JSR Publications

Available Online

J. Sci. Res. **2** (1), 114-126 (2010)

JOURNAL OF
SCIENTIFIC RESEARCH
www.banglajol.info/index.php/JSR

Synthesis and Characterization of Transition Metal Complexes with N,O; N,N and S,N-donor Schifff Base Ligands

Y. Prashanthi[1, 2] and Shiva Raj[1*]

[1]Department of Chemistry, Osmania University, Hyderabad- 500 007, India
[2]Indian Institute of Chemical Technology, Hyderabad-500 007, India

Received 25 June 2009, accepted in final revised form 22 December 2009

Abstract

The Schiff bases namely MIMFMA, MIMTMA and MIPMA have been prepared by reacting 3-amino-5-methyl isoxazole with 5-methyl furan-2-carboxyaldehyde, 5-methyl thiphene-2-carboxaldehyde and pyridine-2-carboxaldehyde. The Cu(II), Ni(II), Co(II), Zn(II) and VO(IV) have been prepared by reacting metal chlorides with those Schiff bases in an alcholic medium. The complexes are electrolytes in DMSO. These have been characterized by using elemental analysis, IR, UV-VIS, ^{1}H, ^{13}C, mass spectra, magnetic susceptibility, conductance measurements and thermo gravimetric studies. The complexes were found to have composition ML2. On basis of elemental and spectral studies, six coordinated geometry is assigned for these complexes. The Schiff bases act as neutral and bidentate and coordinate through the azomethine nitrogen and furfural oxygen, thiophene sulphur and pyridine nitrogen, respectively. The synthesized ligands and their metal complexes were screened against bacteria and fungi. The activity data show that the metal complexes are more potent than the parent Schiff bases.

Keywords; Schiff bases; Transition metal complexes; Spectral studies; Antimicrobial studies.

DOI: 10.3329/jsr.v2i1.2732 J. Sci. Res. **2** (1), 114-126 (2010)

1. Introduction

Schiff bases are considered as a very important class of organic compounds which have wide applications in many biological aspects [1]. Transition metal complexes of Schiff bases are one of the most adaptable and thoroughly studied systems. These complexes have also applications in clinical and analytical and industrial in addition to their important roles in catalysis and organic synthesis [2]. Some of Schiff base complexes are used as model molecules for biological oxygen carrier systems, as metal indicators in

---

[*] *Corresponding author*: shivaraj_sunny@yahoo.co.in

complexometric titrations and colorimetric reagents, in addition to biochemical research [3]. A wide range of biological activities of isoxazole derivatives include pharmacological properties such as antibacterial, anticancer, anti HIV activity and also agrochemical properties and also have applications as pesticides and insecticides [4]. Metal complexes of Schiff bases derived from 3-amino-5-methyl isoxazoles and substituted salicylaldehydes were reported earlier and found that the activity enhances upon complexation [5].

However a brief survey of literature reveal that not much work has been carried out on the chelating tendency of Schiff bases derived from 3-amino-5-methyl isoxazole and heterocyclic aldehydes with bivalent transition metal ions. In view of the above observations it appeared worthwhile to study the synthesis, characterization and antimicrobial activity of metal complexes of MIMFMA, MIMTMA and MIPMA.

2. Experimental

Materials

All the chemicals and solvents used were of Analar grade. Solvents such as water, methanol, acetone, petroleum ether and chloroform were purified by standard procedures [6].

Physical measurements

^{1}H NMR spectra of the ligands were recorded at 200 MHz and 300 MHz on Varian Gemini Unity Spectrometer using TMS as an internal standard. ^{13}C NMR spectra were recorded at 100.6 MHz on Varian Gemini Spectrometer. The EI mass spectra were recorded on a VG micro mass 7070–H Instrument, ESIMS spectra were recorded on VG AUTOSPEC mass spectrometer. IR spectra of the ligand and complexes were recorded using KBr pellets in the range (4000-400cm^{-1}) on Perkin-Elmer Infrared model 337. Electronic spectra of metal complexes in DMSO were recorded on Schimadzu UV-VIS 1601 spectrophotometer. Magnetic susceptibilities of the complexes were determined on Gouy balance model 7550 using $Hg[Co(NCS)_4]$ as standard. The diamagnetic corrections of the complexes were computed using Pascal’s constants. TGA of complexes were carried on Mettler Toledo Star system in the temperature range of 0-1000°C. Melting points of the ligands and decomposition temperature of complexes were determined on Polmon instrument (model No. MP-96). The conductivity measurements were measured in DMSO solutions (0.001 M) using Digisun Electronic Digital conductivity meter of model: DI-909 having a dip-type cell calibrated with KCl solution. The percentage composition of C, H, N for the complexes and ligands were determined by using micro analytical techniques on Perkin Elmer 240C (USA) elemental analyzer. The EPR spectra of the Copper complexes were recorded on EPR Varian-E-112 at RT. The percent composition of metal ions in solid metal complexes was determined by EDTA titration procedure.

