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Synthesis, spectral studies and antibacterial activity of Cu(II), Co(II) and Ni(II) complexes of 1-(2-hydroxyphenyl)-3-phenyl--2-propen-1-one, N^2-[(3,5-dimethyl-1*H*-pyrazol--1-yl)methyl]hydrazone

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Abstract: A new series of Cu(II), Co(II) and Ni(II) complexes with the 1-(2--hydroxyphenyl)-3-phenyl-2-propen-1-one, N^2-[(3,5-dimethyl-1*H*-pyrazol-1--yl)methyl]hydrazone ligand, $C_{21}H_{22}N_4O$ (LH), were synthesized by the reaction of 1-(2-hydroxyphenyl)-3-phenyl-2-propen-1-one, hydrazone with (3,5-dimethyl-1*H*-pyrazol-1-yl)methanol and characterized. The nature of the bonding and geometry of the complexes were deduced from elemental analysis, IR, electronic and ^{1}H-NMR spectroscopy, and magnetic susceptibility and conductivity measurements. The studies indicated square-planar, tetrahedral and octahedral geometry for the copper(II), cobalt(II) and nickel(II) complexes, respectively. The ESR spectra of the copper(II) complex in acetonitrile at 300 and 77 K were recorded and their salient features are reported. The electrochemical behavior of the copper (II) complex was studied by cyclic voltammetry. The antimicrobial activity of the ligand and its metal complexes were studied against the following strains of microorganism: *Staphylococcus aureus*, *Salmonella enterica typhi*, *Escherichia coli* and *Bacillus subtilis* by the well diffusion method. Metal complexes showed enhanced antimicrobial activity compared with that of the free ligand.

Keywords: 3,5-dimethyl-1-(hydroxymethyl)pyrazole; 2'-hydroxychalcone; metal complexes; pyrazole; Cu(II), Co(II) and Ni(II) complexes; antimicrobial activity.

INTRODUCTION

Pyrazoles belong among the most representative five-membered heterocyclic systems. Despite the fact that the pyrazole ring is rarely a constituent of natural products, numerous synthetic compounds containing the pyrazole moiety have

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been the focus of medicinal chemists for the last 100 years because of their outstanding pharmacological, agrochemical, photographic, catalytic, liquid crystals, antitumor drugs and other applications.[1–16] Transition-metal complexes containing the pyrazole heterocycle are well studied. The variety of the coordination modes of pyrazole and its derivatives is due to the different chemical natures of the nitrogen atoms in a pyrazole molecule.[17,18] In the present study, 1-(2-hydroxyphenyl)-3-phenyl-2-propen-1-one, N^2-[(3,5-dimethyl-1*H*-pyrazol-1-yl)methyl]-hydrazone was synthesized *via* the reaction of 1-(2-hydroxyphenyl)-3-phenyl-2--propen-1-one, hydrazone with (3,5-dimethyl-1*H*-pyrazol-1-yl)methanol and characterized by spectral and analytical techniques.

EXPERIMENTAL

The chemicals acetylacetone (A.R.), 2-hydroxyacetophenone (A.R.) and hydrazine hydrate (L.R.) were obtained from E. Merck (India). All the metal salts (L.R.) and solvents (A.R.) were purchased from S. D. Fine Chemicals and used without further purification. The UV–Vis spectra of the ligand and metal complexes were recorded in dichloromethane using a Jasco V-530 spectrophotometer. The IR spectra in KBr discs were recorded on a Shimadzu spectrophotometer Model FTIR-8400S. Cyclic voltammetric measurements were performed using a voltammograph BAS-50 at room temperature in acetonitrile under N_2 using a three electrode cell: a 0.1M Ag/AgCl reference electrode, a Pt wire auxiliary electrode and a glassy carbon working electrode with TBAP as the supporting electrolyte. The ^{1}H-NMR spectra were recorded in $CDCl_3$ using a Bruker DRX-300, 300 MHz NMR spectrometer. The ESR spectra were recorded in the solid state at 300 and 77 K using a JEOL TES 100 ESR spectrometer. The magnetic moments of the complexes were measured by a VSM model 7404 at Pondicherry University. The effective magnetic moments were calculated using the formula $\mu_{eff} = 2.228 (\chi_M T)^{1/2}$, where χ_M is the corrected molar susceptibility. The molar conductance of the complexes was measured in methanol at room temperature using a Systronic type conductivity bridge (Oswal).

