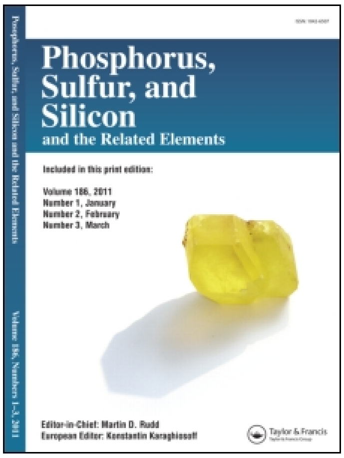

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New Schiff Bases Containing Silicon and Their Co(II) and Cu(II) Complexes: Synthesis, Complexation, Characterization, and Antimicrobial and Electrochemical Properties

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New Schiff Bases Containing Silicon and Their Co(II) and Cu(II) Complexes: Synthesis, Complexation, Characterization, and Antimicrobial and Electrochemical Properties

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Two novel Schiff base ligands, 4-((3-(trimethoxysilyl)propylimino)methyl)benzene–1,2,3-triol (L^1H) and 4-((3-(triethoxysilyl)propylimino)methyl)benzene–1,2,3-triol (L^2H), have been synthesized by the reaction of 2,3,4-trihydroxybenzaldehyde with 3-aminopropyltrimethoxysilane and 3-aminopropyltriethoxysilane, respectively. The mononuclear Co^{II} and Cu^{II} complexes of these Schiff bases were prepared. The complexes of the Schiff bases are formed by coordination of N, O atoms of the ligands. The proposed structures were confirmed by elemental analyses, FT-IR, and UV-visible spectroscopy, magnetic susceptibility, and conductance measurements; the ^1H NMR spectra of the ligands were also recorded. The analytical data show that the metal to ligand ratio in the complexes containing silicon is 1:2. The electrochemical properties of the complexes have been investigated at 100 mVs^{-1} scan rate in DMSO. In addition, the antimicrobial activity of L^1H and L^2H Schiff ligands, and their $[M(L^1)2]$ and $[M(L^2)2]$ type coordination compounds, were investigated.

Keywords Antimicrobial activity; characterization; cyclic voltammetry; Schiff base complexes

INTRODUCTION

Schiff bases are an important class of ligands, such ligands and their metal complexes having a variety of applications including biological, clinical, analytical, and industrial, in addition to their important roles in catalysis and organic synthesis.[1–7]

The metal complexes with the Schiff base as ligands have been playing an important part in the development of inorganic chemistry as a

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whole.[8] The metal oxidation state and the type and number of donor atoms, as well as their relative disposition within the ligand, are major factors determining structure–activity relationship of the metal complexes.[9] Although the redox behavior of a number of metal complexes containing Schiff-base ligands is known, the electrochemical properties of such complexes are not completely clear.[10] Schiff base complexes have been among the most widely studied coordination compounds in the past few years since they are becoming increasingly important as biochemical, analytical, and antimicrobial reagents.[11]

Many Schiff base complexes show excellent catalytic activity in various reactions at high temperature ($>100^\circ$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, hence the need for a review article highlighting the catalytic activity of Schiff base complexes realized.[1,12]

A wide variety of cobalt(II) complexes are known to bind dioxygen more or less reversibly, and therefore they are frequently studied as model compounds for natural oxygen carriers and for their use in O_2 storage, as well as in organic synthesis due to their catalytic properties under mild conditions. In this respect, Co(II) complexes with N-donor ligands containing binding units suitable either for the coordination of a single metal ion or for assembling dimetallic centers have been shown to be particularly useful.[13] In aprotic solvents, at atmospheric pressure and room temperature, cobalt chelated with Schiff bases catalyzes the oxygenation of indols, phenols, flavones, nitroalkanes, hydrazones, olefins, etc.[14]

Silanes are organofunctional hybrid organic–inorganic chemicals, historically used as coupling agents for adhesion between organic and inorganic materials, such as glass fiber-reinforced polymeric composites.[15,16] They concluded that polysiloxanes with an ethylenediamine moiety with both primary and secondary amino groups in their structure can be used to effectively extract aldehydes, lactones, and most ketones by chemical reactions with carbonyl compounds through the formation of carbon–nitrogen double bonds. The strong interactions also occur in the case of alcohols.[17]

This article describes the synthesis, spectroscopic characterization, and redox properties of the Co(II) and Cu(II) complexes from Schiff bases formed from 2,3,4-trihydroxybenzaldehyde with 3-aminopropyltrimethoxysilane and 3-aminopropyltriethoxysilane, respectively.