Synthesis of ligands: MIMFMA / MIMTMA / MIPMA

3-amino-5-methyl isoxazole (0.05 mol) was dissolved in hot methanol to which 5-methyl furan-2-carboxaldehyde / 5-methyl thiophene-2-carboxyaldehyde / pyridine-2-aldehyde (0.05 mol) was added and the mixture was refluxed for 3 hours under nitrogen atmosphere. The dark yellow product formed was filtered and washed with petroleum ether and recrystallised from methanol. Purity of the compounds was checked by TLC. Yield: 80-85%.

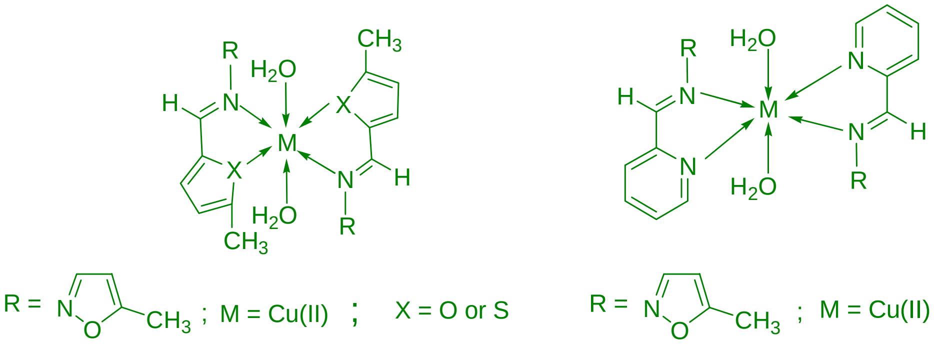
The above-mentioned Schiff bases were also synthesized by microwave irradiation and ultrasonic methods [7, 8]**.** The products obtained were highly pure with good yield.

Synthesis of metal complexes

A) Binary complexes (general method)

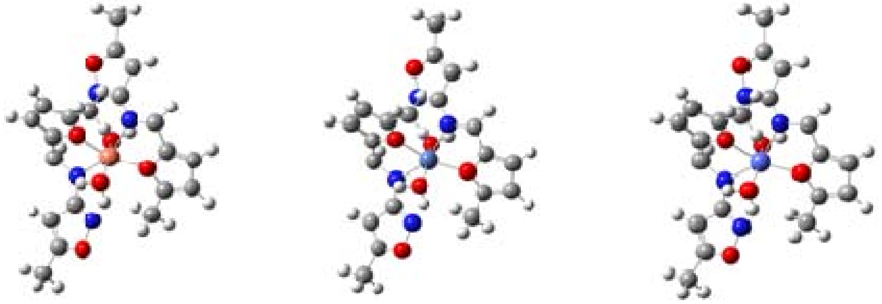
In the preparation of the metal complexes (scheme 1), the metal and the ligands were mixed in 1:2 molar ratio using required quantities of methanol.

Hot methanolic solution of ligand (0.01 mol) and hot methanolic solution of corresponding metal salts (0.005 mol) (MX_2 , where M = Cu(II), Ni(II), Co(II), Zn(II) and VO(IV) ; X = Cl/acetates ; for VO(IV); X = SO_4) were mixed together with constant stirring. The mixture was refluxed for 2-3 hours at 70-80°C on water bath. On cooling, colored solid metal complexes were precipitated out. The products were filtered, washed with cold methanol and dried under vacuum over P_4O_{10}.



Scheme 1: Proposed structures of Cu(II) complexes.

Molecular modeling studies



Cu(II) - MIMFMA(15.698 kcal/mol)

Ni(II) - MIMFMA(11.023 kcal/mol)

Co(II) - MIMFMA(13.231 kcal/mol)

Molecular modeling structure for Cu(II), Ni(II) and Co(II) complexes

In the absence of an X-ray crystal structure data the 3-dimensional structure of the molecules can not be entirely unambiguous. However, recent major advances in the computational chemistry tools provides an alternative, albeit approximate, approach for obtaining the three dimensional structures of the compounds. The configuration possible for the Cu(II), Ni(II) and Co(II) complexes were evaluated using the semiemperical and the density functional theory calculations respectively. PM3, a semiemperical self-consistent field method was employed to obtain the 3D-geometries and relative energies of the possible isomers of Cu(II), Ni(II) and Co(II) complexes. The most stable structure among the possible ones is judged as the probable structure.

3. Results and Discussion

Characterization of Ligands

All the prepared ligands are yellow in colour and are stable. They are soluble in all organic solvents.

1) **MIMFMA**

IR (KBr) : 1625cm^{-1} (C=N); 1253 cm^{-1} (C-O-C).
UV (MeOH) : 332 nm(λ_{max}); 288 (λ_{max}).
^{1}H NMR(DMSO- d$_6$) (200 MHz): δ 8.51 (s, CH=N), 6.97 (d, H-3'); 6.19 (d, H-4'); 6.04 (s, H-4); 2.43 (s, 5-CH$_3$); 2.42 (s, 5'-CH$_3$).
^{13}C spectrum (CDCl$_3$+DMSO) (100.6MHz): 170.5 (C-3); 169.7(C-5); 157.8(CH=N); 152.64(C-5'); 149.72(C-2'); 122.0(C-4'); 109.72(C-3'); 95.1 (C-4); 13.6 (C-5'-CH$_3$); 12.3(C-5- CH$_3$).

