Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry

2016, 5 (1): 111-115

(International Peer Reviewed Journal)

Synthesis and Characterization of Azo Linked Schiff Bases And Their Bimeric Iron (III) Complexes

Santosh S. Chandole and S.G. Shirodkar*

1. Department of Chemistry, Shri Guru Budhhiswami Mahavidyalaya, Purna (Jn.) Nanded Maharashtra, **INDIA**
2. P. G. Department of Chemistry and Research Centre N.S.B. College, Nanded, Maharashtra-431602, **INDIA**

Email: shirodkar_1@hotmail.com, schandole@rediffmail.com

Accepted on 5th December 2015

ABSTRACT

Azo linked Schiff base compounds were synthesized by coupling of benzenediazonium chloride with 4-hydroxy-6-methyl-3-(1-(alkyliminoethyl)-2H-pyran-2-one in alkaline conditions. New Fe (III) complexes of the azo Schiff base ligands were also prepared. These complexes were characterized by elemental analysis, magnetic moment, and molar conductance along with electronic and infrared spectral analysis. Octahedral geometry around these metal ions has been proposed on the basis of magnetic and spectral studies.

Keywords: Dehydroacetic acid, Azo Schiff base, azomethine group, diazotization and coupling.

INTRODUCTION

Heterocyclic azo Schiff base and their complexes with transition metal ions are important due to their complexing, catalytically biological properties.[1,2] These exhibit chemotherapeutic and antiseptic properties.[3] They also have variety of application such as redox indicator dyeing food stuff and preserving food grains.[4] Recently, azometal chelates have attracted increasing attention due to their interesting electronic and geometrical features in connection with their application for molecular memory storage, nonlinear optical elements and printing systems.[5]

The common oxidation states shown by iron are +2 and +3. Almost all the aqueous chemistry of iron is confined to the +2 and +3 oxidation states. Fe (III) ions form a large number of complexes than Fe(II) ion. In most of these, the coordination number of Fe(III) ion is six and the complexes formed are octahedral.[6] In view of these factors, we have synthesized new bimeric complexes of Fe(III) ions with tridentate azo linked Schiff bases containing oxygen and nitrogen donor atoms.

MATERIALS AND METHODS

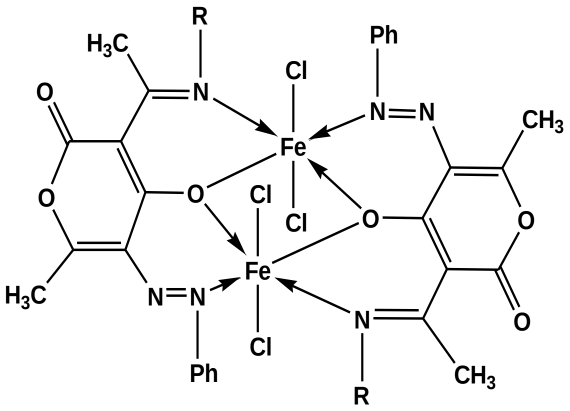
3-acetyl-6-methyl-(2H)-pyran-2,4(3H)-dione (Dehydroacetic acid; DHA), methyl amine, ethyl amine, propyl amine, ethanol amine and aniline were used as supplied by S.D. fine chemicals Ltd. All other chemical and solvents used including iron (III) salts were of A.R. grade.

The C, H and N contents of ligands and complexes were determined on CHN analyzer. The metal contents were determined by atomic absorption spectra on Perkin-Elmer atomic absorption spectrophotometer (Model 2380). The conductivity of dilute solutions ($1x10^{-4}$M) in DMSO is measured on conductivity meter. Magnetic measurements at room temperature were carried out using Gouy's balance. The IR spectra of the ligands and their metal complexes were recorded on Perkin–Elmer (1430) FTIR spectrophotometer using KBr pellets. The electronic spectral measurements were made on Schimadzu UV-visible spectrophotometer (model 150).

