Synthesis of 4-Dicyclohexylaminomethyl Antipyrine and Its Metal Complexes: Spectral Characterization and Evaluation of Thermodynamic Parameters¹

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Abstract—Complexes of Fe(III), Co(II), Ni(II), and Cu(II) with 4-dicyclohexylaminomethyl antipyrine (DCHAMA, L) were prepared and characterized by elemental and chemical analyses, IR, electronic absorption, ¹H NMR and EPR spectroscopies, thermal analysis, and magnetic susceptibility measurements. The stoichiometry of the complexes was found to be MLX₂, MLX₃, or MLX₂(H₂O)₂ where X = Cl or NO₃. The ligand exhibits a bidentate mode of coordination. Thermal analysis of the chloro complexes shows a three stage decomposition pattern for the Cu(II) complex and a two stage decomposition pattern for Fe(III) and Co(II) complexes to yield the respective metal oxides as the end product. Kinetic and thermodynamic parameters such as *n*, *E_a*,

 $\Delta H^{\#}, \Delta S^{\#}, \text{and } \Delta G^{\#}$ were calculated using Coats–Redfern and Madhusudhanan–Krishnan–Ninan integral methods. The coordination number of the metal atom is found to influence the thermal stability of the complexes. The antimicrobial screening shows that the four-coordinated complexes are more active than the five- and six-coordinated ones and DCHAMA.

INTRODUCTION

Antipyrine and its metal complexes have been reported to possess important medicinal properties. They act as anti-inflammatory [1], antirheumatic [2], antipyretic [3], and analgesic [4] drugs. The carbonyl group in antipyrine is a potential donor due to the large dipole moment and strong basic character [5]. In the metal complexes of antipyrine, the ligand was found to act as a monodentate ligand bonding through its carbonyl oxygen atom [6–8]. Antipyrine can be converted into an effective chelating ligand by substitution of groups containing donor atoms. We have previously reported some Mannich bases of antipyrine and their metal complexes [9–12]. In view of the varying possibilities of structural type and biological activity, an attempt is made to synthesize and structurally characterize a new Mannich base of antipyrine and its metal chelates.

EXPERIMENTAL

All the reagents used for synthesizing the ligand and its metal chelates were of analytical or reagent grade and the solvents were purified by the standard methods of distillation.

Synthesis. 4-Dicyclohexylaminomethyl antipyrine (DCHAMA) is synthesized by adding acidified dicyclohexylamine (prepared by mixing 19.9 ml of dicyclo-

hexylamine (0.1 mol) with catalytic amount (~1 ml) of concentrated HCl at ice cold condition) to a mixture of 8.6 ml of formaldehyde (0.1 mol) and 18.8 g of antipyrine (0.1 mol) maintained at 0°C with constant stirring and left at room temperature for about 24 h. Chloroform extract of the reaction mixture is evaporated on a steam bath. Pale yellow colored waxy solid separates out. The crude product is washed with ether and dried in a desiccator and crystallized from ethanol. The iron(III), cobalt(II), nickel(II), and copper(II) chloro complexes and the nitrato complex of copper(II) are prepared by refluxing the methanol solution of the ligand with the metal salts in 1 : 1 molar ratio for about 3 h. The complexes obtained as insoluble precipitates after reflux are washed with chloroform and dried in a desiccator. The cobalt(II) nitrato complex is prepared by mixing the salt solution in EtOH with the ligand in CHCl₃. The resulting mixture obtained is kept overnight in a freezer. Pink colored product obtained is washed with chloroform and dried in a vacuum oven.

Physical measurements. The elemental analyses (C, H, and N) were carried out using LECO-CHN analyzer. Metal contents in the complexes were analyzed using standard procedures. Conductance measurements were made using 10^{-3} M solutions of the complexes in DMF with the help of Systronic Direct Reading Conductivity Bridge. IR spectra of the compounds were recorded as KBr discs using Perkin Elmer-1430 ratio recording spectrophotometer. The far-IR spectral measurements of the compounds on a polyethylene support were made using Bruker IFS 66V FT-IR spectropho-

¹This article was submitted by the auhors in English.