MS: m/z at 190 (M^+). Other fragments are at m/z 162,147,133,121, 98, 79, 75, 53 and 43.
Analysis (%): Found C, 63.10; H, 5.16; N, 14.53. $C_{10}H_{10}N_2O_2$ requires C, 63.15; H, 5.26; N, 14.73.
Melting point: 117 ^{0}C.

2) MIMTMA

IR (KBr) : 1629cm^{-1} (C=N); 888cm^{-1} (C-S-C).
UV (MeOH) : 324 nm(λ_{max}); 272 nm (λ_{max}).
^{1}H NMR (DMSO- d_6) (200 MHz): δ 8.76 (s, CH=N); 7.04 (s, H-3'); 6.83 (d, H-4'); 6.15 (s, H-4); 2.49 (s, 5-CH_3); 2.40 (s, 5'- CH_3).
^{13}C spectrum ($CDCl_3$+DMSO) (100.6MHz): 170.5 (C-3); 167.3(C-5); 159.2(CH=N); 147.9 (C-5'); 139.0 (C-2'); 136.5 (C-4'); 127.3 (C-3'); 95.2 (C-4); 15.6 (C-5'-CH_3); 12.3 (C-5- CH_3).
MS: m/z at 207 (M+H). Other fragments are found at 191, 175, 147, 133, 115, 91, 79 and 73.
Analysis: Found **C**, 58.15; H, 4.65; N, 13.79. $C_{10}H_{10}N_2OS$ requires C, 58.25; H, 4.85; N, 13.59.
Melting point: 113 ^{0}C.

3) MIPMA

This ligand was reported earlier. The spectral data obtained under present experimental conditions are agreed with the literature data [9].
IR (KBr) : 1631cm^{-1} (C=N); 1593cm^{-1} (Py-N).
UV (MeOH) : 396 nm(λ_{max}); 208 nm (λ_{max}).
^{1}H NMR (DMSO- d^6) (200 MHz): δ 8.59 (CH=N); 6.93-8.62 (m, H-3', 4’, 5’, 6’); 6.15 (s, H-4); 2.53 (s, 5-CH_3).
^{13}C spectrum ($CDCl_3$+DMSO) (100.6MHz): 169.2 (C-5); 168.5 (CH=N); 164.2 (C-3); 157.5 (C-2'); 149.5 (C-6'); 148.5 (C-3'); 124.5 (C-4'); 123.5 (C-5'); 94.8 (C-4); 12.5 (C-5-CH_3).
MS : m/z 187(M^+). Other fragment found at 169.
Analysis (%): Found **C**, 64.15; H, 4.65; N, 22.79. $C_{10}H_9N_3O$ requires C, 64.17; H, 4.81; N, 22.45.
Melting point: 116 ^{0}C.

Characterization of metal complexes

All the complexes are stable at room temperature and are non-hygroscopic. On heating, they decompose at high temperatures. The complexes are insoluble in water but are soluble in DMSO.

Elemental analysis

It is clear from the data that the experimental values shown for each of the complexes, are in good agreement with the theoretical values calculated for 1:2 ratio. The composition assigned to the complexes may, therefore be formulated as presented in the Table 1.

Table 1. Analytical data of metal complexes.

