SYNTHESIS, POTENTIOMETRIC AND ANTIMICROBIAL STUDIES ON METAL COMPLEXES OF THIAZOLE SCHIFF BASE

ABDEL-NASSER ALAGHAZ
Department of Chemistry, Faculty of Science, Al-Azhar University, Cairo, Egypt|Department of Chemistry, Faculty of Science, Jazan, KSA

REDA AMMAR
Department of Chemistry, Faculty of Science, Al-Azhar University, Cairo, Egypt

SYNTHESIS, POTENTIOMETRIC AND **ANTIMICROBIAL** STUDIES ON METAL COMPLEXES OF THIAZOLE SCHIFF BASE

ABDEL-NASSER M. A. ALAGHAZ* and REDA A. A. AMMAR

Department of Chemistry, Faculty of Science, Al-Azhar University, Cairo, Egypt

*** Department of Chemistry, Faculty of Science, Jazan, KSA*

Abstract

The synthesis of the Schiff base ligand salicylidene-3-phenyl-2-aminothiazole (LH_2) and their Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Cd(II) metal complexes have been reported. The structure of ligand and their complexes was investigated using elemental analysis, IR, UV-Vis, ^1H NMR, magnetic susceptibility and conductance measurements. Protonation constants of Schiff base and stability constants of their binary metal complexes have been determined potentiometrically in 50% DMSO–water media at 25°C and ionic strength 0.10 M sodium perchlorate. Antimicrobial activity of the ligand and metal complexes were tested using the disc diffusion method and the strains Bacillus megaterium and Candida tropicalis. The stability constants were found to follow the order: Cr(III) < Mn(II) < Co(II) < Ni(II) < Cu(II) > Fe(III).

Keywords: Thiazole Schiff base; Transition metal complexes; Infrared; Stability constants

Introduction

A large number of Schiff bases and their metal complexes have been studied because of their interesting and important properties such as their ability to reversibly bind oxygen[1], and their use in catalyses for: oxygenation and oxidation reactions of organic compounds[2], redox systems in biological processes[3], Aldol reactions[4], degradation of industries[5], reduction of thionyl chloride[6] and oxidation of DNA[7]. Also Schiff bases can be used in degradation of organic compounds[8] and in radiopharmaceuticals[9]. For these applications, we are extending this field in synthesis of novel mono and binuclear Schiff base complexes. The present study deals with the preparation of some salicylidene-3-phenyl-2-aminothiazole (LH_2) and their chelates with some transition metal ions, e.g. Cr(III), Mn(II), Fe(III), Co(II), Ni(II) Cu(II) and Cd(II). The solid complexes have been synthesized and studied by elemental analyses and IR. The DC electrical behaviour of salicylidene-3-phenyl-2-aminothiazole (LH_2) and its chromium(III), manganease (II), iron(III), cobalt(II), nickel(II), copper(II) and cadmium(II) complexes at different temperatures is investigated. The mechanism of conduction is explained. The study further deals

with the potentiometric determination of the protonation constants of the Schiff base and stability constants of the complexes by the potentiometric titration method in 50% DMSO–water media at 25.00 ± 0.02 °C and ionic strength 0.10 M sodium perchlorate. Data were evaluated using a computer program MINIQUAD[10].

Experimental

Materials

All chemicals used in the present investigation were of Analar or the highest purity grade from BDH used as received without further purification. The solvents used were methanol, ethanol, isopropanol, *n*-hexane, dimethylsulfoxide (DMSO), and chloroform, either of spectroscopic pure from BDH or purified according to recommended procedures[11].

Potentiometric titrations

Potentiometric measurements were made using a Metrohni 686 titioprocessor (Switzerland) equipped with a 665 Dosiniat. The electrode and titroprocessor were calibrated with standard buffer solutions prepared according to NBS specifications[12].

All Potentiometric measurements in this study were carried out in water- DMSO mixtures containing 50% DMSO because of low solubility of Schiff base and possible hydrolysis in aqueous solutions.

Procedure of potentiometric measurements

Potentiometric titrations were carried out at constant temperature and an inert atmosphere of nitrogen with Co_2- free standardized 0.1M NaOH in 40 ml solution containing 0.1M $NaClO_4$: (i) 3.0×10^{-3} M HNO_3+ 1.5×10^{-3} M Schiff base (for the protonation constant of the Schiff base); (ii) 3.0×10^{-3} M HNO_3 +1.5×10^{-3} M Schiff base + 7.5×10^{-4} M metal (II) ions (for the stability constant of the complexes).

