

Synthesis and Mossbauer spectroscopy of macrocyclic complexes of iron(III)

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Abstract. The article deals with a fresh series of the complexes of the type: [Fe(III)(TML)Cl]Cl₂; where TML is a tetra-dentate macrocyclic ligand; has been synthesized by condensation of o-phenylenediamine, diethyl malonate and diazonium ion in the ethanolic medium, through refluxing with FeCl₃. The synthesized metal complexes were characterized by Mossbauer spectroscopy. Mossbauer measurements were carried out using standard PC-based spectrometer equipped with Weissel velocity drive operating in the constant acceleration mode. Mossbauer study interprets paramagnetic nature of complexes. Mossbauer measurement of complex 1 and 2 has been taken to find out the value of isomer shift and quadrupole splitting and oxidation state after complexation.

1. Introduction

In all metals, iron has a relevant position due to its indispensability in life, since it takes part in processes such as oxygen transport and electron transfer and DNA syntheses. Iron metal complexes possess a variety of structures and are of current interest not only in bioinorganic chemistry [1] but also in material science, since they can find technological applications due to their promising magnetic, electronic and catalytic properties [2, 3], that are related to their structural characterization. It has been reported that metal complexation alters the various physiological properties especially the cytotoxic and antitumor activities of many naturally occurring compounds [4] It also shows antifungal potential against *Alternaria alternate*, *Fusarium oxysporum* and *Myrothecium roridum* by inhibiting spore germination [5]. It is also demonstrated that the coordination of metal ions with bioactive ligands can actually improve the pharmaceutical activity of drugs [6, 7].



2. Experimental Detail:

2.1. Chemicals and Solvent.

All chemicals (sodium nitrite, sodium acetate, O-phenylenediamine, diethyl malonate, ferric chloride and anilines) are of Loba Chemie and solvents (absolute ethyl alcohol) are of Loba Chemie all are laboratory reagent grades and were used without further purifications.

2.2. Experimental analysis.

Mössbauer spectroscopy is a spectroscopic technique based on the Mössbauer effect which was discovered by Rudolf Mössbauer in 1957, observed in recoil-free, resonant absorption and emission of gamma rays in solids. Mössbauer spectroscopy probes tiny changes in the energy levels of an atomic nucleus in response to its environment. Typically, three types of nuclear interaction may be observed: an isomer shift, quadrupole splitting and magnetic splitting. Due to high energy and extremely narrow line widths of gamma rays, Mössbauer spectroscopy is one of the most sensitive techniques in terms of energy resolution, capable of detecting change in just a few parts per 10^{11} . In its most common form, Mössbauer absorption spectroscopy a solid sample is exposed to a beam of gamma rays and detector measures the intensity of the beam transmitted through the sample. The atom in the source emitting the gamma rays must be of the same isotope as the atoms in the sample absorbing them. In the resulting spectra, gamma ray intensity is plotted as a function of the source velocity. At velocities corresponding to the resonant energy levels of the sample, a fraction of the gamma rays is absorbed, resulting in a drop in the measured intensity and a corresponding dip in the spectrum. The number, position, and intensity of the dips (also called peaks; dips in transmitted intensity are peaks in absorbance) provide information about the chemical environment of the absorbing nuclei and can be used to characterize the sample. Mössbauer spectroscopy is a versatile technique that can be used to provide information in many areas of science such as physics, chemistry, biology and Metallurgy. It can give very precise information about chemical, structural and magnetic properties of a material [8]. Mössbauer measurements of iron complex were carried out using standard PC-based spectrometer equipped with Weissel velocity drive operating in the constant acceleration mode. The data was fitted with the NORMOS-SITE program, and the obtained parameters are with respect to natural iron.

2.3.1. Synthesis of complex 1.

The ligand was prepared by diazotization process. A freshly prepared diazonium ion from sodium nitrite, 2-Chloroaniline and hydrochloric acid in equimolar proportion, is added drop wise with diethyl malonate in continuous stirring. Keep remember that the temperature of reaction should not be more than 10^0C other wise diazonium salt will be decomposed. After keeping the mixture in refrigerator for one day, precipitated it and dry in air for few hours, TML1 is formed. Place O-phenylenediamine, TML 1 and Ferric chloride (equimolar proportion) in round bottom flask containing 25 ml of ethyl alcohol. Reflux it for 2-3 hours (Figure 1). Remove the flask from the heat source and allow for cooling until just warm to the touch. Separate the precipitate from the solution and allow it for drying in air for 1 hour. Complex 1 is formed.