Compound		Λ_{M} ,				
	С	Н	Ν	А	М	$\Omega^{-1} \mathrm{cm}^2 \mathrm{mol}^{-1} *$
DCHAMA	75.54/75.59	9.18/9.18	11.00/11.02			
[Fe(DCHAMA)Cl ₃]	52.99/53.01	6.43/6.44	7.76/7.77	19.59/19.0	10.28/10.28	68.0
[Co(DCHAMA)Cl ₂]	56.36/56.37	6.84/6.85	8.21/8.22	13.88/13.9	11.52/11.53	67.0
[Co(DCHAMA)(NO ₃) ₂]	51.06/51.07	6.20/6.20	12.40/1241	21.97**/28	10.44/10.45	76.0
[Ni(DCHAMA)(H ₂ O) ₂ Cl ₂]	52.66/52.67	7.13/7.13	7.67/7.68	12.98/12.8	10.73/10.73	42.0
$[Cu(DCHAMA)(H_2O)_2Cl_2]$	52.20/52.21	7.07/7.07	7.60/7.61	12.86/12.7	11.52/11.52	20.0
[Cu(DCHAMA)(NO ₃) ₂]	50.64/50.65	6.15/6.15	12.30/12.31	21.80**/21.1	11.17/11.17	81.0

Table 1. Analytical and conductance data of DCHAMA and its Fe(III), Co(II), Ni(II), and Cu(II) complexes

* For 10^{-3} M solution in DMP.

** Obtained from the difference between the mass of the complex and the mass of the other constituents excluding anion.

tometer. The electronic absorption spectra of the complexes in the UV-Visible region were measured using JASCO UVIDEC-430B double beam spectrophotometer and Hitachi UV-VIS-NIR spectrophotometer. The room temperature (305 K) magnetic moment measurements of the complexes were carried out using a Gouy magnetic balance. A Varian E₄XE₄ Band ESR spectrometer was used for recording the EPR spectra. The mass spectral studies were carried out using Finningam MAT-8320 mass spectrometer. NMR spectra were recorded using JEOL GSX 400NB, 400 MHz spectrometer and TMS as internal standard and CDCl₃ as solvent at ambient temperature. TG/DTG measurements of the complexes were recorded on Shimadzu Thermal Analyzer DT-40 in an atmosphere of air at a heating rate of 10°C/min in the range from ambient to 1000°C. The TG curves were analyzed as percentage mass loss as a function of temperature. The number of decomposition steps was identified from the TG curves. From the $TG/DT\bar{G}$ pattern of the compounds, kinetic and thermodynamic parameters such as $n, E_a, \Delta S^{\#}, \Delta H^{\#}$, and $\Delta G^{\#}$ were evaluated using Coats-Redfern (CR) [13] and Madhusudhanan-Krishnan-Ninan (MKN) [14] equations. The turbidity of the bacterial suspensions was measured using Systronics Nephelo Turbidity Meter-131.

The serial tube dilution method [15] is employed for the antimicrobial screening. A nutrient broth medium containing 1% (w/v) sodium chloride is prepared in distilled water and sterilized by autoclaving at 100°C for about 30 min. A standard volume (10 ml) of the nutrient broth medium that would support the growth of the test organism is added to several labeled sterile stoppered identical assay tubes. A solution of each test compound is prepared in DMF and a series of dilutions are prepared. The concentrations tested are 25, 50, 75, 100, 125, and 150 µg/ml of the compound under investigation, a wide spectrum antibiotic, the respective metal salt and the blank (DMF). A control tube containing no test compound is also included. All these operations are carefully carried out under aseptic conditions. The assay tubes are incubated at $37 \pm 1^{\circ}$ C. The resultant turbidities at 24 and 48 h are measured in a nepheloturbidity meter. The minimum inhibitory concentration of the test compound is the least concentration showing no visible turbidity. However, the percentage bacterial growth inhibition produced by a particular concentration of the test compound is calculated from the measure of the turbidities of the control and the particular treatment, provided the influence of the solvent and the metal ion on the growth of the organism is negligible. The relation used is inhibition (%) = $[(T_c - T_t)/T_c] \times$ 100, where T_c is the turbidity of the control and T_t is the turbidity of the specific treatment or the test compound. The organisms selected are *Staphylococcus* (S.) aureus and Escherichia (E.) coli. The inhibition of the growth of the gram-positive and gram-negative organisms by the compounds is compared with that for streptomycin.

