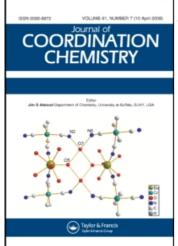
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Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information: http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, characterization, and antimicrobial activities of nickel(II) and copper(II) Schiff-base complexes

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First published on: 08 October 2009

To cite this Article Rajasekar, M., Sreedaran, S., Prabu, R., Narayanan, V., Jegadeesh, R., Raaman, N. and Kalilur Rahiman, A.(2010) 'Synthesis, characterization, and antimicrobial activities of nickel(II) and copper(II) Schiff-base complexes', Journal of Coordination Chemistry, 63: 1, 136 - 146, First published on: 08 October 2009 (iFirst)

To link to this Article: DOI: 10.1080/00958970903296362 URL: http://dx.doi.org/10.1080/00958970903296362

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Synthesis, characterization, and antimicrobial activities of nickel(II) and copper(II) Schiff-base complexes

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(Received 29 January 2009; in final form 8 July 2009)

Ni(II) and Cu(II) metal complexes of simple unsymmetrical Schiff-base ligands derived from salicylaldehyde/5-methylsalicylaldehyde and ethylenediamine or diaminomaleonitrile (DMN) were synthesized. The ligands and their complexes were characterized by elemental analysis, $^{\rm l}$ H NMR, FT IR, and mass spectroscopy. The electronic spectra of the complexes show d–d transitions in the region at 450–600 nm. Electrochemical studies of the complexes reveal that all mononuclear complexes show a one-electron quasi-reversible reduction wave in the cathodic region. ESR spectra of the mononuclear copper(II) complexes show four lines, characteristic of square-planar geometry, with nuclear hyperfine spin 3/2. The copper(II) complexes show a normal room temperature magnetic moment value $\mu_{\rm eff}$ = 1.70–1.74 BM which is close to the spin only value of 1.73 BM. Kinetic studies on the oxidation of pyrocatechol to o-quinone using the copper(II) complexes as catalysts were also carried out. The *in vitro* antimicrobial activity of the investigated compounds was tested against human pathogenic bacterias such as Staphylococcus aureus, Bacillus subtilis, Klebsiella pneumonia, Pseudomonas aeruginosa and Escherichia coli. The antifungal activity was tested against Candida albicans. Generally, the metal complexes have higher antimicrobial activity than the free ligands.

Keywords: Schiff-base ligands; Cyclic voltammetry; Catecholase activity; Antimicrobial activity

1. Introduction

Schiff-base ligands derived from the condensation of salicylaldehyde with diamines and their complexes [1, 2] played an important part in the development of inorganic chemistry, as widely studied coordination compounds are increasingly important as biochemical, analytical, and antimicrobial reagents. Tetradentate Schiff-base complexes of transition metal ions [3–5] have attracted considerable attention as promising materials due to interesting magnetic exchange and spectroscopic characteristics [6–9].

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Complexes of Schiff bases have been used as antibacterial, antifungal, anticancer, antitubercular, hypertensive, and hypothermic reagents [10–12]. Salen complexes of transition metals have also been used as biomimetic catalysts for oxygen atom transfer [13].

Structure–activity relationships of the metal complexes are determined by the oxidation state of metals, the type and number of donor atoms, and relative disposition within the ligand [14]. Parashar *et al.* [15] reported copper(II), cobalt(II), and nickel(II) complexes of the Schiff-base ligands obtained from 2-substituted anilines, and salicylaldehyde exhibit good antifungal and antibacterial activity.

Phenolic compounds are universal inhibitors of free-radical processes, retarding both oxidation and free-radical fragmentation reactions of important biomolecules (lipids, peptides, carbohydrates, vitamins, etc.) and many phenolic compounds have antibacterial activities [16]. In the presence of metal ions these phenolic compounds are believed to damage the cytoplasmic membrane, which is related to their bactericidal activity [17]. These data provide a good basis for attempts to use simple phenolic ligands in the syntheses of new bioactive metal complexes.

As part of our continuing efforts to synthesize and characterize transition metal complexes of simple and inexpensive Schiff bases, in this article we describe the synthesis, characterization, and antimicrobial activities of Schiff bases and their Ni(II) and Cu(II) complexes derived from salicylaldehyde/5-methylsalicylaldehyde and ethylenediamine or diaminomaleonitrile (DMN).

