Volume-04
Issue-05
May-2019

ISSN: 2455-3085 (Online)
RESEARCH REVIEW International Journal of Multidisciplinary
www.rrjournals.com[UGC Listed Journal]

Synthetic and Structural Studies of Iron (II) Complexes with Schiff's bases Derived from Amino Acids and Heterocyclic Aldehydes

[1]Sonal Sengar, [2]S.K. Singh and [3]M. K. Gupta

[1]Research Scholar, School of Applied Sciences, Suresh Gyan Vihar University, Jaipur, Rajasthan, India.
[2]Associate Professor, School of Applied Sciences, Suresh Gyan Vihar University, Jaipur, Rajasthan, India.
[3]Associate Professor, Department of Chemistry, LBS (P.G.) College, Jaipur, Rajasthan, India

ARTICLE DETAILS

Article History
Published Online: 25 May 2019

Keywords
Synthetic, Heterocyclic, Amino Acids.

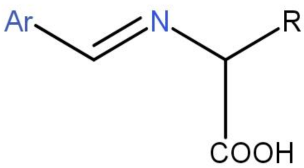
ABSTRACT

Reaction of iron (II) chloride with Schiff's's bases derived by condensation of 2-hydroxy-1-naphthaldehyde and salicylaldehyde with glycine, alanine, valine, isoluciene and tryptophan in 1:1 molar ratio gave a new series of Iron (II) complexes. The coordination behavior of Schiff's bases through phenolic and acidic oxygen and azomethine nitrogen towards iron atom has been investigated by elemental analysis, conductance measurements, molecular weight determinations, IR, UV and ^{1}H NMR spectral studies

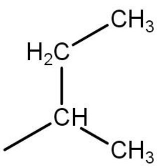
1. Introduction

The Schiff's bases derived from the condensation of amino acids with the carbonyl compounds constitute another series of ligand with ON donor system and their metal complexes have been studied with great interest[1-6].

It was therefore, considered of interest to synthesize Fe(II) derivatives of Schiff's bases derived by the condensation of 2-hydroxy-1-naphthaldehyde or salicylaldehyde with amino acids. In this paper, we are communicating the results of these studies. The structure of the Schiff's bases are shown in fig 1

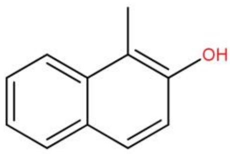


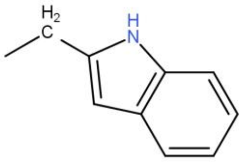
R= H, $-CH_3$, $-CH(CH_3)_2$,



,

Ar=





2. Results and Discussion

Reaction of iron (II) chloride with the neutral ligands and pyridine in 1:1:1 molar ratio may be represented as follows

$$FeCl_2 + HO{\sim}N{\sim}OH + C_5H_5N \longrightarrow Fe(O{\sim}N{\sim}O).C_5H_5N + 2HCl$$

Where HO~N~OH represent the bi-functional tridentate Schiff's base. The resulting complexes are coloured solids (Table 1), which are soluble in DMSO and DMF. These are however susceptible to moistureand aerial oxidation. Low values of molar conductance (5-20 ohm^{-1}cm^{-1}mol^{-1}) indicate that these complexes behave like as an electrolyte. The Rast Camphor Method indicates their monomeric nature and also determines the molecular weight of the complexes.

