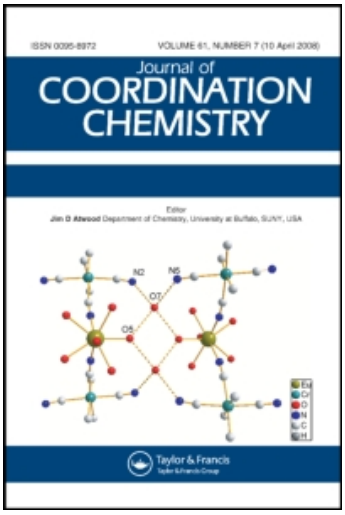

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Synthesis, spectral characterization, and antimicrobial activity of copper(II), cobalt(II), and nickel(II) complexes of 3-formylchromoniminopropylsilatrane

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Synthesis, spectral characterization, and antimicrobial activity of copper(II), cobalt(II), and nickel(II) complexes of 3-formylchromoniminopropylsilatrane

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A new series of Cu(II), Ni(II), and Co(II) complexes have been synthesized from 3-formylchromoniminopropylsilatrane ($C_{19}H_{24}O_5N_2Si$) (**2**) and 3-formylchromoniminopropyltriethoxysilane (**1**). Silatrane ligand ($C_{19}H_{24}O_5N_2Si$) (**2**) has been synthesized by the reaction between 3-aminopropyltriethoxysilane and 3-formylchromone followed by a treatment with triethanolamine. The nature of bonding and the geometry of the complexes have been deduced from elemental analyses, magnetic susceptibility, infrared, electronic, ^{1}H NMR, ^{13}C NMR, and ESR spectral studies. The electronic absorption spectra and magnetic susceptibility measurements of the complexes indicate square planar geometry for Cu(II) and Ni(II) and tetrahedral geometry for Co(II). The redox behavior of copper complexes was studied by cyclic voltammetry. The biological activity of the ligand and metal complexes has been studied on *Klebsiella pneumoniae*, *Staphylococcus aureus*, *Escherichia Coli*, and *Bacillus subtilis* by the well diffusion method using acetonitrile as solvent. The zone of inhibition values were measured at 37°C for 24 h. Antimicrobial screening tests show better results for the metal complexes than the ligand.

Keywords: Formylchromone; 3-Aminopropyltriethoxysilane; Silatrane; Metal complexes; Antimicrobial activity

1. Introduction

Formylchromones have been of synthetic and biological interest because of their synthetic utility based on the three electrophilic carbons and the biological activities associated with the formylchromone derivatives [1–3]. Silatranes constitute a unique class of pentacoordinate silicon compounds and have been extensively important because of the stereoelectronic influence of the silatranyl group in shaping the reactivity of the exocyclic functional group apical to the transannular bond [4–9]. Silanes are used as coupling agents for adhesion between organic and inorganic materials, such as glass fiber-reinforced polymeric composites [10–12].

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Chemically bonded stationary phases containing amino groups in their structure have been known since the 1970s; Haken *et al*. [13] were one of the first groups to prepare and test them. These molecules were synthesized because of their importance in medicine and agriculture [14–16]. To understand the structure–reactivity relationship in these type of compounds by incorporating modifications in the silatranyl group, in this work we report the synthesis, characterization, redox properties, and the biological activity of transition metal complexes of a silatrane-based ligand derived from 3-formylchromone and 3-aminopropyltriethoxysilane.

2. Experimental

All chemicals were obtained from Aldrich Chemical & Co. and used without purification. The UV–Vis spectra of the ligand and metal complexes were recorded in dichloromethane using a JASCO V-530 spectrophotometer. IR spectra were recorded on a Shimadzu FT-IR 8400 s spectrophotometer in National Engineering College, Kovilpatty. Cyclic voltammetry measurements were carried out at room temperature in acetonitrile under N_2 (Model BAS-50 voltammograph) using a three electrode cell containing a reference 1 M KCl Ag/AgCl electrode, Pt wire auxiliary electrode and glassy carbon working electrode in acetonitrile with TBAP as supporting electrolyte. Elemental analyses were performed at Central Drug Research Institute, Lucknow. ^{1}H and ^{13}C NMR spectra (300 MHz) of the samples were recorded in $CDCl_3$ with TMS as internal standard at Madurai Kamaraj University. ESR spectra were recorded with a JEOL TES 100 ESR spectrometer and magnetic moment of the complexes was measured by VSM model 7404 at Pondicherry University. 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. Molar conductances of the complexes were measured in methanol at room temperature using a Systronic conductivity bridge (OSWAL).