Preparation of ligands: The ligands 4-hydroxy-6-methyl-3-(1-(methylimino)ethyl)-5-(phenyldiazenyl)-2H-pyran-2-one(L_1), 3-(1-(ethylimino)ethyl)-4-hydroxy-6-methyl-5-(phenyldiazenyl)-2H-pyran-2-one(L_2), 4-hydroxy-6-methyl-3-(1-(propylimino)ethyl)-5-(phenyldiazenyl)-2H-pyran-2-one (L_3) and 4-hydr oxy-3-(1-(2-hydroxyethylimino) ethyl)-6-methyl-5-(phenyldiazenyl)-2H-pyran-2-one (L_4) were prepared in two different steps. The first step involves refluxing of equimolar mixture of dehydroacetic acid and primary aliphatic amine (methyl amine, ethyl amine, propyl amine, ethanol amine) for 4 hours. Upon cooling, the separated solid Schiff base were filtered, washed with portions of dry methanol and dried. Further azo linked Schiff bases were prepared by coupling the Schiff bases with benzene diazonium chloride as described in the literature.[7]

Preparation of metal complexes: To a hot solution of ligand (0.02mol) in 30mL methanol, the ferric chloride (0.01mol) in methanol was added drop wise. The pH of the solution was adjusted to 7 to 8.5 by adding alcoholic ammonia. The contents were digested for 4 h. The Fe (III) complexes were filtered in hot condition, washed with hot methanol followed by petroleum ether (40-60^{0}C) and dried in vacuum. The structure of metal complexes is shown below.

Structure of Fe(III)Complexes with Ligand L_1 to L_4



The elemental and metal analysis of iron complexes is given in table 1.

Table.1 Elemental and Metal Analysis of Iron (III) Complexes

Sr. No.	**Molecular formula**	**Elemental Analysis Found (Calculated)**					**Magnetic Moment μ BM**	**Conductivity**
		%C	**%H**	**%N**	**%Cl**	**%Fe**		
1	$[Fe_2(C_{15}H_{14}O_3N_3Cl_2)_2]$	42.95 (43.83)	3.22 (3.43)	10.12 (10.22)	16.89 (17.25)	13.20 (13.59)	4.84	Non electrolyte
2	$[Fe_2(C_{16}H_{16}O_3N_3Cl_2)_2]$	44.90 (45.21)	3.25 (3.79)	9.55 (9.89)	16.02 (16.68)	12.55 (13.14)	4.94	Non electrolyte
3	$[Fe_2(C_{17}H_{18}O_3N_3Cl_2)_2]$	45.55 (46.50)	4.37 (4.13)	9.28 (9.57)	15.75 (16.15)	12.25 (12.72)	4.75	Non electrolyte
4	$[Fe_2(C_{16}H_{16}O_4N_3Cl_2)_2]$	43.20 (43.57)	3.21 (3.66)	9.20 (9.53)	16.00 (16.08)	12.20 (12.66)	5.03	Non electrolyte

RESULTS AND DISCUSSION

All the complexes are coloured solid, stable to air and non-hygroscopic. They are insoluble in water and methanol but slightly soluble in DMF, DMSO. The molar conductance values of all the complexes in DMSO at a concentration of 10^{-4} M fall in the range 17.76 – 26.47 mho cm^2 mol^{-1}. This very low molar conductance value indicates non-electrolytic nature of complexes [8].

The Infrared spectra of the metal complexes were recorded between 4000-300 cm^{-1}. The examination of the IR spectra of all the complexes reveals that: All the IR spectra have identical bands at their respective positions. Most of the bands appeared in the spectra of ligands are observed at the similar position in the IR spectra of metal complexes. In IR spectra of free ligands, the band observed in the range 1639-1583cm^{-1} were assigned to the C=N stretching frequencies. In the IR spectrum of metal complexes, medium to strong bands of the same appeared in the region 1614-1523 $cm^{-1.}$ A downward shift of this band by 10-30 cm^{-1} on complexation indicates that C=N group of the ligands is coordinated to the metal ion via its azomethine nitrogen [9]. In ligands, medium to strong intensity band in the region 1397-1307 $cm^{-1}$are assigned to C-N stretching vibration. The medium to strong intensity bands in the region 1300-1231 cm^{-1} appeared in the spectra of metal complexes were assigned to enolic C–O stretching frequency. These bands in the corresponding free ligands spectra were observed in the region 1274-1218 cm^{-1}. Thus the observed upward shift of this band by 5-30 cm^{-1} on chelation indicates the participation of enolic oxygen of DHA moiety of ligand in the complex formation. [10] In the infrared spectra of transition metal complexes of azo schiff bases the medium to strong bands appeared in the region 1491-1460 cm^{-1} were assigned to aryl azo (N=N) stretching vibrations. The bands due to N=N bond in the corresponding free ligand spectra were found in the region 1480-1438cm^{-1}. The shift of this band to lower frequency side by 10-25cm^{-1} on complexation suggests the involvement of one of the azo nitrogen atoms in bonding with the metal ion. [11] All the ligands exhibited a broad weak band at 2760-2550 cm^{-1} assignable to O-H---N stretching vibration. It is known that, strong hydrogen bonding causes a shift of the O-H stretching band to a lower frequency and broadens the band. Absence of these bands in the spectra of complexes confirms the deprotonation of enolic -O-H and subsequent coordination of enolic oxygen with metal forming Fe-O bond. The strong evidence of bonding is revealed by the appearance of band at 480-520 cm^{-1}(Fe-O), 440-470 cm^{-1}(Fe-N) [12] and in the spectra of around 350 cm^{-1} is assigned for (Fe-Cl) bonding.