2. Experimental

2.1. Physical measurements

Elemental analyses of the complexes were obtained using a Haereus CHN rapid analyzer. IR spectra were recorded on a Shimadzu FT-IR 8300 series spectrophotometer on KBr disks from 4000 to 400 cm⁻¹. ¹H NMR spectra were recorded using a JEOL GSX 400 MHz NMR spectrometer. Atomic absorption spectral data were recorded using a Varian spectra AA-200 model atomic absorption spectrophotometer. Mass spectra were obtained on a JEOL DX-303 mass spectrometer. Electronic spectral studies were carried out on a Hitachi 320 spectrophotometer from 200 to 1100 nm. Cyclic voltammograms were obtained on a CHI-600A electrochemical analyzer under oxygen-free conditions using a three-electrode cell in which a glassy carbon electrode was the working electrode, a saturated Ag/AgCl electrode was the reference electrode, and platinum wire was the auxiliary electrode. A ferrocene/ferrocenium (1+) couple was used as an internal standard and $E_{1/2}$ of the ferrocene/ferrocenium (Fc/Fc⁺) couple under the experimental condition was 470 mV. Tetra(n-butyl)ammonium perchlorate (TBAP) was used as the supporting electrolyte. Room temperature magnetic moments were measured on a PAR vibrating sample magnetometer Model-155. X-band EPR spectra were recorded at 25°C on a Varian EPR-E 112 spectrometer using diphenylpicrylhydrazine (DPPH) as the reference. Catalytic oxidation of catechol to o-quinone by the copper complexes was studied in 10^{-3} M dimethylformamide solutions. The reactions were followed spectrophotometrically with the strongest absorption band of o-quinone at 390 nm and monitoring the increase in absorbance. A plot of $\log(A_{\infty}/A_{\infty} - A_{\rm t})$ versus time was made for each complex and the rate constants for the catalytic oxidations were calculated.

2.2. Materials and safety note

5-Methyl salicylaldehyde [18] was prepared by following the literature method. Glycerol, boric acid, *p*-cresol, THF, and hexamethylenetetramine were purchased from Qualigens and used as received. Analytical grade methanol, ethanol, chloroform, and dimethylformamide were purchased from Qualigens. TBAP used as supporting electrolyte in electrochemical measurement was purchased from Fluka and recrystal-lized from hot methanol. (Caution: TBAP is potentially explosive; perchlorate complexes are also potentially explosive; and hence, care should be taken in handling the compounds. However, the small quantities used in this study were not found to present a hazard.) All other chemicals and solvents were of analytical grade and used as received.

2.3. Synthesis of L^1

5-Methy1 salicylaldehyde (10 mmol, 1.38 g) and ethylenediamine (10 mmol, 0.7 mL) were added to chloroform (50 mL) and the mixture was refluxed for 18 h. The resulting yellow solution was cooled to room temperature and the yellow needles were collected by filtration, washed with hexane, and recrystallized from THF. The product (10 mmol, 1.78 g) obtained was refluxed with salicylaldehyde (10 mmol, 1.04 mL) in ethanol (50 mL) for 16 h. The resulting yellow solution was cooled in ice to give yellow precipitate which was filtered, washed with hexane, and dried under vacuum. Recrystallization from THF gave yellow crystals.

Yield (for monocondensed Schiff base): 0.62 g (34.8%). m.p.: 158°C. Anal. Calcd for $C_{10}H_{14}N_2O$ (%): C, 67.39; H, 7.92; N, 15.72. Found (%): C, 67.12; H, 7.98; N, 15.50. ESI MS: (m/z) (%) 179.16, Calcd av. m/z 178.28. Yield (L¹): 0.4 g (14.2%). m.p.: 128°C–132°C. Anal. Calcd for $C_{17}H_{18}N_2O_2$ (%): C, 71.81; H, 6.43; N, 9.92. Found (%): C, 71.72; H, 6.34; N, 9.81. ESI MS: (m/z) (%) 283.20, Calcd av. m/z 282.34. ¹H NMR: δ (ppm in CDCl₃): 2.25 (s, 3H, Ar–CH₃), 3.91–3.92 (d, 4H, N–CH₂), 6. 82–6.86 (t, 1H), 6.92–6.94 (d, 1H), 7.0 (d, 1H), 7.07–7.09 (d, 1H), 7.21–7.28 (t, 1H), 8.28–8.29 (d, 2H, –CH=N), 12.97 (s, Ar–OH).

2.4. Synthesis of L^2

A solution of 5-methyl salicylaldehyde (4.70 mmol, 0.64 g) and diaminomaleonitrile (DMN) (4.65 mmol, 0.503 g) in THF was refluxed for 18 h. The resulting brown solution was cooled to give brown precipitate which was washed with hexane. The product (2 mmol, 0.45 g) was refluxed with a solution of salicylaldehyde (2 mmol, 0.210 mL) in THF (50 mL) for 16 h. The resulting brown solution was cooled in ice to give brown precipitate, which was collected, washed with hexane and dried under vacuum. Recrystallization from chloroform gave brown solid.