The species formed were characterized by the general equilibrium process (1), whereas the formation constants for these generalized species are given by Eq. (2) (charges are omitted for simplicity).

$$pM + qL + rH \quad \overleftarrow{\quad\quad} \quad M_pL_qH_r \tag{1}$$

$$\beta_{\mathbf{pqr}} = \frac{[M_pL_qH_r]}{[M]^p[L]^q[H]^r} \tag{2}$$

Where M, L, H stand for the metal ion, ligand and proton, respectively. The calculations were performed using the computer program MINIQUAD-75 and were conducted on an IBM computer. The stoichiometries and stability constants of the complexes formed were determined by trying various possible composition models for the systems studied. The model selected was that which gave the best statistical fit and was chemically consistent with the magnitudes of various residuals as described elsewhere [13]. Table (1) lists the stability constants together with their standard deviation and the sum of the squares of the residuals as derived from the output of the program MINIQUAD- 75. The concentration distribution diagrams were obtained with the program SPECIES [14], taking into account the experimental conditions used.

Table 1 Formation Constants of the Metal Complexes .

System	p	q	r^a	$Log \beta^b$	S^c
LH$_2$	0	1	1	8.67(0.01)	3.8×10^{-9}
	0	1	2	11.45(0.02)	
Cu(II)	1	1	0	4.97(0.01)	6.3×10^{-9}
	1	2	0	10.12(0.03)	
	1	1	1	15.23(0.03)	
Cr(III)	1	1	0	4.72(0.02)	2.1×10^{-8}
	1	2	0	9.34(0.02)	
	1	1	1	14.66(0.01)	
Fe(III)	1	1	0	3.90(0.02)	5.8×10^{-8}
	1	2	0	8.01(0.04)	
	1	1	1	14.94(0.03)	
Co(II)	1	1	0	3.57(0.04)	9.3×10^{-7}
	1	2	0	7.63(0.06)	
	1	1	1	15.56(0.02)	
Ni(II)	1	1	0	3.11(0.03)	7.0×10^{-8}
	1	2	0	6.33(0.05)	
	1	1	1	15.74(0.02)	
Cd(II)	1	1	0	3.06(0.01)	9.9×10^{-8}
	1	2	0	6.15(0.06)	
	1	1	1	14.24(0.02)	

[a]p, q and r are the stoichiometric coefficients corresponding to metal ion, ligand and H^+, respectively; [b]Standard deviations are given in parentheses; [c]Sum of square of residuals .

Preparation of the Salicylidene-3-phenyl-2-aminothiazole (LH$_2$)

The Schiff base was prepared by mixing equimolecular amounts of salicylaldehyde (0.122gm; 0.001mmole) and the appropriate 3-phenyl-2-aminothiazole (0.176 g, 0.001 mmol) in 10 ml absolute ethanol in a round bottomed flask equipped with a condenser. The mixture was brought into reflux for 2 h. The products obtained after cooling were filtered off and crystallized from absolute ethanol. The crystallized solids were dried under vacuum and kept dry in a desiccator over anhydrous calcium chloride. Melting points were measured and elemental analysis for the prepared Schiff base was done (Fig. 1).
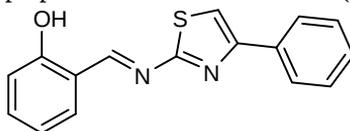
Fig. 1 Proposed structure of LH$_2$ ligand.

Preparation of the solid complexes

The solid complexes were prepared by mixing hot saturated alcoholic solutions of 0.001M of metal salt solutions with the requisite amount of the ligand under study (LH$_2$) sufficient to form 1: 2 (M: L) complexes (Fig. 2). The reaction mixture was stirred on a water bath. If the solid complexes did not separate on standing, diluted ammonia solution 1: 10 was added to the complexes of Cr(III), Fe(III), Co(II) and Ni(II) to maintain the pH at 5–6. The solid complexes were filtered off and washed several times with ethanol until the filtrate becomes colourless. The obtained complexes were kept in a vacuum desiccator.
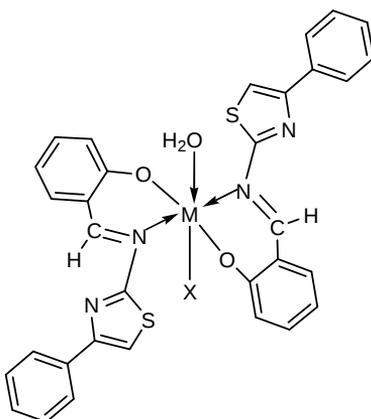
$M=Cr^{3+}$, Fe^{3+}, $X=Cl$; $M= Mn^{2+}$, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, X H_2O

Fig. 2 Suggested structures of LH$_2$ metal complexes.