The Co(II) and Cu(II) complexes of these Schiff base ligands were synthesized, and their structures were confirmed elemental analyses, FT-IR and UV-visible spectroscopy, magnetic susceptibility, and conductance measurements; the ^{1}H NMR spectra of the ligands were also recorded. The analytical data show that the metal to ligand ratio in the Schiff base complexes is 1:2.

RESULTS AND DISCUSSION

In this present work, 4-((3-(trimethoxysilyl)propylimino)methyl) benzene-1,2,3-triol (L^1H) and 4-((3-(triethoxysilyl)propylimino)methyl) benzene-1,2,3-triol (L^2H) Schiff base ligands were prepared by the reaction of 2,3,4-trihydroxybenzaldehyde with 3-aminopropyltrimethoxysilane and 3-aminopropyltriethoxysilane. The impurities were checked by TLC. The complexes were synthesized by the general equations shown below.

$$\mathrm{M(OAc)_2 \cdot \mathit{x}H_2O + 2\,L^1H \longrightarrow [M(L^1)_2] + 2AcOH + \mathit{x}H_2O}$$

$$\mathrm{M(OAc)_2 \cdot \mathit{x}H_2O + 2\,L^2H \longrightarrow [M(L^2)_2] + 2AcOH + \mathit{x}H_2O}$$

x : 4 for Co(II), 1 for Cu(II)

L^1H : 4 – ((3 – (trimethoxysilyl)propylimino)methyl)benzene – 1, 2, 3-triol

L^2H : 4 – ((3 – (triethoxysilyl)propylimino)methyl)benzene – 1, 2, 3-triol

The results of the elemental analyses of the ligands and complexes are in agreement with the chemical formulae. The Schiff base ligands (E)-4-((3-(trimethoxysilyl)propylimino)methyl)benzene–1,2,3-triol (L^1H) and (E)-4-((3-(triethoxysilyl)propylimino)methyl)benzene–1,2,3-triol (L^2H) were synthesized in good yields in PhMe. The ligands and their complexes are stable at room temperature and soluble in DMSO and DMF. Based on the analytical and spectroscopic characterization, these mononuclear complexes are presumed to have the coordination environment shown later in Figures 3 and 4. The analytical data for the ligands and their complexes are listed in Table I. The molar conductances of the metal complexes are also given in Table I. Condutivity values for the $[Co(L^1)_2]$, $[Cu(L^1)_2]$, $[Co(L^2)_2]$, and $[Cu(L^2)_2]$ compounds in MeOH are in the range of 7.3–13.2 (Ω^{-1} cm^3 mol^{-1}) indicating that they are non-electrolytes. Single crystals of the compounds could not be isolated from any organic solution, thus no definitive structures can

TABLE I Some Analytical and Physical Data for the Ligands and Their Complexes

				Found (Calcd)%			
Compound	Color	Yield (%)	Mp (°C)	C	N	H	Λ_M[a]
L^1H	Dark yellow	74	>250[b]	49.6 (49.5)	4.5 (4.4)	6.7 (6.7)	1.4
$[Co(L^1)_2]$	Dark green	65	>300[b]	45.4 (45.4)	4.1 (4.0)	5.9 (5.9)	7.3
$[Cu(L^1)_2]$	Brown	68	>300[b]	45.1 (45.0)	4.1 (4.0)	5.9 (5.8)	10.8
L^2H_2	Yellow	75	>250[b]	53.8 (53.7)	4.0 (3.9)	7.7 (7.6)	1.5
$[Co(L^2)_2]$	Reddish brown	71	>300[b]	49.8 (49.7)	3.7 (3.5)	6.9 (6.7)	8.1
$[Cu(L^2)_2]$	Dark brown	69	>300[b]	49.5 (49.1)	3.7 (3.6)	6.8 (6.6)	13.2

[a] Ω^{-1} cm^3 mol^{-1}.
[b] Decompose.

be described. However, the analytical and spectroscopic data enables us to predict probable structures as shown in Figures 1–4.

