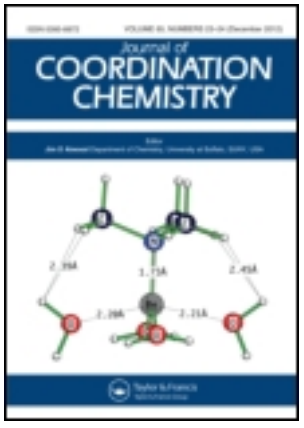

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Spectral, biological screening, and DNA studies of metal chelates of 4-[N,N-bis-(3,5-dimethyl-pyrazolyl-1-methyl)]aminoantipyrine

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Spectral, biological screening, and DNA studies of metal chelates of 4-[*N*,*N*-*bis*-(3,5-dimethyl-pyrazolyl-1-methyl)]aminoantipyrine

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Tridentate chelate complexes of Co(II), Ni(II), and Cu(II) have been synthesized from 4-[*N*,*N*-*bis*-(3,5-dimethyl-pyrazolyl-1-methyl)]aminoantipyrine. Microanalytical data, UV-Vis, magnetic susceptibility, Infrared, ^{1}H- ^{13}C-NMR, mass, thermal gravimetric analysis and electron paramagnetic resonance (EPR) techniques were used to confirm the structures. The electronic absorption spectra and magnetic susceptibility measurements suggest a distorted octahedral geometry for the metal. EPR spectra of the copper(II) complex at 77 K confirm the distorted octahedral geometry of the copper(II) complex. The antimicrobial activities of the ligand and metal complexes against the bacteria such as *Xanthomonas maltophilia*, *Chromobacterium violaceum*, *Acinetobacter*, *Staphylococci*, *Streptococci,* and the fungus *Candida albicans* have been carried out. A comparative study of minimum inhibitory concentration values of the ligand and its metal complexes indicates that metal complexes exhibit higher antibacterial and antifungal activity than the free ligand. The electrochemical behavior of copper(II) complex was studied by cyclic voltammetry. The complexes show nuclease activity in the presence of oxidant.

Keywords: Pyrazolyl aminoantipyrine; Metal complexes; Biological screening; DNA cleavage studies

1. Introduction

Transition metal complexes of pyrazolone derivatives are of interest due to their appreciable biological activities, especially antipyrine derivatives. Among the pyrazolone derivatives, 4-aminoantipyrine forms a variety of Schiff bases with aldehydes/ketones, and they are reported to be superior reagents in biological, pharmacological, clinical and, analytical applications [1–15].

The carbonyl group in 4-aminoantipyrine is a potential donor due to the large dipole moment (5.48 D) and strong basic character. Pyrazole derivatives have a unique position in drug discovery due to their broad range of biological activities, including

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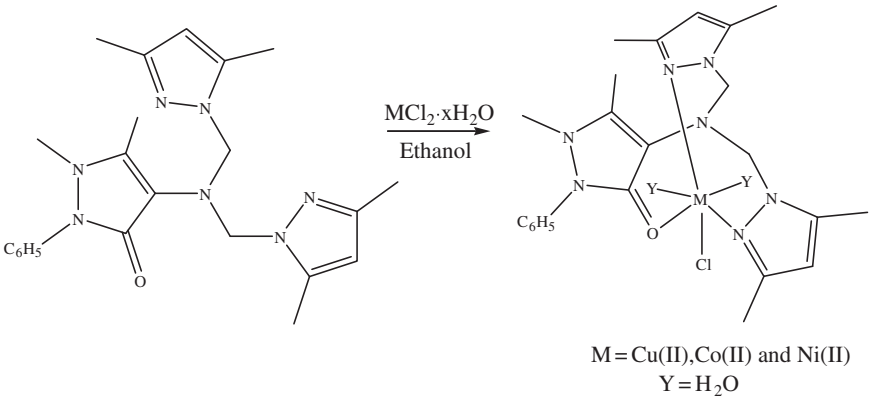
anti-inflammatory, antiangiogenic, antibacterial, antimicrobial, anticancer, and antidepressant activities [16–21]. Based on the number and the position of the pyrazole ring, the number of coordination sites may be increased. Reactions of 3,5-dimethy-1-(hydroxymethyl)-pyrazole and its derivatives with transition metals have been studied [22–27]. Condensation product derived from 4-aminoantipyrine and 3,5-dimethy-1-(hydroxymethyl)-pyrazole has not been studied. We present studies on metal complexes of Cu(II), Ni(II), and Co(II) with 4-[*N*,*N*-*bis*-(3,5-dimethyl-pyrazolyl-1-methyl)] aminoantipyrine(L) with their biological activities and DNA cleavage studies.