2.3.2. Synthesis of complex 2.

The ligand was prepared by same analogy as we discussed above only difference is that 2-Chloroaniline is replaced by O-Toluidine. Now place O-phenylenediamine, TML 2 and Ferric chloride (equimolar proportion) in round bottom flask containing 25 ml of ethyl alcohol. Place this flask for reflux for 2-3 hours (Figure 1). Remove the flask from the heat source and allow for cooling until just

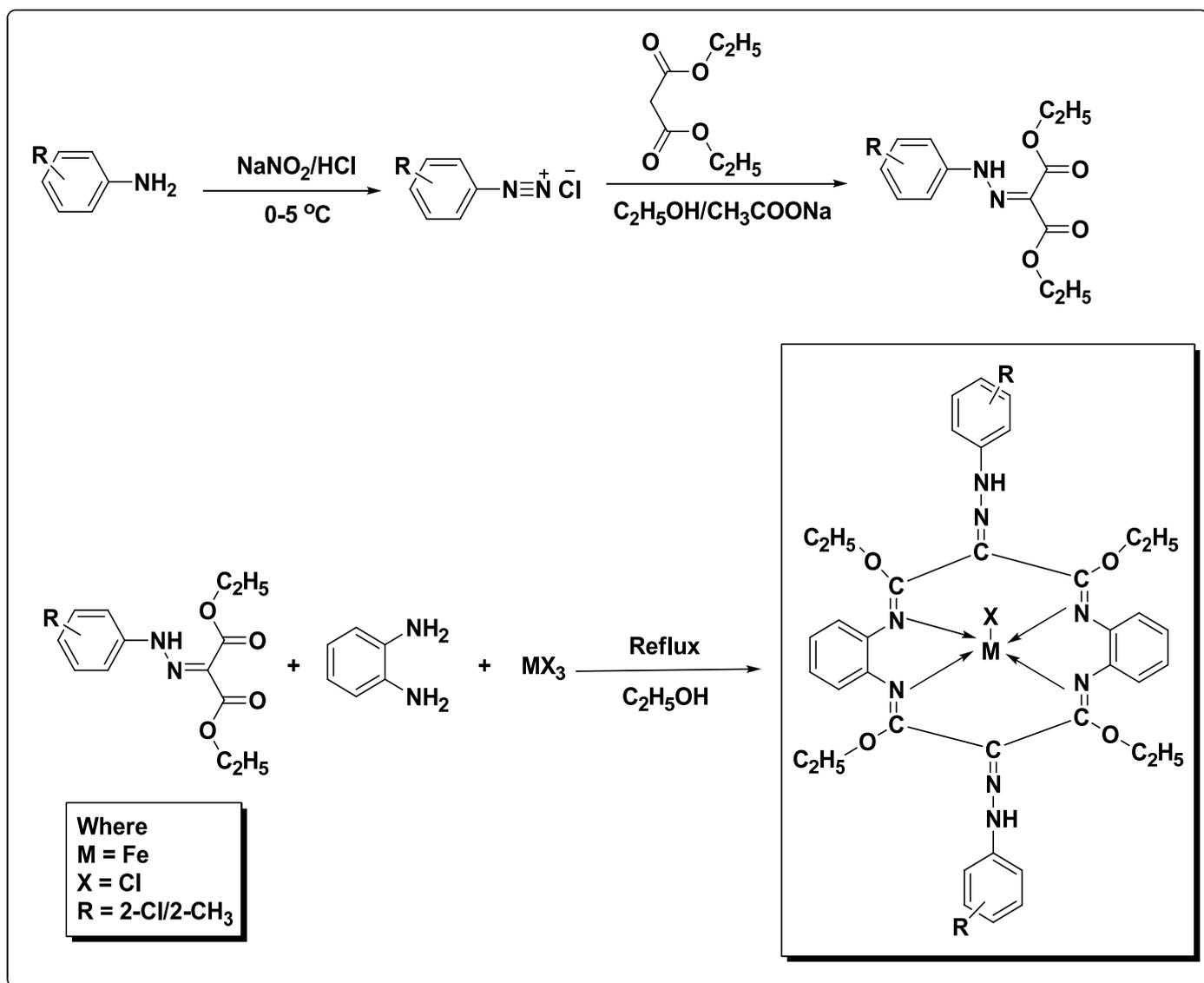


Figure 1. Schematic overview of synthetic strategy for ligand and metal complexes; R=Cl & CH₃ for complex 1 and complex 2 respectively.