Table 1: Synthesis and characteristics of Iron(II) complexes

Sr. No.	Products (Colour& State)	Melting Point (°C)	Elemental analysis (%) Found (calcd)					Mol. Wt. Found (Calc.)
			Fe	C	H	N	O	
01	($C_{18}H_{14}N_2O_3Fe$) Light Yellow Solid (R=H, Ar=N)	140d	15.39 (15.42)	59.91 (59.97)	3.69 (3.90)	7.12 (7.74)	13.05 (13.25)	361.59 (362.16)
02	($C_{19}H_{16}N_2O_3Fe$) Greenish yellow solid (R=CH_3, Ar=N)	210	14.14 (14.84)	60.18 (60.66)	4.05 (4.29)	7.18 (7.45)	12.56 (12.76)	376.01 (376.19)
03	($C_{21}H_{20}N_2O_3Fe$) Black Solid (R=$CH(CH_3)_2$, Ar=N)	95d	13.16 (13.81)	62.13 (62.39)	4.45 (4.99)	6.23 (6.93)	11.56 (11.87)	404.05 1(404.24)
04	($C_{22}H_{22}N_2O_3Fe$) Dark Brown Solid (R=$CH(CH_3)C_2H_5$, Ar=N)	90d	13.05 (13.35)	62.85 (63.17)	5.05 (5.30)	6.34 (6.70)	11.12 (11.48)	418.08 (418.27)
05	($C_{27}H_{21}N_3O_3Fe$) Yellow Solid R=CH_2-C_8H_6N, Ar=N	270	11.07 (11.37)	65.78 (66.00)	4.03 (4.31)	8.23 (8.55)	8.90 (9.11)	491.06 (491.32)
06	($C_{14}H_{12}N_2O_3Fe$) Black Solid (R=H, Ar=S)	190	17.58 (17.89)	53.34 (53.88)	3.35 (3.88)	8.49 (8.98)	15.08 (15.38)	312.02 (312.10)
07	($C_{15}H_{14}N_2O_3Fe$) Brown Solid (R=CH_3, Ar=S)	145d	17.01 (17.12)	55.12 (55.24)	4.07 (4.33)	8.32 (8.59)	14.46 (14.72)	325.98 (326.13)
08	($C_{17}H_{18}N_2O_3Fe$) Light Brown Solid (R=$CH(CH_3)_2$, Ar=S)	215	15.70 (15.77)	57.55 (57.65)	5.10 (5.12)	7.88 (7.91)	13.45 (13.55)	354.02 (354.18)
09	($C_{18}H_{20}N_2O_3Fe$) Light Pink Solid (R=$CH(CH_3)C_2H_5$, Ar=S)	195	15.10 (15.17)	58.62 (58.71)	5.38 (5.47)	7.55 (7.61)	12.88 (13.04)	368.12 (368.21)
10	($C_{21}H_{19}N_3O_3Fe$) Light Yellow Solid (R=CH_2-C_8H_6N, Ar=S)	220	13.10 (13.38)	60.32 (60.45)	4.23 (4.59)	9.95 (10.07)	11.43 (11.50)	417.12 (417.24)

*Ar = S means salicylaldehyde, Ar=N means 2-hydroxynaphthaldehyde

On comparing the IR spectra of the ligands as well as their correspondingironcomplexes, it can be concluded that the chelate formation takes place through the oxygen and nitrogen of the ligand moieties. In the infrared spectra of the ligands, medium intensity bands appearing in the region,~3300 $cm^{-1}$was assigned to the hydrogen bonded νOH vibrations[7-9], which disappear in the resulting complexes suggesting the possible deprotonation on complexation and the formation of Fe-O bond.

All the ligands display sharp and strong band in the region, 1610-1625 cm^{-1} and which is due to the νC=N stretching frequency in the free ligands[10]. It gets shifted to the lower frequency region (~10 cm^{-1}) in the spectra of complexes. The lowering in the frequency may be attributed to the decrease in the C=N bond order as a result of Fe←N bond formation. Further new bands in the region, 600-400 cm^{-1} in the Iron complexes may be attributed to ν(Fe-O) and ν(Fe←N) vibrations[11].

A strong band at ~1280 cm^{-1} in the ligands may be due to the phenolic C-O stretching vibrations. In the resulting complexes, a shift of this band to the higher frequency (~1300 cm^{-1}) indicates the bonding of the ligand through the phenolic oxygen.

In addition, the formation of iron complexes with pyridine, a sharp band at 1600 $cm^{-1}$was observed due to vC=N vibration and other bands at 1140, 1080, 1030, 1010, 800 cm^{-1} are observed due to different vibrational modes of pyridine.

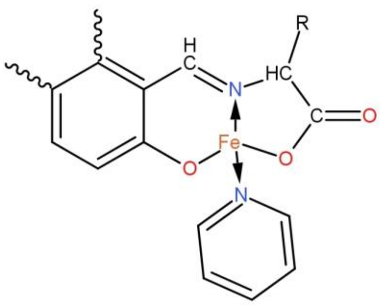
^{1}H NMR Spectra

The proton magnetic resonance of all ligands and their corresponding iron complexes has been recorded in DMSO-d_6 using TMS as internal standard. The spectrum of ligands exhibit -OH proton signal at δ13.10 ppm and the -COOH proton signals at δ11.00 ppm, respectively. These absorptions disappear in the corresponding metal complexes. In the case of the ligand, the proton signal for the azomethine proton signals atδ8.50-ppm shifts downfield in the spectra of the corresponding metal complexes due to the formation of a co-ordinate linkage between the nitrogen and metal atom. The ligand shows a complex multiplet signal in the region at 7.65 to 6.80 ppm for the aromatic protons and it remains in almost the same position [-CH_2, -$CH(CH_3)_2$, -$CH(CH_3)$-CH_2-CH_3 at δ3.2 ppm, δ2.8 ppm and δ1.45-δ3.15 ppm in the metal complexes respectively.

