



Synthesis and characterization of transition metal complexes of 2-(salicylimino)-3-hydroxypyridine

Kamini J. Donde

Department of Chemistry, Ramnarain Ruia College, Matunga (E), Mumbai, India

ABSTRACT

The Cu(II), Fe(II), Mn(II) and Zn(II) metal complexes of Schiff base 2-(salicylimino)-3-hydroxypyridine (SIHP) were prepared and characterized by various analytical techniques such as FTIR, UV-Visible spectroscopy and elemental analyses. The magnetic moment values suggested octahedral geometry for these transition metal complexes. Thermal stability of the compounds synthesized was also studied. The compounds were also screened against various microorganisms to study their antimicrobial effect. The complexes synthesized were non toxic, non electrolytic and stable solids.

Keywords: Schiff base; Complexes; thermal stability; antimicrobial effect; non electrolytic

INTRODUCTION

Schiff's base is a functional group or type of chemical compound containing a carbon nitrogen double bond with the nitrogen atom connected to an aryl group or an alkyl group but not hydrogen [1]. Schiff bases are formed by condensation of an amine and the carbonyl group of aldehydes. Schiff for the first time reported condensation of this kind and hence the condensation products are referred as Schiff bases. Many procedures have been described in literature for the synthesis of Schiff bases [2]. The simplest method appears to be the one in which equimolar quantities of amines and aldehydes are condensed by boiling in methanol or ethanol [3, 4].

Schiff bases are an important class of ligands in coordination chemistry and find extensive applications in different fields. Schiff bases derived from the salicylaldehydes are well known as polydentate ligands coordinating in neutral forms. The interaction of these donor ligands and metal ions give complexes of different geometries and these complexes are potentially biologically active. A large number of Schiff bases and their complexes have been studied for their interesting and important properties, e.g., their ability to reversibly bind oxygen, catalytic activity in hydrogenation of olefins and transfer of an amino group, photochromic properties, and complexing ability towards some toxic metals. The high affinity for the chelation of the Schiff bases towards the transition metal ions is utilized in preparing their solid complexes [3, 4].

Many Schiff base complexes showed excellent catalytic activity in various reactions at high temperature (>100°C) and in the presence of moisture. Over the past few years, there have been many reports on their applications in homogeneous and heterogeneous catalysis [5, 6]. In the past two decades, the synthesis, structure and properties of Schiff base complexes have stimulated much interest for their noteworthy contributions in single molecule-based magnetism, material science, catalysis of many reactions like carbonylation, hydroformylation, reduction, oxidation,

epoxidation and hydrolysis, etc [7, 8]. A great deal of work has been reported on the synthesis, structural investigations, various crystallographic features, mesogenic characteristics, structure-redox relationships and catalytic properties of different types of Schiff bases and their complexes with transition and non-transition element [9-12].

The lot of attention is being given to the study of Schiff bases containing salicylaldehyde and their metal complexes [10,11]. In recent years metal complexes of Schiff bases derived from salicylaldehyde have attracted considerable attention due to their remarkable antifungal, antibacterial, antitumor and anticancer activity [9,12]. Thus the main aim of this study was to design new Schiff base containing salicylaldehyde unit and its metal complexes could be synthesized in a novel way. To fulfill this Schiff base 2-(salicylimino)-3-hydroxypyridine (SIHP) was selected as a starting point and the Cu(II), Fe(II), Mn(II) and Zn(II) complexes were prepared and characterized.