2.1. *Synthesis of 3-formylchromoniminopropyltriethoxysilane ($C_{19}H_{27}O_5NSi$) (1)*

About 1.76 g (10 mmol) of 3-formylchromone dissolved in 20 mL benzene was mixed with 2.2 mL (10 mmol) of 3-aminopropyltriethoxysilane dissolved in 20 mL benzene in a round bottomed flask. This reaction mixture was refluxed for 7 h under nitrogen and then volume of the solution was reduced to small amount and petroleum ether was added. The red-orange product was filtered off and dried under vacuum. m.p.: $>280^\circ$C. ^{1}H NMR ($CDCl_3$): (6.9–7.60 δ, m, Ar–H), (3.89, m, 6H, CH_2), (2.25 δ, t, 9H, CH_3–CH_2–O), (0.62 δ, t, 2H, Si–CH_2), (1.40–1.37 δ, m, 2H, –N–CH_2–CH_2–CH_2–); ^{13}C-NMR ($CDCl_3$) 120–156 δ phenyl ring carbon, at 187.9 δ carbonyl carbon, 51.2 δ O–CH_2, 17.6 δ (O–CH_2–CH_3), 9.18 δ (Si–CH_2), N–CH_2 at 15.5, N–CH_2–**C**H_2 at 56.2 δ. ^{13}C-NMR ($CDCl_3$): (120–156 δ, Ar–C), (187.9 δ, C=O), (O–CH_2, 1.2 δ), (17.6 δ, O–CH_2–CH_3), (9.18 δ, Si–CH_2), (15.5 δ, N–CH_2) (N–CH_2–CH_2 at 56.2 δ).

2.2. *Synthesis of 3-formylchromoniminopropylsilatrane ($C_{19}H_{24}O_5N_2Si$) (2)*

About 3.89 g (10 mmol) of **1** dissolved in 20 mL benzene was mixed with 1.49 g (10 mmol) of triethanolamine dissolved in 20 mL benzene. This reaction mixture was

refluxed for 1 h, volume of the solution was reduced and petroleum ether was added. The red product thus obtained was filtered off and dried under vacuum. m.p.: $>280^{\circ}$C.; ^{1}H NMR $CDCl_3$: (6.9–7.60 δ, m, Ar–H), (3.74 and 2.15 δ, t, 2H, N–CH_2–CH_2–O), (0.58 δ, t, –$2H_2$, Si–CH_2), (1.45–1.38 δ, m, 2H, –N–CH_2–CH_2–CH_2–); ^{13}C-NMR ($CDCl_3$): (120–156 δ, Ar–C), (187.9 δ, C=O), (57.2 δ, O–CH_2), (9.3 δ, Si–CH_2), (50.5, N–CH_2), (16.2 δ, N–CH_2–CH_2).

2.3. *Synthesis of metal complexes*

About 1 mmol of silatrane-based ligand was dissolved in 20 mL of dichloromethane and 2 mmol of anhydrous MCl_2 (M = Cu(II), Co(II), and Ni(II)) was added. This reaction mixture was stirred for 3 h. The resulting precipitated complexes were filtered and dried under vacuum.

3. Results and discussion

The 3-formylchromoniminopropyltriethoxysilane (**1**) was synthesized by condensation of 3-aminopropyltriethoxysilane with 3-formylchromone (figure 1). It was then treated with triethanolamine to form 3-formylchromoniminopropylsilatrane ($C_{19}H_{24}O_5N_2Si$) (**2**). Combination of Cu(II), Co(II), and Ni(II) with **1** and **2** gave powders with high melting points, not soluble in ethanol and water but soluble in dichloromethane, acetonitrile, chloroform, and more soluble in DMF.

Elemental analyses (table 1) suggests that the complexes have 1 : 2 (metal : ligand) stoichiometry (figures 2 and 3). Based on the elementary chemical analysis, the formula ML_2 was suggested for all compounds. The conductance values support the electrolytic nature of metal complexes.