Synthesis of 1-(2-hydroxyphenyl)-3-phenyl-2-propen-1-one, hydrazone

2'-Hydroxychalcone and 3,5-dimethylpyrazole were synthesized by adopting the literature method.[19,20] An ethanolic solution of 2'-hydroxychalcone (2.24 g, 10.0 mmol) was added dropwise at room temperature and with stirring over 1 h to hydrazine hydrate (2.5 g, 50 mmol). After completion of the addition, the mixture was stirred for 10 min, and upon cooling in ice, a pale yellow solid appeared, which was collected by filtration, washed with diethyl ether and dried under vacuum.

Synthesis of 1-(2-hydroxyphenyl)-3-phenyl-2-propen-1-one, N^2*-[(3,5-dimethyl-1*H*-pyrazol-1--yl)methyl]hydrazone (**1**) (Fig. 1)*

3,5-Dimethyl-1-(hydroxymethyl)pyrazole (3.15 g, 25.0 mmol) in 25 ml of dichloromethane and 1-(2-hydroxyphenyl)-3-phenyl-2-propen-1-one, hydrazone (5.95 g, 25 mmol) in 15 ml dichloromethane were stirred for 3 h and kept at room temperature for 50 h. The excess water was removed by the addition of anhydrous $MgSO_4$ and filtrated. The filtrate solution was reduced to one third on a water bath and the thus obtained yellow colored solid was filtered and then dried under vacuum.

Compound ***1***. Yield: 68 % (11.8 g), m.p. 124 °C. Anal. Calcd. for $C_{21}H_{22}N_4O$: C, 72.83; H, 6.30; N, 16.18 %. Found: C, 72.37; H, 6.28; N, 16.04 %. IR (KBr, cm^{-1}): 1599 (C=N stretching of pyrazole ring), 3342–3360 (O–H stretching of aromatic ring). ^{1}H-NMR (300

MHz, $CDCl_3$, δ / ppm): 7.00–7.43 (9H, *m*, aromatic ring protons), 10.6 (1H, *s*, phenolic O–H), 5.84 (1H, *s*, pyrazole ring proton), 2.8 (6H, *s*, pyrazole ring methyl protons), 5.2 (2H, *s*, N–CH_2–N), 5.6 (1H, *d*, CH=CH), 6.3 (1H, *d*, CH=CH). UV–Vis (CH_3CN, 10^{-3} M) (λ_{max} / nm (cm^{-1})): 318 (31440), 250 (40000), 231 (43290).

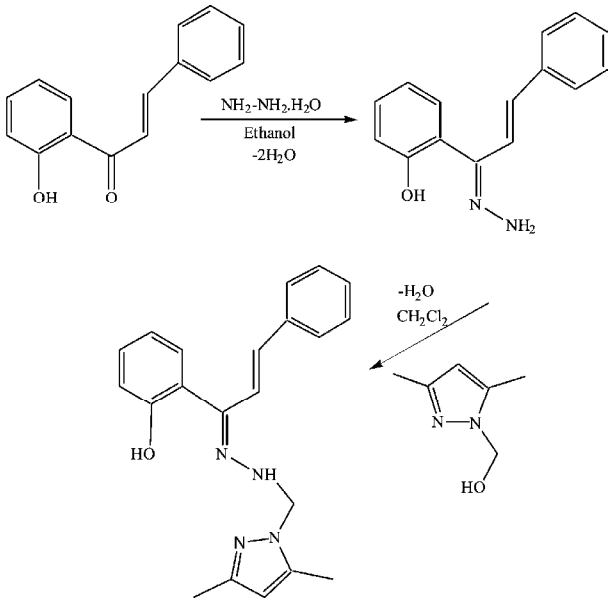
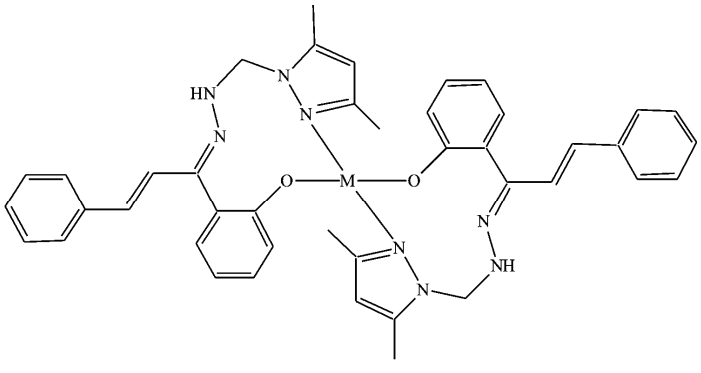


Fig. 1. Synthetic route to the ligand 1-(2-hydroxyphenyl)-3-phenyl-2-propen-1-one, N^2-[(3,5-dimethyl-1*H*-pyrazol-1-yl)methyl]hydrazone (**1**).