Physical measurements

All melting points were taken on a Stuart apparatus and are uncorrected. Microanalyses for C, H, N, S and Cl were performed by the microanalytical unit at Cairo University, Egypt. The infrared spectra of all ligands and their complexes were recorded (4000–200 cm^{-1}) using a Perkin-Elmer FTIR 2000 spectophotometer applying the KBr disc technique. The UV–visible absorption spectra were recorded using Jasco V-350 recording spectrophotometer at room temperature. ^{1}H NMR spectra in D$_6$-DMSO with TMS as internal standard were obtained from a Jeol-FX-90Q Fourier NMR Spectrometer at Cairo University, Egypt. The metal content of the prepared complexes was determined[11]. The conductometric measurements in solutions were carried out using conductivity TDS model 72.

Results and discussion

The ligand was found to be soluble in CHCl$_3$, EtOH, MeOH, DMF, DMSO, THF, and insoluble in diethyl ether and water, slightly soluble in benzene and n-hexane. The structure of the ligand **(LH$_2$)** was elucidated by elemental analyses, IR, electronic, ^{1}H NMR techniques. The assignment of the proposed structure for **LH$_2$** is based on the elemental analyses data listed in Table 2. The ^{1}H NMR spectrum of the ligand **(LH$_2$)** showed the following characteristic proton signals at: δ (13.22) ppm is assigned for O–H proton, which disappeared on the addition of D$_2$O due to the proton exchange. The presence of a sharp singlet signal at δ= 8.82 ppm due to the azomethine proton clearly indicates the Schiff-base formation. The spectrum also shows, the multi-signals within the range δ= 7.68-6.97 ppm which are assigned to the aromatic protons.

Table 2 Physical data of Ligand (LH₂) and corresponding Metal Complexes

[Compound] M. F. (M.Wt)	m.p. (°C)	Color [Yield (%)]	Elemental analyses % calculated (found)						Λ_m (Ω^{-1} mo^{-1}cm^2)
			C	H	N	S	Cl	M	
[LH₂] C₁₆H₁₂N₂OS[280.34]	160	Orange [98]	68.55 (68.05)	4.31 (4.11)	9.99 (9.57)	11.44 (11.34)	--	--	--
[Cr(L)₂H₂O Cl] C₃₂H₂₄ClCrN₄O₃S₂ [664.14]	>300	Gray [89]	57.87 (57.26)	3.64 (3.44)	8.44 (8.25)	--	5.34 (5.15(	7.83 (7.80 (	14.54
[Fe(L)₂H₂O Cl] C₃₂H₂₄ClFeN₄O₃S₂ [667.99]	>300	Yellow [88]	57.54 (57.32)	3.62 (3.49)	8.39 (8.20)	9.60 (9.54)	5.31 (5.45 (	8.36 (8.37 (	18.05
[Mn (L)₂(H₂O)₂] C₃₂H₂₆MnN₄O₄S₂ [649.64]	>300	Green [90]	59.16 (59.03)	4.03 (3.80)	8.62 (8.87)	9.87 (10.05)	--	8.46 (8.46 (	17.33
[Co(L)₂(H₂O)₂] C₃₂H₂₆CoN₄O₄S₂ [653.64]	>300	Green [91]	58.80 (58.60)	4.01 (3.80)	8.57 (8.32)	--	--	9.02 (9.00 (	17.63
[Ni(L)₂(H₂O)₂] C₃₂H₂₆NiN₄O₄S₂ [653.4]	>300	Green [90]	58.82 (58.80)	4.01 (4.00)	8.57 (8.56)	9.81 (9.78)	--	8.98 (8.97 (	17.63
[Cu(L)₂(H₂O)₂] C₃₂H₂₄CuN₄O₄S₂ [658.25]	>300	Orange [84]	58.39 (58.31)	3.98 (3.73)	8.51 (8.46)	9.74 (9.76)	--	9.65 (9.62 (	10.85
[Cd (L)₂(H₂O)₂] C₃₂H₂₄CdN₄O₄S₂ [707.11]	>300	Orange [88]	54.35 (54.33)	3.71 (3.73)	7.92 (7.73)	--	--	15.90 (15.90 (	10.85

Infrared spectra of the free ligands and their metal complexes

The metal complexes of ligand (LH₂) with Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Cd(II) were prepared and subjected to many analytical tools such as elemental analyses C, H, N and S (Table 2), IR and UV-Vis analysis. In order to give conclusive idea about the structure of the metal complexes, the main IR bands were compared with those of the free ligand.