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 using a JASCO V-530 spectrophotometer. Infrared (IR) spectra in KBr discs were recorded on a SHIMADZU FT-IR 460plus spectrophotometer at USIC, Madurai Kamaraj University, Madurai. Cyclic voltammetry measurements were carried out at room temperature in DMSO (CH Instruments, USA, voltammograph) using a three electrode cell containing a reference Ag/AgCl electrode, Pt wire auxiliary electrode and glassy carbon working electrode with tetrabutylammonium perchlorate as supporting electrolyte. Elemental analyses were performed at SAIF, CDRI, Lucknow. ^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ using a Bruker DRX-300, 300 MHz NMR spectrometer. Electron-ionization (EI) mass spectra were recorded by JEOL-GC MATE-2 at IIT, Madras-Chennai. Thermal gravimetric analysis (TGA) studies were done on a TGA 50 SHIMADZU MAKE- SOFTWARE TA-60WS at Thiagarajar Engineering College, Madurai. Electron paramagnetic resonance (EPR) spectrum was recorded at SAIF, IIT, Mumbai. Magnetic Susceptibility of the complexes was measured on a MSB mark 1 Sherwood, UK at Thiagarajar College, Madurai. Effective magnetic moments were calculated using the formula $(\mu_{\text{eff}} = 2.828\chi_{\text{M}}\,\text{T})^{1/2}$, where χ_{M} is the corrected molar susceptibility. Molar conductances of the complexes (10^{-3} mol L^{-1}) were measured in DMSO at room temperature using a Systronic conductivity bridge.

2.1. *Synthesis of 4-[N,N-bis-(3,5-dimethyl-pyrazolyl-1-methyl)]aminoantipyrine(L)*

To 4.06 g (20 mmol) of 4-aminoantipyrine dissolved in 20 mL of dichloroethane was added 5.04 g (40 mmol) of 3,5-dimethyl-1-(hydroxymethyl)-pyrazole(hmdmp) [28] in 15 mL of dichloroethane and the mixture was stirred at room temperature for 24 h. After the reaction was over, the reaction mixture was concentrated under reduced pressure and oily liquid was washed with water and then extracted with diethylether. A cream colored solid obtained after refrigeration was recrystallized from dichloromethane. Elemental analysis (Found: C, 64.12; H, 6.55; N, 22.84; $C_{23}H_{30}N_7O$. Calcd: C, 65.71; H, 7.14; N, 23.33.) ν_{max} (KBr) cm^{-1} 1662 (C=O), 1589 (C=N), 1286 (N–N); ^{1}H-NMR (300 MHz; $CDCl_3$), 2.80 (12H, s, CH_3), 5.763 (2H, s, Py–H), 7.253–7.471 (5H, m, C_6H_5), 4.873 (4H, S, N–$(CH_2)_2$). ^{13}C-NMR ($CDCl_3$, δ, ppm) $\delta = 8.5$–13.241 (CH_3); 36.5 (N–CH_3); 59.9 (N–CH_2–N); 66.1 (C=O); 103–139 (aromatic and pyrazole carbons); 146–164 (C=N in pyrazole moiety). The EI mass spectrum of L gives a



Scheme 1. Synthesis of metal(II) complexes.

molecular ion peak m/z at 418. The mass fragmentation of the ligand is given in on-line "Supplementary material".