warm to the touch. Separate the precipitate from the solution and allow it for drying in air for 1 hour. Complex 2 is formed.

3. Result and Discussions.

The Mossbauer effect provides a powerful probe to chemical state and the environment of iron atoms. The Mossbauer spectrum for iron complexes at room temperature is shown in Figure 2. The various Mössbauer parameters obtained from the computations of spectral data are presented in Table 1. These spectra were least-square fit with a superposition of two doublets with Lorentzian line shape. The fitted parameters are given in the table 1. According to the collected data presented in table, least square fitting and Lorentzian line shape were used for the spectral plot, which indicates two doublets corresponding to low and high spin states. Values for the isomer shift yield information on the degree of covalency in the metal ligand bond. Fe²⁺ has higher isomer shift values than Fe³⁺ because a decrease

in number of d electron with increasing iron oxidation state increases s electron density at the nucleus. This in turn, tends to decrease the value of isomer shift for Fe^{3+} state of iron [9]. The spectra of quadrupole splitting at room temperature suggest that the presence of electric field gradient at the metal ion is due to the presence of ligand around the ion. This may be due to the distorted octahedral geometry. According to collected data the isomer shift of complex 1 is 0.32 ± 0.020 and 0.46 ± 0.05 mm/s and for complex 2 has isomer shift of 0.22 ± 0.06 and 0.37 ± 0.03 mm/s and quadrupole splitting of complex 1 is 0.50 ± 0.05 and 1.15 ± 0.16 mm/s and for complex 2 is 0.43 and 0.71 mm/s.