The IR spectra of the ligands and their complexes have been studied in order to characterize their structures. The characteristic IR data of the Schiff base ligands and their metal complexes are listed in Table II. In the ligands' and complexes' spectra, both ligands and complexes exhibit bands at 3409–3426 cm^{-1} and 3055–3062 cm^{-1} that are assignable to ν(OH) and ν(Ar-CH).[18,19] The strong bands around 1606–1642 cm^{-1} can be attributable to the azomethine ν(-CH=N-) stretching. This band in the complexes is shifted towards the lower frequencies as a result of coordination of the azomethine nitrogen atom to the metal ion.[20] In the complexes, new weak bands in the 563–610 and 415–441 cm^{-1} range may be attributed to ν(M-O) and ν(M-N) stretching respectively.[21] The bands at 1030–1046 cm^{-1} are due to the vibration of the Si-O bands in both ligands and complexes.[22]

The electronic absorption spectral data for the ligands and their metal complexes were obtained in 10^{-3} M DMSO solutions at room temperature, and magnetic moment data are given in Table III. The

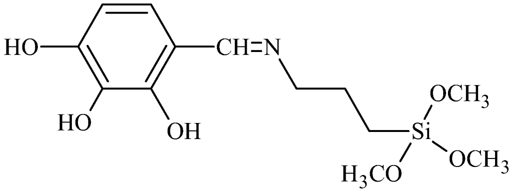


FIGURE 1 The proposed structure of L^1H Schiff base ligand.

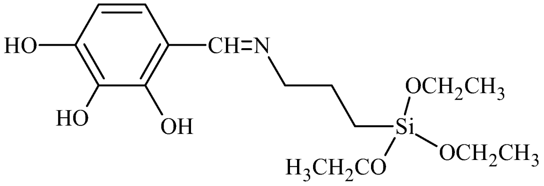


FIGURE 2 The proposed structure of L^2H Schiff base ligand.

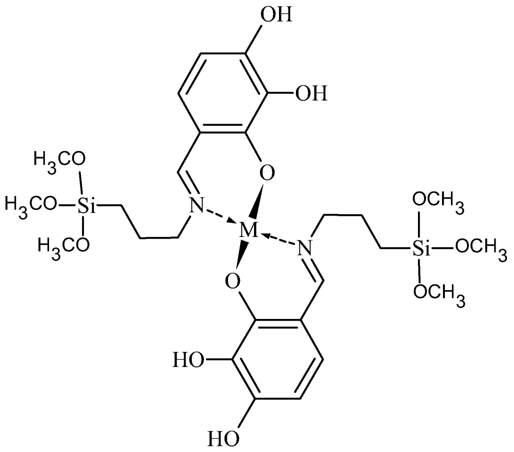
UV-visible spectra of the Schiff base ligands and their metal complexes in DMSO showed absorption bands between 617 and 265 nm. The bands at higher energies (~286–281 nm range) are associated with benzene $\pi \rightarrow \pi^*$ transitions. The spectra of the complexes show intense bands in the high-energy region at 306–397 nm which can be assigned to charge transfer L → M bands.[23,24] The bands at λ_{max} 420 and 423 nm assigned to $n \rightarrow \pi^*$ transitions of the azomethine groups in the L^1H and L^2H ligands. In the spectra of the complexes, the bands of the azomethine $n \rightarrow \pi^*$ transitions are shifted to lower frequencies, indicating that the imine nitrogen atom is involved in coordination to the metal ion. The spectra of all complexes contain an absorption band in the 617, 603, 585, and 539 nm, which may be assigned to the d–d transition of metal ions. The Co(II) complexes show bands at 603 and 617 nm. This indicates tetrahedral geometry for the Co(II) complexes. In general, due to Jahn–Teller distortion, square planar Cu(II) complexes give a broad absorption band between 600 and 700 nm, and the peak at 510 nm merges with the broad band. In the electronic spectra of Cu(II) complexes, the observed bands are at 585 and 539 nm.[25] This suggests square planar geometry for the Cu(II) complex.

The $Cu(L^1)_2$ and $(CuL^2)_2$ complexes exhibit 1.78–1.81 BM values, suggesting that the Cu(II) ion has square-planar geometry. The values

TABLE II IR Spectral Data of the Ligands and Their Complexes (cm^{-1}, KBr)

Compound	ν(OH)	ν(ArC-H)	ν(aliph.C-H)	ν(CH=N)	ν(Si-O)	ν(M-O)	ν(M-N)
L^1H	3413 s	3075 m	2929–2871*m*	1640 s	1034 w	—	—
$[Co(L^1)_2]$	3409 m	3055 m	2926–2883*m*	1611 s	1030 w	594 w	417 w
$[Cu(L^1)_2]$	3411 m	3038 m	2927–2881*m*	1609 s	1031 w	599 w	415 w
L^2H_2	3426 s	3058 m	2930–2878*m*	1642 s	1046 m	—	—
$[Co(L^2)_2]$	3419 m	3051 m	2928–2880*m*	1618 s	1036 w	663 w	441 m
$[Cu(L^2)_2]$	3416 m	3062 m	2933–2879*m*	1606 m	1042 m	610 w	421 w

s: strong; m: medium; w: weak.