2.2. *Preparation of complexes*

All the complexes were prepared from hydrated metal salts. To a solution of 4.20 g (10 mmol) 4-[*N*,*N*-*bis*-(3,5-dimethyl-pyrazolyl-1-methyl)]aminoantipyrine in 20 mL ethanol was added 10 mmol of $MCl_2 \cdot xH_2O$ (M=Cu(II), Co(II), and Ni(II)). The solution was refluxed at 70–80°C with constant stirring for 3 h and the resulting solution was refrigerated for 1 day. The complexes were precipitated by adding petroleum ether (60–80°C). The colored complexes were filtered and washed with hot water and dried under vacuum (scheme 1).

3. Results and discussion

The ligand was obtained as a low melting solid and stored in vacuum desiccators. The ligand forms stable complexes in ethanol. The analytical data of the ligand and the complexes with their physical properties are given in table 1. The ligand is a tridentate chelating ligand. The elemental analyses of the complexes were in good agreement with calculated data for 1 : 1 (M : L) ratio. Based on elemental analysis, spectra, TGA and conductance data the formula $[ML(H_2O)_2Cl]Cl$ was suggested. Lee *et al.* [27] characterized the cobalt complex of [*N*,*N*-*bis*-(3,5-dimethyl-pyrazolyl-1-methyl)]*N*,*N*-dimethylethylenediamine in which the ligand acts as (NNNN) donor and the geometry reported was square pyramidal. The present NNO donor ligand derived from condensation between 4-aminoantipyrine and 3,5-dimethy-1-(hydroxymethyl)-pyrazole leads to octahedral geometry on complexation with metal(II) ions.

Table 1. Physical characterization, analytical, molar conductance data Λ_M of the ligand, and its metal complexes.

No.	Compound	Color	m.p. (°C)	Experimental (Calcd) % FW(g mol^{-1})	C	H	N	Λ_M (Ω^{-1} cm^2 mol^{-1})
1	$C_{23}H_{30}N_7O$(L)	Yellow	60	420	64.12 (65.71)	6.55 (7.14)	22.84 (23.33)	–
2	$[CuL(H_2O)_2Cl]Cl$	Pale green	110	590.46	49.25 (46.74)	4.98 (5.08)	16.23 (16.59)	60
3	$[CoL(H_2O)_2Cl]Cl$	Blue	130	585.85	47.00 (47.11)	4.88 (5.12)	16.00 (16.73)	62
4	$[NiL(H_2O)_2Cl]Cl$	Green	122	585.61	47.03 (47.13)	4.89 (5.12)	16.31 (16.73)	59

3.1. *Electronic spectra and magnetic moment*

Electronic spectra recorded in ethanol are presented in table 2. The ligand shows strong peaks at 34,965 and 41,152 cm^{-1} which are attributed to π–π* and n–π* transitions, respectively. The copper(II) chelate shows a broad band at 11,248 cm^{-1} assignable to $^2B_{1g} \rightarrow {}^2A_{1g}$ characteristic of octahedral Cu(II) split under the influence of the tetragonal distortion; the others, $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$, remain unresolved, in agreement with the general observation of Cu(II) d–d transitions [8]. The electronic spectrum of cobalt(II) shows three peaks at 15,037, 15,625, and 16,778°cm^{-1} assigned to $^4A_{2g} \rightarrow {}^4T_{2g}$, $^4A_{2g} \rightarrow {}^4T_{1g}$(F) and $^4A_{2g} \rightarrow {}^4T_{1g}$(P), suggesting the octahedral environment around Co(II) [29]. Nickel complex exhibits absorptions at 9514 and 15,220 cm^{-1} assignable to $^3A_{2g} \rightarrow {}^3T_{2g}$ and $^3A_{2g} \rightarrow {}^3T_{1g}$(F), indicating octahedral geometry of the complex [30].