Yield (for monocondensed Schiff base): 0.43 g (40.6%). m.p.: 120°C. Anal. Calcd for $C_{12}H_{10}N_4O$ (%): C, 63.71; H, 4.46; N, 24.77. Found (%): C, 63.53; H, 4.61; N, 24.65.

ESI MS: (m/z) (%) 227.40, Calcd av. m/z 226.24. Yield (L²): 0.17 g (25.8%). m.p.: 210°C (dec). Anal. Calcd for C₁₉H₁₄N₄O₂ (%): C, 69.08; H, 4.27; N, 16.96. Found (%): C, 68.96; H, 4.32, N, 16.88. ESI MS: (m/z) (%) 331.41, Calcd av. m/z 330.35. ¹H NMR: δ (ppm in CDCl₃): 2.27 (s, 3H, Ar–CH₃), 6. 83–6.85 (t, 1H), 6.92–6.94 (d, 1H), 7.0 (d, 1H), 7.15–7.19 (d, 1H), 7.21–7.28 (t, 1H), 8.34–8.46 (d, 2H, –CH=N), 12.93 (s, Ar–OH).

2.5. Synthesis of metal complexes

Metal complexes were synthesized by mixing 1:1 methanolic solution of L^1/L^2 and the appropriate metal perchlorate salts. The resulting mixture was refluxed for 8–12 h in a water bath, then concentrated to ca 15 mL and ca 15 mL of ether was added and the reaction mixture was cooled to 0° C. The precipitated metal complexes were obtained by filtration, washed with ether, recrystallized from chloroform, and dried under vacuum.

 $Ni(II)L^{I}$: Yield: 2.14 g (63%). m.p.: >250°C (dec). Anal. Calcd for $C_{17}H_{16}N_{2}O_{2}N_{16}$ (%): C, 60.22; H, 4.76; N, 8.26; Ni, 17.31. Found (%): C, 60.17; H, 4.72; N, 8.22; Ni, 17.28. ESI MS: (m/z) (%) 338.12, Calcd av. m/z 339.02.

*Cu(II)L*¹: Yield: 2.83 g (82%). m.p.: >250°C (dec). Anal. Calcd for C₁₇H₁₆N₂O₂Cu (%): C, 59.38; H, 4.69; N, 8.15; Cu, 18.48. Found (%): C, 59.32, H, 4.65; N, 8.12; Cu, 18.46. ESI MS: (m/z) (%) 344.76, Calcd av. m/z 343.87. EPR: $g_{||}$, 2.29; g_{\perp} , 2.05; $A_{||}$, 153. *Ni(II)L*²: Yield: 2.53 g (65%). m.p.: >250°C (dec). Anal. Calcd for C₁₉H₁₂N₄O₂Ni (%): C, 58.97; H, 3.12; N, 14.48; Ni, 15.17. Found (%): C, 58.92; H, 3.10; N, 14.43; Ni, 15.14. ESI MS: (m/z 386.20 M⁺, Calcd av. m/z 387.02).

 $Cu(II)L^2$: Yield: 3.10 g (79%). m.p.: > 250°C (dec). Anal. Calcd for C₁₉H₁₂N₄O₂Cu (%): C, 58.24; H, 3.09; N, 14.30; Cu, 16.22. Found (%): C, 58.12; H, 2.94; N, 14.13; Cu, 16.14. ESI MS: (m/z) (%) 390.63, Calcd av. m/z 391.88. EPR: $g_{||}$, 2.26; g_{\perp} , 2.06; $A_{||}$, 165.

3. Results and discussion

Schiff bases have been synthesized by condensation reaction of 5-methylsalicylaldehyde/salicylaldehyde and ethylenediamine or DMN (scheme 1); metal complexes (figure 1) were prepared by using 1:1 ratio of ligand and appropriate metal complexes as per the following known equation:

$$M^{n+} + H_2L \rightarrow ML + 2H^+$$

Attempts to grow single crystals of the complexes by diffusion of diethyl ether vapor into DMF or recrystallization of the complexes from acetonitrile only gave brown/yellow powder or micro crystals.

3.1. Spectroscopic studies

The FT IR spectrum of 5-methy1salicylaldehyde shows $\nu(C=0)$ at $1642\,\mathrm{cm}^{-1}$. The ligands as well as 5-methy1salicylaldehyde show bands at $3400\,\mathrm{cm}^{-1}$ corresponding

Scheme 1. (a) Synthesis of ligand L¹; (b) Synthesis of ligand L².