The absence of the broad band at 3100 cm^{-1} due to v(OH) of the intramolecularly bonded N-OH in the spectra of the complexes indicates the deprotonation of the salicylaldimine moiety of ligand in the complexation. The shift of the characteristic imine (>CH=N) band from 1650 to 1615–1622 cm^{-1}, demonstrates the coordination of the azomethine nitrogen to the nickel atom. Furthermore, the bands observed at 450–650 cm^{-1} assigned to M-O and M-N bending vibrations, supporting the ligand and Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) or Cd(II) ion coordination[15]. The most significant conclusion drawn from the proceeding arguments is that ligands act as monobasic bidentate ligand towards the central metal ion to form cationic six-coordinate chelates.

Conductimetric titrations

The calculated molar ratio [L]/[M] are plotted against the corrected molar conductance values. The results indicate that the conductance increases with the addition of the metal ion solutions due to the release of the highly conducting hydrogen ions as a result of chelation. Inspection of the titration curves shows the presence of two distinctive breaks at metal to ligand molar ratios of 1M: 2 L[16].

Electronic spectra and magnetic measurements

Electronic spectral data of the ligand (LH$_2$) was recorded in DMF solution. The electronic spectrum of ligand (LH$_2$) exhibited five absorption bands at 278, 307, 335, 418 and 430 nm. In this case, the first and third bands correspond to $^1L_a \leftarrow ^1A_1$ and $^1L_b \leftarrow ^1A_1$ transitions of the phenyl ring[17]. The second band at 307 nm corresponds to the $\pi \rightarrow \pi^*$ transition of the C=O group. The fourth band at 418 nm corresponds to the $\pi \rightarrow \pi^*$ transition of the azomethine group, and the last band at 430 nm corresponds to the $n \rightarrow \pi^*$ due to the lone pairs of the oxygen and nitrogen[18].

The Cu(II) complex [Cu(L)$_2$(H$_2$O)$_2$] gave a band at 560 nm, suggesting the existence of a transition from $d_{xy} \rightarrow d^2_z$ and $d_{xz} \rightarrow d_{yz}$ transfer to the antibonding and half-filled $d^2x - d^2y$ level which is consistent with an octahedral configuration[19, 20]. The observed magnetic moment of the Cu(II) complex is 1.81 B.M., which confirms the octahedral structure of this complex[21].

The electronic spectrum of [Ni(L)$_2$(H$_2$O)$_2$] is consistent with the octahedral geometry showing one broad d–d transition band at 795 nm assigned to $^3T_1g(F) \leftarrow ^3A_2g(F)$ transition. Magnetic moment of 2.93B.M. is an additional evidence for the octahedral structure[22].

The electronic spectrum of the blue complex, [Co(L)$_2$(H$_2$O)$_2$] exhibits an intense band at 545 nm assignable to the $^4A_2g(F) \leftarrow ^4T_1g(F)$ transition and a shoulder at 630 nm due to spin coupling, indicating octahedral geometry for this complex[23]. The blue color as well as the magnetic moment of 5.13 B.M are a further indication for the octahedral geometry[24].

The electronic spectrum of the [Mn(L)$_2$(H$_2$O)$_2$] complex shows a strong band at 774 nm which is assigned to the $^6A_1g \rightarrow ^4T_1g (^4G)$ transition. The other characteristic bands for d-d transitions are difficult to recognize in this complex and thus the ligand field parameters could not be calculated. The magnetic moment

value is 5.52 B.M which indicates the presence of Mn(II) complex in octahedral structure[19, 20].

From the electronic spectrum it is observed that, the Fe(III) chelate exhibits a band at 452 nm, which may be assigned to the $^6A_1g \rightarrow T_2g(G)$ transition in octahedral geometry of the complexes[22]. The $^6A_1g \rightarrow {}^5T_1g$ transition appears to be split into two bands at 590 and 740 nm. The spectrum shows also a band at 360 nm which may be attributed to ligand to metal charge transfer[22]. The observed magnetic moment value of Fe(III) complex [Fe(L)$_2$H$_2$O Cl] is found to be 5.58 B.M., indicating octahedral geometry around the Fe(III) complex[21].