The magnetic moment data (table 2) indicate paramagnetic Cu(II), Co(II), and Ni(II). The magnetic moment value of 1.98 B.M. for copper complex falls within the range normally observed for octahedral Cu(II) complexes [31]. For cobalt(II) complex, the magnetic moment is 4.88 B.M. (normal range for octahedral Co(II) complex is 4.7–5.2 B.M.), which is an indicative of distorted octahedral geometry [32]. The Ni(II) complex reported has a room temperature magnetic moment of 3.57 B.M., which indicates that the complex of Ni(II) is six-coordinate and probably octahedral [33, 34]. The slight deviation from the normal range may be due to distortion from perfect octahedral geometry.

3.2. *IR spectra*

The IR spectral data of the ligands and their metal complexes are presented in table 3. The strong band at 1662°cm^{-1} in spectra of the ligand is assigned to ν(C=O) of the antipyrine [35]. A considerable shift (~56 cm^{-1}) of the carbonyl frequency in complexes indicates coordination through carbonyl oxygen. The band at 1589 cm^{-1} assigned to pyrazole ring nitrogen ν(C=N) of the ligand shifted to lower frequency (~14–27 cm^{-1}) in the complexes, indicating coordination of ring nitrogen to metal [36, 37]. The broad band at 3416 cm^{-1} indicates coordination of water ν(O–H) to the metal.

Table 2. Electronic spectral data of ligand and their metal complexes.

Compound	λ_{max} (cm^{-1})	Transition	Geometry	μ_{eff} (B.M.)
$C_{23}H_{30}N_7O$ (L)	34,965	INCT	–	–
	41,152	INCT		
$[CuL(H_2O)_2Cl]Cl$	11,248	$^2B_{1g} \rightarrow {}^2A_{1g}$	Distorted octahedral	1.98
$[CoL(H_2O)_2Cl]Cl$	15,037	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	Distorted octahedral	4.88
	15,625	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$		
	16,778	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$		
$[NiL(H_2O)_2Cl]Cl$	9514	$^3A_{2g} \rightarrow {}^3T_{2g}$	Distorted octahedral	3.57
	15,220	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$		

Table 3. IR spectral data of the ligand and their metal complexes.

Compound	ν(O–H)	ν(C=O)	ν(C=N) ring	ν(N–N)
Ligand(L)	–	1662	1589	1286
Cu complex	3394	1610	1570	1270
Co complex	3423	1606	1575	1245
Ni complex	3446	1623	1562	1278

3.3. *Mass spectra*

The mass spectrum of ligand(L), Cu(II), Co(II), and Ni(II) complexes are recorded (on-line Supplementary material). The molecular ion peak for L was observed at 418 m/z, whereas molecular ion peaks of Cu(II), Co(II), and Ni(II) complexes were observed at 554, 548 and 547 m/z, respectively, which corresponds to $[ML(H_2O)_2Cl]^+$. Fragmentation pattern of mass spectra is compared with TGA data and the percentage loss of water and chlorine and organic moiety is found to be in good agreement.

3.4. *Thermogravimetric studies*

Thermogravimetric studies carried out from 29°C to 800°C (on-line Supplementary material) are listed in table 4. In the first step all the complexes lose one molecule of water, then the second step is removal of chlorine and water at 139°C–321°C. The third step corresponds to removal of two pyrazoles from 321°C to 506°C and the fourth step corresponds to loss of antipyrine group at 504°C–691°C leaving metal oxide as residue. In the mass spectra of cobalt complex molecular ion peaks m/z at 530, 483, 208, and 173 are due to loss of water, chlorine and water, pyrazole, and antipyrine group, respectively.