Figure 1. Metal complexes of nickel and copper.

to ν (–OH). The absence of these peaks in the complexes indicates the absence of OH due to complexation. Ligands and complexes show a sharp band at 1618–1629 cm⁻¹ due to C=N group. Formation of this new peak and the disappearance of ν (C=O) and ν (–OH) in the complexes indicate Schiff-base condensation [12, 19, 20]. For the complexes bands at 466–430 cm⁻¹ could be assigned ν (M–O). Other weak bands at lower frequency could be assigned to ν (M–N) [21]. A strong band at 1260 cm⁻¹ in the free Schiff bases has been assigned to phenolic C–O stretch. Upon complexation, this band shifts to higher frequency (~1300 cm⁻¹) showing coordination through phenolic oxygen [22].

	λ_{max} (nm) (ε (M ⁻¹ cm ⁻¹)] in methanol			
Compound	d-d	Charge transfer		
Ni(II)L ¹	457 (5688)	261 (35,348), 328 (55,600), 385 (75,692)		
Cu(II)L ¹ Ni(II)L ²	574 (2084) 461 (5704)	273 (48,840), 363 (12,856) 262 (41,120), 335 (58,480), 381 (84,184)		
$Cu(II)L^2$	583 (1640)	265 (25,196), 328 (14,036)		

Table 1. Electronic spectral data of the complexes.

CDCl₃ was used as solvent for ¹H NMR spectra (Supplementary material). A singlet at 2.2–2.4 ppm is assigned to methyl of the Schiff base. Aromatic protons were observed at 6.8–7.4 ppm, the aromatic hydroxyl protons at 12.8–13.0 ppm, and two equivalent imine protons (–CH=N) as a singlet at 8.2–8.4 ppm, respectively.

Electronic spectra of the complexes were recorded in CH_3OH (table 1). The band below 280 nm is due to intraligand transition $(\pi - \pi^*)$. The band between 325 and 390 nm is due to LMCT $(n-\pi^*)$. The nickel(II) complexes exhibit four bands in their electronic spectra with the band at \sim 460 nm attributed to the d-d transition. Schiff-base copper(II) complexes exhibit three bands in their UV-vis region with the band at \sim 580 nm attributed to the d-d transition. The electronic spectral values of these complexes are close to the reported square planar Schiff-base ligands [23–26]. This shows the existence of complexes in square planar structures. The electronic spectra of the complexes show a "red shift" in the d-d absorption band upon introducing an electron-withdrawing group in the side arm.

3.2. ESR spectra

Solid state ESR spectra of the copper(II) complexes were recorded in the X-band region at room temperature. The ESR spectrum of Cu(II)L² (Supplementary material) shows four lines [27] with nuclear hyperfine spin 3/2 due to hyperfine splitting. The observed $g_{||}$ values are less than 2.3 indicating considerable covalent character in the M–L bonds [28]. The $g_{||}$ values of Cu(II)L¹ and Cu(II)L² are 2.29 and 2.26 and g_{\perp} values are 2.05 and 2.06, respectively, indicating square-planar geometry. The absence of the half-field signal at 1600 G, corresponding to $\Delta Ms = \pm 2$ transition, ruled out Cu–Cu interaction [29], consistent with mononuclear complexes.

The hyperfine $A_{||}$ splitting falls in the range of $150-165 \times 10^{-4} \, \mathrm{cm}^{-1}$, indicative of an electron interacting with only one copper nucleus. The relation $g_{||} > g_{\perp}$ is typical of d⁹ copper(II) complexes in a ground state doublet with the unpaired electron in a $\mathrm{d}_{x^2-y^2}$ orbital [30–32]. The order $g_{||} > g_{\perp} > 2$ and the ESR parameters coincide with related systems suggesting the square-planar geometry [33]. In the axial spectra, the g values are related to the exchange interaction term G by the expression

$$G = (g_{\parallel} - 2.0023)/(g_{\perp} - 2.0023)$$

According to Hathaway and Tomlinson [34], if G > 4.0, exchange is negligible because the local tetragonal axes are aligned parallel or are slightly misaligned. If G < 4.0, exchange is considerable and the local tetragonal axes are misaligned. The observed G values for the complexes are higher than 4.0.

Complexes	$E_{\rm pc}$ (V)	$E_{\mathrm{pa}}\left(\mathrm{V}\right)$	$E_{\frac{1}{2}}$ (V)	$\Delta E \text{ (mV)}$
Cu(II)L ¹	-1.16	-0.88	-1.02	280
$Cu(II)L^2$	-1.10	-0.90	-1.00	200
$Ni(II)L^1$	-1.28	-0.94	-1.11	340
Ni(II)L ²	-1.16	-0.86	-1.01	300

Table 2. Electrochemical data of Ni(II) and Cu(II) complexes (reduction at cathodic potential).

