



Synthesis, Characterization and Antimicrobial Studies of Co(II), Ni(II), Cu(II) Cr(III), Mn(III), Fe(III), VO(IV), Zr(IV) and UO₂(VI) with Tetradentate Schiff base having N₂O₂ donor group

S. R. Kelode¹ and P. R. Mandlik²

¹ Department of Engg. Chemistry, Jagadambha College of Engineering and Tech. Yavatmal

² P. G. Department of Chemistry, Shri Shivaji Science College, Amravati

ABSTRACT

The new tetradentate Schiff base have been synthesized by condensing 2-hydroxy-5-bromo acetophenone with ethylene diamine. The metal complexes were obtained as a result of interaction of Schiff base ligand and metal ions: Co (II), Ni (II), Cu (II), Cr (III), Mn (III), Fe (III) VO (IV), Zr (IV) and UO₂ (VI). The complexes have been characterized on the basis of elemental analysis, infrared, molar conductance and magnetic Susceptibilities. The bioefficacy of the ligands and their complexes have been examined against the growth of bacteria to assess their antimicrobial potential.

Keywords: Tetradentate Schiff base, Spectra, Molar conductance, Antimicrobial

INTRODUCTION

Schiff base complexes have an important and popular area of research due to their simple synthesis, versatility and diverse range of applications (Taylor and Relinski, 2004; Yamada, 1999). The Schiff bases play a significant role in the area of coordination chemistry. The Schiff base prepared by using variety of aldehydes and amines possessed antitubercular, antitumor, anticancer, fungicidal medicinal and agrochemical activities [1,2]. Schiff base and their metal complexes are becoming increasingly important in recent years due to their biological activity [3] and their used as catalysts [4,5], photoluminescent and electroluminescent properties [6]. Antimicrobial screening and biological great significance of Schiff base metal complexes research [7,8] Schiff bases and their complexes have a variety of applications in biological clinical and analytical fields [9-11]. Recently there has been a considerable interest in the chemistry of hydrazine and hydrazone compounds because of their potential pharmacological applications [12].

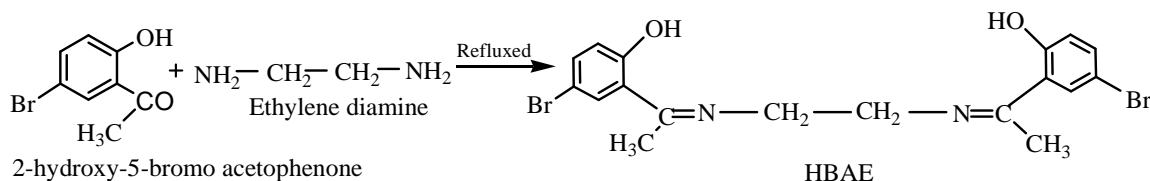
This paper discusses the molar conductance, magnetic Susceptibilities and biological activity for Schiff base complexes of Co (II), Ni (II), Cu (II), Cr (III), Mn (III), Fe (III) VO (IV), Zr (IV) and UO₂ (VI).

EXPERIMENTAL SECTION

All the chemicals were of A.R. grade and used as received ethylene diamine and 2-hydroxy-5-bromo acetophenone (HBA) was prepared by known methods [13]. The solvents were purified by standard methods [14].

Synthesis of 2-Hydroxy-5-bromoacetophenone-N,N'-ethylenediimine (HBAE):

A hot ethanolic solution of ethylene diamine (0.05 mol) was added to an ethanolic solution of respective acetophenone (0.05 mol). The reaction mixture was refluxed in a water-bath for 4-5 h. The colour product was filtered off and recrystallised. Yield 70%. M. P. 270°C



Preparation of complexes:

All the metal complexes were prepared in a similar way by following method. To a hot solution of ligand HBAE (0.02M) in 25ml of ethanol a suspension of respective metal salts was added drop wise with constant stirring. The reaction mixture was refluxed on a water bath for 4-6 h. The precipitated complexes were filtered, washed with ethanol followed by ether and dried over fused calcium chloride. Yield : 45-50%