Complex	Formula	Mol.wt.	C	H	N	M
$[Cu(MIMFMA)_2(H_2O)_2]^{+2}$	$[CuC_{20}H_{24}N_4O_6]$	479.5	50.05 (50.00)	5.00 (5.01)	11.67 (11.98)	13.24 (13.28)
$[Cu(MIMTMA)_2(H_2O)_2]^{+2}$	$[CuC_{20}H_{24}N_4O_4S_2]$	511.5	46.92 (46.09)	4.69 (4.99)	10.94 (10.02)	12.41 (12.90)
$[Cu(MIPMA)_2(H_2O)_2]^{+2}$	$[CuC_{20}H_{22}N_6O_4]$	473.5	50.68 (50.80)	4.64 (4.24)	17.74 (17.82)	13.41 (13.20)
$[Ni(MIMFMA)_2(H_2O)_2]^{+2}$	$[NiC_{20}H_{24}N_4O_6]$	474.7	50.55 (50.00)	5.05 (5.02)	11.79 (11.00)	12.36 (12.32)
$[Ni(MIMTMA)_2(H_2O)_2]^{+2}$	$[NiC_{20}H_{24}N_4O_4S_2]$	506.7	47.36 (47.23)	4.73 (4.65)	11.05 (11.00)	11.58 (11.02)
$[Ni(MIPMA)_2(H_2O)_2]^{+2}$	$[NiC_{20}H_{22}N_6O_4]$	468.7	51.20 (51.35)	4.69 (4.26)	17.92 (17.00)	12.52 (12.25)
$[Co(MIMFMA)_2(H_2O)_2]^{+2}$	$[CoC_{20}H_{24}N_4O_6]$	474.9	50.53 (50.15)	5.05 (4.95)	11.79 (11.09)	12.40 (12.01)
$[Co(MIMTMA)_2(H_2O)_2]^{+2}$	$[CoC_{20}H_{24}N_4O_4S_2]$	506.9	47.34 (47.21)	4.73 (4.61)	11.04 (11.24)	11.61 (11.09)
$[Co(MIPMA)_2(H_2O)_2]^{+2}$	$[CoC_{20}H_{22}N_6O_4]$	468.9	51.18 (51.29)	4.69 (4.23)	17.91 (17.87)	12.56 (12.67)
$[Zn(MIMFMA)_2(H_2O)_2]^{+2}$	$[ZnC_{20}H_{24}N_4O_6]$	481.3	49.86 (49.96)	4.15 (4.05)	11.63 (11.69)	13.56 (13.06)
$[Zn(MIMTMA)_2(H_2O)_2]^{+2}$	$[ZnC_{20}H_{24}N_4O_4S_2]$	513.3	46.75 (46.25)	4.67 (4.91)	10.90 (10.11)	12.72 (12.69)
$[Zn(MIPMA)_2(H_2O)_2]^{+2}$	$[ZnC_{20}H_{22}N_6O_4]$	475.3	50.49 (50.69)	4.62 (4.67)	17.67 (17.00)	13.73 (13.75)
$[VO(MIMFMA)_2(H_2O)]^{+2}$	$[VOC_{28}H_{20}N_4O_5]$	464.94	51.61 (51.21)	4.73 (4.03)	12.04 (12.21)	14.39 (14.00)
$[VO(MIMTMA)_2(H_2O)]^{+2}$	$[VOC_{20}H_{22}N_4O_3S_2]$	496.94	48.29 (48.09)	4.42 (4.24)	11.26 (11.36)	13.47 (13.00)
$[VO(MIPMA)_2(H_2O)]^{+2}$	$[VOC_{20}H_{20}N_6O_3]$	458.94	52.29 (52.96)	4.35 (4.02)	18.30 (18.11)	14.58 (14.27)

Conductivity

The conductance values for all complexes of MIMFMA, MIMTMA and MIPMA are high (195-235 Ohm^{-1} cm^{2} mol^{-1}) indicating their electrolytic nature in the solvent [10].

Thermal Analysis

Representative thermogram of Cu-MIMFMA is given in Fig. 1. From the figure it is found that the heating rates were suitably controlled at 10^{o}C min^{-1} under nitrogen atmosphere and the weight loss was measured from the ambient temperature upto 1000 ^{0}C. In metal complexes water molecules may present as lattice water and/or coordinated water. Lattice water is lost at lower temperature regions between 60-120 ^{0}C whereas the loss of coordinated water requires 150 ^{0}C or above 150 ^{0}C. The thermogram above this temperature is a horizontal and the final product of decomposition corresponds to their metal oxides. Presence of water molecules is further confirmed by the endothermic bands observed in the respective DTA curve in the temperature region where the TGA curves indicates loss in weight. In addition to the endothermic bands, the DTA curves of complexes also show exothermic bands. These bands appeared at higher temperatures which represent phase transition, oxidation and/or decomposition of the compound.

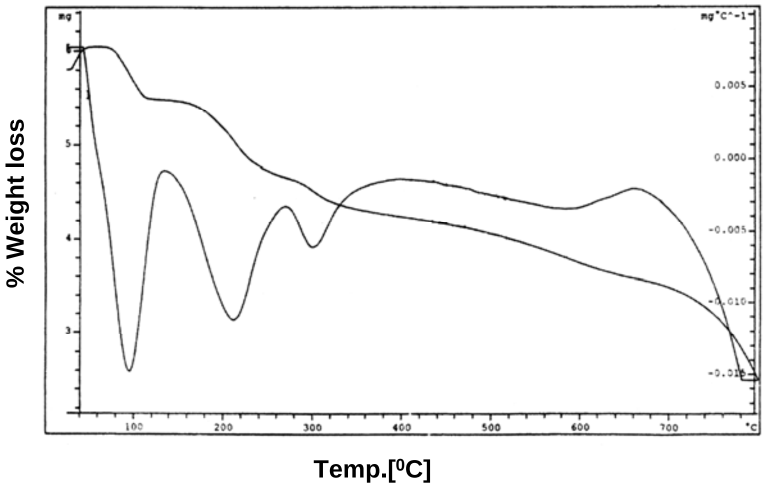


Fig. 1. Thermogram of Cu(II)-MIMFMA.

IR spectra: In order to study the binding mode of the Schiff base to the metal ion in complexes, the IR spectra of the free ligands are compared with the spectra of corresponding complexes. The important absorption frequencies of all complexes with their ligands and their assignments are given in Table 2.

Table 2. IR Absorption frequencies of metal complexes.