Synthesis of metal complexes

A solution of MCl_2, M = Cu(II), Co(II) or Ni(II), (10 mmol) in 15 ml of ethanol was mixed with **1** (20 mmol) in 15 ml ethanol. This mixture was refluxed for 3 h and then the solution was reduced to minimum volume. The thus obtained metal complexes (Figs. 2 and 3) were filtered, washed with ether and dried under vacuum.



M = Cu(II), Co(II)

Fig. 2. Suggested structure of the Cu(II) and Co(II) complexes.

$$2LH + MCl_2 \rightarrow ML_2 + 2HCl$$

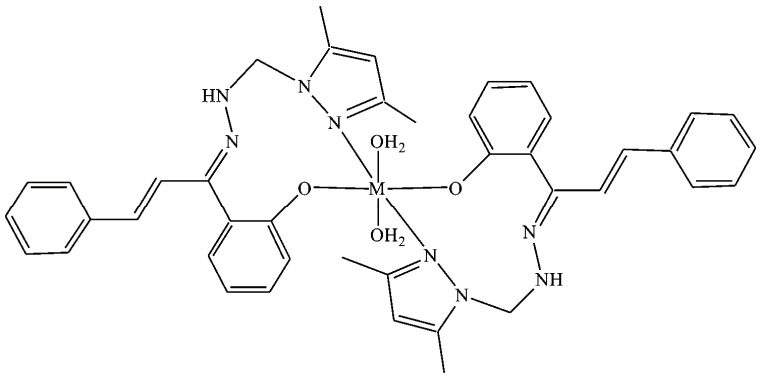


Fig. 3. Suggested structure of the Ni(II) complex.

RESULTS AND DISCUSSION

The analytical data of the ligand and its metal complexes are given in Table I. The found values were in good agreement with the theoretical ones, and correspond well with the general formula $[ML_2]$, for M = Cu(II) and Co(II), and $[ML_2(H_2O)_2]$, for M = Ni(II) and L = $C_{21}H_{22}N_4O$. The metal complexes were dissolved in acetonitrile and the molar conductivities of their 10^{-3} M solutions were measured at 25±2 °C. The low molar conductivity values of the metal complexes indicate that they are non-electrolytes. The structure of the complexes was predicted based on analytical, spectroscopic and magnetic moment data.

TABLE I. Physical characterization, analytical and molar conductance data of the ligand and its metal complexes

Compound	Found (Calcd.), %						
	Color	M	C	H	N	M. p. / °C	Λ_M / S cm^2 mol^{-1}
Ligand (LH)	Yellow	–	72.37 (72.83)	6.28 (6.36)	16.04 (16.18)	124	–
$[CuL_2]$	Pale Green	8.10 (8.42)	66.12 (66.87)	5.13 (5.61)	14.58 (14.85)	293	13.31
$[CoL_2]$	Green	7.53 (7.86)	67.17 (67.28)	5.65 (5.36)	14.95 (14.65)	245	14.08
$[NiL_2(H_2O)_2]$	Blue	7.02 (7.47)	64.04 (64.22)	5.54 (5.90)	14.10 (14.26)	278	11.20