3.5. *EPR spectra*

The EPR spectra of the copper(II) complex were recorded at 300 and 77°K. No splitting was observed in room temperature spectra, however, in the LNT spectrum all three components were resolved (figure 1). The g values $g_{||} = 2.47$ and $g_{\perp} = 2.185$ suggest a tetragonal distortion around Cu(II) corresponding to elongation along the fourfold

Table 4. Thermogravimetric data of Co(II), Ni(II), and Cu(II) complexes.

Complex	Temperature (°C)	%Weight loss observed (Calcd)	Process
$[CoL(H_2O)_2Cl]Cl$	29–140	3.86(3.35)	Loss of one molecule of water
	139–321	10.289(9.62)	Loss of Cl and water molecules
	321–506	30.95(31.65)	Loss of two pyrazole moiety
	504–691	34.28(34.55)	Loss of antipyrine group
	>700	Residue	CoO
$[NiL(H_2O)_2Cl]Cl$	29–140	3.16(3.37)	Loss of one molecule of water
	139–321	10.35(9.72)	Loss of Cl and water molecules
	321–506	31.25(31.75)	Loss of two pyrazole moiety
	504–691	34.28(34.65)	Loss of antipyrine group
	>700	Residue	NiO
$[CuL(H_2O)_2Cl]Cl$	29–140	3.86(3.35)	Loss of one molecule of water
	139–321	10.3(9.62)	Loss of Cl and water molecules
	321–506	29.95(30.65)	Loss of two pyrazole moiety
	504–691	32.28(32.55)	Loss of antipyrine group
	>700	Residue	CuO

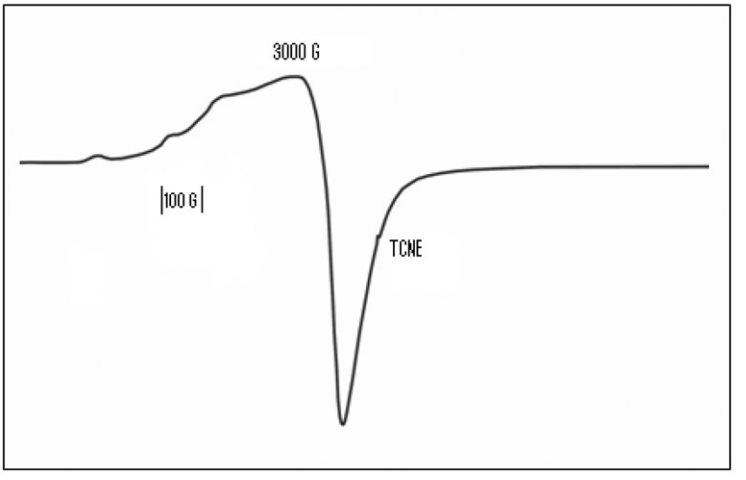


Figure 1. EPR spectrum of $[CuL(H_2O)_2Cl]Cl$ at 77 K.

symmetry Z-axis [38]. The $g_{||}$ value (2.47) for the complex is greater than 2.3, suggesting significant ionic character of the metal ligand bond. Calculated values of $g_{||}$ and $g_{\perp}$ show the order $g_{||} > g_{\perp} > g_e$ (2.0023), which is consistent with the $d_{x^2-y^2}$ ground state [39, 40]. The odd electron may be located in the B_{1g} antibonding orbital.

The geometric parameter G (2.96) estimated from the expression $G = (g_{||} - 2.0023)/(g_{\perp} - 2.0023)$ $G < 4$ suggests significant exchange coupling is present and the misalignment is appreciable. The covalency parameter α^2 is calculated using the following equation.