Six coordinated Cr(III) complexes with octahedral symmetry show three spin allowed bands in the range of 555–333 nm. While the complex [Cr(L)$_2$H$_2$O Cl] under study shows four bands in the range of 588–260 nm. This type of complex may have either C$_4$v or D$_4$h symmetry. The Cr(III) complex [Cr(L)$_2$H$_2$O Cl] display bands at 555, 364, 364, and 260 nm, respectively. These bands may be assigned to $^4B_1g \rightarrow {}^4E_1g(v_1)$, $^4B_1g \rightarrow {}^4B_2g(v_2)$, $^4B_1g \rightarrow {}^4E_1g(v_3)$ and $^4B_1g \rightarrow {}^4A_1g(v_4)$ transitions, respectively, arising from the lifting of the degeneracy of the orbital triplet (in octahedral symmetry) in the order of increasing energy and assuming D$_4$h symmetry[21]. The C$_4$v symmetry has been ruled out because of higher splitting of the first band. This suggests it possess distorted octahedral geometry[21]. Chromium(III) complex shows magnetic moments corresponding to three unpaired electrons, i.e. 3.82 B.M., expected for high-spin octahedral chromium(III) complexes[22].

The Cd (II) complex Cd(L)$_2$(H$_2$O)$_2$] is diamagnetic and octahedral geometry is proposed for this complex.

Protonation constants of Schiff base

The study of complex formation by the studied Schiff base cannot be carried out in aqueous solution because of the nature of the compounds involved. These metal complexes as well as the ligand themselves are insoluble in water. This solvent has been most widely used for potentiometric determination of stability constants. The mixture DMSO–water 50: 50% was the chosen solvent for our study. In such a medium, the studied Schiff base and their metal complexes are soluble giving stable solutions. The use of this mixed solvent has some advantages over pure DMSO. Thus, pure DMSO is very hygroscopic and controlling its water content is difficult[25]. This fact would affect reproducibility of our experiments. However, DMSO–water 50:50% mixture has only a small hygroscopic character.

The stoichiometric protonation constants of the investigated Schiff base LH_2 was determined in 50% DMSO–water at 25°C and these constants are tabulated in Table 1. As the titration curve of the ligand in Fig 3., it can be seen that there are two end – points at a = 1 and a = 2. According to the results obtained from this titration curve it can be concluded that the Schiff base have two protonation constants. Log K_{OH} and Log K_{NH} values are amounting to 8.67 and 2.78 respectively, as Fig 4. The highest value due to the protonation of phenolic oxygen while the other value due to the imine nitrogen proton. The concentration distribution diagram of the protonated forms of the ligand are shown in Fig. 5.
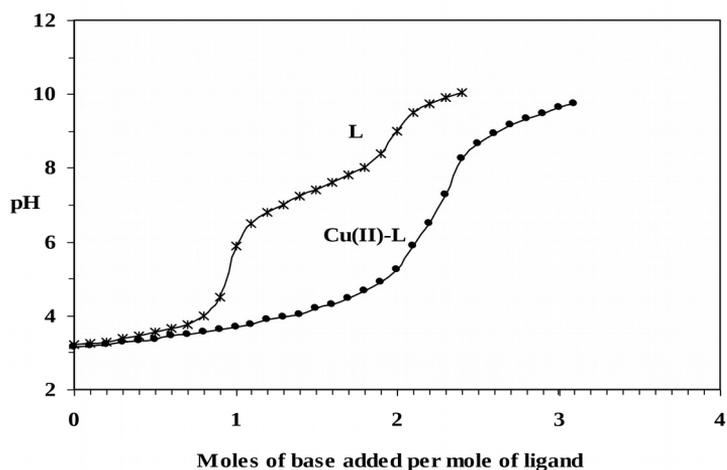
Fig. 3. Potentiometric titration curve of the Cu(II)-L system
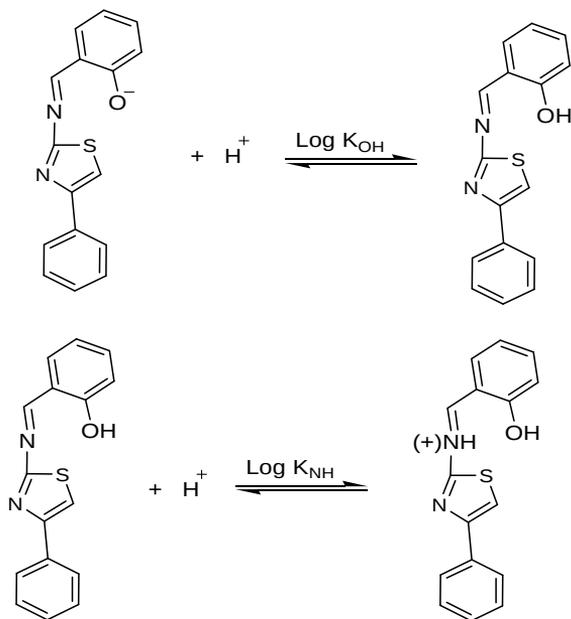
Fig. 4. The log K_{OH} and log K_{NH} equilibrium reactions of the ligand LH_2
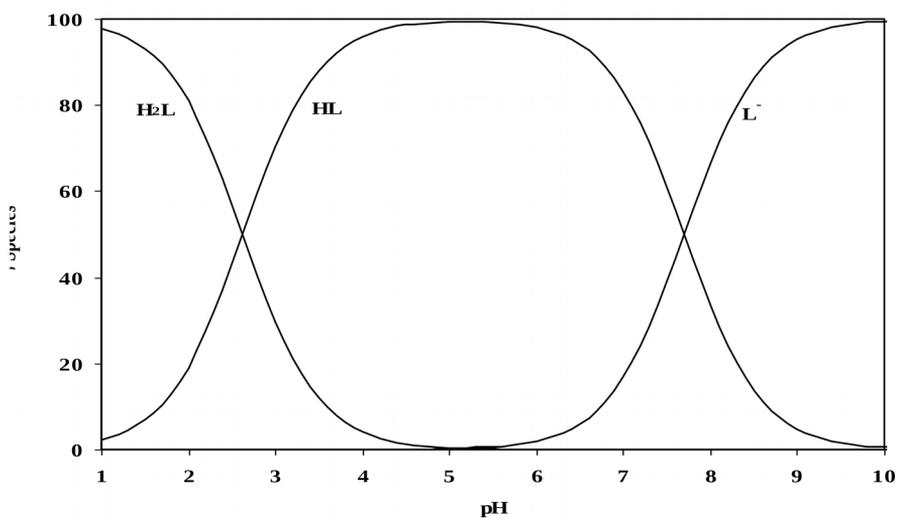
Fig. 5. Species distribution diagram for the systems L Schiff base (LH_2) as a function of pH.