RESULTS AND DISCUSSION

DCHAMA is a pale yellow colored waxy solid and its melting point is 78°C. Yield of the product is 75%. It is readily soluble in chloroform and moderately soluble in methanol, ethanol, 1-propanol, and 2-propanol and slightly soluble in acetone. The elemental analysis of the crystallized product is given in Table 1. Comparison of the IR spectrum of antipyrine with that of DCHAMA indicates that new bands appear in the spectrum of DCHAMA which are due to the substitution of an additional moiety on antipyrine. A new and sharp intense absorption band at 1153 cm⁻¹ is due to v(C-N-C) of dicyclohexylamino moiety. The effect of substitution on the antipyrine was indicated by a negative shift of about 40 and 12 cm⁻¹ in the ν (C=O) and pyrazolone ring bending modes, respectively. The important IR absorption bands are listed in Table 2.

The ¹H NMR spectrum of DCHAMA in CDCl₃ exhibits a signal at $\delta = 2.22$ ppm that is assigned to $-N-(C_6H_{11})_2$ moiety. Protons of the benzene ring appear at

Compound	v(C=O)	Pyrazolo- ne ring stretch	Pyrazolo- ne ring bend	N–Phenyl stretch	v(C-N-C)	v(M*–O)	ν(M=N)	v(M–Cl)
Antipyrine	1668 s*	1482 s	1464 m*	1170 w*				
DCHAMA	1649 s	1490 s	1452 m	1170 w	1153 s			
[Fe(DCHAMA)Cl ₃]	1620 s	1492 s	1470 w	1178 w	1143 s	380	316	277
[Co(DCHAMA)Cl ₂]	1600 s	1491 s	1449 w	1187 w	1099 s	390	330	290
[Co(DCHAMA)(NO ₃) ₂]	1581 s	1490 s	1455 w	1188 w	1143 s	380	320	
[Ni(DCHAMA)(H ₂ O) ₂ Cl ₂]	1602 s	1492 s	1456 m	1167 w	1076 s	380	300	260
[Cu(DCHAMA)(H ₂ O) ₂ Cl ₂]	1575 s	1495 s	1385 w	1198 w	1133 s	500	430	300
[Cu(DCHAMA(NO ₃) ₂]	1638 s	1492 s	1389 w	1195 w	1099 s	428	390	

Table 2. II	R data of ((cm^{-1})) DCHAMA	and its	Fe(III),	Co(II)	, Ni(II),	and Cu(II)) complexes
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* s, strong; w, weak; m, medium; M, metal.

 δ = 7.26–7.45 ppm almost in the same position as in the spectrum of antipyrine. The >N–CH₃ and C–CH₃ protons of antipyrine ring appear at δ = 3.07 and 3.05 ppm, respectively. The signal at δ = 2.25 ppm is assigned to –CH₂– group that links dicyclohexylamino moiety and antipyrine. The intensity for the signals correlates well with the total number of protons under each type.

The mass spectrum of DCHAMA exhibits the molecular ion peak at m/z = 381, which corresponds to the proposed molecular weight of the compound. Upon fragmentation, it exhibits a signal at m/z = 298, which indicates the loss of $-C_6H_{11}$ fragment from DCHAMA. The intermediate species further loses $^+N-C_6H_{11}$ and registers a peak at m/z = 201. Based on the above data, the structure proposed for DCHAMA is the following.



All the complexes synthesized are soluble in polar solvents DMF and DMSO. Λ_M values (Table 1) suggest all the complexes to be nonelectrolytes. The analytical data indicate a 1 : 1 stoichiometry for the metal and ligand (Table 1).