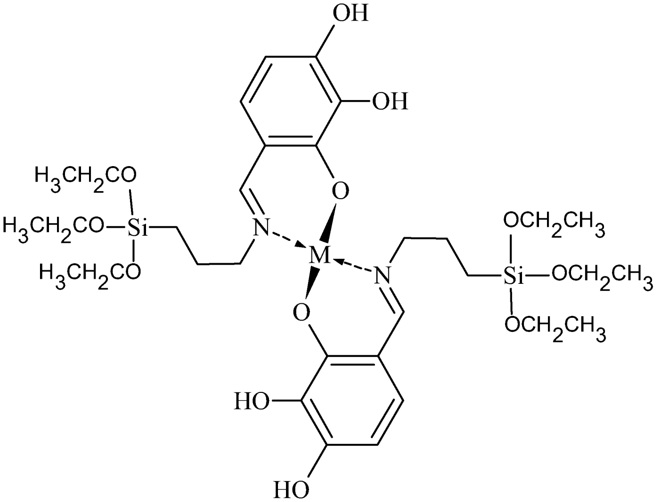


M: Cu^{II} and Co^{II}

FIGURE 3 The proposed structures of the complexes of the L^1H.

of 4.20 and 4.27 BM observed for $Co(L^1)_2$ and $(CoL^2)_2$ reveal tetrahedral geometry around the Co(II) ion.[26]

In the ^1H NMR spectra of the ligands, L^1H and L^2H exhibit singlet signals in the 13.49–9.01 ppm and 8.19–8.21 ppm ranges, which are



M : Cu^{II} and Co^{II}

FIGURE 4 The proposed structures of the complexes of the L^2H.

TABLE III Electronic Spectral and Magnetic Moment Data for the Complexes

Compound	λ_{max}, nm	μ_{eff}, BM
$Co(L^1)_2$	603,412, 362, 265	4.20
$Cu(L^1)_2$	585,421, 395, 288	1.81
$(CoL^2)_2$	617,402, 397, 278	4.27
$(CuL^2)_2$	539,409, 375, 283	1.78

attributed to the OH group and azomethine group protons, respectively. In the spectra of the ligands, in DMSO-d_6 resulted in peaks corresponding to the aromatic protons at 6.57–7.68 ppm and 6.58–7.12 ppm as multiplets.[27] In the ligands, signals at 0.82–3.86 ppm and 0.97–2.12 ppm may be assigned to the $[Si-(CH_2)_3-]$ protons.[28] In the L^1H Schiff base ligand, there is a singlet for $(-OCH_3)$ protons at 3.39 ppm. In the spectrum of L^2H ligand, there is a triplet at 1.23 ppm and a quartet at 3.21 ppm for $(-OCH_2CH_3)$ protons.[11,29] The ^1H NMR spectrum of L^1H is taken as a represantive example and shown in Figure 5.

Electrochemical Studies

The redox properties of the metal complexes were investigated in DMSO solution (in nitrogen atmosphere) by cyclic voltammetry (Table IV) in the potential range +1.0 to −1.0 V. The cyclic voltammograms have been recorded at 100 mVs^{-1}. The cyclic voltammograms of the complexes (Figures 6–9) show the complexes have cathodic and anodic peaks.

Electrochemical studies of the complexes were investigated as metal-centered. In the scan rate 100mVs^{-1}, the Schiff-base complexes consist

TABLE IV Electrochemical Data for the Obtained Complexes

Compound	E_{pa} (V)	E_{pc} (V)	ΔE (V)
$[Co(L^1)_2]$	0.120	0.730	−0.610
$[Cu(L^1)_2]$	−0.050, −0.82	0.680	−0.870
$[Co(L^2)_2]$	−0.090	0.500	−0.590
$[Cu(L^2)_2]$	−0.140	0.900	−0.1040

Supporting electrolyte: [NBu4](ClO4) (0.05 M); concentrations of the compounds: 0.001 M. All the potentials are referenced to Ag/AgCl; where *Epa* and *Epc* are anodic and cathodic potentials, respectively. $\Delta Ep = Epa—Epc$. The data have been obtained at 100 mVs^{-1} scan rate.