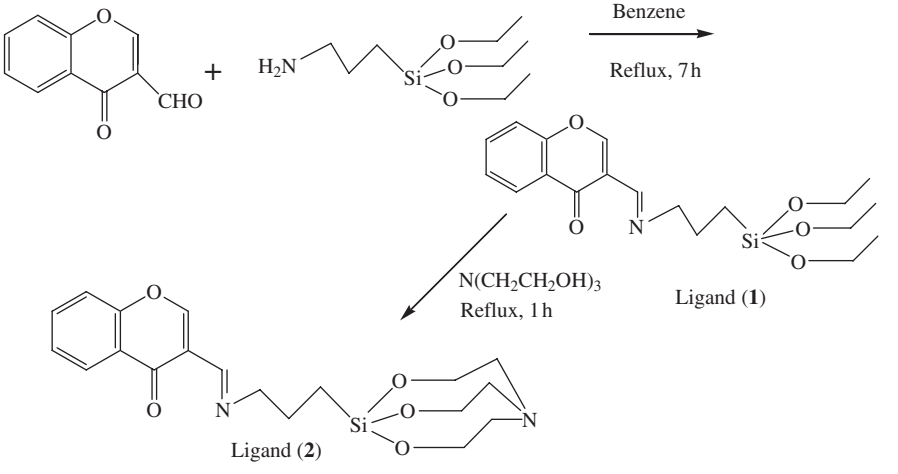

Figure 1. Synthesis of **1** and **2**.

Table 1. Elemental analysis data of the ligands and metal(II) complexes.

Compound	Analysis found (Calcd) (%)				Λ_M ($\Omega^{-1}\,cm^2\,mol^{-1}$)
	M	C	H	N	
$C_{19}H_{27}O_5NSi$ (**1**)	–	60.12	7.05	3.48	–
	–	(60.45)	(7.21)	(3.71)	
$[C_{38}H_{54}O_{10}N_2Si_2Cu]Cl_2$ (**3**)	6.98	51.15	6.02	3.04	110
	(7.14)	(51.31)	(6.12)	(3.15)	
$[C_{38}H_{54}O_{10}N_2Si_2Co]Cl_2$ (**4**)	6.15	51.22	6.04	3.09	90
	(6.66)	(51.58)	(6.15)	(3.17)	
$[C_{38}H_{54}O_{10}N_2Si_2Ni]Cl_2$ (**5**)	6.23	51.12	6.03	2.94	97
	(6.64)	(51.59)	(6.15)	(3.17)	
$C_{19}H_{24}O_5N_2Si$ (**2**)	–	58.12	6.10	7.02	–
	–	(58.74)	(6. 23)	(7.21)	
$[C_{38}H_{48}O_{10}N_4Si_2Cu]Cl_2$ (**6**)	6.37	49.82	5.24	6.03	120
	(6.97)	(50.07)	(5.31)	(6.15)	
$[C_{38}H_{48}O_{10}N_4Si_2Co]Cl_2$ (**7**)	6.13	50.10	5.11	5.85	110
	(6.50)	(50.33)	(5.34)	(6.18)	
$[C_{38}H_{48}O_{10}N_4Si_2Ni]Cl_2$ (**8**)	6.08	50.16	5.24	6.04	125
	(6.48)	(50.34)	(5.34)	(6.18)	

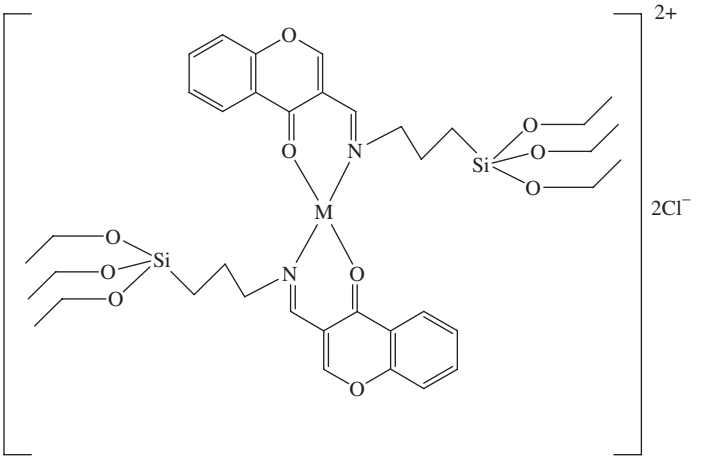

Figure 2. Proposed structures of metal(II) complexes of **1** (M = Cu, Co, and Ni).