The Fe (III) complexes show magnetic moment values are in the range 4.75 - 5.03 B.M. at room temperature suggesting bimeric high spins octahedral geometry [13]. The bimeric nature is also supported by elemental analysis. The low magnetic moment value than the normal value of the complexes is also due to high metal-metal interaction. Further, the geometry by electronic spectra shows three absorption bond in the region (17241cm^{-1}) 580 nm (V_1), (23696 cm^{-1}) 422 nm (V_2) and (27472-26246 cm^{-1}) 364-381 (V_3) can be assigned to $^6A_{1g}\rightarrow{}^4T_{2g}$ (D), $^6A_{1g}\rightarrow{}^4T_{1g}$ and $^6A_{1g} \rightarrow {}^4T_{2g}$ transition respectively [14].

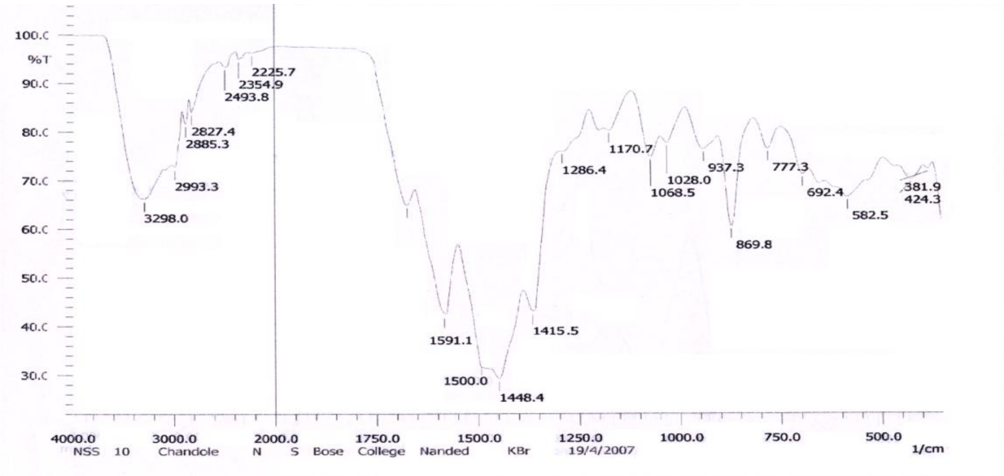


Fig.1 Infrared Spectrum of Fe (III) Complex with ligand L_4

APPLICATIONS

Azo Schiff bases (L_1 and L_3) and their Fe (III) complexes were screened (at 300 and 500 ppm) in vitro for their antifungal activity against *Aspergillus niger*. The ligands showed 60-70% inhibition (Table 2). The complexes had greater antifungal activity than the corresponding ligands.

Table 2. Yield of mycelial dry weight (MDW) in mg

Growth of GN Media Control	**Growth in Presence of Ligands**		**Ligands**	**Growth of Iron complex**	
	300 PPM	**500 PPM**		**300 PPM**	**500 PPM**
335	255	202	**L_1**	303	179
366	333	271	**L_3**	287	140

CONCLUSIONS

In the present paper, we report the synthesis of Fe(III) complexes of azo linked Schiff base ligand derived from coupling reaction of benzenediazonium chloride with 4-hydroxy-6-methyl-3-(1-(alkylimino)ethyl)-2H-pyran-2-one. Infrared spectral studies suggest the metal-ligand coordination at azo, azomethine and enolic C–O groups. Further, by elemental analysis, molar conductivity measurements, magnetic susceptibilities, electronic absorption, structure for these Fe(III) complexes is assigned as bimeric high spin octahedral structures.