Stability constants of the Schiff base complexes

The potentiometric titration curves of the Cu(II)-L system, taken as a representative, are given in Fig.3. The titration curve of the Cu(II)–L complex is lowered from that of the free Schiff base(L) curve, indicating formation of Cu(II) complex by displacement of protons. The formation constants were determined by fitting potentiometric data on the basis of possible composition models. The selected model with the best statistical fit was found to consist of CuL (110), CuL_2 (120) and CuLH (111) complexes. The stability constants of their complexes are given in Table (1). The concentration distribution for the Cu(II) complex, taken as a representative, is given in Fig. 6. The CuL complex starts to form at pH value 4, reaching a maximum concentration (88.61%). On the other hand, CuL_2 complex concentration was found to increase with increasing the pH and becomes predominant (95.14%) at pH=10.2. Protonated complex (CuLH) species have been found to be most favoured at lower pH values.
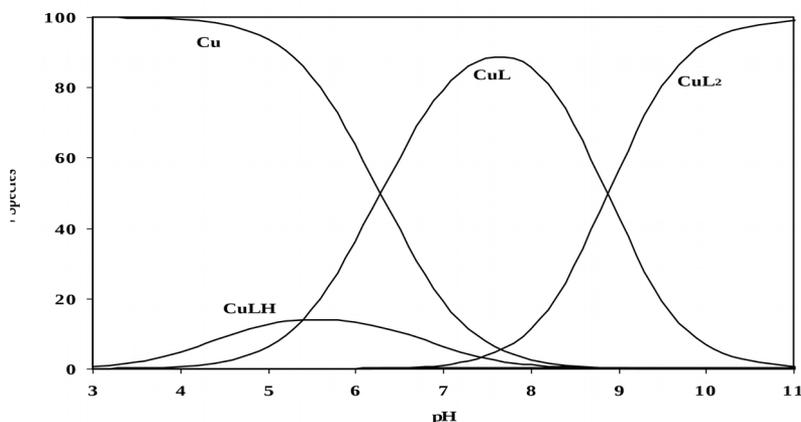
Fig. 6. Species distribution diagram for the systems Cu(II)- Schiff base (LH$_2$) as a function of pH.

The results show that the stability of the metal chelates follows the order Co<Ni<Cr<Cu>Cd. This order is in good agreement with that found by Mellor and Naley[26] and by Irving and Williams[27] for 3d transition metal ions. The classic sharp maximum for the Cu(II) complex is due to the stabilizing contribution of the Jahn-Teller effect[28] With respect to increasing electronegativity of the metals, the electronegativity difference between metal atom and donor atom of the ligand will

decrease, hence the metal-ligand bond would have more covalent character which may result in greater stability of the metal chelates

