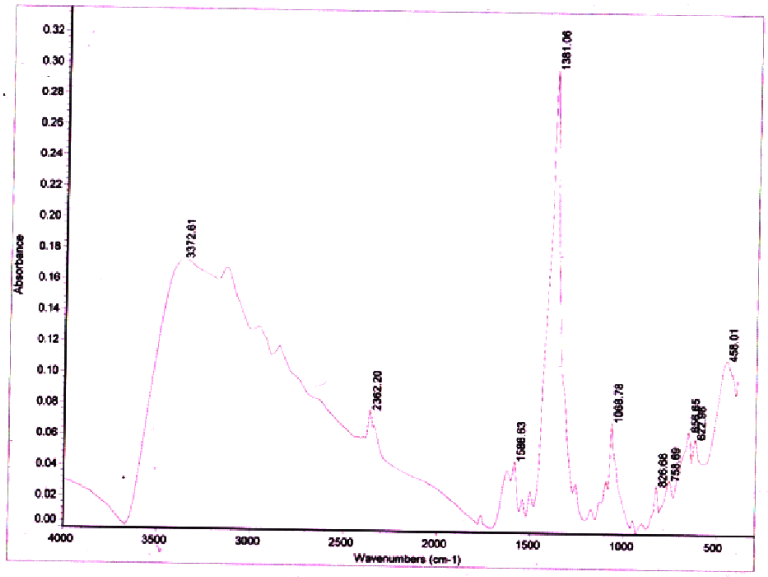


Fig. 1. IR Spectrum of $[Fe\ (im)_4(H_2O)_2](NO_3)_3$; im= imidazole