IR Spectra

The IR spectral data of the ligand and its complexes are given in Table II. In order to study the binding mode of the ligand in the metal complexes, the IR spectrum of the free ligand was compared with those of the corresponding metal

complex. The free ligand exhibited a strong band at 3342 cm^{-1} assignable to the ν(N–H) stretching vibration. The hydrogen bonded ν(O–H) shows a broad band in the region 3320–2990 cm^{-1}, which is obviously absent in the spectra of the complexes, indicating the deprotonation and the involvement of the phenol O in the chelation. The absorption bands around 1304, 1599 and 976 cm^{-1} may be assigned to ν(C–O), ν(C=N) and ν(N–N), respectively. The ν(C–O) band has a positive shift of 20–40 cm^{-1} in the complexes due to chelation of the phenolic oxygen atom to the metal ion. On coordination, the negative shift in ν(C=N) and positive shift in ν(N–N) (15–55 cm^{-1}) are indicative of the coordination of the tertiary nitrogen of pyrazoline to the metal. The increased ν(N–N) stretching frequency in the complexes may be attributed to the loss of the repulsive forces of the lone pair on the nitrogen atom. The ν(NH) stretching frequency shows irregular variation in the complexes, which ruled out the possibility of its coordination. The oxygen and nitrogen coordination to the metal ion is proved by the bands that appeared in the range 590–550 cm^{-1} and 450–400 cm^{-1}, assigned to M–O and M–N modes,[21–23] respectively. In the Ni(II) complex, IR bands of coordinated water appeared at 832 and 1469 cm^{-1}, indicating the binding of water molecules to the metal ion.[24]

TABLE II. IR Spectral data of the ligand and its metal complexes

Compound	Frequency, cm^{-1}						
	ν(O–H)	ν(C–O)	ν(C=C)	ν(C=N)	ν(N–N)	ν(M–O)	ν(M–N)
Ligand (LH)	3342–3360	1304	1627	1599	976	–	–
$[CuL_2]$	–	1328	1643	1573	980	435	574
$[CoL_2]$	–	1331	1634	1582	985	465	537
$[NiL_2(H_2O)_2]$	3450 (Coordinated water)	1338	1642	1569	976	443	549

Magnetic properties and electronic absorption spectra

The magnetic moments and electronic spectral data of the ligand and its complexes are summarized in Table III. The spectrum of the ligand in acetonitrile showed three prominent bands at 31440, 40000 and 43290 cm^{-1}, which were assigned as intra-ligand charge transfer (INCT) bands. The spectrum of the copper(II) complex showed a broad band at 16120 cm^{-1}, which was assigned as a ($^2B_{1g} \rightarrow {}^2A_{1g}$) d–d transition and is interpreted in terms of square-planar geometry. The absence of any bands below 10000 cm^{-1} eliminates the possibility of a tetrahedral or pseudo tetrahedral environment in this complex. The magnetic moment of Cu(II) complex is 1.78 μ_B, indicating square-planar geometry.[25,26] The Co(II) complex exhibited three bands, *viz.* 14410, 15010 and 15870 cm^{-1}, which were assigned as $^4A_{2g} \rightarrow {}^4T_{2g}(F)$, $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ and $^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$ transitions, respectively. The intensity and band width strongly suggested tetrahedral geometry. The magnetic moment of the Co(II) complex was 3.59 μ_B,

which is characteristic for a tetrahedral environment. The electronic spectrum of the Ni(II) complex showed three prominent bands at 10449, 15878 and 19920 cm^{-1}, which may be tentatively assigned to $^3A_{2g} \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions, arising from octahedral geometry.[27] The Ni(II) complex possessed a magnetic moment value of 2.84 μ_B found for a regular octahedral arrangement.

TABLE III. Electronic spectral data and magnetic moments of the prepared compounds

Compounds	Frequency, cm^{-1}	Transition	Geometry	μ_{eff} / μ_B
Ligand (LH)	31440	INCT	–	–
	40000	INCT		
	43290	INCT		
$[CuL_2]$	16120	$^2B_1g \rightarrow {}^2A_1g$	Distorted octahedral	1.71
$[CoL_2]$	14410	$^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$	Octahedral	3.59
	15010	$^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$		
	15872	$^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$		
$[NiL_2(H_2O)_2]$	10449	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	Octahedral	2.84
	15878	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$		
	19920	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$		

Adduct formation

The tendency of the Co(II) complex to form additional compounds with coordinating bases, such as pyrazole and imidazole, was studied in solution. The variations of the peak pattern in the electronic spectra upon addition of heterocyclic bases, indicating geometrical changes in the Co(II) complex due to adduct formation, are shown in Figs. 4 and 5. The addition of pyrazole and imidazole to the chelate complex revealed the weak nature of the ligand field, which was susceptible for further coordination to give six-coordinated complexes.