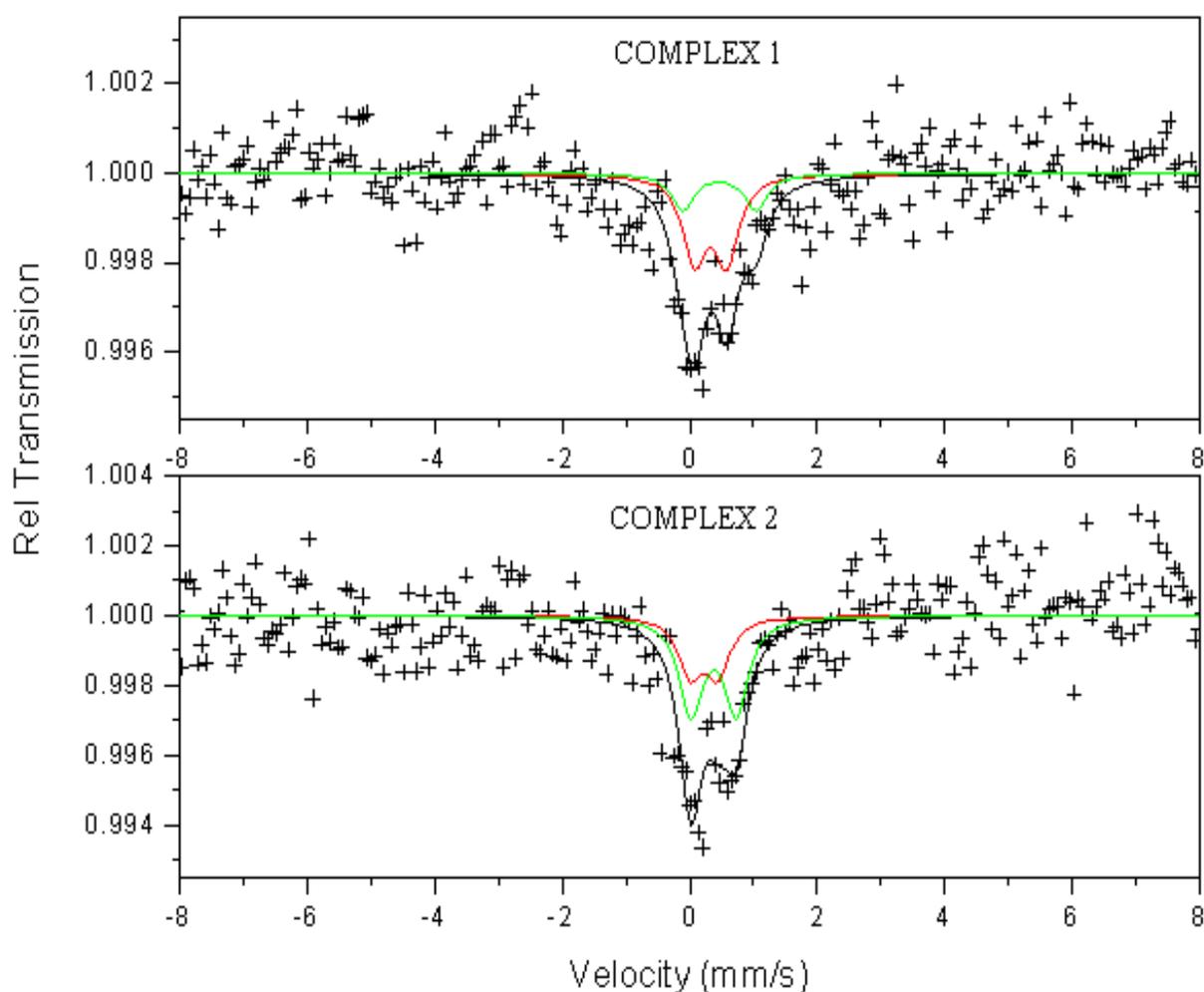


Figure 2. Mössbauer spectra of Complex 1 and Complex 2.

Table1. Parameters from Mossbauer spectra of iron complexes

Sample	Isomer shift (mm/s)	FWHM (mm/s)	Quadrupole splitting (mm/s)	Area
Complex 1	0.32 ± 0.02	0.45	0.50 ± 0.05	69.7
	0.46 ± 0.05	0.45	1.15 ± 0.16	30.3
Complex 2	0.22 ± 0.06	0.45	0.43	36.6
	0.37 ± 0.03	0.45	0.71	63.4

4. Conclusion

Complexation of Fe with tetra-dentate macrocyclic ligand has been successfully done via chemical route method. Mössbauer fitting reveals the value of isomer shift and quadrupole splitting of the complexes. It exhibits that the complexes possess distorted octahedral geometry.

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References

- [1] Tanase S, Bouwman E, Long G J, Shahin A M, Gelder R de, Mills A M, Spek L A, Reedijk J 2005 *Polyhedron* **24** 41 b) Xu X, Persson H L, Richardson D R 2005 *Mol. Pharmacol.* **68** 261
- [2] Chaudhuri P, 2003 *Coord. Chem. Rev.* **243** 143; Soler M, Wernsdorfer W, Folting K, Pink M, Christou G 2004 *J. Am. Chem. Soc.* **126** 2156.
- [3] Be´nisvy L, Chottard J - C, Marrot J, Li Y 2005 *Eur. J. Inorg. Chem.* **999**.
- [4] Thompson K H, Böhmerle K, Polishchuk E, Martins C, Toleikis P, Tse J, Yuen V, Mcneill J H and Orvig C 2004 *Journal of Inorganic Biochemistry* **98** 2063
- [5] Hothi H S, Makkar A, Sharma J R & Manrao M R 2006 *Eur J Med Chem* **41** 253
- [6] Zhang S, Tu C, and Wang X 2004 *European Journal of Chemistry* **98** 4028
- [7] Dutta S, Murugkar A, Gandhe N, and Padhye S 2001 *Metal-Based Drugs* **8** 183
- [8] Mishra A, Mishra N, Malviya P, Awate R 2014 *International Journal of Scientific Research in Physics and Applied Sciences* **2** 2348
- [9] Mishra A, Sharma R, & Shrivastava B D 2011 *Indian Journal of pure & Applied physics* **49** 740