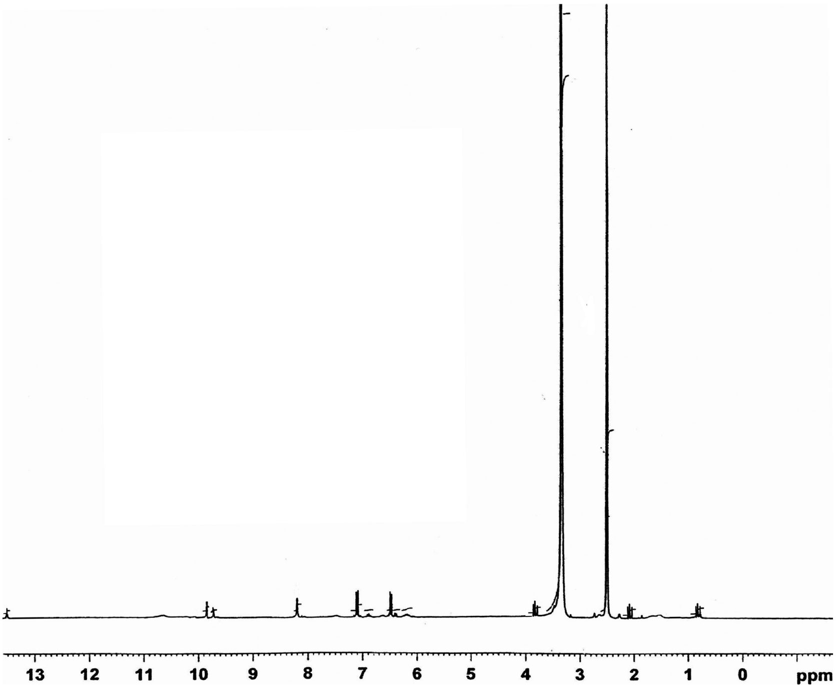


FIGURE 5 The ^{I}H NMR spectrum of L^1H.

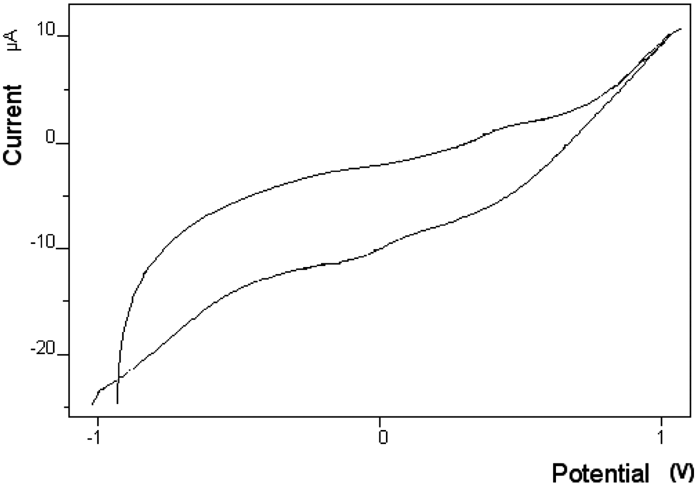


FIGURE 6 Cyclic voltammograms of the complex $[Co(L^1)_2]$.

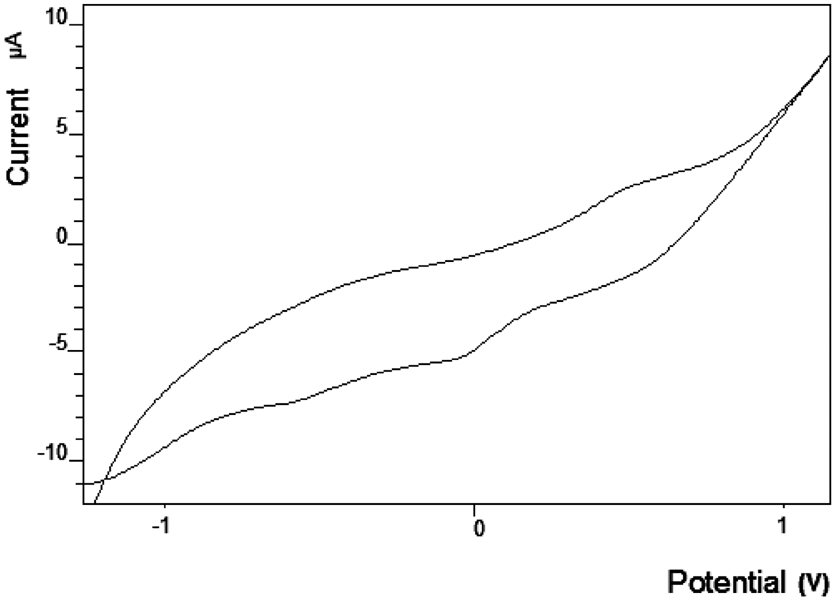


FIGURE 7 Cyclic voltammograms of the complex $[Cu(L^1)_2]$.