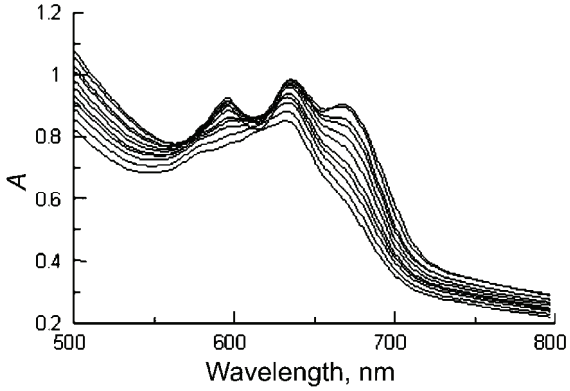


Fig. 4. Electronic spectra of the Co(II) complex in acetonitrile after addition of pyrazole.

In order to study the effect of coordination bases on the geometry of the $[CoL_2]$ complex, a comparison of electronic spectra of the $[CoL_2Y_2]^-$ (Y = 3,5-

-dimethylpyrazole) complex (formed by the addition of 3,5-dimethylpyrazole) with that of [CoL_2] showed that the band at around 15010 cm^{-1} decreased in intensity due to adduct formation. The bands at 14410 and 15870 cm^{-1} of the Co(II) complex vanished completely in pyrazole solution. Thus the Co(II) complex in pyrazole solution showed adduct formation with a possible change in geometry from tetrahedral to octahedral.[28]

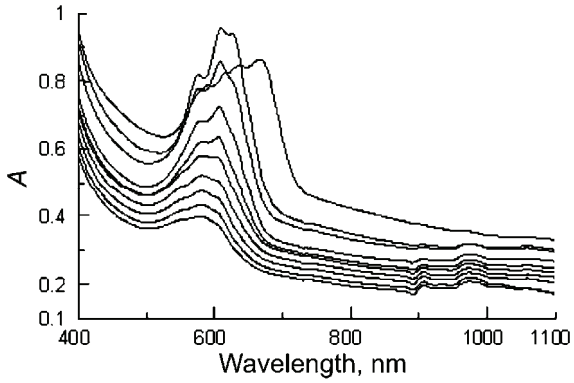


Fig. 5. Electronic spectra of the Co(II) complex in acetonitrile after addition of imidazole.

The electronic spectra of the Co(II) complex in imidazole solution gave rise to a new band at 10362 cm^{-1} and the bands at 15010 and 15870 cm^{-1} were shifted to 16393 and 16863 cm^{-1}, respectively, with a decrease in intensity due to interaction of the base with the metal ion. This led to a change in geometry to octahedral. The ligand exchange behavior on the chelated complex was also studied with acetylacetone. Addition of a small amount of acetylacetone shifted the broad band in the spectrum of the Co(II) complex to 16025 cm^{-1} (Fig. 6).

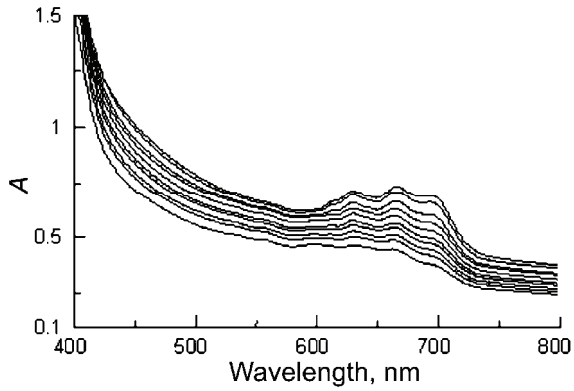


Fig. 6. Electronic spectra of the Co(II) complex in acetonitrile after addition of acetylacetone.

ESR Spectra

ESR spectra of the Cu(II) complex were recorded at room temperature and liquid nitrogen temperature (Fig. 7). There are four well resolved peaks in the low field region corresponding to $g_{\parallel}$ (2.264) and $g_{\perp}$ (2.0419). The trend $g_{\parallel}$ (2.264) > g (2.0419) > g_e (2.0023) observed for the copper complex suggests that the unpaired electron is localized in the $d_{x^2-y^2}$ orbital of the copper ion.[29,30] The fact that the unpaired electron lies predominately in the $d_{x^2-y^2}$ orbital is also supported by the value of the exchange interaction term G estimated from expression:

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

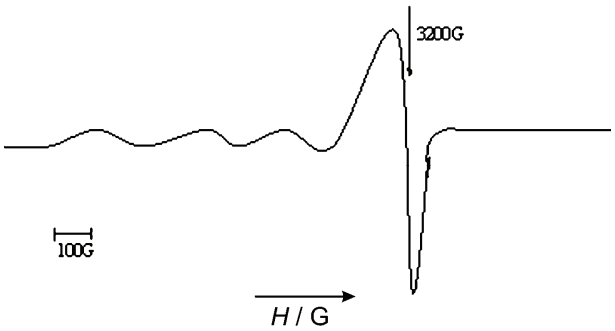


Fig. 7. ESR spectrum of the Cu(II) complex in acetonitrile at 77 K.