Infrared spectra. The IR spectra of all the complexes show perceptible shifts by about 75–25 and 55–20 cm⁻¹ (Table 2) in the stretching frequencies of C=O and C–N–C relative to DCHAMA. This observation suggests that in all the complexes the ligand is bonded to the metal atom through the same atoms, i.e., the O atom of C=O and the N of C–N–C moieties. In the nickel(II) chloro complex, the absorption bands around 3551, 1640, 870, and 590 cm⁻¹ indicate the presence of

coordinated water molecules. The bands at 1439, 1286, and 1034 cm⁻¹ for the nitrato complex of cobalt(II) can be assigned to the $v_1(A_1)$ (v(N= \overline{O})), $v_5(B_2)(v_a(NO_2))$, and $(A_1)(v_s(NO_2))$. These bands indicate a bidentate behavior of the nitrato group. Similarly, the nitrato complex of Ni(II) shows absorption bands at 1470, 1303, and 1021 cm⁻¹, which can be assigned to v(N=O) (v_1) , $v_a(NO_2)$ (v_5) , and $v_s(NO_2)$ (v_2) , respectively, of the nitrato group. The v_5 and v_2 are the split bands of v_4 in the free NO₃⁻. A value of 167 cm⁻¹ for $v_5 - v_1$ indicates a bidentate mode of coordination. In the IR spectrum of copper(II) nitrato complex, three strong bands overlapping with the ligand bands are observed at 1418, 1320, and 1046 cm⁻¹. These are assigned to v_4 , v_1 , and v_2 vibrations, respectively, of the nitrato group. The bands at 1418 and 1320 cm⁻¹ are the split bands of v_3 mode of free nitrate group and the difference is 98 cm⁻¹, which indicates that the nitrato groups are monodentate. Far IR spectra of these complexes show absorption bands corresponding to M–O, M–N, and M–Cl stretching frequencies (Table 2).

Electronic absorption spectral and magnetic susceptibility measurements. The electronic absorption spectrum of iron(III) chloro complex shows an intense band at 31400 cm⁻¹ and another weak band at 17600 cm⁻¹ which are presumably due to the charge transfer (CT) and spin forbidden transitions, respectively. The μ_{eff} value for the complex is 5.35 $\mu_{\rm B}$. Based on the above, a trigonal bipyramidal geometry is assigned to the iron(III) chloro complex. The diffuse reflection spectrum of cobalt(II) chloro complex exhibits three absorption bands at 16393, 9107, and 5464 cm⁻¹. These absorptions are due to ${}^{4}A_{2}(F) \longrightarrow {}^{4}T_{1}(P), {}^{4}A_{2}(F) \longrightarrow$ ${}^{4}T_{1}(F)$, and ${}^{4}A_{2}(F) \longrightarrow {}^{4}T_{2}(F)$ transitions. The magnetic moment of the Co(II) chloro complex is 4.60 μ_B which is well within the range of 4.30–4.80 $\mu_{\rm B}$ expected for Co(II) in a tetrahedral environment [16]. The number

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Parameter	[Co(DCHAMA)Cl ₂]	[Co(DCHAMA)(NO ₃) ₂]	[Ni(DCHAMA)(H ₂ O) ₂ Cl ₂]
v_3, cm^{-1}	16393	19431	25000
v_2, cm^{-1}	9107	15151	15873
v_1 , cm ⁻¹	5464	7048	10220
v_3/v_1	3.00	2.76	2.45
v_2/v_1	1.66	2.15	1.55
v_3/v_2	1.80	1.28	1.58
ν_3/B	27.00	21.84	36.71
B, cm^{-1}	607	889	681
Dq/B	0.90	0.93	1.50
Dq, cm^{-1}	546.43	822.88	1021.00
β	0.62	0.90	0.98
β, %	38	10	2
LFSE, kcal/mol**	18.74	27.77	35.00
Color	Bluish green	Pink	Green
μ_{eff}, μ_B	4.60	5.10	2.89

Table 3. Ligand field parameters of Co(II) and Ni(II) complexes of DCHAMA*

* Free ion value for Co(II) is 971 cm⁻¹ and for Ni(II) is 1041 cm⁻¹.