EXPERIMENTAL SECTION

Water used in present investigation was redistilled in a glass distillation assembly. The distilled water was having pH of about 6.98 to 7.00. All solvents used for synthesis and characterization experiments were HPLC grade and AR grade. The solvents such as ethanol, dimethylsulfoxide (DMSO) were purchased from Merck India Ltd, and s. d. fine Chemical Ltd, Mumbai and were used without purification. The metal salts were purchased from science house. All amino acids were purchased from Sigma-Aldrich Ltd. 2-amino-3-hydroxypyridine of AR grade was purchased from s. d. fine Chemical Ltd, Mumbai. The glassware's were used made of pyrex or corning glass. An analytical balance of 100 μ g sensitivity was used for weighing samples. Thermolyses of compounds were performed with Perkin-Elmer / Pyris Diamond TG-DTA assembly. FTIR spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrophotometer in KBr discs. UV-visible spectra were recorded by Shimadzu UV-2100 spectrophotometer. ¹H NMR spectra were recorded on a Bruker AMX-300 spectrometer in CDCl₃/DMSO and chemical shifts were reported in δ ppm values relative to an internal standard tetramethyl silane (TMS). Room temperature magnetic susceptibility measurements for all metal complexes were made by the Guoy's method using Hg[Co(SCN)₄] as calibrant [10]. The crystallite size of complexes was evaluated with X-ray powder diffraction. Diffraction patterns were obtained using an XPERT-PRO diffractometer (PANalytical). The elemental analyses of C, H, N were carried out with a Thomas and Coleman Analyser-Carlo Erba 1106. Melting points were uncorrected and determined by capillary tube method. A digital pH meter model EQ-660 was used for pH measurement. A digital Conductometer, model ELICO LI-120 was used for conductance measurement and the measurements were made at room temperature using DMF as a solvent.

Scheme 1.

Synthesis of SIHP

An ethanolic solution of 2-amino-3-hydroxypyridine (5g, 1 mmol) was added to the ethanolic solution of salicylaldehyde (5.54 g, 1mmol) in 250 ml round bottom flask. To this reaction mixture 3-4 drop of Conc. HCl was added with vigorous stirring. The reaction mass was refluxed on water bath at 80 °C for 6 hr with constant stirring. The hot reaction mass was then quenched on crushed ice. Yellow crystals obtained were filtered, washed with hot water and recrystallized twice from distilled ethanol (Figure 1).

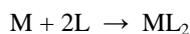
Scheme 2

Synthesis of the metal complexes

Aqueous solution of metal salt (1mmol) was mixed with warmed ethanolic solution of SIHP (2 mmol). To this reaction mixture 3-4 drop of Conc. HCl was added with vigorous stirring. The reaction mass was refluxed on water bath at 90-100 °C for 3 hr with constant stirring. The appropriate pH of the solution was maintained by adding 0.1N NH₄OH solution. The precipitate obtained was cooled, filtered, washed with warm water followed by 50 % ethanol and dried in vacuum.

RESULTS AND DISCUSSION

The metal complexes of SIHP were represented by the general formula ML₂.



The metal complexes were insoluble in water but soluble in dilute alkali indicating the presence of one free -OH

group in the complexes. This was further supported by the infrared data for these complexes, discussed later and their poor solubility in common oxygenated organic solvents like alcohol, methanol and acetone. However, all the metal complexes were somewhat more soluble in more polar solvent dimethyl formamide (DMF). The molar conductance was measured using 10^{-2} M solution in DMF. The lower conductance values indicated their non-ionic in nature [13,14].

Magnetic Susceptibility Measurements

The closed ring structure for brown-green coloured complexes was supported by UV and IR spectra [10,11]. The green Cu(II) complex was paramagnetic at room temperature. The magnetic moments at 299K for Cu(II) complex was 1.50 B.M. which suggested the octahedral geometry [9-12]. Similarly magnetic moment values of other metal complexes suggested octahedral geometry (Table 1).

^1H NMR Spectra

The paramagnetic nature and the limited solubility in the solvents CDCl_3 and DMSO, metal complexes leads to noisy base line and broadening of the signals, and did not yield ^1H NMR spectra to satisfactory quality. The NMR signals for SIHP are shown in the Table 2.

FTIR Spectra

The infrared spectra of the complexes are quite complex, however, important bands have been assigned on the basis of their correlation with other similar complexes [15,16]. A characteristic FTIR bands of the compounds are shown in Table 3. The frequency due to O-H vibrations observed in the spectrum of SIHP (3329 cm^{-1}) was also present in the spectra of complexes, which suggested presence of one -OH group. This observation confirmed the replacement of proton of one -OH group by metal ion during complexation, where as other -OH group was remained unchanged after complexation. The sharp band observed at 1576 cm^{-1} in spectrum of SIHP was assigned for C=N stretching vibrations, these vibrations were remained unchanged in the spectra of complexes. This observation also suggested non involvement of C=N in the complexation [10,11].

