

Structural and Thermodynamic Studies of Aqueous Chelating Agent and its Metal Complexes

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ABSTRACT

The Schiff base ligand diethylene triamine Penta acetic acid was synthesized from choro acetic acid and diethylene triamine tetra acetic acid. Fe (III) complexes of the Schiff base were prepared from Fe(III) salts in an ethanolic medium. The ligand and Fe (III) complexes were characterized by elemental analysis, molar conductance measurements, magnetic susceptibility, IR and electronic absorption spectra. The Fe(III) complexes were electrolytic nature due to higher values of their molar conductivities. The Schiff base behaves as trianionic tridentate ligand and coordinating through amino nitrogen and oxygen atom of -COOH group. The analytical and spectral data show the formula of metal complexes have been found to be $[Fe(L)(B)_3]$ where L = ligand, B = water, ammonia, quinoline, phenyl isocyanide and α -picoline. Thus, on the basis of elemental analysis and spectral data all the Fe (III) complexes have been found to be octahedral in geometry.

Keywords: -Diethylene triamine tetra acetic acid, Chloro acetic acid, Schiff base, Metal complexes.

1. INTRODUCTION

Schiff bases are most important class of organic ligands and they are synthesized by condensation between primary amine and carbonyl compounds. Schiff bases and their metal complexes have important applications in biological, pharmaceuticals, catalysis, dyes, polymers and analytical chemistry. Coordination chemistry employs Schiff base have achieved prime importance in this era. There numerous ligands containing nitrogen, oxygen and sulphur donor atoms, oxygen donor Schiff base ligands are widely used in pharmaceuticals. Aliphatic and aromatic carbonyl compounds are condensation with primary amine to form Schiff base ligands, but aromatic carbonyl compounds form stable Schiff base complexes than aliphatic carbonyl compounds due to effective conjugation. The azomethine group present in the Schiff bases, which is responsible for their reactivity, stability and biological activity. The biological activity of Schiff base enhances after complexation with metal. We report here the structural and thermodynamic studies of Schiff base ligand diethylene triamine Penta acetic acid and its iron (III) complexes.

2. EXPERIMENTAL

2.1 Chemicals: - All the chemicals used in the present work obtained from BDH/Aldrich and they were used without further purification. They are chloro acetic acid, ethylene diamine, ethylene dibromide, ammonium hydroxide, ethanol, iron salt, picoline, pyridine, phenyl isocyanide, DMSO and DMF.

2.2 Physical measurements: - The elemental analysis of carbon, hydrogen and nitrogen were determined by using Perkin-Elmer elemental analyzer. The infrared spectra of Schiff base ligand and its complexes were recorded on Perkin-Elmer 577 spectrophotometer using KBr disc. The electronic absorption spectra of the iron complexes were recorded by using Schimadzu UV-1601 using DMF as solvent. The molar conductivities of the complexes were measured by digital molar conductivity at room temperature.

2.3 Synthesis of Schiff base ligand (L): - The Schiff base ligand diethylene triamine Penta acetic acid was prepared by adding 0.01 mol of diethylene triamine tetra acetic acid in 25 ml ethanol and 0.01 mol of chloro acetic acid in 25 ml ethanol. The reaction mixture was stirring for 1 h and cooled. A coloured precipitate was obtained, which was filtered, washed with ethanol and dried over anhydrous CaCl_2 .

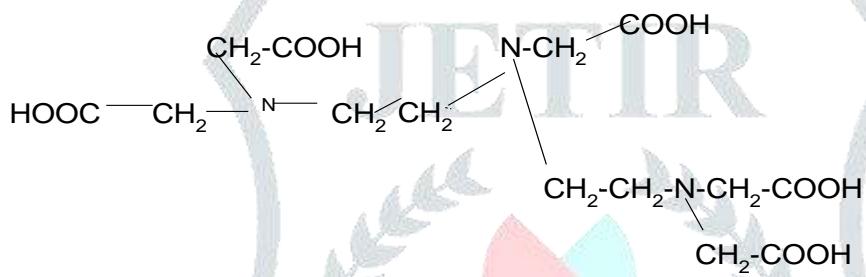


Fig1. Structure of Schiff base ligand

2.4 Synthesis of complexes: -

2.4(a) Synthesis of $[Fe(C_{14}H_{20}N_3O_{10})(H_2O)_3]$: - 0.4g (0.001 mol) of the ligand was completely dissolved in ethanol. 0.28 g (0.001 mol) of Fe (III) chloride hexahydrate was completely dissolved in water. Both the solutions were mixed together and shaken well. The resulting solution was heated on water bath under reflux with regular shaking. After heating for 3 h, a brownish solid was obtained in the solution. The solid was separated by filtration and washed with ethanol, the solid was crystallized with methanol.