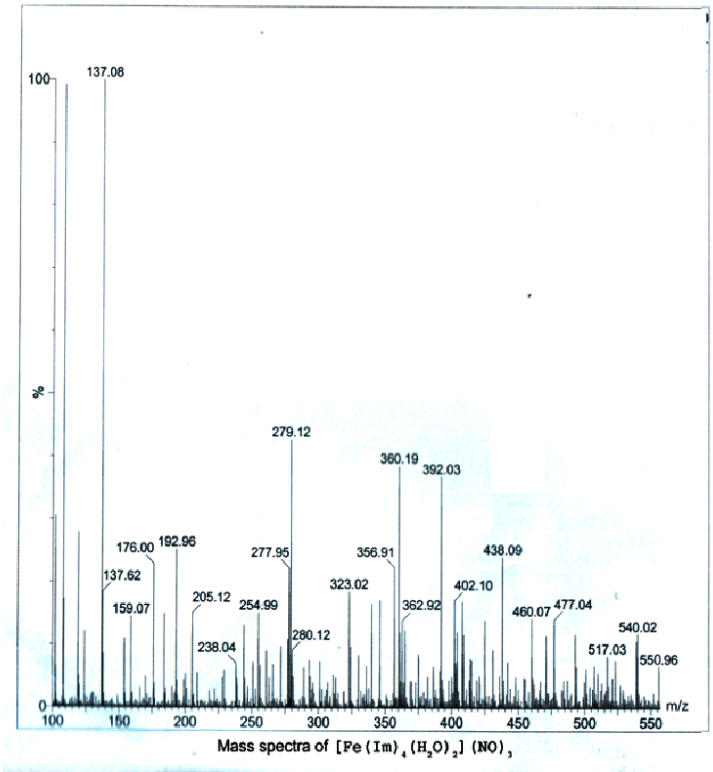
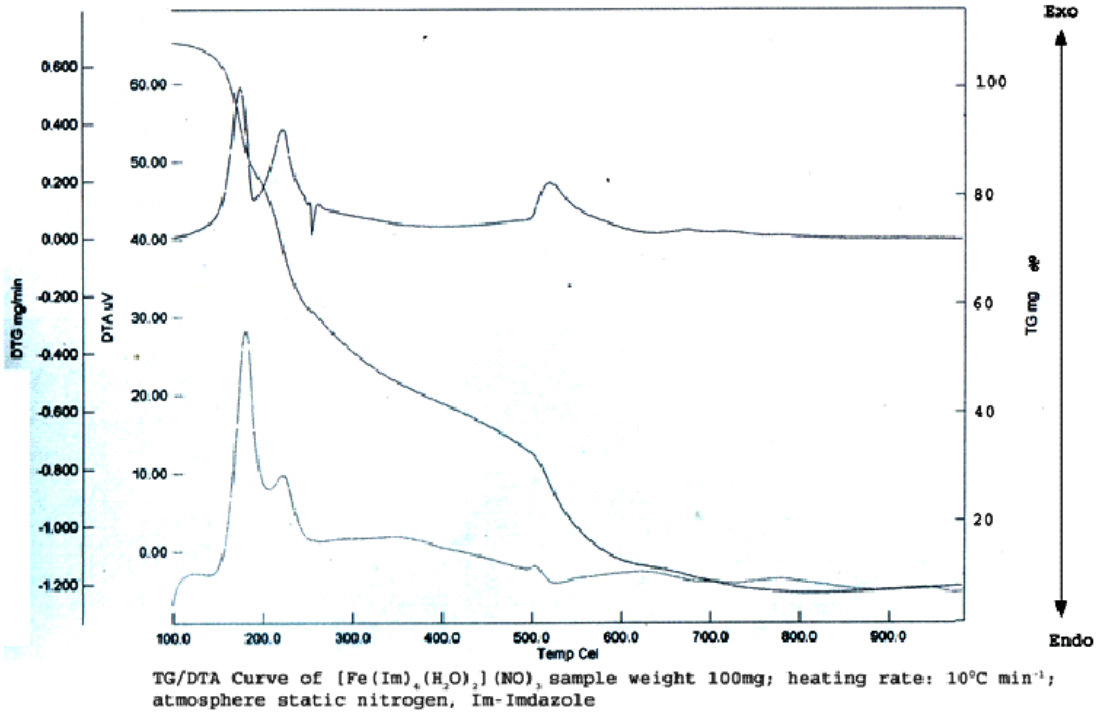