MICROBIAL ASSAY

Antimicrobial Screening

The synthesized Schiff base ligand LH_2 and their complexes were tested for the in vitro growth inhibitory activity against pathogenic fungi, *Alternaria cymopsidis and Macrophomina phaseolina* and bacteria *Escherichia coli* (-) and *Staphylococcus aureus* (+). The proper temperature, necessary nutrients and growth media were employed for the preparation of cultures of the fungi and bacteria using aseptic technique.[29]

Antifungal Screening

The antifungal Screening Schiff base ligand LH_2 and their complexes has been evaluated against *Alternaria cymopsidis and Macrophomina phaseolina*. The Radial Growth Method[30] using Czapek's agar medium having the composion glucose 20 g, starch 20 g, agar-agar-20 g and distilled water 1000 mL was employed for measure fungicidal activity. The compounds were mixed directly with the medium in different concentrations. Spores of the fungi were placed on the medium with the help of an inoculum needle. The petri dishes were wrapped in polythene bags containing a few drops of alcohol and were placed in an incubator at 30 ± 1^0C. Controls were also run and three replicates were used in each case. The linear growth of the fungus was obtained by measuring the fungal colony diameter after 4 days. The amount of growth inhibition in each of the replicates was calculated by the equation (C-T) $100C^{-1}$, where C is the diameter of the fungal colony on the control plate and T is the diameter of the fungal colony on the test plate.

Antibacterial Screening

Antibacterial activity was evaluated by the Paper Disc Plate method.[31] Foe this purpose, pure cultures of the organisms were dissolved in peptone-water (1: 1) and then uniformly seeded on the nutrient agar plates having the composition peptone 5g, beaf extract 5g, NaCl 5g, agar-agar 20g, and distilled water 1000mL. The compounds were dissolved in 500- and 1000-ppm concentrations. Paper discs of Whatman No.1 with a diameter of 5 mm were soaked in different solutions of the compounds. These discs were placed on the medium previously seeded with the

organisms in the petri dishes at suitable distances. The petri dishes were stored in an incubator at $30 \pm 20C$ for 24 h. The zone of inhibition thus formed around each disc containing the test compound was measured accurately in mm. The organisms used in the present investigations included *Escherichia coli* (-) and *Staphylococcus aureus* (+).

Mode of action

The Schiff base ligand LH_2 and their corresponding chromium, manganese, ferric, nickel and copper complexes were screened against the selected pathogenic fungi and bacteria to examine their growth-inhibiting potential towards the test organism. The results show that these compounds exhibit antimicrobial properties. Cr(II), Mn(II), Fe(III), Ni(II) and Cu(II) complexes show more inhibitory effects than the parent Schiff base ligand LH_2 (Table 3 and 4). The Schiff base ligand with nitrogen and oxygen donor system might have inhibited enzyme productions since enzymes, which require reactive groups for their activity, appear to be especially susceptible to deactivation by the complexes. The complexes facilitate their diffusion through the lipid layer of the spore membrane to the site of action, ultimately killing them by combining with the reactive groups of certain cell enzymes. The results show that the activity is enhanced by undergoing chelation.[31] It is a well known fact that the concentration plays a vital role in increasing the degree of inhibition. As the concentration increases, the activity increases. The fungicidal activity was better when compared to the bactericidal activity.

Table 3 Fungicidal Screening Data of the Schiff base, LH_2, ligand and their metal complexes   (Average % Inhibition after 96 h, Concentration in ppm)

Compd	*Alternaria cymopsidis*		*Macrophomina phaseolina*	
	100 ppm	200 ppm	100 ppm	200 ppm
$[LH_2]$	38	51	37	52
$[Cr(L)_2H_2O\ Cl]$	41	61	82	100
$[Mn(L)_2(H_2O)_2]$	86	100	41	52
$[Fe(L)_2H_2O\ Cl]$	42	63	42	52
$[Co(L)_2(H_2O)_2]$	46	65	46	62
$[Ni(L)_2(H_2O)_2]$	43	64	82	53
$[Cu(L)_2(H_2O)_2]$	46	66	46	62
$[Cd(L)_2(H_2O)_2]$	49	63	48	60
Bavistin	86	100	82	100

Table 4 Antibacterial Activity of the Schiff base, LH$_2$, ligand and their metal complexes (Diameter of Inhibition zone after 30 h, Concentration in ppm)

Compd	Alternaria cymopsidis		Macrophomina phaseolina	
	100 ppm	200 ppm	100 ppm	200 ppm
[LH$_2$]	31	50	37	86
[Cr(L)$_2$H$_2$O Cl]	40	100	82	54
[Mn (L)$_2$(H$_2$O)$_2$]	40	62	41	52
[Fe(L)$_2$H$_2$O Cl]	42	66	42	58
[Co(L)$_2$(H$_2$O)$_2$]	86	65	40	53
[Ni(L)$_2$(H$_2$O)$_2$]	46	63	46	61
[Cu(L)$_2$(H$_2$O)$_2$]	48	70	88	91
[Cd (L)$_2$(H$_2$O)$_2$]	60	69	76	85
Bavistin	86	100	82	100