Complex	υC=N	Coordinated Water	υM-N	υM-O	COC	CSC
MIMFMA	1624	-	-	-	1253	-
$[Cu(MIMFMA)_2(H_2O)_2]^{+2}$	1613	762	440	543	1271	-
$[Ni(MIMFMA)_2(H_2O)_2]^{+2}$	1611	-	430	510	1288	-
$[Co(MIMFMA)_2(H_2O)_2]^{+2}$	1607	764	434	544	1275	-
$Zn(MIMFMA)_2(H_2O)_2]^{+2}$	1577	-	491	524	1275	-
$[VO(MIMFMA)_2((H_2O)]^{+2}$	1575	743	417	509	1282	-
MIMTMA	1628	-	-	-	-	888
$[Cu(MIMTMA)_2(H_2O)_2]^{+2}$	1616	774	420	544	-	928
$[Ni(MIMTMA)_2(H_2O)_2]^{+2}$	1617	-	509	430	-	938
$[Co(MIMTMA)_2(H_2O)_2]^{+2}$	1613	738	554	461	-	898
$[Zn(MIMTMA)_2(H_2O)_2]^{+2}$	1617	-	525	482	-	932
$[VO(MIMTMA)_2(H_2O)_2]^{+2}$	1624	750	436	542	-	898
MIPMA	1627	-	-	-	-	-
$[Cu(MIPMA)_2(H_2O)_2]^{+2}$	1615	775	467	531	-	-
$[Ni(MIPMA)_2(H_2O)_2]^{+2}$	1604	-	486	544	-	-
$[Co(MIPMA)_2(H_2O)_2]^{+2}$	1611	772	472	551	-	-
$[Zn(MIPMA)_2(H_2O)_2]^{+2}$	1580	-	462	545	-	-
$[VO(MIPMA)_2(H_2O)]^{+2}$	1618	771	455	512	-	-

A medium intensity band around 1636 cm^{-1} due to **υ**C=N shifted to higher frequency region to the extent 10-25 cm^{-1} in complexes, indicating the nitrogen of azomethine is coordinated to the metal ion [11,12]. Medium to sharp bands, due to **υ**C-O-C of furan, appeared at 1253 cm^{-1} in MIMFMA and the sharp band at 888 cm^{-1} due to **υ**C-S-C group in MIMTMA are shifted to higher frequency region in their complexes suggesting the bonding of oxygen of furan moiety in MIMFMA and sulphur of thiophene moiety in MIMTMA with the metal ion [13 14]. The strong band at 1593 cm^{-1} due to the **υ**C=N of pyridine nitrogen and ring deformation bands at 611 and 405 cm^{-1} of MIPMA ligand are shifted to higher frequency region indicating the participation of pyridine nitrogen in the complex [10, 15]. Appearance of a broad band around 3400 cm^{-1} region was observed in the spectra of complexes indicating the presence of coordinated water molecules. This band was followed by another non-ligand band at 762-795 cm^{-1}, suggesting the presence of water molecules, which may be coordinated water molecules. This fact is also supported by the results of elemental analysis, T.G.A of complexes and also by the appearance of non-ligand bands at appropriate positions in the far infrared region (526-596 cm^{-1} and 420-469 cm^{-1}) due to **υ**M-O and **υ**M-N vibrations, respectively [16].

Magnetic susceptibility and electronic spectra

The electronic spectra and magnetic moment of the metal complexes are listed in Table 3. The magnetic moment values of Cu(II) complexes are 1.87-1.98 B.M. falls within the normal range observed for distorted octahedral complexes. In the present studies, all Cu(II) complexes each show, a single broad band in the range 18,920 cm^{-1} due to transition between $^2E_g \rightarrow ^2T_{2g}$ suggesting tetragonal geometry. Tetragonal or square planar Cu(II) complexes, are expected to give three bands. However, these three bands usually overlap in tetragonal complexes, to give one broad absorption band [17]. The electronic spectra and magnetic moment data for all Cu(II) complexes coupled with the analytical, conductance data obtained for them, suggest the tetragonal geometry for all the complexes.

The Ni(II) complexes of MIMFMA, MIMTMA and MIPMA show three bands around 9363- 12400 ; 16309 – 19200 and 24096 – 27900 cm^{-1}. These have been assigned respectively to the transitions $^3A_{2g}$ (F) → $^3T_{2g}$ (F) (ν_1); $^3A_{2g}$ (F) → $^3T_{1g}$ (F) (ν_2) and $^3A_{2g}$ (F)→ $^3T_{1g}$ (P) (ν_3) of octahedral geometry[18]. The octahedral geometry for these complexes is further supported by the values of ν_2 / ν_1 in the range 1.60 -1 .72 [19]. These values are lower than the ν_2/ν_1 value of 1.80 observed for the regular octahedral $[Ni(H_2O)_6]^{+2}$. The lowering of the value in the present cases may be attributed to the presence of asymmetric environment around Ni(II). Further, the B values for these complexes are lower than the free ion value (B') of 1030 cm^{-1}, which is an indication of orbital overlap and delocalization of d orbitals [20]. The covalent factor β equal to B/B' for the complexes is less than one suggesting considerable amount of covalent character of the metal - ligand bonds. The energy separation between $^3A_{2g}$ (F) and $^3T_{2g}$ (F) is equal to 10 DQ and the values of 10 DQ in octahedral Ni(II) complexes vary between 6400 and 12700 cm^{-1}, depending on the position of the ligand in the spectrochemical series [21].