** LFSE (Ligand Field Splitting Energy) = 12 Dq, kcal/mol = 350 cm^{-1} .

and energy positions of the absorption bands suggest a tetrahedral geometry around cobalt(II). The diffuse reflection spectrum of Co(II) nitrato complex in MgCO₃ medium registers absorption maximum at 7058 cm⁻¹, which arises due to ${}^{4}T_{1g}(F) \longrightarrow {}^{4}T_{2g}$ transition. The next two bands at 15151 and 19431 cm⁻¹ can be attributed to ${}^{4}T_{1g}(F) \longrightarrow {}^{4}A_{2g}$ and ${}^{4}T_{1g}(F) \longrightarrow {}^{4}T_{1g}(P)$ transitions, respectively. The magnetic moment is 5.1 $\mu_{\rm B}$ due to the spin orbit coupling in an octahedral environment. Diffuse reflection spectrum recorded for Ni(II) chloro complex exhibits three intense absorption bands at 25000, 15873, and 10220 cm⁻¹ that are assigned to ${}^{3}A_{2g} \longrightarrow {}^{3}T_{2g}(P)(v_3), {}^{3}A_{2g} \longrightarrow {}^{3}T_{1g}(F)(v_2)$, and ${}^{3}A_{2g} \longrightarrow {}^{3}T_{2g}(v_1)$, respectively. These three bands are characteristic of six-coordinated nickel(II) complex. The magnetic moment value is 2.89 μ_B , which does not differ much from the only spin value. The μ_{eff} value supports the octahedral geometry proposed for Ni(II) chloro complex based on UV-VIS spectral studies. The electronic absorption spectrum of copper(II) chloro complex exhibits a broad band at 13474 cm⁻¹ which is assigned to ${}^{2}E_{g} \longrightarrow {}^{2}T_{2g}$ suggesting a distorted octahe-dral environment [17, 18] in this complex. Though three transitions ${}^{2}B_{1} \longrightarrow {}^{2}A_{1}(v_{1}), {}^{2}B_{1} \longrightarrow {}^{2}B_{2}(v_{2})$, and ${}^{2}B_{1} \longrightarrow {}^{2}E(v_{3})$ are expected in copper(II) complexes of D_2h symmetry due to Jahn–Teller distortion, they are often close in energy and give rise to a single broad band. The intense band that appears near 38000 cm⁻¹ might be of charge transfer origin. The room temperature magnetic moment of the complex is 1.83 $\mu_{\rm B}$. The diffuse reflection spectrum of Cu(II) nitrato complex exhibits a broad band centered at 16571 cm⁻¹ along with two less intense bands at 13774 and 10204 cm^{-1} .

The latter two absorption bands rule out tetrahedral geometry for the complex since tetrahedral complex usually shows no *d*–*d* bands in the range 10000–20000 cm⁻¹. These transitions are assigned to ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$, ${}^{2}B_{1g} \rightarrow {}^{2}B_{2g}$, and ${}^{2}B_{1g} \rightarrow {}^{2}A_{2g}$, respectively, which arise due to the Cu²⁺ in a square planar crystal field. The magnetic moment value of this complex is 2.18 µ_B. Various electronic spectral parameters calculated for some of the complexes by taking recourse to Tanabe–Sugano diagram are given in Table 3.

Electron paramagnetic resonance spectra. In the EPR spectrum of copper(II) chloro complex, g_{\parallel} is less than 2.3, which indicates a covalent environment. The g_{\parallel} and α^2 values are 2.283 and 0.86, respectively, suggest that the bond is sufficiently covalent in nature and the unpaired electron spends 14% of its time on the ligand donor atom. Inspection of the EPR data indicates four hyperfine lines on the g_{\parallel} feature due to the interaction of the unpaired electron with nuclear spin of the copper(II) nucleus (I = 3/2, 2I + 1 = 4). Super hyperfine lines are seen on the g_{\perp} feature in some cases with a very low resolution and a decrease in the number of lines, which is expected if the N atom is the donor atom. Based on the spectral data and magnetic moment values, distorted octahedral geometry is assigned to the copper(II) chloro complex. The EPR spectrum of copper(II) nitrato complex exhibits four clear bands in the g_{\parallel} region and a clear g_{\perp} band with values of $g_{\parallel} = 2.182$ and $g_{\perp} = 2.097$ expected for copper(II) complexes. Hyperfine splitting constant A_{\parallel} of the complex is 175 G which is typical of square planar complexes. The α^2 value of 0.96 indicates that the bond is covalent in nature and the unpaired electron spends 4% of its time on the ligand donor atom. From the $g_{\parallel} > g_{\perp}$ trend, it is clear that unpaired electron lies predominantly on the $d_{x^2 - y^2}$ orbital. The EPR spectral parameters are given