2.4(b) Synthesis of $[Fe(C_{14}H_{20}N_3O_{10})(NH_3)_3]$: - 0.4g (0.001 mol) of the ligand was completely dissolved in ethanol. 0.28 g (0.001 mol) of Fe (III) chloride hexahydrate was completely dissolved in water. Both the solutions were mixed together and shaken well, 3-4 drops of ammonium hydroxide were added to the resulting solution. The resulting solution was heated on water bath under reflux with regular shaking. After heating for 3 h, a brown solid was obtained in the solution. The solid was separated by filtration and washed with ethanol, the solid was crystallized with methanol.

2.4(c) Synthesis of $[Fe(C_{14}H_{20}N_3O_{10})(C_9H_7N)_3]$: - 0.4g (0.001 mol) of the ligand was completely dissolved in ethanol. 0.28 g (0.001 mol) of Fe (III) chloride hexahydrate was completely dissolved in water. Both the solutions were mixed together and shaken well, 3-4 drops of quinoline was added to the resulting solution. The resulting solution was heated on water bath under reflux with regular shaking. After heating for 3 h, a faint brown solid was obtained in the solution. The solid was separated by filtration and washed with ethanol, the solid was crystallized with methanol.

2.4(d) **Synthesis of [Fe (C₁₄H₂₀N₃O₁₀) (C₆H₅NC)₃]:** - 0.4g (0.001 mol) of the ligand was completely dissolved in ethanol. 0.28 g (0.001 mol) of Fe (III) chloride hexahydrate was completely dissolved in water. Both the solutions were mixed together and shaken well, 3-4 drops of phenyl isocyanide was added to the resulting solution. The resulting solution was heated on water bath under reflux with regular shaking. After heating for 3 h, a light brown solid was obtained in the solution. The solid was separated by filtration and washed with ethanol, the solid was crystallized with methanol.

2.4(e) **Synthesis of [Fe (C₁₄H₂₀N₃O₁₀) (C₅H₅N)₃]:** - 0.4g (0.001 mol) of the ligand was completely dissolved in ethanol. 0.28 g (0.001 mol) of Fe (III) chloride hexahydrate was completely dissolved in water. Both the solutions were mixed together and shaken well, 3-4 drops of pyridine was added to the resulting solution. The resulting solution was heated on water bath under reflux with regular shaking. After heating for 3 h, a brown solid was obtained in the solution. The solid was separated by filtration and washed with ethanol, the solid was crystallized with methanol.

2.4(f) **Synthesis of [Fe (C₁₄H₂₀N₃O₁₀) (C₅H₄NCH₃)₃]:** - 0.4g (0.001 mol) of the ligand was completely dissolved in ethanol. 0.28 g (0.001 mol) of Fe (III) chloride hexahydrate was completely dissolved in water. Both the solutions were mixed together and shaken well, 3-4 drops of α picoline was added to the resulting solution. The resulting solution was heated on water bath under reflux with regular shaking. After heating for 3 h, a brown solid was obtained in the solution. The solid was separated by filtration and washed with ethanol, the solid was crystallized with methanol.

3. RESULTS AND DISCUSSION

The analytical data of the metal complexes are given in Table-1. The iron (III) complexes are coloured and stable in air. The analytical data show the general formula of Fe (III) complexes have been found to be [Fe (L)(B)₃] where L = ligand, B =water, ammonia, pyridine, phenyl isocyanide, quinoline and α -picoline. The higher molar conductivities of iron complexes in DMSO solution indicate their electrolytic nature.

3.1 FTIR spectra: - The ligand behaves as tripodal molecule. After the complex formation, there are appreciable change in the frequencies of – OH group while the bond at 1720 cm⁻¹ due to ν (C=O)vibrations remains the same in the complexes. A sharp band obtained at 2530 cm⁻¹ in free ligand molecule due to H-bonded OH group disappearance in the all complexes, which indicating the deprotonation of – OH group of carboxylic acid. A sharp and medium band obtained in the ligand molecule at 1520 cm⁻¹ due to ν (C=O) vibration has been increased by 30-50 cm⁻¹ indication the deportation of -OH group. A medium and sharp band obtained at 1280 cm⁻¹ due to ν (C=N) vibration has been decreased by 20-25 cm⁻¹ in the complexes which indicate the participation of imino nitrogen in bond formation with iron ion. A sharp and medium band obtained in the complexes at 2930 cm⁻¹ and 1560 cm⁻¹ due to the vibration of ν (C-H) and carboxylate anion stretching also indicates the deprotonation of carboxylic acid group. The Schiff base ligand behaves as tri-anionic tridentate and forming the complexes with Fe (III) ion in presence of various bases containing nitrogen and oxygen atom as their donor sites. Three inner carboxylic acid groups after deprotonation take part in complex formation with Fe (III) ion. Even after complex formation there are a band obtained 2785 cm⁻¹ in the complexes due to H- bonded - OH group of carboxylic acid. The participation of amino nitrogen and oxygen atom of -COOH groups are further confirmed by appearance of medium and sharp bands at 415 and 460 cm⁻¹ due to ν (M-N) and ν (M-O) vibrations respectively.