The magnetic moments of the present Co(II) complexes lie in the range 4.82-5.05 B.M. with high-spin octahedral geometry. All the present Co(II) complexes show each three characteristic peaks around 12093-14692; 19074 - 23125 and 25411-29012 cm^{-1} assignable respectively to the transitions $^4T_{1g}$(F) → $^4T_{2g}$ (F) (ν_1) , $^4T_{1g}$(F) → $^4A_{2g}$ (F) (ν_2) and $^4T_{1g}$(F) →$^4T_{1g}$ (P) (ν_3) of octahedral geometry[22]. The assignment of octahedral geometry to the complexes is further supported by their ν_2/ν_1 which lies in the range 1.80 - 2.20 [23].

The ligand field parameters and ligand field splitting energies of complexes are shown in Table 3. The β values for the present complexes are less than one suggesting considerable amount of covalent character of the metal-ligand bonds.

All the Zn(II) complexes have been found to be diamagnetic in nature. On the basis of analytical, conductance and spectral data the Zn(II) complexes of MIMFMA, MIMTMA and MIPMA are assigned to octahedral geometry [24].

Table 3. Electronic spectral data, magnetic susceptibility and ligand field parameters.

Complex	Frequency	v_2/v_1	B	B'	10 Dq	μ_{eff}
$[Cu(MIMFMA)_2(H_2O)_2]^{+2}$	18,920 ; -	-	-	-	-	1.87
$[Ni(MIMFMA)_2(H_2O)_2]^{+2}$	12400;19200;27900	1.54	660	0.64	12400	3.42
$[Co(MIMFMA)_2(H_2O)_2]^{+2}$	12,890;20,800;27,300	1.61	642	0.66	7910	5.00
$[Zn(MIMFMA)_2(H_2O)_2]^{+2}$	-	-	-	-	-	-
$[VO(MIMFMA)_2(H_2O)]^{+2}$	18019; 26501	-	-	-	-	1.96
$[Cu(MIMTMA)\ (H_2O)_2]^{+2}$	19607 ; -	-	--	-	-	1.83
$[Ni(MIMTMA)_2(H_2O)_2]^{+2}$	11800;18100;25052	1.53	516	0.50	11800	3.81
$[Co(MIMTMA)_2(H_2O)_2]^{+2}$	13181 ; 22831 ; 27467	1.61	642	0.66	7910	5.00
$[Zn(MIMTMA)_2(H_2O)_2]^{+2}$	- -	-	-	-	-	-
$[VO(MIMTMA)_2(H_2O)]^{+2}$	18520 ; 28507	-	-	-	-	1.93
$[Cu(MIPMA)_2(H_2O)_2]^{+2}$	18520 ; -	-	-	-	-	1.86
$[Ni(MIPMA)_2(H_2O)_2]^{+2}$	12459 ;21252 ;27847	1.70	781	0.80	12459	2.85
$[Co(MIPMA)_2(H_2O)_2]^{+2}$	12980 ;21750 ;26540	1.67	623	0.64	8770	4.91
$[Zn(MIPMA)_2(H_2O)_2]^{+2}$	-	-	-	-	-	-
$[VO(MIPMA)_2(H_2O)]^{+2}$	18019 ; 26501	-	-	-	-	1.87

The observed magnetic moment values for VO(IV) are in the range of 1.76-1.97 B.M. Which suggest octahedral geometry for these complexes [25]. The higher value may be due to the presence of orbital contribution. In the present studies, all VO(IV) complexes show two bands around 18000-25059 cm^{-1} which can be assigned for transitions $^2B_2 \rightarrow {}^2B_1$ and $^2B_2 \rightarrow {}^2A_1$. The low frequency band corresponding to $^2B_2 \rightarrow 2E$ is not clearly resolved in the spectrum. Based on the two bands observed octahedral geometry is proposed for the above complexes.

^{1}H NMR Spectra: A peak at δ 8.75- 9.01 due to azomethine proton has shifted to the downfield region indicating that the coordination of azomethine (>C=N-) to the metal ion.

FAB mass: The fast atom bombardment (FAB) spectrum exhibits molecular ion peak (M^+) at m/z 601, , which corresponds to mass of $[Zn(MIMFMA)_2(H_2O)_2]$ complex. Wherein, the metal to ligand ratio is 1:2.

ESR spectra

The solid state ESR spectra of all the present Cu(II) complexes at room temperature are anisotropic, each consisting of two peaks, one of small intensity towards low field region and the other of large intensity towards high field region. The ESR spectra of Cu(II) complexes are shown in Fig. 2. The $g_{\parallel}$ is less than 2.30(2.053) gives covalent character between M-L. $g_{\parallel} > g_{\perp} > 2.303$ suggests unpaired electron is localized in d_{x2-y2} orbital and spectral features are characteristic of axial geometry and tetragonally elongated geometry i.e. tetragonal geometry.