References

1. S. PARK, V. K. MATHUR AND R. P. PLANAP, Polyhedron, **17**, 325 (1998).

2. A. NASHINAGA, H. OHARA, H. TOMITA AND T. MATSUURA, Tetrahedron Lett., **24**, 213 (1983).

3. L. F. LINDOY (Ed.), The Chemistry of Macrocyclic Ligand Complexes, Cambridge University Press, Cambridge, (1989).

4. K. MARUYAMA, K. KUBO, Y. TODA, K. KAWASA, T. MASHINO AND A. NISHINAGA, Tetrahedron Lett., **36**, 5609 (1995).

5. T. NAKAMURA, K. NIWA, M. FUJIWARA, T. MATSUSHITA, Chem. Lett., 1067 (1999).

6. Y. K. CHOI, W. S. KIM, K. I. CHUNG, M. W. CHUNG AND H. P. NAM, Microchem., **65**, 3 (2000).

7. C. J. BURROWS, J. G. MULLER, G. T. POULTER AND S. E. ROKITA, Acta Chem. Scand., **50**, 337 (1996).

8. H. YOON, T. R. WAGLER, K. J. O'CONNOR AND C. J. BURROWS, J. Am. Chem. Soc., **122**, 4568 (1990).

9. M. A. GREEN, H. LUO AND P. E. FANWICK, Inorg. Chem., **37,** 1127 (1998).

10. A. SABATINI, A. VACCA AND P. GANS, Talanta, 21, 53 (1974).

11. I. VOGEL, A Text Book of Practical Organic Chemistry, 4th ed., Longman, London, 1978, p. 925.

12. R. C. BATES, "Determination of pH - Theory and Practice" 2nd Edn., Wiley Interscience, New York (1975).

13. P. GANS, A. SUBATINI, A. VACCA, Inorg. Chim. Acta 18 (1976) 237.

14. L. Pettit, University of Leeds (personal communication).

15. A. KUMARI, J. P. TANDON AND R. V. SINGH, Appl. Organomet. Chem., **7**, 655 (1993).

16. M. ABD-ELLAH, B. A. EL-SAYED, M. A. EL-NAWAWY AND A. M. A. ALAGHAZ, J. Phosphorous, sulfur and Silicon, **177**, 2895 (2002).

17. R. PLATT, J. Chem. Phys., **17**, 484 (1949).

18. N. N. GREENWOOD AND A. EARNSHAW, Chemistry of the Elements, Pergamon Press, New York (1984).

19. A. B. P. LEVER, Inorganic Electronic Spectroscopy, 2nd ed., Elsevier, New York (1997).

20. A. A. EMARA, Synth. React. Inorg. Met.-Org. Chem., **29**, 87 (1999).

21. F. A. COTTON AND G. WILKINSON, Advanced Inorganic Chemistry, A Comprehensive Text, 4th ed., John Wiley and Sons, New York (1986).

22. C. BAILAR, H. J. EMELEUS, R. NYHOLM AND A. F. TROTMAN-DICKENSON, Comprehen-sive Inorganic Chemistry, Vol. 3, Pergamon Press, New York (1975).

23. Nakamoto, Infrared Spectra of Inorganic Coordination Compounds, 4th ed., Wiley/Interscience, New York (1980).

24. G. ABD EL-WAHED, A. BARAKAT AND H.A. HAMMAD, Bol. Soc. Quim. Peru LXII, 30 (1996).

25. D. MARTIN, H.G. HAUTHAL, Dimethyl Sulphoxide, Van Nostrand Reinhold, Wokingham, UK (1975).

26. D. P. MELLOR AND L. MALEY, Nature, **159**, 370 (1947).

27. H. IRVING AND R. J. P. Williams, Analyst, **71**, 813 (1952).

28. COTTON AND G. WILKINSON, Advanced Inorganic Chemistry, Wiley, New York (1980).

29. GURSOY AND N. KARAH, European Journal of Medicinal Chemistry, **38,** 633 (2003).

30. S. LEE, K. YANG YI, S. KIM, J. Suh, N. Kim and S. Yoo, European Journal of Medicinal Chemistry, **38,** 459 (2003).

31. D. H. HEILMAN, Proc. Staff Meetings Mayo Clinic, **20**, 145 (1945).

☿