Table 1. Analytical data and molar conductance of the compounds

Compounds	Colour	Mol.wt.	Analysis % Found (calc.)					μ_{eff} B.M.	Λ_{M} ($\Omega^{-1} \text{cm}^2$ mol^{-1})
			M	C	H	N	Cl		
$\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_2\text{Br}_2$	Yellow	453.8	--	47.83 (47.59)	3.85 (3.96)	6.07 (6.17)	--	--	--
$[\text{CoL}(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$	Brown	564.7	10.32 (10.43)	38.12 (38.25)	3.72 (3.89)	4.80 (4.95)	--	4.27	6.1
$[\text{NiL}] \cdot \text{H}_2\text{O}$	Black	528.5	11.02 (11.10)	40.72 (40.87)	3.25 (3.40)	5.17 (5.29)	--	Dia	5.6
$[\text{CuL}(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$	Brown	587.3	10.61 (10.81)	36.61 (36.77)	3.95 (4.08)	4.62 (4.76)	--	2.02	18.8
$[\text{CrL}(\text{H}_2\text{O})\text{Cl}] \cdot 2\text{H}_2\text{O}$	Yellow	593.3	8.66 (8.76)	36.22 (36.40)	3.52 (3.70)	4.58 (4.71)	5.77 (5.98)	3.86	21.2
$[\text{MnL}(\text{OAc})] \cdot 2\text{H}_2\text{O}$	Brown	601.7	9.02 (9.12)	39.78 (39.88)	3.62 (3.82)	4.53 (4.65)	--	5.6	12.8
$[\text{FeL}(\text{H}_2\text{O})\text{Cl}] \cdot \text{H}_2\text{O}$	Green	579.2	9.58 (9.65)	37.13 (37.29)	3.32 (3.45)	4.72 (4.83)	6.02 (6.12)	6.0	18.8
[VOL]	Green	518.8	9.41 (9.83)	41.12 (41.63)	3.01 (3.08)	5.09 (5.39)	--	1.78	14.5
$[\text{ZrL}(\text{OH})_2] \cdot 2\text{H}_2\text{O}$	Yellow	613.0	14.72 (14.87)	35.08 (35.23)	3.47 (3.58)	4.38 (4.56)	--	Dia	31.9
$[\text{UO}_2\text{L}]$	Orange	721.9	32.87 (32.98)	29.82 (29.92)	2.08 (2.21)	3.75 (3.87)	--	Dia	23.6

The complexes are soluble in DMSO and DMF but insoluble in water and common organic solvents. The metal chloride content of complexes were analyzed by standard methods¹¹.

The ^1H NMR spectra of ligand was recorded and obtained from RSIC Chandigarh. IR spectra of the compounds were recorded on Perkin Elmer 842 spectrophotometer in the region 400-4000 cm^{-1} , Carbon, Hydrogen and Nitrogen analysis were carried out at RSIC, Punjab University, Chandigarh. The molar conductance of the complexes at 10^{-3} M dilution in DMF were determined using equiptronic digital conductivity meter EQ-660 with a cell constant 1.00 cm^{-1} at room temperature. The magnetic moment measurement were made on a Gouy balance at room temperature using $[\text{HgCo}(\text{SCN})_4]$ as the calibrant. The thermogravimetric analysis were performed on laboratory set up apparatus in air atmosphere at 10^0C min^{-1} heating rate. The molecular weights of the complexes were determined by Rast method.

RESULTS AND DISCUSSION

The Schiff base ligand HBAE and its complexes have been characterized on the basis of ^1H NMR, IR spectral data, elemental analysis, molar conductance and magnetic susceptibility. All these values and analytical data is consistent with proposed molecular formula of ligand. All the compounds are coloured solid and stable in air. They are insoluble in water but soluble in coordinating solvents like DMF and DMSO. The molar conductance values in DMF (10^{-3} M) solution at room temperature (Table 1) shows all the complexes are non electrolytes[11].

The ^1H NMR spectra of ligand HBAE shows signals: δ 15.97 (1H, s, phenolic OH); 8.06 (1H, s, phenyl); 7.67 and 7.31(2H, m, phenyl), 3.29(4H, s, $\text{CH}_2\text{-CH}_2$); 2.51 ppm (3H, s, methyl)[15-24]