The room temperature (at 298 K) magnetic moments of the complexes were determined by vibrating sample magnetometer (VSM). The nickel(II) complexes are diamagnetic in nature due to the square planar geometry [27]. The magnetic moments of copper(II) complexes show a $\mu_{\rm eff}$ in the range of 1.70–1.74 BM, close to the spin-only value of copper(II) [35]. The room temperature magnetic data of the copper(II) complexes do not provide conclusive evidence for the geometry; however, the electronic spectral data coupled with magnetic moment values indicate the square planar geometry for both nickel(II) and copper(II) complexes.

3.3. Electrochemical studies

The electrochemical properties of the complexes were studied by the cyclic voltammetry in the potential range of 0 to -2.0 V versus Ag/AgCl using DMF and 10^{-1} M TBAP as supporting electrolyte. The cyclic voltammograms of Ni(II)L² and Cu(II)L² are shown in Supplementary material (data are summarized in table 2).

3.3.1. Reduction at negative potential. All the complexes show one quasi-reversible reduction wave at negative potential. ΔE increases with increasing scan rate and is always greater than 60 mV. Controlled potential electrolysis carried out at 100 mV more negative than the reduction wave consumes one electron per molecule [36].

The Ni(II) complexes show a well-defined quasi-reversible reduction peak at -0.96 to -1.16 V which correspond to Ni^{II} \longrightarrow Ni^I [37–40].

The Cu(II) complexes show a well-defined quasi-reversible reduction peak at -0.96 to $-1.12\,V$ which corresponds to $Cu^{II} \Longrightarrow Cu^{I}$. The electrochemical behavior of the copper complexes agree with that observed for other neutral copper(II) Schiff-base complexes [41]. Complexes of L^2 are reduced at lower negative potential than L^1 due to the presence of two electron-withdrawing groups in the side arm.

3.3.2. Oxidation at positive potential. The cyclic voltammogram for Ni(II) complexes recorded at anodic potential in the range 0 to $+1.6\,\mathrm{V}$ shows one quasi-reversible oxidation wave at a positive potential (+1.21 to $+1.36\,\mathrm{V}$) (Supplementary material). The $E_{\frac{1}{2}}$ values of oxidation correspond to reported values [39, 40]. Controlled potential electrolysis carried out at $100\,\mathrm{mV}$ more negative than the reduction wave indicates consumption of one electron per molecule. Thus, the one electron process occurred at the electrode surface is

$$Ni^{II} \longrightarrow Ni^{III}$$

3.4. Kinetic studies of oxidation of pyrocatechol (catecholase activity)

In most of the catecholase activity studies pyrocatechol has been employed as the substrate. The product o-quinone is stable and shows a strong absorption at $\lambda_{\text{max}} = 390 \text{ nm}$ [12, 36, 42]. Thus, the activities and reaction rates, respectively, can be determined using electronic spectroscopy by following the appearance of the absorption of o-quinone.

Catalytic activity of the copper(II) complexes was carried out using pyrocatechol as the model substrate for identification of the functional models for metalloenzymes [43, 44]. The oxidation of catechols (i.e., o-diphenols) to the corresponding quinones is known as catecholase activity (scheme 2). Solutions (10⁻³ mol dm⁻³) of complexes in dimethylformamide were treated with 100 equivalents of pyrocatechol in the presence of air. The course of the reaction was followed spectrophotometrically at 390 nm for 45 min at time intervals of 5 min. The slope was determined by the method of initial rates by monitoring the growth of the 390 nm band of the product o-quinone. A linear relationship for initial rate and the complex concentration obtained for the copper(II) complexes shows a first-order dependence on the complex concentration for the systems.

Plots of $\log(A_{\infty}/A_{\infty}-A_{\rm t})$ versus time for catecholase activity of the copper(II) complexes are shown in figure 2. The observed kinetics show a first-order dependence on complex concentration. Initial rate constant values show that $Cu(II)L^2$ has higher activity $(7.4 \times 10^{-3}\,{\rm min}^{-1})$ than $Cu(II)L^1$ $(5.1 \times 10^{-3}\,{\rm min}^{-1})$. Reactivity of the complexes differs significantly by introducing electron-withdrawing group on the side arm.

Scheme 2. Oxidation of catechol.