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

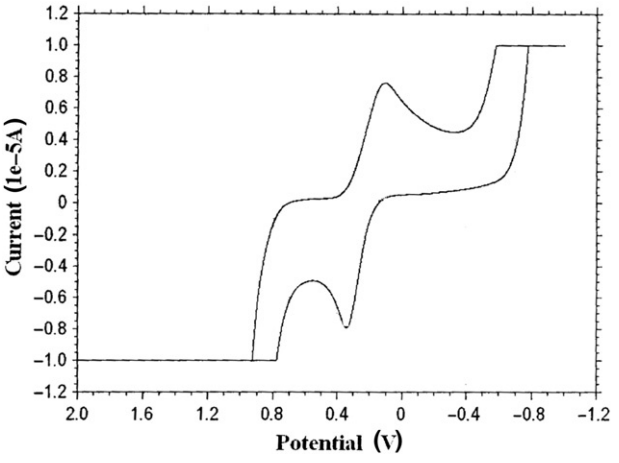


Figure 2. Cyclic voltammogram of copper(II) complex in DMSO.

where $\alpha^2 = 0.5$ indicates complete covalent bonding and $\alpha^2 = 1$ suggests complete ionic bonding. The observed value of $\alpha^2 = 1.4582$ indicates that the complex has ionic character. The orbital reduction factor K was calculated using the expression $K^2 = K_{||}^2 + 2K_{\perp}^2/3$, where $K_{||}$ and $K_{\perp}$ are the parallel and perpendicular components of the orbital reduction factor. The high value of K (1.1927) also indicates the ionic nature of the complex.

3.6. *Electrochemical studies*

Cyclic voltammetry of the copper complex with scan rate $0.1\,\mathrm{V\,s^{-1}}$, figure 2, shows a well-defined redox process corresponding to formation of Cu(II)/Cu(I) couple at $E_{pa} = 0.344\,\mathrm{V}$ and $E_{pc} = 0.103\,\mathrm{V}$. This couple is quasireversible with $\Delta Ep = 0.241\,\mathrm{V}$ and the ratio of anodic to cathodic peak currents ($I_{pc}/I_{pa} \approx 1$) corresponding to a simple one electron process. The ΔE_p ($E_{pa} - E_{pc}$) values are greater than 200 mV, indicating quasireversible reduction and a chemical change occurring with electron transfer [41].

3.7. *Molar conductance*

The molar conductances of the complexes of copper, cobalt, and nickel, given in table 1, indicate that the complexes are 1 : 1 electrolytes. One chloride was also confirmed by silver nitrate test [42].

3.8. *Biological activities*

Most Schiff bases of 4-aminoantipyrine show antibacterial, antimalarial, and antitumor activities [1]. Similarly the 4-aminoantipyrine derivative obtained by condensing amino group and hydroxyl group of pyrazole shows remarkable antimicrobial activities. The well diffusion method was employed for screening the antibacterial and antifungal

Table 5. MIC of the synthesized compounds against growth of bacteria and fungi ($\mu g\,mL^{-1}$).

Compounds	*X. maltophilia*	*C. violaceum*	*Acinetobacter*	*Staphylococci*,	*Streptococci*	*C. albicans*
$C_{23}H_{30}N_7O(L)$	58	56	65	65	75	80
$[CuL(H_2O)_2Cl]Cl$	20	23	30	38	40	40
$[NiL(H_2O)_2Cl]Cl$	24	28	32	40	42	42
$[CoL(H_2O)_2Cl]Cl$	16	14	20	25	30	35
Amikacin	10	11	12	15	16	–
Ketokonazole	–	–	–	–	–	20

Each value observed is within the error limits of ±2.

activities [43]. The bacteria used are *Xanthomonas maltophilia*, *Chromobacterium violaceum*, *Acientobacter* (Gram-negative) and *Staphylococci*, *Streptococci* (Gram-positive). The fungus used is *Candida albicans*. Stock solution (0.001 mol) was prepared by dissolving the compounds in ethanol and the solutions were serially diluted to find the minimum inhibitory concentrations (MICs) values ($\mu g\,mL^{-1}$). The diameters of the inhibition zones were measured in millimeters. Antimicrobial activities were performed in triplicate and the average was taken as the final reading. MICs of the compounds are summarized in table 5. A comparative study of the MIC values for the ligands and their complexes indicates that the complexes exhibit higher antimicrobial activity [44, 45]. The diameter of the inhibition zones was measured in millimeters. Cobalt complex was more active than the other two complexes.