in Table 4. Based on the above discussion of the physical characteristics of the complexes, the tentative structure types are assigned as follows:



Thermal studies and evaluation of thermodynamic parameters. The TG/DTG of DCHAMA shows a two-stage decomposition pattern. DCHAMA is stable up to 150°C. A gradual mass loss is observed up to 400°C. The second stage decomposition temperature range is 425–600°C. An exotherm at 525°C suggests an oxidative degradation of the ligand. In the TG curve of [Fe(DCHAMA)Cl₃], the first stage of the decomposition starts at 300°C and mass loss occurs up to 400°C which may be due to the loss of one of the cyclohexyl moieties (calcd. 15.3%, obs. 15.0%). The second stage of the decomposition starts at 400°C and ends at 675°C. The mass of the final residue corresponds to the formation of Fe₂O₃ (calcd. 29.5%, obs. 29.0%). The TG curve of the [Co(DCHAMA)Cl₂] suggests two-stage decomposition. The complex is thermally stable up to 325°C. The first stage decomposition temperature range is 325-425°C. The second stage of the decomposition starts at 500°C and ends at 675°C. The mass of the final residue corresponds to the formation of Co₂O₃ (calcd. 32.47%, obs. 33.0%). The TG curve of the [Cu(DCHAMA)(H₂O)₂Cl₂] complex records a threestage decomposition pattern. It registers a mass loss at 120°C corresponding to the elimination of two coordinated water molecules (calcd. 6.5%, obs. 7.0%). The anhydrous complex is thermally stable up to 150°C as indicated by a plateau in this region. The subsequent mass loss corresponds to the removal of one of the cyclohexyl moieties from the complex (calcd. 15.0%, obs. 16.0%). The second stage of the decomposition occurs in the temperature range 275-375°C. The third stage of the decomposition occurs in the 650–775°C range and the mass of the final residue does not correspond to any definite product. The thermal stabilities of the metal chloro complexes of DCHAMA are found to be as follows:

$$[Co(DCHAMA)Cl_2] > [Fe(DCHAMA)Cl_3]$$

> DCHAMA > $[Cu(DCHAMA)(H_2O)_2Cl_2].$

The bonding atoms being the same in all the complexes, the thermal stability is influenced by the geometry of the complexes. Among the complexes investigated, it is found that the lower the coordination number the higher the thermal stability.

Table 4. EPR spectral parameters of Cu(II) complexes of DCHAMA

Parameters	[CuDCHAMA(H ₂ O) ₂ Cl ₂]	[Cu(DCHAMA)(NO ₃) ₂]
<i>g</i> ₁₁	2.283	2.182
g_{\perp}	2.099	2.097
g_{av}	2.160	2.182
G	2.91	3.69
<i>A</i> ₁₁ , G	150	175
A_{11} , cm ⁻¹	159.89×10^{-4}	192.22×10^{-4}
$A_{\perp}, \mathrm{cm}^{-1}$	5.88×10^{-3}	7.34×10^{-3}
A_{av} , cm ⁻¹	9.25×10^{-3}	11.30×10^{-3}
α^2	0.86	0.96