The another sharp band observed at 1455 cm^{-1} in the spectrum of SIHP was assigned for C-N vibrations of pyridine, these vibrations were shifted to lower frequency ($1281\text{-}1396\text{ cm}^{-1}$) in the FTIR spectra of metal complexes. This observation suggested that, the nitrogen atom on pyridine ring formed coordinate bond during the complexation. The weak intensity bands observed around $533\text{-}618$ and $466\text{-}547\text{ cm}^{-1}$ in the FTIR spectra of the metal complexes were assigned to M-N and M-O stretching modes, respectively. These assignments are based on the fact that oxygen is more electronegative than nitrogen, the M-O bond tends to be more ionic than the M-N bond and, therefore, M-O vibrations were expected to appear at lower frequencies than the M-N vibration [10,11].

Electronic Spectra

Various electronic absorption bands exhibited by metal complexes in solution and their tentative assignments are summarized in Table 4. The spectral features indicated distorted octahedral geometry for the Cu(II) complexes. A broad band in the region $11,389\text{-}13,679\text{ cm}^{-1}$ and another bands in the region $28,735\text{ cm}^{-1}$ were observed in the spectrum of the Cu(II) complexes. The former band may be assigned to the $^2E_g \rightarrow ^2T_{2g}$ transitions, suggested a distorted octahedral geometry for these complex, whereas latter two bands can be attributed to a L-M charge transfer band. The band at $16,949\text{ cm}^{-1}$ observed in the Cu(II) complexes was due to the green coloration of the complex. Only one absorption band is expected for octahedral Cu(II) complexes. Since the 2E_g state is highly susceptible to *Jahn-Teller* distortion, the Cu(II) complexes possess a distorted octahedral geometry [10,11].

The electronic spectra of Co(II) complex showed two spin-allowed transitions at $17,857$ and $21,739\text{ cm}^{-1}$ assignable to $^4T_{1g}(F) \rightarrow ^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$ transitions respectively, which were in conformity with octahedral arrangements for Co(II) ion [18]. The electronic spectra of the Fe(II) complex showed two weak bands at $10,989$ and $11,574\text{ cm}^{-1}$ due to the $^5T_{2g} \rightarrow ^5E_g$ transition and is characteristic of octahedral symmetry. Mn(II) complex showed three bands $20,283$, $18,939$ and $13,831\text{ cm}^{-1}$, which lie in the same range as reported for octahedrally coordinated Mn(II) ion [18]. The magnetic moment 4.57 B.M. was an additional evidence for an octahedral structure. The electronic spectrum of the Zn(II) complex showed an absorption band at $27,472\text{ cm}^{-1}$ attributed to the LMCT transition, which suggested an octahedral structure [19].

Thermal Analysis

The study demonstrated that the complexes were crystalline solids; however, all decomposed exothermically at

about their melting points. Polycrystalline mixtures or undesirable solvates were not detected. The thermogravimetric analysis of complexes synthesized was carried out between 28°C and 1000°C at heating rate of 10°C per minute in the nitrogen atmosphere. The thermograms of the metal complexes showed appreciable mass loss up to 150°C indicating the presence of water molecules (Table 5). The thermal analysis of the complexes showed that they were thermally stable to a varying degree in the range 210-850 °C. With further increase in temperature in the range investigated, all the complexes showed two step decomposition with loss of two water molecules (first step) and ligand molecules (second step), final residue was corresponding metal oxides .

Antimicrobial Screening

The compounds synthesized in the present investigation have been subjected to various biological screening programmes based on their structural features so as to ascertain their suitability as potential chemotherapeutic agents. The various screening programmes conducted have been in the *in vitro* study by the serial tube dilution technique [10,11]. For the biological evaluation, some representative examples were screened against seven different microorganisms (four *bacteria* and three *fungi*) using. The solvent used was DMF, and the sample concentrations were 200, 100, 50, 25, 12.5 ppm. The test results obtained are listed in Table 6. The data showed that these compounds generally exhibited moderate toxicity in the selected concentrations towards many of the biological strains tested.