Fig. 2. Mass spectra of $[Fe\ (im)_4(H_2O)_2](NO_3)_3$; Im = imidazole



TG/DTA Curve of $[Fe(Im)_4(H_2O)_2](NO_3)_3$ sample weight 100mg; heating rate: 10°C min^{-1}; atmosphere static nitrogen, Im-Imdazole

Fig. 3. TG/DTA Curve of $[Fe\ (Im)_4(H_2O)_2]\ (NO_3)_3$

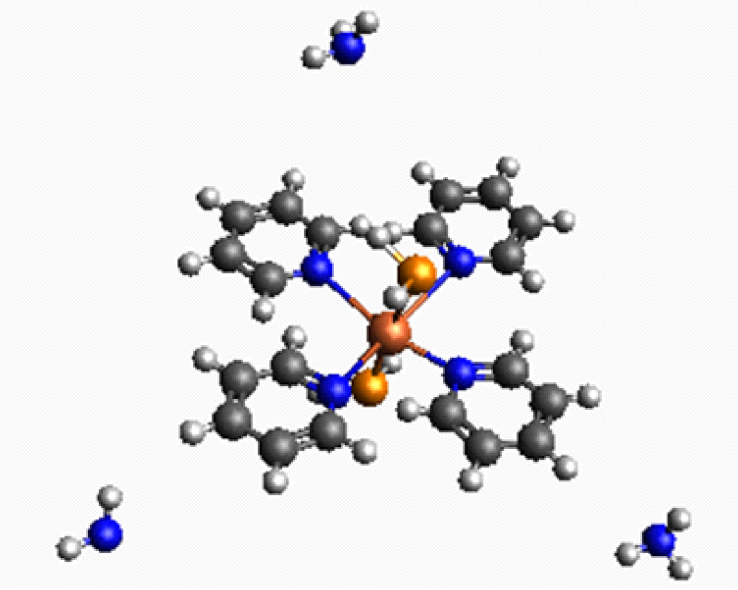


Fig. 4. $[Fe\ (py)_4(H_2O)_2](NO_3)_3$; py=pyridine

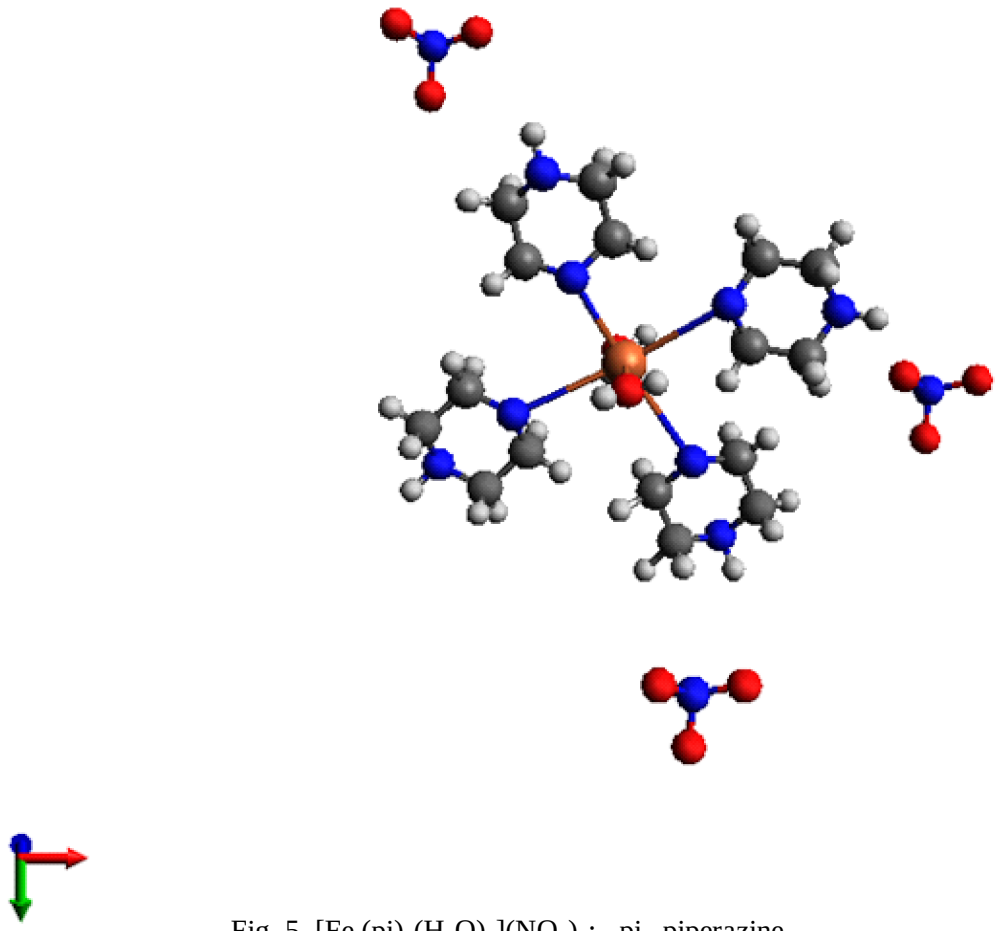


Fig. 5. $[Fe\ (pi)_4(H_2O)_2](NO_3)_3$; pi = piperazine

Acknowledgements

The authors thank the authorities of the central research facility (CRF) IIT, Kharagpur for UV, IR Spectra and for thermo-gravimetric analysis. Thanks are due to the IICB, Kolkata for providing mass spectra. One of us (S.C.Nayak) is thankful to the university grants commission (UGC), Kolkata unit for financial support under a minor research project.

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