Table – 1. Analytical data of complexes

Compounds	Elemental analysis found (calc) %			
	Colour	C	H	N
[Fe (C ₁₄ H ₂₀ N ₃ O ₁₀) (H ₂ O) ₃]	Brownish	33.36(33.60)	5.22(5.20)	8.44(8.40)
[Fe (C ₁₄ H ₂₀ N ₃ O ₁₀) (NH ₃) ₃]	Brown	33.52(33.80)	5.80(5.83)	16.92(16.90)
[Fe (C ₁₄ H ₂₀ N ₃ O ₁₀) (C ₉ H ₇ N) ₃]	Faint brown	58.80(59.03)	4.90(4.92)	10.12(10.08)
[Fe (C ₁₄ H ₂₀ N ₃ O ₁₀) (C ₆ H ₅ NC) ₃]	Light brown	58.74(59.06)	4.90(4.92)	10.12(10.08)
[Fe (C ₁₄ H ₂₀ N ₃ O ₁₀) (C ₅ H ₅ N) ₃]	Brown	50.48(50.86)	5.10(5.12)	12.30(12.27)
[Fe(C ₁₄ H ₂₀ N ₃ O ₁₀) (C ₅ H ₄ NCH ₃) ₃]	Brown	52.80(52.96)	5.67(5.65)	11.60(11.57)

3.2 Electronic spectra: - The ground term for Fe (III) containing d⁵ system is ^6S. The remaining excited state terms are ^4G, ^4P, ^4D, ^4F The extinction coefficient is very low as all the five d- orbitals are singly occupied, the transition of the electron most result in the spin pairing in one of the five orbitals. Thus, the d-d transition is spin forbidden. The transition of one electron from t_{2g} to eg is LaPorte forbidden, in case of d⁵ system of octahedral complexes are totally forbidden. The absorption spectrum has a lot of bands. This obvious from the energy level diagram which has many states lying close together to give closely spaced multiple absorption bands.

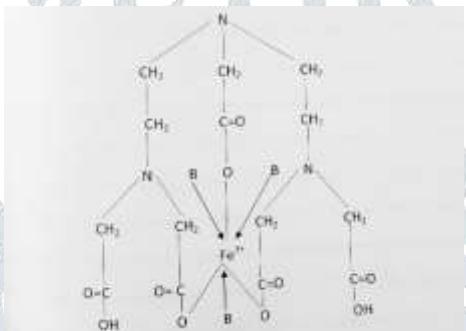


Fig 2. Proposed structure of Fe(III) complexes.

4. CONCLUSION

The Schiff base ligand diethylene triamine Penta acetic acid was synthesized by condensation of diethylene triamine tetra acetic acid and chloro acetic acid. The ligand and Fe (III) complexes were characterized by micro elemental analysis and spectroscopic techniques. The metal complexes are electrolytic nature due to higher values of molar conductivity. The Schiff base behaves as tri anionic and tridentate ligand. Thus, on the basis of elemental analysis, magnetic susceptibility and spectral data of the Fe (III) complexes suggest octahedral geometry.

REFERENCES

1. Reddy, K.R, Reddy, K.L, and Reddy, K.A. Ind. J. Chem. 1989, 5, 28A, 961.
2. Khulbe,R.C, Bhoon, Y.K and Singh,R.P. J. Ind. Chem. Soc. 1981, 58, 840.
3. Patel,M.N and Patel, V.J. Ind. J. Chem. 1989, 28A, 428.
4. Sandhu, S.S and Sharma Sanjay. Ind. J. Chem. 1989, 28A, 574.
5. Geary, W.J. Coord. Chem. Rev. 1971, 7, 81.
6. Raman,M and Ali, M.A. Ind. J. Chem. 1989, 28A, 453.

7. Bertrand, J.A and Eller, P.G. Inorg. Chem, 1974,13,1928.
8. Hodgson, D.J. Prog. Inorg. Chem. 1975,19,173.
9. Sonn, E and Harris, C.M. Coord. Chem. Rev. 1958,11,371.
10. Zhao Guoliang. Asian. J.Chem. 2008, 20(4),2769-2773.
11. Rai B.K and Sharma K.K. Oriental. J.Chem.2011,27(1),143-146.
12. Tiwari Vivek and Singhai Rashmi. Asian.J.Chem. 2003, 15(1), 435-438.