REFERENCES

[1] Nurcan Kurtoglu, Synthesis, characterization, chelation with transition metal ions, and antibacterial and antifungal studies of the 4-[(E)- -phenyldiazenyl]-2-[(E)-(phenylimino)methyl]phenol dye, *J. Serb. Chem. Soc*, **2009,** *74* (8–9) 917–926.

[2] B.B. Mahapatra, P. Ray, Dinuclear Complexes of Bivalent Mn, Co, Ni, Cu, Zn, Cd and Hg with Bis-Bidentate Oxygen Donor Azodye Ligands, *J. Indian Chem. Soc*, **2002,** 79, 536-537.

[3] B.B. Mahapatra, P. Ray, Polymetallic Complexes, Part-LXXVII, Complexes of MnII, CoII, NiII, CuII, ZnII, CdII and HgII with NOON and ONOONO Donor Azodye Ligands, *J. Indian Chem. Soc*, **2002,** 79, 609-610.

[4] A.K. Ghoneium, R.M. Isa, H.A. Dessouki and M.M. Mustafa, Co(II), Ni(II) and Cu(II) complexes of some phenylazosalisylaldehyde derivative, *J. Indian Chem. Soc,***1984,** 61, 286.

[5] Saijun Wu, Wei Qian, Zongju Xia, Yinghua Zou, Shuangqing Wang, Shuyin Shen, Huijun Xu, Investigation of third-order nonlinearity of an azo dye and its metal-substituted compounds, **2000**, *Chem. Phys. Lett*, 330, 535-540.

[6] F.A. Cotton and G. Wilkinson, "*Advanced Inorganic Chemistry*," 6th edition., wiley Eastern, New Delhi, **1999**.

[7] A. I. Vogel, "*A Text Book of Practical Organic Chemistry*", ELBS, **1994,** 946.

[8] Ramachandra Akkasali, Nirdosh Patil and S. D. Angadi, Synthesis, characterization and microbial activities of metal complexes with coumarine derivatives, *Rasayan J. Chem*, **2009,** 2(1), 81-86**.**

[9] M.L. Harikumarran Nair and V.L. Siji, Synthesis, spectral, thermal and antimicrobial studies of oxomolybdenum(V) and dioxomolybdenum(VI) complexes of Schiff base derived from 4-aminoantipyrine and 2,4-dihydroxyacetophenone, *J. Indian Chem.Soc*, **2009,** 86, 441-448.

[10] D.S. Revankar, J.C. Ajbani, M. Revanasiddappa, M.V. Swamy and S. Shankar, Synthesis, Characterization and Biological Studies on Riluzole Schiff base Metal Complexes, *J. Applicable Chem,* **2014,** 3 (4),1447-1459.

[11] M.L. Harikumarran Nair and K.P. Lalitha, Synthesis, Physicochemical Characterization and Structure Determination of Some Novel Nickel (II) Complexes, *Journal of Applied Chemistry*, **2014,** Vol.6 (6), 15-20.

[12] M.R. Anil Kumar, S. Shanmukhappa, B.E. Rangaswamy and M. Revanasiddappa, Synthesis, Characterization and Antimicrobial Activity of Some Transition Metal Complexes with Schiff Base Ligand, *J. Applicable Chem,* **2014,** 3 (4),1440-1446.

[13] Abbas Noor Al-Shareefi, Salih Hadi Kadhim and Waleed Abbas Jawad, Synthesis and study of Fe(III), Co(II), Ni(II) and Cu(II) complexes of new Schiff's base ligand derived from 4-amino antipyrine, **2013,** *J. Applicable Chem.,* 2 (3),438-446.

[14] R. L. Dutta, A. Syamal, "*Elements of Magneto Chemistry*", 2nd edition, East-west Press, New Delhi, **1999**.

AUTHORS' ADDRESSES

1. **Santosh S. Chandole**
Asst. Prof., Department of Chemistry,
Shri Guru Budhhiswami Mahavidyalaya, Purna (Jn.) Nanded Maharashtra, India
Email: schandole@rediffmail.com, Mob no: 09689010099

2. **S.G. Shirodkar**
Asso. Prof. and Head, P. G. Department of Chemistry and Research Centre,
N.S.B. College, Nanded, Maharashtra, India
Email: shirodkar_1@hotmail.com, Mob no: 09421928129