Electronic Spectra

The electronic spectra of ligands and their ironcomplexes have also recorded in DMF. The spectra of ligands show broadband at ~370 and ~350 nm and which can be assigned to n-π* transition of azomethine group. This band shifts in the iron complexes and appears at ~415 and 400 nm respectively indicating the coordination of azomethine nitrogen to iron atom.

On the basis of spectral data and element analysis the following structure can be assigned to these newly synthesized derivatives as shown below:



3. Experimental

The entirechemicals used in this work areof AR grade, the solvents were dried by standard method and all reactions were carried out under an anhydrous and oxygen free atmosphere.

The Schiff's bases were synthesized by the condensation of 2- hydroxyl-1-naphthaldehyde andsalicylaldehyde with amino acids, viz. Glycine, alanine, valine, isoleucine and tryptophan in 1:1 molar ratio using methanol as the reaction medium and were then refluxed for 6h. On cooling, crystals of the Schiff's bases separated out which were washed with methanol. These were dried and recrystallized from acetone.

4. Measurements

Nitrogen was estimated by Kjeldahl's method. The complexes were analyzed as reported earlier[11-1]. The infrared spectra were recorded on a Perkin-Elmer-577 spectrophotometer in the region 400-200 cm^{-1} using KBr disks. A Perkin-Elmer Mode RB-12 spectrometer was used for obtaining the PMR spectra employing DMSO-d_6 as the solvent and TMS as internal standard. Molar conductance measurements were made in anhydrous DMF at 36 ±1°C using a systronics conductivity bridge model 3-5. Molecular weight determinations were carried out by the Rast camphor method.

5. Synthesis of Iron(II) Complexes

The ligand and pyridine with iron (II)chloride were mixed in a 1:1:1 molar ratio in dry methanol as the reaction medium. The contents were refluxed for 6 hours on a fractionating column and the liberated hydrochloric acid was estimated at regular intervals to ascertain the completion of the reaction. The resulting complexes, after being washed with dry cyclohexane, were dried in vacuo. Their physical properties and elemental analysis are given in (Table 1).

Acknowledgement

The authors are thankful to the Principal, Department of chemistry, LBS PG CollegeJaipur for providing the laboratory facilities.

References

1. Bowden, F. L.; Carpenter, R.P.: Parrish, R.V. and Pollock, R. D. Inorg. Chem. Acta 1977,23,35
2. Percy, G.C. and Slenton, H.S. J. Inorg. Nucl. Chem. 1976, 38, 1255.
3. Percy, G.C. J. Inorg. Nucl. Chem. 1975, 37, 2071.
4. Hodgson J. H. and Percy, G.C. SpectrochemActa, Part A 1976, 32 1291.
5. Burrows, R. C. and Bailar, J.C. Jr. J. Am. Chem. Soc. 1966, 88, 4150.
6. Singh, H. L.; Sharma, M.; Gupta, M.K. and Varshney, A.K. Bull. Pol. Acad. Sci. Chem. 1999, 47, 103.
7. Nath, M.; Sharma, N. and Sharma, C.L. Synth. React. Inorg. Met. Org. Chem. 1999, 21, 51.
8. Lal, R.A.; Adhikari, S.;Kumar, A. and Pal, M.L. J. Indian Chem. Soc. 1998, 75, 345.
9. Varshney A. K. and Tandon, J.P. Proc. Ind. Acad. Sci. Chem. 1985,94, 509.
10. Dashora, R.; Singh, R.V and Tandon, J.P. Indian, J. Chem. 1986, 25A, 188.
11. Varshney, A.K.; Varshney, S.; Sharma, M. and Singh, H.L. Main group Met. Chem., 1998, 21, 495.
12. Marta A. Fik; Marta Loffler; MarekWeselski; MaciejKubicki; Maria J. Korabik and ViolettaPatroniak, Polyhedron, Volume 102, 2015, Pages 609-614
13. NevinTuran, AhmetSavci, KenanBuldurun, Yusuf Alan, RagıpAdigüzel, Letters in Organic Chemistry, Volume 13 , Issue 5 , 2016.
14. K. Jayanthi, R. P. Meena, K. Chithra, S. Kannan, W. Shanthi, R. Saravana, M. Suresh, D. Satheesh, Journal of Pharmaceutical, Chemical and Biological Sciences, 2017, 205-215
15. G. Osigbemhe, M. E. Khan, A. Mutairu and I. F. Esekhaigbe, Communication in Physical Sciences 2020, 5(2) 106-116