3.1. *IR spectra*

IR spectral data of the ligands and metal complexes are presented in table 2. Compared to the IR spectrum of the ligands, the frequency of $\nu_{C=N}$ (1678, 1687 cm^{-1}) moves to lower energy in the spectra of the complexes, confirming coordination of the azomethine nitrogen to the metal.

For **1** and **2**, $\nu_{C=O}$ (cyclic keto group present in the phenyl ring: 1608, 1610 cm^{-1}) moved to a lower frequency in complexes, suggesting coordination via the C=O oxygen [11, 12]. The proof of N and O coordination is demonstrated by bands in the spectra of complexes in the regions 525–564 cm^{-1} and 411–428 cm^{-1} assigned to M–N and M–O modes, respectively [17, 18]. The IR spectra of the ligands and metal complexes show bands in the region 985–1100 cm^{-1}, assigned to ν_{Si-O} [12, 19].

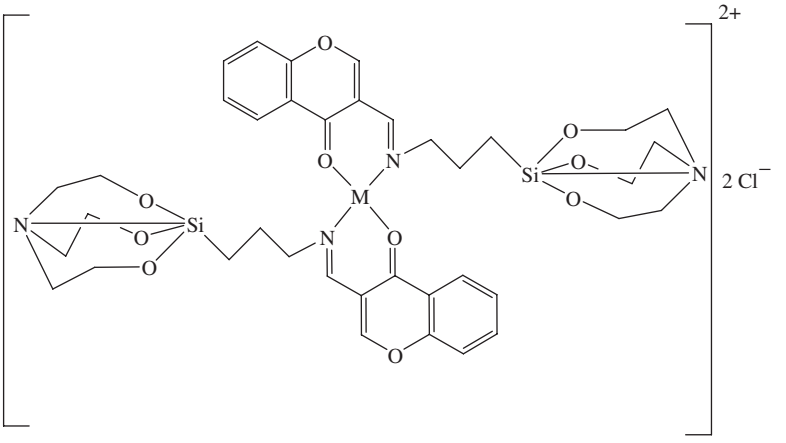

Figure 3. Proposed structures of metal(II) complexes of **2** (M = Cu, Co, and Ni).

Table 2. Characteristic IR bands of the ligands and metal complexes.

	Frequency (cm^{-1})				
Compound	$\nu_{C=O}$	$\nu_{C=N}$	Si–O	M–N	M–O
1	1688	1608	1078	–	–
3	1617	1575	1030	525	412
4	1637	1560	985	564	428
5	1644	1568	1013	540	436
2	1678	1610	1094	–	–
6	1631	1542	1093	539	419
7	1615	1564	990	548	420
8	1622	1572	1010	537	442

3.2. *Electronic spectral and magnetic moment data of the metal complexes*

The electronic spectral and magnetic moment data of metal complexes are listed in table 3. The spectra of Cu(II) complexes (**3** and **6**) show absorption in the region 24, 750–24, 937 cm^{-1}, which could be attributed to the $^2B_{1g} \rightarrow {}^2A_{1g}$ transition characteristic of Cu(II) in a square planar geometry [11, 20, 21]. Square planar geometry of Cu(II) ion in the complex is confirmed by magnetic moment values of 1.73–1.82 B.M.

The Co(II) complexes (**4** and **7**) exhibit a band at 16,977–17,000 cm^{-1} assigned to $^4T_1(F) \rightarrow {}^4T_1(P)$ transition and another band at 14,684–14,641 cm^{-1} due to $^4A_2(F) \rightarrow {}^4T_1(F)$, which indicates tetrahedral geometry. The four coordinated Co(II) complexes show magnetic moment values of 4.2–4.46 B.M., consistent with tetrahedral geometry [22].