If G > 4.0, the local axes are aligned parallel or only slightly misaligned. If G < 4.0, significant exchange coupling is present and the misalignment is appreciable. The observed value for the exchange interaction parameter for the Cu(II) complex (G = 6.60) suggests that the local tetragonal axes are aligned parallel or slightly misaligned and that the unpaired electron is present in the $d_{x^2-y^2}$ orbital. The spin orbit coupling constant, λ (value: –15938 cm^{-1}), calculated using the relation, $g_{av} = 1/3(g_{\parallel} + 2\ g_{\perp})$ and $g_{av} = 2(1 - 2\lambda/10Dq)$, is less than that for the free Cu(II) ion, –12019 cm^{-1}, which also supports the covalent character of M–L band in the complex. The covalency parameter, α^2, was calculated using the following equation:

$$\alpha^2(\mathrm{Cu}) = A_{\parallel}/p + (g_{\parallel} - 2.0023) + 3/7(g_{\perp} - 2.0023) + 0.004$$

The observed value of α^2 of the complex is less than unity and slightly higher than 0.5, which indicates that the complex had some covalent character in the ligand environment.[31] The observed $g_{\parallel}$ value for the copper complex was less than 2.3, suggesting a covalent character of the M–L bond, which is in agreement with the observation of Kivelson and Neiman.

Redox behavior

The redox behavior of the Cu(II) complex was investigated in acetonitrile by cyclic voltammetric studies using a glassy carbon working electrode. The cathodic current function values were found to be independent of the scan rate. The repeated scans as well as the different scan rates showed that dissociation of this complex did not occur. The reduction peak of the Cu(II)/Cu(I) couple for the copper complex (Fig. 8) was observed in the potential range from E_{pa} = 0.450 V *vs*. Ag/AgCl to E_{pc} = 0.575 V *vs*. Ag/AgCl, which is similar to the value reported earlier. The ratio of the anodic and cathodic peak currents ($I_{pc}/I_{pa} \approx 1$) corresponds to a one electron process. Copper complex had a large separation between the cathodic and anodic peak of 125 mV, indicating a quasi-reversible character.[32,33]

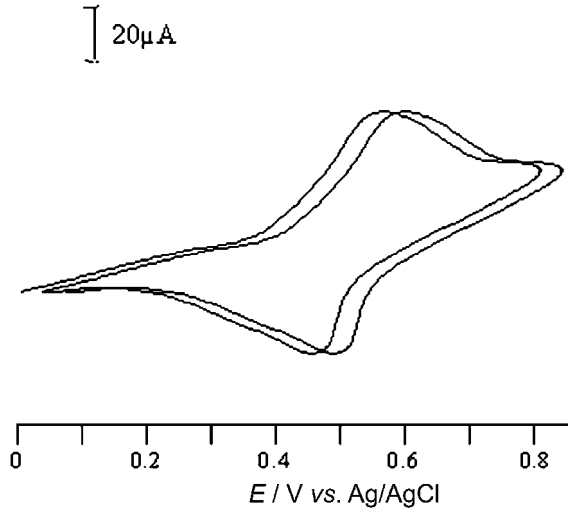


Fig. 8. Cyclic voltammograms of the Cu(II) complex in acetonitrile solution at various scan rates, *viz*. 50 and 150 mV s^{-1}.

Antibacterial activity

The antimicrobial activity of the ligand and its metal complexes were tested against the following stains of bacteria: *Staphylococcus aureus*, *Escherichia coli*, *Salmonella enterica typhi* and *Bacillus subtilis* by the well diffusion method.[34] The test solutions were prepared in acetonitrile, nutrient agar was used as the culture medium. The zone of inhibition was measured in mm and the values of the investigated compounds are summarized in Table IV.