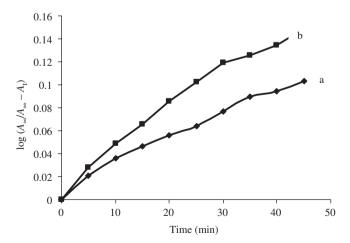


Figure 2. Catecholase activity of (a) Cu(II)L¹ and (b) Cu(II)L².

Structural features and electrochemical properties are important factors in determining the catalytic activity of complexes. If the reduction potential is too negative, the complex has decreased the catalytic activity due to a more difficult reduction to metal(I). Literature reports [45, 46] also show that complexes containing electron-withdrawing groups have higher catalytic activity than complexes with electron-donating substituents.

3.5. Antifungal and antimicrobial activities

Antifungal and antibacterial activities of the complexes were tested by the well diffusion method using Sabouraud dextrose agar and Muller Hinton agar [47]. The zone of inhibition was recorded on the completion of the incubation and the mean diameter for each complex at $100 \, \mu \mathrm{g \, mL^{-1}}$ was recorded. The zone of inhibition was recorded in millimeters (mm). Stock solutions of tested compounds were prepared in dimethyl sulfoxide. The diameters of the zone of inhibition produced by the compounds were compared with the standard antibiotics Streptomycin $10 \, \mu \mathrm{g}$ per well and Azithromycin $15 \, \mu \mathrm{g}$ per well (for *Candida albicans*). Each experiment was repeated three times to minimize the error.

3.5.1. Inoculum preparation. Fresh bacterial cultures were used for the antibacterial susceptibility test. Inoculate five ATCC colonies of the strains to Tryptic soy or Brain Heart Infusion broth incubate at 37° C for 22-24 h. The turbidity was adjusted with sterile broth to correspond to the 0.5 Mc Farland standard; standard inoculum of the microorganism of 1.5×10^{6} colony forming units CFU mL⁻¹ diluted 1:100 gives suspension of turbidity equal to a Mc Farland standard 0.5. The turbidity was adjusted to match a Mc Farland 0.5 barium sulfate, prepared by adding 0.5 mL of 1.175% w/v (0.048 m) hydrate (BaCl₂ · 2H₂O) to 99.5 mL of 1% w/v (0.36) sulfuric acid.

3.5.2. Antifungal activity. We have evaluated the antifungal activity of the ligands and complexes against *C. albicans*. The screening data are reported in table 3.

Table 3. Antibacterial and antifungal activity data of Schiff-base ligands and their complexes.

		Representation zone of inhibition (diameter in mm)						
		Antibacterial activity (100 µg mL ⁻¹)						
Sample	S.a	B.s	K.p	P.a	E.c	C.a		
L ¹ L ² Ni(II)L ¹ Cu(II)L ¹ Ni(II)L ² Cu(II)L ²	$ \begin{array}{c} -\\ 13 \pm 2\\ 12.0 \pm 0.5\\ 16 \pm 1\\ 15 \pm 1 \end{array} $	$ \begin{array}{c} -12.0 \pm 0.6 \\ 12 \pm 1 \\ 14 \pm 2 \\ 17 \pm 2 \\ 16 \pm 1 \end{array} $	$ \begin{array}{c} -\\ 14 \pm 1\\ 12.0 \pm 0.6\\ 15 \pm 1\\ 14.0 \pm 0.6 \end{array} $	- 16±2 - 18±2	$ \begin{array}{c} - \\ 14.0 \pm 0.6 \\ 11.0 \pm 0.6 \\ 9 \\ 18 \pm 0.6 \\ 14.0 \pm 0.6 \end{array} $	$ \begin{array}{c} -\\ 14 \pm 1\\ 14 \pm 2\\ 10 \pm 1\\ 16 \pm 2\\ 18 \pm 2 \end{array} $		

 $S.a = Staphylococcus \ aureus \ (ATCC 12600); \ B.s = Bacillus \ subtilis \ (ATCC 6633); \ K.p = Klebsiella \ pneumonia \ (ATCC 13883); \ P.a = Pseudomonas \ aeruginosa \ (ATCC 10145); \ E.c = Escherichia \ coli \ (ATCC 11775); \ and \ C.a = Candida \ albicans. The values are the arithmetic mean of zone of inhibition <math>\pm$ standard deviation.

Generally, Ni(II) and Cu(II) complexes show higher activity than their corresponding ligands and complexes of L^2 show higher activity than complexes of L^1 .