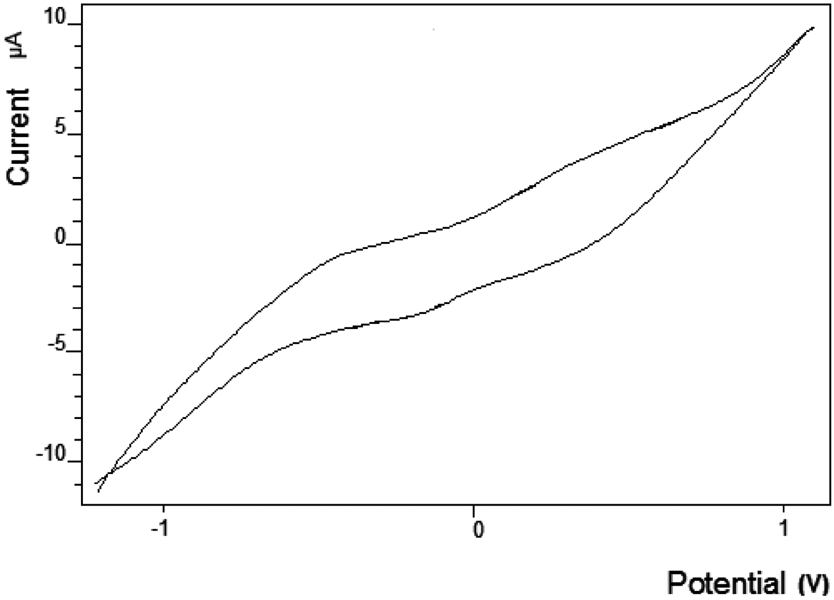


FIGURE 8 Cyclic voltammograms of the complex $[Co(L^2)_2]$.

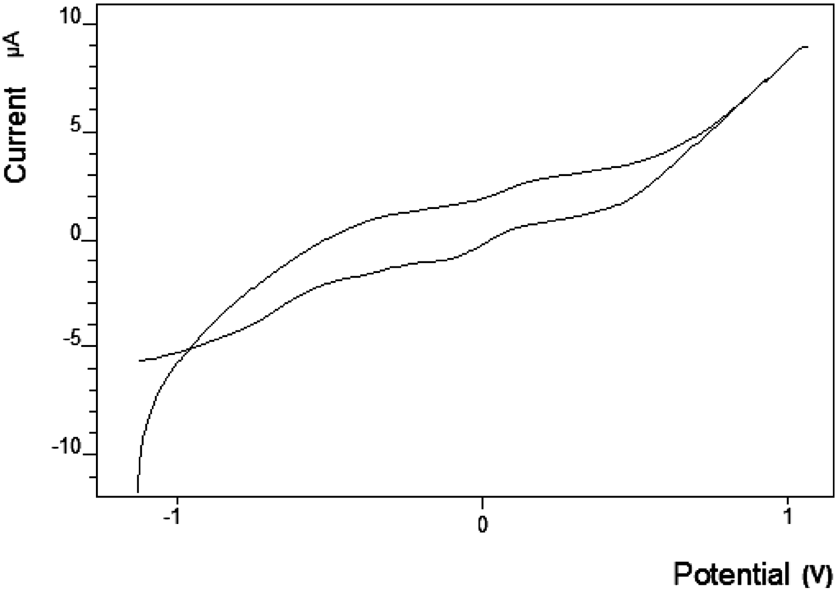


FIGURE 9 Cyclic voltammograms of the complex [Cu(L^2)$_2$].

of a single cathodic peak at potentials ranging from 0.500–0.900 V; anodic wave occurs at potentials ranging from −0.140–0.120 V in the reverse scan. The oxidation peaks of the [Cu(L^1)$_2$], [Co(L^2)$_2$], and [Cu(L^2)$_2$] complexes, except for the [Co(L^1)$_2$] complex, have negative values. The [Cu(L^1)$_2$] complex has two anodic peak potentials at −0.050 and −0.82 V. In other words, the same complex has only one cathodic peak potential at +0.68 V. This situation shows that the Cu(II) ion, first reduces to the Cu(I) ion at the cathodic region, and then it oxidizes to the Cu(II) and Cu(III) ions at the anodic peak potentials, respectively, whereas, all the complexes have positive reduction peak potentials. The ratio of anodic to cathodic peak currents (Ipc/Ipa) indicates an irreversible redox potential.[29]

Antimicrobial Activity

In the present study, the ligands and their metal complexes have been tested for their effects on the growth of microbial cultures using the diffusion method.[30] The antifungal activities of the compounds against four fungi, namely *Rhodatorula rubra MC 12*, *Kluyveromyces merxianus*, *Aspergullis fumigatus*, and *Mucar pussilus*, are presented in Table III. The results showed that all of the compounds exhibit