The values indicate that the metal complexes had a higher antibacterial activity than the free ligand. Such increased activity of the metal complexes can be explained on the basis of the overtone concept[35] and chelation theory.[36] According to the overtone concept of cell permeability, the lipid membrane that surrounds the cell favors the passage of only lipid soluble materials, due to which liposolu-

bility is an important factor controlling the antimicrobial activity. On chelation, the polarity of the metal ion is reduced to a great extent due to the overlap of the ligand orbital and the partial sharing of the positive charge of the metal ion with donor groups. Furthermore, it increases the delocalization of electrons over the whole chelate ring and enhances the lipophilicity of the complex. This increased lipophilicity enhances the penetration of the complex into the lipid membrane and blocks the metal binding sites on the enzymes of the microorganism. However, the antibacterial activities of the ligand and its metal complexes were lower than those found for the standard antibacterial drug ciprofloxacin.

TABLE IV. Antibacterial activity data of the ligand and its metal complexes; concentration of the test solutions: 10^{-3} M; diameter of the well: 7 mm

Compound	Zone of inhibition, mm			
	Gram (+)		Gram (–)	
	Bacillus subtilis	*Staphylococcus aureus*	*Escherichia coli*	*Salmonella enterica typhi*
Ligand (LH)	10	11	14	13
$[CuL_2]$	16	17	18	18
$[CoL_2]$	19	14	16	16
$[NiL_2(H_2O)_2]$	17	17	19	15
Ciprofloxacin	23	24	22	23

CONCLUSIONS

The available experimental data suggest that the prepared 1-(2-hydroxyphenyl)-3-phenyl-2-propen-1-one, N^2-[(3,5-dimethyl-1*H*-pyrazol-1-yl)methyl]hydrazone possesses four coordinating sites. Physical and spectroscopic characterization of the complexes revealed that the OH group of the chalcone and the azomethine nitrogen of pyrazole were involved in the coordination and that the Cu(II) complex had square-planar geometry, whereas the Ni(II) and Co(II) complexes had octahedral and tetrahedral geometry, respectively. On addition of bases to the Co(II) complex, a change in geometry occurred due to adduct formation. Generally, antimicrobial activity is due to the hetero atom of multiple bonds or a cyclic ring system. The metal complexes had more pronounced antibacterial activities than the free ligand, probably due to a reduction of the polarity of the metal ion.

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ИЗВОД

СИНТЕЗА, СПЕКТРАЛНО ПРОУЧАВАЊЕ И АНТИБАКТЕРИЈСКА АКТИВНОСТ Cu(II), Co(II) И Ni(II) КОМПЛЕКСА СА N^2-[(3,5-ДИМЕТИЛ-1*H*-ПИРАЗОЛ-1-ИЛ)МЕТИЛ]ХИДРАЗОНОМ 1-(2-ХИДРОКСИФЕНИЛ)-3-ФЕНИЛ-2-ПРОПЕН-1-ОНА

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Нова серија комплекса Cu(II), Co(II) и Ni(II) са N^2-[(3,5-диметил-1*H*-пиразол-1-ил)метил]хидразоном 1-(2-хидроксифенил)-3-фенил-2-пропен-1-она као лигандом, $C_{21}H_{22}N_4O$ (LH), добијена је реакцијом хидразона 1-(2-хидроксифенил)-3-фенил-2-пропен-1-она са (3,5-диметил-1*H*-пиразол-1-ил)метанолом и окарактерисана. Природа везе и геометрија комплекса су изведени на основу елементалне анализе, IR, електронских и ^{1}H-NMR спектара, магнетне сусцептибилности и мерења проводљивости. Проучавање је показало квадратну, тетраедарску и октаедарску геометрију за бакар(II), кобалт(II), односно никал(II) комплексе. ESR спектри бакар(II) комплекса у ацетонитрилу на 300 и 77 K су снимљени и дате су њихове истакнуте карактеристике. Електрохемијско понашање бакар(II) комплекса изучавано је цикличном волтаметријом. Антимикробна активност лиганда и његових металних комплекса тестирана је на следећим сојевима микроорганизама: *Staphylococcus aureus*, *Salmonella enterica typhi*, *Escherchia coli* и *Bacillus subtilis* дифузионом методом. Метални комплекси показали су повећану антимикробну активност у односу на слободни лиганд.

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