3.5.3. Antibacterial activity. The Schiff-base ligands and their complexes were subjected to antibacterial activity against *Pseudomonas aeruginosa* (ATCC 10145), *Staphylococcus aureus* (ATCC 12600), *Bacillus subtilis* (ATCC 6633), *Klebsiella pneumonia* (ATCC 13883), and *Escherichia coli* (ATCC 11775). The screening results are shown in table 3. The activity reported by the present complexes is comparable with salicylaldehyde derived Schiff-base complexes [48]. Complexes containing electron-withdrawing group show higher activity. The complexes show higher activities against *S. aureus*, *P. aeroginosa*, *K. pneumonia*, *B. cearus*, and *E. coli*. [49]. Further studies are needed to understand the functions responsible for antifungal and antibacterial activities of the complexes.

4. Conclusion

Simple Schiff-base complexes have been synthesized and their coordination chemistry and antibacterial activity are investigated. Electronic spectra of Ni(II) and Cu(II) complexes indicate square planar geometry; cyclic voltammetry exhibit one electron quasi-reversible process. The copper complexes show higher catalytic activity on introducing an electron-withdrawing group. All the complexes show antimicrobial activity and the presence of an electron-withdrawing group enhances the antimicrobial activities. The observed variation in the activity of the metal complexes and their corresponding ligands across the various classes of organisms studied may be attributable to the differences in cell wall and/or membrane construction. All these studies of the complexes agree well with established trends.

Acknowledgements

The authors express their sincere thanks to the Management, Principal, and Prof. A.G. Md. S. Oolvi, HOD, PG, and Research Department of Chemistry, The New College, Chennai, for providing research facilities. We also thank Dr S. Sriman Narayanan, Professor, Department of Analytical Chemistry, University of Madras, Chennai, for providing cyclic voltammetry facility.

References

- [1] L.J. Boucher, C.G. Coe. Inorg. Chem., 14, 1289 (1975).
- [2] A.R. Oki, D.J. Hodgson. Inorg. Chim. Acta, 170, 65 (1990).
- [3] A. Nishinaga, T. Tsutsui, H. Moriyama. J. Mol. Catal., 83, 117 (1993).
- [4] A. Bottcher, T. Takeuchi, K.I. Hardcastle, T.J. Meade, H.B. Gray, D. Cwikel, M. Kapon. *Inorg. Chem.*, 36, 2498 (1997).
- [5] L.A. Kovbasyuk, I.O. Fritzy, V.N. Kokozay, T.S. Iskendevov. Tetrahedron, 16, 1723 (1997).