3.9. *CT-DNA cleavage study*

The cleavage of CT-DNA was determined by agarose gel electrophoresis. The gel electrophoresis experiments were performed by incubation of the samples containing 30 $\mu mol\,L^{-1}$ CT-DNA, 50 $\mu mol\,L^{-1}$ copper complex and 50 $\mu mol\,L^{-1}$ H_2O_2 in tris–HCl/NaCl buffer (pH 7.2) at 37°C for 2 h. After incubation, the samples were electrophoresed for 2 h at 50 V on 1% agarose gel using tris–acetic acid–EDTA buffer (pH 7.0). The gel was then stained using 1 $\mu g\,cm^{-3}$ ethidiumbromide and photographed under ultraviolet light at 360 nm. All the experiments were performed at room temperature. The cleavage efficiency of the complexes compared to that of the control is due to their efficient DNA-binding ability. The metal complex is able to convert supercoiled DNA into open circular DNA. General oxidative mechanisms account for DNA cleavage by hydroxyl radicals *via* abstraction of a hydrogen from sugar units and predict the release of specific residues arising from transformed sugars, depending on the position from which the hydrogen is removed [46]. The cleavage is inhibited by free radical scavengers, implying that hydroxyl radicals or peroxy derivatives mediate the cleavage reaction. The reaction is modulated by a bound hydroxyl radical or a peroxo species generated from H_2O_2. In this study, the CT-DNA gel electrophoresis experiment was conducted at 35°C using the synthesized complex in the presence of H_2O_2 as an oxidant. As can be seen from figure 3, at very low concentration, copper and cobalt complexes exhibit nuclease activity in the presence of H_2O_2. Control experiments using DNA alone do not show significant cleavage of CT-DNA even on longer exposure time.

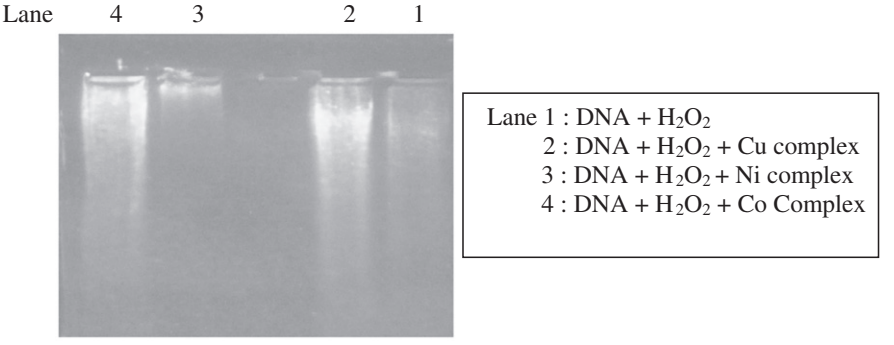


Figure 3. DNA cleavage studies.

From the observed results, the complexes cleave DNA as compared to control DNA. Further, the presence of a smear in the gel diagram indicates radical cleavage [47].

4. Conclusion

Complexes of 4-[*N*,*N*-*bis*-(3,5-dimethyl-pyrazolyl-1-methyl)]aminoantipyrine with Cu(II), Co(II), and Ni(II) were synthesized and characterized by various analytical techniques. The ligand is a tridentate (NNO) chelate and yields complexes with distorted octahedral geometry. EPR studies of copper complex confirm the ionic character of the metal ligand linkage. The ligand and all metal complexes possess appreciable antibacterial and antifungal activities and the cobalt(II) complex was found to be more potent than the other two complexes. Gel electrophoresis experiment indicates that the complexes cleave DNA in the presence of hydrogen peroxide.

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