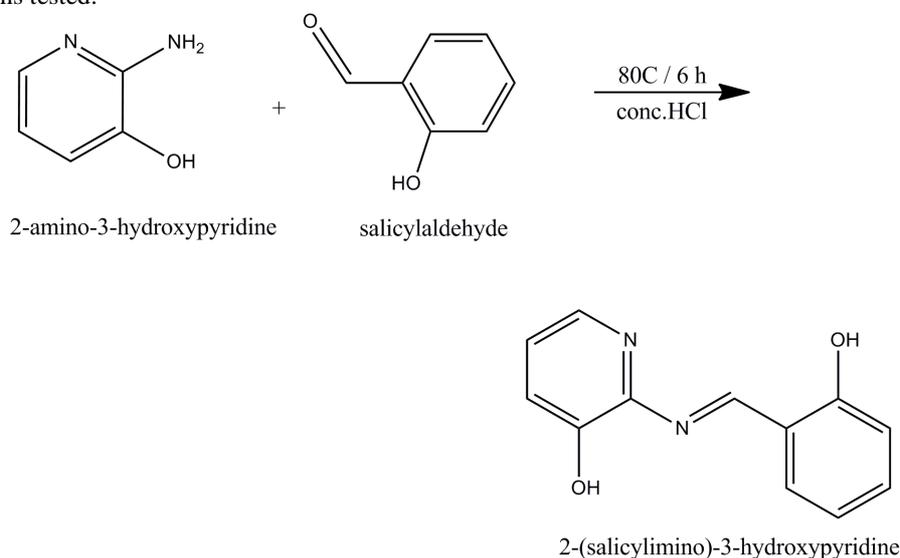


Figure 1 : Reaction scheme for SIHP

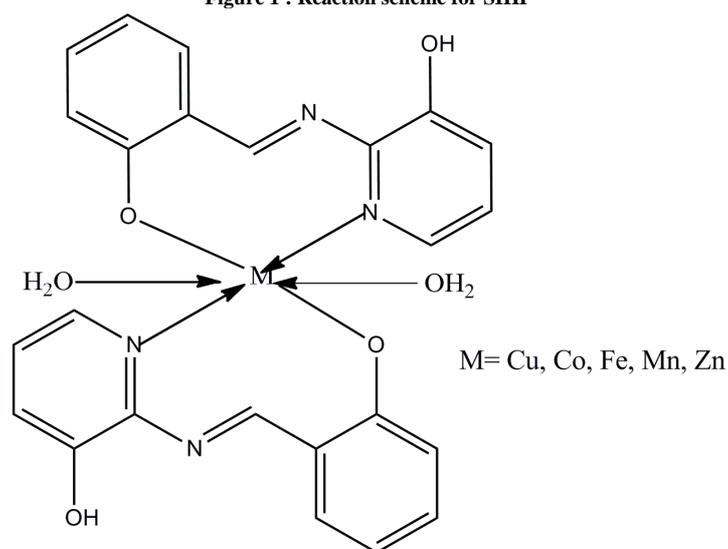


Figure 2 : Probable geometry of metal complexes

Table 1: Physicochemical properties

Compound	Colour	pH	M.P./Decomp. temp./MP	Yield %	Molar Cond. (Ohm ⁻¹ cm ² mol ⁻¹)	μ_{eff} B.M.	Elemental analysis in %				
							Obs (Cal)				
							C	H	N	O	M
SIHP	Brown	--	80	58	0.00	1.50	62.15 (62.29)	4.56 (4.67)	13.25 (13.08)	20.04 (19.96)	-
[Cu(SIHP) ₂ (H ₂ O) ₂]	Green	6	>270	76	0.01	2.70	54.60 (54.80)	4.55 (4.57)	10.65 (10.66)	17.80 (17.88)	12.00 (12.09)
[Co(SIHP) ₂ (H ₂ O) ₂]	Dark Brown	9	>280	63	0.03	2.90	55.19 (55.29)	4.40 (4.22)	10.63 (10.75)	18.27 (18.43)	11.69 (11.31)
[Fe(SIHP) ₂ (H ₂ O) ₂]	Reddish Brown	6	>280	58	0.01	4.57	55.28 (55.62)	4.06 (4.25)	9.80 (9.27)	20.00 (20.08)	10.86 (10.78)
[Mn(SIHP) ₂ (H ₂ O) ₂]	Brown	9.5	>300	38	0.02	0.00	55.52 (55.71)	4.13 (4.26)	8.99 (9.29)	20.89 (20.11)	10.47 (10.63)
[Zn(SIHP) ₂ (H ₂ O) ₂]	Light Green	9	>300	52	0.01	--	54.23 (54.61)	4.56 (4.17)	9.27 (9.10)	19.19 (19.72)	12.75 (12.40)