- [6] P. Mukherjee, M.G.B. Drew, M. Estrader, C. Diaz, A. Ghosh. Inorg. Chim. Acta, 361, 161 (2008).
- [7] A. Fortunelli, R. Colle, O. Salvetti. *Inorg. Chem.*, 30, 2388 (1991).
- [8] F.L. Urbach, R.D. Bereman, J.A. Topich, M. Hariharan, B.J. Kalbacher. J. Am. Chem. Soc., 96, 5063 (1974).
- [9] B. Ortiz, S.M. Park. Bull. Korean Chem. Soc., 21, 405 (2000).
- [10] P.K. Radhakrishanan, P. Indrasen, C.G.R. Nair. Polyhedron, 18, 67 (1998).
- [11] E. Ispir, M. Kurtoğlu, F. Purtas, S. Serin. Trans. Met. Chem., 30, 1042 (2005).
- [12] S. Sreedaran, K. Shanmuga Bharathi, A. Kalilur Rahiman, K. Rajesh, G. Nirmala, L. Jagadish, V. Kaviyarasan, V. Narayanan. *Polyhedron*, 27, 1867 (2008).
- [13] S. Mohebbi, D.M. Boghaei, A.H. Sarvestani, A. Salimi. Appl. Catal. A: Gen., 278, 263 (2005).
- [14] A.M. Amado, P.J.A. Ribeiro-Claro. *Inorg. Biochem.*, 98, 561 (2004).
- [15] R.K. Parashar, R.C. Sharma, A. Kumar. Inorg. Chim. Acta, 151, 201 (1988).
- [16] N.V. Loginova, T.V. Koval'chuk, R.A. Zheldakova, A.A. Chernyavskaya, N.P. Osipovich, G.K. Glushonok, H.I. Polozov, V.L. Sorokin, O.I. Shadyro. Central. Eur. J. Chem., 4, 440 (2006).
- [17] N. Yamashita, H. Tanemura, S. Kawanishi. Mutat. Res., 425, 107 (1999).
- [18] J.C. Duff. J. Chem. Soc., 547 (1941).
- [19] R.M. Silverstein, G.C. Bassler. Spectrometric Identification of Organic Compounds, John Wiley & Sons, New York (1991).
- [20] G. Das, R. Shukala, S. Mandal, R. Singh, P.K. Bharadwaj, J.V. Singh, H. Whitmire. *Inorg. Chem.*, 36, 323 (1997).
- [21] N.M. EI-Metwally, I.M. Gabr, A.M. Shallaby, A.A. EI-Asmy. J. Coord. Chem., 58, 1154 (2005).
- [22] P. Viswanathamurthi, N. Dharmaraj, S. Anuradha, K. Natarajan. Trans. Met. Chem., 23, 337 (1998).
- [23] J. Manonmani, M. Kandaswamy, V. Narayanan, S. Shanmuga Sundara Raj, G. Shanmugam, M.N. Ponnuswamy, H.K. Fun. *Polyhredron*, 20, 3039 (2001).
- [24] E. Tas, M. Aslanoglu, A. Killic, O. Kaplan, H. Temel. J. Chem. Research, 242 (2006).
- [25] A.B.P. Lever. Inorganic Electronic Spectroscopy, 2nd Edn, Elsevier, New York (1984).
- [26] D. Fraser, B. Bosnich. Inorg. Chem., 33, 338 (1994).
- [27] A. Bottcher, H. Elias, E.G. Jager, H. Langfelderova, M. Mazur, L. Muller, H. Paulus, P. Pelikan, M. Rudolph, M. Valko. *Inorg. Chem.*, 32, 4131 (1993).
- [28] D. Kivelson, R. Neiman. J. Chem. Phys., 35, 149 (1961).
- [29] A.L. Sharma, I.O. Singh, M.A. Singh, H.R. Singh, R.M. Kadam, M.K. Bhide, M.D. Sastry. *Trans. Met. Chem.*, 26, 532 (2001).
- [30] S. Zhu, F. Kon, H. Lin, E. Lin. Inorg. Chem., 35, 3848 (1996).
- [31] R.C. Agarwal, N.K. Singh, R.P. Singh. Inorg. Chem., 20, 2794 (1981).
- [32] R.K. Ray, G.B. Kauffman. Inorg. Chim. Acta, 153, 207 (1989).
- [33] N. Raman, A. Kulandaisamy, C. Thangaraja, K. Jeyasubramanian. Trans. Met. Chem., 28, 29 (2003).
- [34] B.J. Hathaway, A.A.G. Tomlinson. Coord. Chem. Rev., 5, 1 (1970).
- [35] J.D. Gane, D.E. Fenton, J.M. Latour, A.J. Smith. J. Chem. Soc., Dalton Trans., 2279 (1991).
- [36] S. Sreedaran, K. Shanmuga Bharathi, A. Kalilur Rahiman, K. Rajesh, G. Nirmala, V. Narayanan. J. Coord. Chem., 61, 3594 (2008).
- [37] I.C. Santos, M. Vilas-Boas, M.F.M. Piedade, C. Friere, M.T. Duarte, B. DeCastro. *Polyhydron*, 19, 655 (2000).
- [38] L. Gomes, E.S. Periera, B. de Castro. J. Chem. Soc., Dalton Trans., 1373 (2000).
- [39] A. Kapturkiewicz, B. Behr. Inorg. Chim. Acta, 69, 247 (1983).
- [40] C. Freire, B. de Castro. J. Chem. Soc., Dalton Trans., 1491 (1998).
- [41] G.S. Patterson, R.H. Holm. Bioinorg. Chem., 4, 257 (1975) and references therein.
- [42] J. Reim, B. Krebs. J. Chem. Soc., Dalton Trans., 3793 (1997).
- [43] A. Neves, L.M. Rossi, A. Horn, I. Vencato, A.J. Bortoluzzi, C. Zucco, A.S. Mangrich. *Inorg. Chem. Commun.*, 8, 334 (1999).
- [44] A. Neves, L.M. Rossi, I. Vencato, V. Drago, W. Hasse, R. Werner. Inorg. Chim. Acta, 281, 111 (1998).
- [45] V. Alexander. Chem. Rev., 95, 273 (1995).
- [46] R. Mahalakshmy, R. Venkatesan, P.S. Sambasiva Rao, R. Kannappan, T.M. Rajendiran. Trans. Met. Chem., 29, 623 (2004).
- [47] S. Magaldi, S. Mata-Essayag, C.H. de Capriles, C. Perez, M.T. Colella, C. Olaizola, Y. Ontiveros. Int. J. Infectious Disease, 8(1), 39 (2004).
- [48] M.S. Refat, I.M. El-Deen, Z.M. Anwer, S. El-Ghol. J. Coord. Chem., 62, 1709 (2009).
- [49] B.G. Tweedy. Phytopathology, 55, 910 (1964).