Table 2. IR spectra of ligand and metal complexes

Compound	$\nu(\text{O-H})$ hydrogen bonded	$\nu(\text{C=N})$ imine	$\nu(\text{C-O})$ phenolic	$\nu(\text{M-O})$	$\nu(\text{M-N})$	H_2O
$\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_2\text{Br}_2$	2900	1614	1480	--	--	-----
$[\text{CoL}(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$	--	1589	1440	520	455	3400, 1640, 815, 770
$[\text{NiL}] \cdot \text{H}_2\text{O}$	--	1586	1460	510	495	3326, 1630
$[\text{CuL}(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$	--	1595	1440	590	490	3406, 1642, 818, 780
$[\text{CrL}(\text{H}_2\text{O})\text{Cl}] \cdot 2\text{H}_2\text{O}$	--	1600	1436	570	460	3390, 1635, 830, 745
$[\text{MnL}(\text{OAc})] \cdot 2\text{H}_2\text{O}$	--	1590	1446	580	495	3330, 1628
$[\text{FeL}(\text{H}_2\text{O})\text{Cl}] \cdot \text{H}_2\text{O}$	--	1602	1463	530	425	3395, 1638, 845, 740
[VOL]	--	1600	1455	525	480	-----
$[\text{ZrL}(\text{OH})_2] \cdot 2\text{H}_2\text{O}$	--	1601	1440	565	460	3335, 1628
$[\text{UO}_2\text{L}]$	--	1590	1420	560	470	-----

Antimicrobial activity:

The ligand HBAE and its complexes[25-33] are found to show considerable bacteriocidal activity against *E. coli*, *A. aerogenes*, *S. aureus* and *B. subtilis* and are almost inactive against *B. megatherium*, *P. vulgaris* and *P. fluorescen*. The ligand inhibits the growth of *S. aureus* more than all its complexes. In contrast, bacteriostatic nature of the ligand is dominated by its complexes against *S. aureus*. All the complexes show moderate to good zone of inhibition against *S. aureus*. The Cu(II) and Fe(III) complexes are resistant towards *E. coli*, *B. subtilis*, *B. megatherium* and *P. fluorescen* but shows moderate activity towards other bacterial species. The Co(II) and Zr(IV) complexes strongly inhibits the growth of *B. subtilis* and has no activity against *E. coli*. The ligand Cr(III), Mn(III), VO(IV) complexes show considerable activity against *E. coli* and *B. subtilis* and almost inactive towards *P. vulgaris* and *P. fluorescen*. The $\text{UO}_2(\text{VI})$ complex exhibits moderate activity against *E. coli*, *A. aerogenes*, *S. aureus*, *B. megatherium* and is almost resistant towards the other bacteria. The results reveals that the sensitivity of the ligand HBAE and its complexes is shows in (Table 3)

Table 3. Antimicrobial activity

Ligand and its complexes	<i>B. subtilis</i> (mm)	<i>P. vulgaris</i> (mm)	<i>S. aureus</i> (mm)	<i>E. coli</i> (mm)	<i>P. fluorescen</i> (mm)	<i>A. aerogenes</i> (mm)	<i>B. megatherium</i> (mm)
HBAE	S ₈	R	S ₁₄	S ₁₃	R	R	R
Co- HBAE	S ₁₅	S ₇	S ₁₈	R	S ₁₆	R	S ₁₁
Ni- HBAE	S ₁₁	S ₁₃	S ₁₀	R	S ₁₇	S ₁₆	R
Cu- HBAE	R	S ₁₇	S ₁₂	R	R	S ₁₁	R
Cr- HBAE	S ₁₃	R	S ₁₁	S ₁₄	R	S ₁₂	R
Mn- HBAE	S ₁₃	R	S ₁₅	S ₉	R	S ₈	S ₉
Fe- HBAE	R	S ₉	S ₁₄	R	R	S ₁₃	R
VO- HBAE	S ₁₁	R	S ₁₃	S ₉	R	S ₁₈	S ₉
Zr- HBAE	S ₁₅	R	S ₁₄	R	R	S ₉	R
UO_2 - HBAE	R	R	S ₁₄	S ₁₂	R	S ₁₂	S ₈

CONCLUSION

The results revealed that the ligands and their complexes show considerable antimicrobial activity. However, the zone of inhibition of ligand varies with organisms as well as metal ions. Thus, it can be concluded that most of our ligands and their complexes possess antimicrobial activities