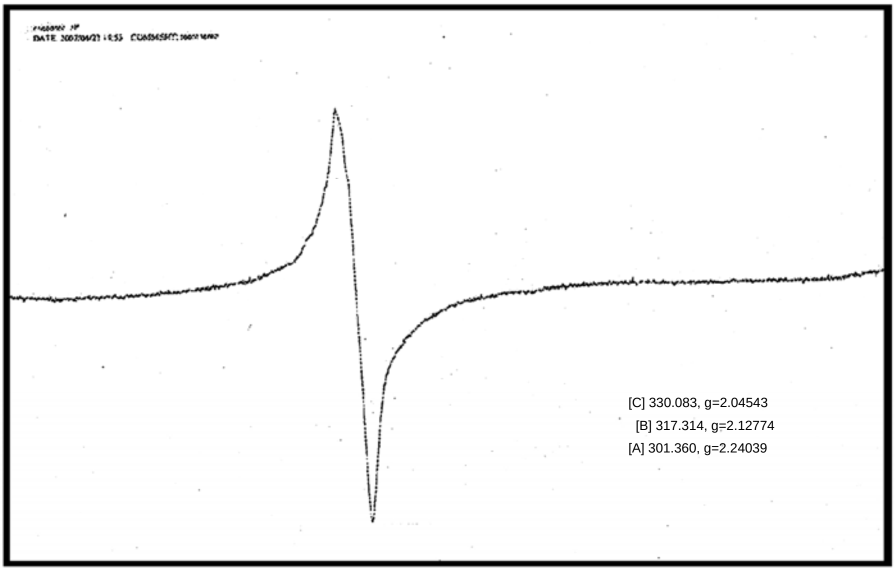


Fig. 2. ESR spectrum of Cu(II) MIMFMA.

Antimicrobial activity: In the present investigation, biological activity of the ligands namely MIMFMA, MIMTMA and MIPMA and their binary complexes with Cu(II), Ni(II), Co(II), Zn(II) and VO(IV) have been screened for antimicrobial activity against bacteria(*E.coli* and *P. aeruginosa)* and fungi(*A.niger* and *R.oryzae)* by paper disc method [26]. The concentration for these samples maintained as 1mg/ml in DMSO. The results thus obtained are explained on the basis of Overtone's concept and Chelation theory [27]. The mode of action of the compounds may involve formation of a hydrogen bond through the azomethine group with the active centers of cell constituents, resulting in an interference with the normal cell process [28].

The variation in the activity of different complexes against different organisms depend either on the impermeability of the cells of the microbes or difference in ribosomes of microbial cells. Comparisons of the biological activity of the synthesized compounds with some known antibiotics (gentamycin) presented in Table 4 show generally the free Schiff base ligand and some of its complexes exhibit better activity than these antibiotics or comparable effect. The antimicrobial activities of complexes are shown in Figs. 3 and 4.

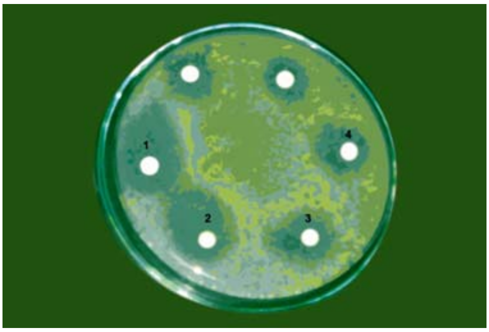


Fig. 3. *A. niger* of 1) Cu(II)-MIMFMA 2) Cu(II)-MIMTMA.

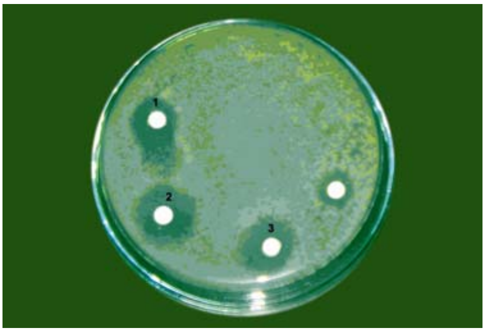


Fig. 4. *A.niger* of 2) Ni(II)-MIMFMA 3) Ni(II)-MIMTMA.

Table 4. Antimicrobial activity of the complexes.

Complex	*E.Coli*	*P.aeruginosa*	*R.oryzae*	*A.niger*
MIMFMA	+	+	+	+
Cu(II)	+++	++	+	++
Ni(II)	++	++	++	++
Co(II)	++	+	+	++
Zn(II)	++	+	+	++
VO(IV)	++	+	+	++
MIMTMA	+	+	-	+
Cu(II)	+++	++	++	+++
Ni(II)	++	++	++	++
Co(II)	++	++	+	+++
Zn(II)	++	++	+	+
VO(IV)	++	+	+	++

* Highly active = +++ (inhibition zone > 15 mm); Moderatively active = ++ (inhibition zone > 10 mm); slightly active = + (inhibition zone > 5 mm); Inactive = -- (inhibition zone < 5mm).