The Ni(II) complexes (**5** and **8**) exhibit a band at 18,692–19,453 cm^{-1} assigned to $^1A_{1g} \rightarrow {}^1A_{2g}$ and another at 20,492–21,121 cm^{-1} due to $^1A_{1g} \rightarrow {}^1B_{1g}$, which strongly favors square planar geometry of the nickel complex, further supported by their diamagnetism.

Table 3. Electronic spectral data (cm^{-1}) and magnetic moments (B.M.).

Compound	Frequency (cm^{-1})	Transition	Geometry	μ_{eff} (B.M.)
1	38,461	INCT	–	–
	29,411	INCT		
3	25,000	INCT	Square planar	1.73
	24,750	$^2B_{1g} \rightarrow {}^2A_{1g}$		
4	16,977	$^4T_1(F) \rightarrow {}^4T_1(P)$	Tetrahedral	4.20
	14,684	$^4A_2(F) \rightarrow {}^4T_1(F)$		
5	40,125	INCT	Square planar	–
	19,453	$^1A_{1g} \rightarrow {}^1A_{2g}$		
	21,121	$^1A_{1g} \rightarrow {}^1B_{1g}$		
2	32,154	INCT	–	–
	39,682	INCT		
6	24,937	$^2B_{1g} \rightarrow {}^2A_{1g}$	Square planar	1.82
	11,862	INCT		
7	17,000	$^4T_1(F) \rightarrow {}^4T_1(P)$	Tetrahedral	4.46
	14,641	$^4A_2(F) \rightarrow {}^4T_1(F)$		
8	38,195	INCT	Square planar	–
	27,145	INCT		
	18,692	$^1A_{1g} \rightarrow {}^1A_{2g}$		
	20,492	$^1A_{1g} \rightarrow {}^1B_{1g}$		

Table 4. ESR spectral data of copper(II) complex.

Compound	$g_\parallel$	$g_\perp$	g_{av}	α^2	$A_\parallel \times 10^{-4}\,cm^{-1}$	$A_\perp \times 10^{-4}\,cm^{-1}$	$g_\parallel/A_\parallel$
3	2.303	2.058	2.135	0.861	178.920	35.725	136.336

3.3. *ESR spectra*

ESR spectra of copper complexes provide important information for studying the metal ion environment. The X-band ESR spectrum of **3** was recorded in acetonitrile at liquid nitrogen temperature and room temperature (300 K). The spin Hamiltonian parameters calculated for the copper complex are given in table 4. The spectrum of the copper complex at room temperature shows one intense absorption in the high field and is isotropic due to tumbling of the molecules. However, this complex in frozen state shows four well-resolved peaks at low field. In square planar complexes, the unpaired electron lies in the $d_{x^2-y^2}$ orbital giving $g_\parallel$ (2.303) > $g_\perp$(2.058) > g_e(2.0023). The fact $g_\parallel > g_\perp$ suggests that the complex is square planar. This is also supported by the fact that the unpaired electron lies predominately in the $d_{x^2-y^2}$ that is evident from the value of the exchange interaction term G, estimated from the expression:

$$G = \frac{g_\parallel - 2.0023}{g_\perp - 2.0023}.$$

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.

Table 5. Cyclic voltammetric data of the copper complexes.

Complexes	Epc(V)	Epa(V)	ΔEp(V)	$E_{1/2}$(V)	Ic/Ia
3	0.559	0.423	0.139	0.491	1.29
6	0.542	0.411	0.131	0.476	1.37

The observed value for the exchange interaction parameter for the copper complex ($G = 5.398$) suggest that the local tetragonal axes are aligned parallel or slightly misaligned and the unpaired electron is in $d_{x^2-y^2}$ orbital [23–26]. The spin orbit coupling constant, λ value ($-24752\,cm^{-1}$) calculated using the relations, $g_{av} = 1/3(g_{\parallel}) + 2/3(g_{\perp})$, is less than the free Cu(II) ion ($-12019\,cm^{-1}$) which also supports the covalent character of M–L bond in the complex. The covalency parameter α^2 is calculated using the following equation:

$$\alpha^2_{Cu} = A_{\parallel}/p + (g_{\parallel} - 2.0023) + 3/7(g_{\perp} - 2.0023) + 0.04.$$

If the $\alpha^2 = 0.5$, it indicates complete covalent bonding, while the value of $\alpha^2 = 1$ suggests complete ionic bonding. The observed value of α^2 of the complex indicates that the complex has some ionic character in the ligand environment [27].