Table 2: ¹H NMR data of compounds

Compound	δ ppm	Assignment
SIHP	5.09	Two protons of aromatic C-OH
	6.82-6.93	Two Ar-CH protons
	7.12	One Ar-CH proton
	7.45-7.53	Three Ar =CH-CH= protons
	8.12	One N=CH proton
	8.44	One Ar C=N-CH= proton

Table 3: Characteristic FTIR bands of the compounds (cm⁻¹)

Compound	OH	C-N	C=N	C=C	M-N	M-O
SIHP	3329	1455	1576	1618	--	--
[Cu(SIHP) ₂ (H ₂ O) ₂]	3321	1369	1570	1606	618	542
[Co(SIHP) ₂ (H ₂ O) ₂]	3350	1306	1566	1602	617	547
[Fe(SIHP) ₂ (H ₂ O) ₂]	3399	1396	1572	1612	595	529
[Mn(SIHP) ₂ (H ₂ O) ₂]	3334	1281	1577	1602	601	513
[Zn(SIHP) ₂ (H ₂ O) ₂]	3498	1299	1576	1607	533	466

Table 4: Visible spectral data of the metal complexes

Compound	ν (λ) cm ⁻¹ (nm)	Assignment
[Cu(SIHP) ₂ (H ₂ O) ₂]	11389-13679 (878-731)	² E _g → ² T _{2g}
	28735(348)	C.T.
	17857 (560)	⁴ T _{1g} (F) → ⁴ A _{2g} (F)
[Co(SIHP) ₂ (H ₂ O) ₂]	21739 (460)	⁴ T _{1g} (F) → ⁴ T _{1g} (P)
	28248 (354)	C.T.
	10,989 (910)	⁵ T _{2g} → ⁵ E _g
[Fe(SIHP) ₂ (H ₂ O) ₂]	11,574 (864)	⁵ T _{2g} → ⁵ E _g
	28011 (357)	C.T.
	13831 (723)	⁴ T _{1g} → ⁶ A _{1g}
[Mn(SIHP) ₂ (H ₂ O) ₂]	18939 (528)	⁴ T _{2g} → ⁶ A _{1g}
	20283 (493)	⁴ A _{1g} → ⁶ A _{1g}
	28571 (350)	C.T.
[Zn(SIHP) ₂ (H ₂ O) ₂]	27472 (364)	C.T.

Solvent – DMF, C.T.- Charge transfer

Table 5: Thermal analysis data

Compound/ M.F./M.W.	TG Temp. Range (°C)	DTA peak temp. (°C)	Expt. loss (%)	Calc. loss (%)	Moiety lost	Residue (%)
SIHP/ C ₁₂ H ₁₀ N ₂ O ₂ /214	120-450	305	96.505	100	Whole molecule	--
[Cu(SIHP) ₂ (H ₂ O) ₂] 525.546	100-210	170	7.11	6.85	2H ₂ O	CuO
[Co(SIHP) ₂ (H ₂ O) ₂] 520.933	230-650	430	80.31	78.01	Two SIHP mol.	(12.18)
[Fe(SIHP) ₂ (H ₂ O) ₂] 517.845	100-190	150	6.89	6.91	2H ₂ O	CoO
[Mn(SIHP) ₂ (H ₂ O) ₂] 516.938	210-700	450	77.25	78.71	Two SIHP mol.	(15.86)
[Zn(SIHP) ₂ (H ₂ O) ₂] 527.380	100-200	145	7.32	6.95	2H ₂ O	FeO
	220-810	500	78.84	79.17	Two SIHP mol.	(13.84)
	100-190	155	6.78	6.96	2H ₂ O	MnO
	210-650	440	80.11	79.31	Two SIHP mol.	(13.11)
	100-210	160	7.40	6.83	2H ₂ O	ZnO
	230-800	570	82.01	77.74	Two SIHP mol.	(10.59)