TABLE V Antimicrobial Activity Studies [Diameter of Inhibition Zone (mm); Concentration 2000 ppm, 30 μL/ disc]

Compound	*Rhodotorula rubra MC 12*	*Kluyveromyces merxianus*	*Aspergullis fumigatus*	*Mucar pussilus*
L^1H	11	9	11	9
$[Co(L^1)_2]$	18	7	10	15
$[Cu(L^1)_2]$	8	15	11	9
L^2H_2	9	8	10	8
$[Co(L^2)_2]$	20	11	9	16
$[Cu(L^2)_2]$	9	16	12	8

moderate activity against all species of fungi. The Schiff base ligands have the highest effect against *Aspergullis fumigatus* fungus in comparison to other three fungi. The results indicate that all the complexes show more activity and the ligands have low activity against same microbes under identical conditions. This would suggest that chelation could facilite the ability of a complex to cross a cell membrane and can be explained by Tweedy's chelation theory.[30] Among the complexes tested, the compounds $[Co(L^1)_2]$ and $[Co(L^2)_2]$ showed higher activity than the other complexes (Table V). Co^{II} complexes of the ligands showed higher activity against *R. Rubra MC 12* then the other compounds. The inhibition activity of the complexes increases with increase in the concentration of the test solution containing the new complexes. The variation in the activity of different complexes against different organisms depends either on the impermeability of the cells of the microbes or differences in ribosomes in microbial cells.[31,32]

EXPERIMENTAL

$Co(OAc)_2{\cdot}4H_2O$ and $Cu(OAc)_2{\cdot}H_2O$, 3-aminopropyltriethoxysilane, 3-aminopropyltrimethoxysilane, and 2,3,4-trihydroxybenzaldehyde were obtained from Fluka. Solvents were analytical grade and were purified by standard procedures.

Physical Measurements

Elemental analyses were carried out by the Instrumental Analysis Laboratory of TUBITAK Marmara Research Centre. ^1H NMR spectra were recorded on a Varian XL-200 NMR instrument. TMS was used as internal standard and deuteriated DMSO as solvent. IR spectra were obtained using KBr discs (4000–400 cm^{-1}) on a Shimadzu

8300 FT-IR spectrophotometer. The electronic spectra in the 200–900 nm range were obtained using DMSO on a Shimadzu UV–160 A spectrophotometer. Magnetic measurements were carried out by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant. Molar conductances of the Schiff base ligands and their transition metal complexes were determined in MeOH ($\sim 10^{-3}$ M) at room temperature using a Jenway Model 4070 conductivity meter.

Cyclic voltammograms were recorded on a Iviumstat Electrochemical workstation equipped with a low current module (BAS PA–1) recorder. The electrochemical cell was equipped with a BAS glassy carbon working electrode (area 4.6 mm^2), a platinum coil auxiliary electrode, and a Ag/AgCl reference electrode filled with tetrabutylammonium tetrafluoroborat ($[CH_3(CH_2)_3]_4NBF_4$, 0.1 M in DMSO, Aldrich) solution and adjusted to 0.00 V vs. SCE. All potentials are reported with respect to Ag/AgCl. The solutions were deoxygenated by passing dry nitrogen through the solution for 30 min prior to the experiments, and during the experiments the flow was maintained over the solution. Digital simulations were performed using DigiSim 3.0 for windows (BAS, Inc.). Experimental cyclic voltammograms used for the fitting process had the background subtracted and were corrected electronically for ohmic drop.

The HL^1 and HL^2 Schiff base ligands and their complexes, $[Co(L^1)_2]$, $[Cu(L^1)_2]$, $[Co(L^2)_2]$, and $[Cu(L^2)_2]$, have been tested for in vitro growth inhibitory activity against the fungi *Rhodatorula rubra MC 12*, *Kluyveromyces merxianus*, *Aspergullis fumigatus*, and *Mucar pussilus*. All the fungi studied were incubated in Malt Extract Broth (Difco) for 48 h. Mueller Hinton Agar (Oxoid), sterilized in a flask and cooled to 45–50°C, was distributed in sterilized Petri dishes having a diameter of 9 cm, by using pipettes to the extent of 15 cm^3 after injecting cultures of bacteria prepared as mentioned above and molded for 24 h in the amount of 0.01 cm^3 103 fungi spores per cm^3, and providing the distribution of food medium in Petri dishes homogenously. All the compounds thus obtained and the standard antibiotics were injected into empty sterilized antibiotic discs having a diameter of 6 mm (Schleicher & Shüll, No. 2668, Germany) in the amount of 50 cm^3. The compounds to be tested were dissolved in DMSO at a final concentration of 2 ppm and soaked in fitler paper. Discs injected with complexes were located on the solid agar medium by pressing slightly. Afterward, the Petri dishes so obtained were placed at 4°C for 2 h, and plates inoculated with fungi were incubated at 25 ± 0.1°C for 24 h. At the end of the period, inhibition zones formed on the food medium were evaluated is millimeters. These studies were performed in triplicate. Gentamicin (Bioanalyse) and Nystatin (Oxoid) were used as a standard.