REFERENCES

- [1] Dincer Sebla, *Indian J. Chem.*, **1996**, 33B, 1335.
- [2] PR Panditrao;SD Deval; SM Gupta; SD Samant; LD Deodhar,*Indian J.Chem.*,**1981**,20B, 929.
- [3] RK Parashar; RC Sharma; A Kumar; *Inorg. Chim. Acta.*, **1988**, 151, 201.
- [4] K Srinivasan; S Perrier; JK Kochi, *J. Mol. Cat.*, **1986**, 36, 297.
- [5] ZY Wu; DJ Xu; ZX Feng, *Polyhedron*, **2001**, 20, 281.
- [6] ME Emam; IM Kenawy; MAH Hafez, *Thermochim. Acta.*, **1995**, 249, 169.
- [7] R Johari; G Kumar; D Kumar; S Singh, *J. Ind. Council Chem.*, **2009**, 26(1), 23.
- [8] R Nair; A Shah; S Baluja and S Chanda, *J. Serb. Chem. Soc.*, **2006**, 71(7), 733
- [9] PS Chittilappilly and KK Mohammed, *Indian J. Chem.*, **2008**, 47A, 848.
- [10] A Prakash; MP Gangwar and KK Singh, *J. Dev. Biol. Tissue Eng.*, **2011**, 3(2), 13.
- [11] N Raman; V Muthuraj; S Ravichandran, *Journal of Chemical Sciences.*, **2003**,115(3):161.
- [12] ZH Chohan; SKA Sherazi, *Metal-Based Drugs*. **1997**, 4(6), 327.
- [13] A Aswar; P Bahad; A Pardhi and N Bhawe, *J. Poym. Mater*, **1988**, 5, 232.
- [14] B Furniss; A Hannaford; P Smith and A Tatchell, *Vogel's practical organic chemistry* 5thEd. (Logman Scientific Technical, John Wiley and Sons), **1989**.
- [15] JD Joshi; NP Patel; SD Patel, *J. Indian Poly.*, **2006**, 15(3), 219.
- [16] N Raman; YP Raja; A Kulandaisamy, *J. Indian Acad. Sci.*, **2001**,113(3), 183.
- [17] B Naik; KR Desai, *Indian J. Chem.*, **2006**, 45B, 267.
- [18] EJ Campbell; ST Nquyen, *J. Tetrahedron*, **2001**, 42, 1221.
- [19] P Pietikainen; A. Haikarainen, *J. Mole. Catalysis*, **2002**, 180, 59.
- [20] M Gottschaldt; R Wegner; H Gorls; P Klufers; EG Jager;D Klemm, *J.Carbohydrate*, **2004**, 339, 1941.
- [21] T Matsushita; T Shono, *J. Polyhedron*, **1986**, 5(3), 735.
- [22] SK Gupta; PB Nutchcock;YS Kushwah;GS Argal, *J. Inorg. Chimica Acta*, **2007**, 360, 2145.
- [23] LH Cai; PZ Hu; XL Du; LX Zhang; Y Liu, *Indian J. Chem.*, **2007**, 46B, 523.
- [24] M Kidwai; PR Poddar; K Singhal, *Indian J. Chem.*, **2009**, 48B, 886.
- [25] N Chauhan; K Vyas; K Nimavat; K Joshi, *J. Chem. Pharm. Res.*, **2012**, 4(2), 1106.
- [26] CI Raj; M Christudhas; GA Raj, *J. Chem. Pharm. Res.*, **2011**, 3(6), 127
- [27] SD Dhumwad; KB. Gudasiand; TR Gaudar, *Indian J. Chem.*, **1994**, 33A, 320.
- [28] UI Singh; RK Singh; WR Devi; CH Singh, *J. Chem. Pharm. Res.*, **2012**, 4(2), 1130.
- [29] S Prakash; VP Vaidya; KM Mahadevan; MK Shivananda1; PA Suchetan; B Nirmala; M Sunitha, *J. Chem.Pharm. Res.*, **2012**, 4(2), 1179.
- [30] IO Adeoye; OO Adelowo; OO Onawumi, *J. Chem. Pharm. Res.*, **2012**, 4(1), 1.
- [31] AK Mapari; KV Mangaonkar, *Int. J. ChemTech Res.*, **2011**, 3(1), 477.
- [32] M. Rajan; V. Kishor Kumar; P. Satheesh Kumar; K. Reddy Swathi, and S. Haritha, *J. Chem. Pharm. Res.*, **2012**, 4(6), 2860
- [33] P. Patel; D. Gor and PS. Patel, *J. Chem. Pharm. Res.*, **2012**, 4(6):2906-2910