Table 6: Results of antimicrobial activities in ppm

Compound	Antibacterial activity				Antifungal activity		
	a	b	c	d	e	f	g
SIHP	25	50	50	25	25	25	50
[Cu(SIHP) ₂ (H ₂ O) ₂]	50	50	50	50	100	100	100
[Co(SIHP) ₂ (H ₂ O) ₂]	25	25	50	25	25	50	25
[Fe(SIHP) ₂ (H ₂ O) ₂]	50	50	25	25	25	50	25
[Mn(SIHP) ₂ (H ₂ O) ₂]	25	100	100	100	50	100	100
[Zn(SIHP) ₂ (H ₂ O) ₂]	25	200	50	25	100	50	100

a. *C. diphtheriae*, b. *E. coli*, c. *S. typhi*; d. *S. aureus*; e. *C. albicans*; f. *A. niger*; g. *S. cerevisiae*,

CONCLUSION

Based on spectroscopic investigations and their correlations with the available data of known compounds, the proposed structures of metal complexes have been illustrated Figure 2. The antimicrobial study showed that the complexes of SIHP exhibited moderate biological activity against all the organisms under study. Therefore, these compounds may be considered as promising candidates for further biological investigations.

REFERENCES

- [1] IJ Patel; SJ Parmar, *E-J.Chem.*, **2010**, 7(2), 617-623.
- [2] Y Farina; SA Shaker; AA Salleh, *Euro. J. Sci. Res.*, **2009**, 33, 702-709.
- [3] GG Mohamed; MM Omkar; AM Hindy, *Turk J. Chem.*, **2006**, 30, 361 – 382.
- [4] P Souza; JA Garcia-Vazquez; JR Masaguer, *Trans.Met. Chem.* **1985**, 10, 410- 412.
- [5] H Naeimi; J Safari; A Heidarneshad, *Dyes Pigments*, **2007**, 73, 251- 253.
- [6] SJ Lippard; JM Berg. Principles of Bioinorganic Chemistry, University Science Books, California, **1994**.
- [7] B Dede; F Karipcin; M Cengiz, *J. Chem. Sci.*, **2009**, 121(2), 163–171.
- [8] R H Holm; M J O' Conner, *Prog. Inorg. Chem.*, **1971**, 14, 241.
- [9] IJ Sallomi; A J Shaheen, *Polyhedron*, **1998**, 19, 1429-1433.
- [10] A.R. Patil, K. J. Donde, S. S. Raut, V. R. Patil and R.S. Lokhande, *J. Chem.Pharm. Res.*, **2012**, 4(2), 1413-1425.
- [11] AR Patil; KJ Donde; SS Raut; V R Patil; RS Lokhande, *J.Pharm.Res.*, **2011**, 4(7), 2256-2260.
- [12] S Baluja; A Solanki; N Kachhadia, *J. Ira.Chem. Soc.*, **2006**, 3(4), 312-317.
- [13] W J Geary, *Coord. Chem. Rev.*, **1971**, 7(1), 81- 122.
- [14] VK Naik; AVaradarajan; A J Kulkarni; SP Malve, *Synth. React. Inorg. Met.Org. Chem.*, **1999**, 29(6), 935- 949.
- [15] R G Deshmukh; NV Thakkar, *Ind. J. Chem.*, **1985**, 24A, 1066- 1070.
- [16] BC Haldar, *J. Ind. Chem. Soc.*, **1974**, 51, 224-230.
- [17] CH Krushna; CM Mohapatra; KC Dush, *J.Inorg. Nucl. Chem.*, **1977**, 39, 1253- 1258.
- [18] MM A Mohammad; M M Shoukry, *Polyhedron*, **2001**, 21(2), 167–173.
- [19] M Sekerci; E Tas, *Heteroatom. Chem.*, **2000**, **11**, 254- 260.