4. Conclusions

The metal chelates of MIMFMA, MIMTMA and MIPMA have been structurally characterized. The metal ligand stiochiometry in all these complexes is 1:2, associated with two water molecules. The complexes of the above ligands are electrolytes in DMSO.

These ligands act as neutral and bidentate coordinating through nitrogen of azomethine and furfural oxygen, thiophene sulphur and pyridine nitrogen respectively. Based on analytical, conductance, magnetic and electronic spectral data, all these complexes are assigned to be in octahedral geometry. Biological studies of these complexes reveal that these complexes show better activity compared to their respective ligands.

References

1. B. S. Tovrog, D. J. Kitko, and R. S. Dragom, J. Am. Chem. Soc. **98**, 5144 (1976). doi:10.1021/ja00433a016
2. H. Sharghi and M. A. Nasseri, Bull. Chem. Soc. (Jpn.). **76**, 137 (2003). doi:10.1246/bcsj.76.137
3. K. B. Gudasi, M. S. Patil, R. S. Vadavi, R. V. Shenoy, S. A. Patil, and M. Nethaji, Trans. Met. Chem. **31**, 580 (2006). doi:10.1007/s11243-006-0031-3.
4. M. V. D. Teresa Pinho e Melo, Current Org. Chem. **9** (10), 925 (2005). doi: 10.1002/chin.200539250
5. Y. Prashanthi, K. Kiranmai, N. J. P. Subhashini, and Shivaraj, Spectrochimica Acta, Part A. **70/1**, 30 (2008).
6. A. I. Vogel., A text book of qualitative Organic analysis, **3rd** ed. (ELBS, London, 1971) p.166.
7. R. N. Gegye and J. V. Weiv, Canadian J. Chem. **76**, 525 (1998). doi:10.1139/cjc-76-5-525
8. K. J. T. Li, J. S. Han, J. H. Yang, and P. S. Li, Ultrasonic Sonochem, **10**, (2003).
9. K. Karunakar, Ph.D thesis, Kakathiya University, Warangal, India (1992).
10. A. P. Mishra and S. K. Gautam, Ind. J. Chem. Soc. **81**, 324 (2004).
11. J. M. Sece, M. Quiros, and M. J. G. Garmendia, Polyhedron, **19,** 1005 (2000). doi:10.1016/S0277-5387(00)00356-9
12. A. A. Soliman and G. G. Mohamed, Thermochim.Acta, **421**, 151 (2004). doi:10.1016/j.tca.2004.03.010
13. A. P. Mishra, V. Shrivastava, and S. K. Shrivastava, Synth. React. Inorg. Met. Org. Chem. **255**, 21 (1995).
14. C. Spinu, A. Kriza, and L. Spinu, Acta Chim. Slov, **48**, 257 (2001).
15. W. R. Paryzek and E. Luks, Polyhedron **13**, 899 (1994). doi:10.1016/S0277-5387(00)83007-7
16. M. N. Kamaluddin and J. Cheema, Ind. J. Chem. Sec A, **32**,108 (1993).
17. J. Sanmartin, M. R. Bermejo, A. M. G. Deibo, M. Maneiro, C. Lage, and A. J. C. Filho, Polyhedron **19**, 185 (2000). doi:10.1016/S0277-5387(99)00341-1
18. D. R. Zhu, Y. Song, Y. Xu, Y. Zhang, S. S. S. Raj, H. K. Fun, and X. Z. You, Poyhedron **19**, 2019 (2000). doi:10.1016/S0277-5387(00)00501-5
19. R. Malhotra, S. Kumar, and K. S. Dhindsa, Ind. J. Chem. Sec A, **32**, 457 (1993).
20. A. B. P. Lever, J. Chem. Edn. **45**, 711 (1966).
21. R. K. Carlin, Trans. Met. Chem. **4**, 199 (1968).
22. N. Mondal, D. K. Dey, S. Mitra, and K. M. A. Malik, Polyhedron **19**, 2707 (2000). doi:10.1016/S0277-5387(00)00584-2
23. N. R. S. Kumar, M. Nethiji, and K. C. Patil, Polyhedron **10**, 365 (1991). doi:10.1016/S0277-5387(00)80158-8
24. M. Imran, J. Iqbal, S. Iqbal, and N. Ijaz, Turk . Biol. **31**, 67 (2007).
25. R. C. Maurya and D. D. Mishra, Synth. React. Inorg. Met. Org. Chem. **27**, 1127 (1995). doi:10.1080/15533179508218298
26. A. P. Mishra, M. Khare, and S. K. Gautam, Synth. React. Inorg. Met. Org. Chem. **32**, 1689 (2002).
27. L. Mishra and V. K. Singh, Ind. J. Chem. **32** (A), 446 (1997).
28. N. Dharmraj, P. Viswanathanmurthhi, and K. Natarajan, Trans. Met. Chem. **26**, 105 (2001). doi:10.1023/A:1007132408648