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			M.K.N. ec	juation		C.R. equation				
Compound	Stage	<i>E_a</i> , kJ/mol	$\Delta S^{\#},$ J/(K mol)	$\Delta H^{\#},$ kJ/mol	$\Delta G^{\#},$ kJ/mol	<i>E_a</i> , kJ/mol	$\Delta S^{\#}, J/(K mol)$	$\Delta H^{\#},$ kJ/mol	$\Delta G^{\#},$ kJ/mol	
DCHAMA	Ι	36.17	-170.56	25.73	132.84	35.85	-171.56	25.41	133.15	
	II	113.89	-86.36	100.62	169.53	113.51	-86.78	100.24	169.49	
[Fe(DCHAMA)Cl ₃]	Ι	112.41	-51.35	101.69	134.81	112.12	-51.64	101.40	134.71	
	II	82.27	-141.69	67.40	194.07	81.83	-142.38	66.96	194.24	
[Co(DCHAMA)Cl ₂]	Ι	115.70	-48.05	105.50	134.98	115.40	-48.34	105.20	134.87	
	II	172.95	-36.21	157.99	190.56	172.57	-36.42	157.62	190.36	
[Cu(DCHAMA)(H ₂ O) ₂ Cl ₂]	Ι	42.82	-125.33	35.62	89.89	42.58	-126.04	35.38	89.96	
	II	60.04	-132.23	50.03	129.64	59.71	-132.95	49.70	129.74	
	III	213.54	-23.50	197.36	220.23	213.12	-23.66	196.94	219.97	

Table 5. Thermodynamic parameters for DCHAMA and its metal complexes

Table 6. Antibacterial activity of DCHAMA and its Fe(III), Co(II), and Ni(II) complexes

			S. aı	ireus			E. coli					
Compound	concentration of compound, µg/ml concentration of compound, µg/ml								nl			
	25	50	75	100	125	150	25	50	75	100	125	150
			% inh	ibition			% inhibition					
Streptomycin	82	89	91	92	94	96	65	72	83	86	90	91
DCHAMA	77	82	87	90	92	92	67	74	86	92	93	94
[Fe(DCHAMA)Cl ₃]	87	90	92	94	96	96	64	70	78	83	84	85
[Co(DCHAMA)Cl ₂]	90	94	94	96	96	96	82	86	90	92	92	92
[Ni(DCHAMA)(H ₂ O) ₂ Cl ₂]	79	84	89	93	96	96	60	69	74	80	81	83

The kinetic and thermodynamic parameters of DCHAMA and its metal complexes evaluated using CR and MKN equations are given in Table 5. Plot of the left-hand side of the CR and MKN equations versus 1/Twas linear and the correlation coefficient value r approached to unity. The order parameter n was found to be 1 for all the complexes. From the slope of the linear plot, E_a is evaluated. A closer view of the TG/DTG curves and their corresponding kinetic data indicates a two/three stage degradation pattern for the ligand and its metal chelates. The DTG curve records an intense sharp peak for the last stage of the decomposition of the complexes. In all the cases the initial stage of decomposition corresponds to the loss of water/degradation of organic moiety and the last stage involves the formation of the metal oxides. Kinetic parameters calculated indicate that the entropy of activation is negative and so transformations take place to a more ordered form and the reactions are slow as inferred from the TG curve.

Biological studies. Concentrations of 100 and 50 μ g/ml of the test compound exhibit maximum inhibition against *E. coli* and *S. aureus*, respectively. Further increase in concentration of the test compounds shows no pronounced increase in activity. The results of

the percentage of inhibition of the bacterial growth are presented in Table 6.

The order of activity of DCHAMA and its metal complexes against *E. coli* is $[Co(DCHAMA)Cl_2] >$ $DCHAMA > Streptomycin > [Fe(DCHAMA)Cl_3] >$ [Ni(DCHAMA))(H₂O)₂Cl₂]. Against S. aureus, the activity order is $[Co(DCHAMA)Cl_2] > [Fe(DCHAMA)Cl_3] >$ [Ni(DCHAMA)(H₂O)₂Cl₂] Streptomycin > DCHAMA. From the above observation it is clear that coordinately unsaturated complexes are found to be more active than the coordinately saturated ones. The higher activity of the coordinately unsaturated complex may be due to the fact that the metal atom in the complex is more prone for further interaction with the ligating sites like the enzymatic functional groups in the biological system in order to increase its coordination number. The metabolism of the microbe is probably inhibited as soon as the metal atom binds with enzymatic functional groups.

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