Synthesis of 4-((3-(Rrimethoxysilyl)propylimino)methyl) benzene-1,2,3-triol (L^1H)

2,3,4-Trihydroxybenzaldehyde (1.54 g, 10 mmol) dissolved in PhMe (10 cm^3) was carefully added with stirring to a solution of 3-aminopropyltrimethoxysilane (1.75 cm^3, 10 mmol) in PhMe (10 cm^3). The resulting mixture was allowed to stir magnetically under reflux for 4 h. After cooling, the resulting precipitate was filtered, washed with cold PhMe, and dried in a vacuum desiccator. ^1H NMR (DMSO-d_6 δ ppm): 13.49 (s, 1 H, O–H), 9.87 (s, 1 H, O–H), 9.73 (s, 1 H, O–H), 8.19 (s, 1 H, CH=N), 6.58–7.12 (m, Ar-H), 3.39 (s, 9 H, OCH_3), 0.82–2.03–3.86 (t, 6 H, Si-$(CH_2)_3$-). UV-Vis (λ_{max}, nm in DMSO): 420, 374, 345, 306, 281.

Synthesis of 4-((3-(triethoxysilyl)propylimino)methyl) benzene-1,2,3-triol (L^2H)

2,3,4-Trihydroxybenzaldehyde (1.54 g, 10 mmol) and 3-aminopropyltriethoxysilane (2.33 cm^3, 10 mmol) were stirred in 30 cm^3 of PhMe until a yellow precipitate appeared. Stirring was continued for 4 h, and then the yellow powder was collected by vacuum filtration, washed with cold PhMe, and dried overnight in a vacuum desiccator. ^1H NMR (DMSO-d_6 δ ppm): 13.23 (s, 1 H, O–H), 9.25 (s, 1 H, O–H), 9.01 (s, 1 H, O–H), 8.21 (s, 1 H, CH=N), 6.57–7.68 (m, Ar-H), 1.23 (t, 9 H, O-CH_2-CH_3), 3.21 (q, 6 H, O-CH_2-CH_3), 0.97–1.33–2.12 (t, 6 H, Si-$(CH_2)_3$-). UV-Vis (λ_{max}, nm in DMSO): 423, 372, 340, 314, 286.

Synthesis of $[Co(L^1)_2]$

$Co(OAc)_2{\cdot}4H_2O$ (0.125 g, 0.5 mmol) was dissolved in 20 mL of DMSO. To this solution, a MeCN solution (30 mL) containing L^1H (0.315 g, 1 mmol) was added. The mixture was stirred for 4 h at room temperature and refluxed for another 4 h. The precipitated dark green compound was filtered, washed with cold acetonitrile, and dried in vacuo.

Synthesis of $[CuL^1)_2]$

To a yellow DMSO solution (30 cm^3) of L^1H ligand (0.315 g, 1 mmol), $Cu(OAc)_2{\cdot}H_2O$ (0.100 g, 0.5 mmol) was added. The brown solution was refluxed for 24 h. The resulting brown precipitate was collected by filtration, washed with cold MeCN, and dried in vacuo.

Synthesis of [Co($L^2{}_2$]

A solution of Co(OAc)$_2$·4H$_2$O (0.125 g, 0.5 mmol) in MeCN (20 cm^3) was added to a solution of the ligand L^2H (0.357 g, 1 mmol) in absolute DMSO (20 cm^3). The mixture was boiled under reflux for 24 h. The precipitated reddish brown compound was filtered, washed with cold MeCN, and dried in vacuo.

Synthesis of [Cu$L^2{}_2$]

This dark brown compound was prepared by the addition of Cu(OAc)$_2$·H$_2$O (0.100 g, 0.5 mmol) in MeCN (20 cm^3) to a refluxing mixture of the ligand L^2H (0.357 g, 1 mmol) in absolute DMSO (30 cm^3). The dark brown compound was separated out on filtration, washed with cold MeCN, and dried in vacuo.

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