3.4. *Redox behavior*

The redox behaviors of **3** and **6** have been studied by cyclic voltammetric glassy carbon as the working electrode in acetonitrile (table 5). The cathodic current function values were independent of scan rate. The repeated scan as well as different scan rate shows that dissociation does not take place in these complexes.

Cyclic voltammograms show well-defined, quasi-reversible processes for the Cu(II)/Cu(I) couple in the range $Epc = 0.559$–0.542 V and $Epa = 0.423$–0.411 V. This couple likely has $n = 1$, but cannot be determined from quasi-reversible cyclic voltammograms which give modestly large ΔEp's. ($\Delta Ep_{a,c}$ at *ca* 130 mV) [28–30].

3.5. *NMR spectra*

The ^{1}H NMR spectrum of **1** recorded in $CDCl_3$ is assigned as follows: phenyl ring as multiplet at 6.9–7.60 δ (m), the peaks at 3.89 (m, 6H) and 2.25 δ (t, 9H) to (CH_3–CH_2–O) group, peak at 0.62 δ (t, –CH_2) due to (Si–CH_2), at 1.40–1.37 δ (m, 2H) due to (–N–CH_2–CH_2–CH_2–). ^{13}C-NMR ($CDCl_3$) spectra assigned as 120–156 δ due to the phenyl ring carbons, carbonyl carbon at 187.9 δ, O–CH_2 at 51.2 δ, 17.6 δ O–CH_2–CH_3, Si–CH_2 at 9.18 δ, N–CH_2 at 15.5, N–CH_2–**C**H_2 at 56.2 δ.

The ^{1}H NMR spectrum of **2** in $CDCl_3$ is assigned as: phenyl ring multiplet at 6.9–7.60 δ (m), 3.74 and 2.15 δ (t, CH_2) to (N–CH_2–CH_2–O) group, 0.58 δ (t, –CH_2) due to (Si–CH_2), 1.45–1.38 δ (m, 2H) due to (–N–CH_2–CH_2–CH_2–). Resonances in **1** at 3.89 δ m, 6H and 2.25 δ t, 12H (–Si–OCH_2–CH_3)$_3$ are shifted in **2** to 3.74 and 2.15 δ (t, 6H) due to the change of Si–(OCH_2CH_3)$_3$ to (Si–O–CH_2–CH_2)$_3$–N. ^{13}C NMR ($CDCl_3$) spectra are assigned as 120–156 δ due to the phenyl ring carbon, carbonyl carbon at 187.9 δ, O–CH_2 at 57.2 δ, Si–CH_2 at 9.3 δ, N–CH_2 at 50.5, and N–CH_2–**C**H_2 at 16.2 δ.

Table 6. Antimicrobial activity of the ligands and metal complexes (zone of inhibition in mm).

Compound	*K. pneumoniae*	*S. aureus*	*E. coli*	*B. subtilis*
1	11	14	12	12
3	16	17	15	17
4	14	17	15	13
5	15	13	17	16
2	13	12	13	13
6	16	17	15	14
7	16	15	14	17
8	14	17	14	15

3.6. *Biological activity*

The antimicrobial activity of the ligands and their metal complexes were tested against the bacterias *K. pneumoniae*, *S. aureus*, *E. coli*, and *B. subtilis* by the well diffusion method [31]. Test solutions were prepared in acetonitrile, and nutrient agar was used as a culture medium. The zone of inhibition was measured in millimeter (table 6). The values indicate that most complexes have higher antimicrobial activity than the free ligands [32].

4. Conclusion

3-Formylchromoniminopropyl silatrane and metal complexes have been synthesized and characterized on the basis of analytical and spectral data. The results of this investigation support the suggested structures of the metal complexes. The copper and nickel complexes have square planar geometry while the cobalt complexes are tetrahedral. Biological activity of the ligand and their metal complexes has shown that the activity of the metal complexes is higher than the ligand. The presence of azomethine moiety and chelation effect with central metal enhances the antimicrobial activities.

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