Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2018, 10(3):1-8

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

A Novel One-Pot Synthesis, Characterization, DNA Binding and Cleavage Studies on Bis(Phenylhydrazoneglyoxylato)Diaqua Metal(II) Complexes

R Pradeep and BN Sivasankar*

Department of Chemistry, Government Arts College, Udhagamandalam, The Nilgiris, Tamilnadu, India

---

ABSTRACT

Phenylhydrazoneglyoxylic acid, $C_6H_5NHN=CHCOOH$, formed in situ by the aqueous condensation between phenyl hydrazine and glyoxylic acid, inthe presence of metal ions such as Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) yielded water insoluble bis(phenylhydrazoneglyoxylato)diaqua metal(II) complexes. These complexes were characterized by analytical, spectral (UV-visible, IR and NMR) and thermal techniques. Infrared, NMR and X-ray powder diffraction patterns reveal the formation and isomorphic nature of $[M(OOCCH=NNHC_6H_5)_2(H_2O)_2]$ complexes. Thermal degradation studies show multi-step degradation behaviour and the final weight losses are in accordance with the formation of respective metal oxides as the end residues. Octahedral geometry around the metal ion has been proposed on the basis of spectral and thermal studies. The interaction of the complexes with CT-DNA has been explored by absorption titration method which revealed that the compounds could interact with CT-DNA through electrostatic interaction. The gel electrophoresis assay demonstrated the zinc complex exhibit good cleavage efficiency, which is concentration dependent.

Keywords: Phenylhydrazoneglyoxylate; Aqueous condensation; Isomorphism; Octahedral; DNA binding and cleavage

---

INTRODUCTION

Condensation between aldehydes and amines or hydrazine derivatives conducted in organic medium has been exhaustively investigated. The hydrazones formed during the condensations have been utilized in the synthesis of variety of biological active coordination compounds. However, the aqueous condensation is not common with amines/hydrazines and aldehydes. Glyoxylic acid, OHCCOOH is a monocarboxylic acid containing aldehyde group and its reactions with ammonia and hydrazine are quite interesting. Carboxylic acids and substituted carboxylic acids react with hydrazine hydrate in aqueous medium yield hydrazinium carboxylates salts [1-6]. In the presence of metal ions, aqueous mixture of carboxylic acids and hydrazine hydrate always yielded hydrazine/hydrazinium metal carboxylates [7,8]. The aldehyde group in glyoxylic acid is not expected to undergo condensation with amino derivatives in aqueous medium though in organic solvents the formations of hydrazones are very common. In the present investigation, novel hydrated phenylhydrazoneglyoxylate complexes have been synthesized by the aqueous condensation between phenyl hydrazine and glyoxylic acid in the presence of metal(II) ions. In spite of wealth of information available on hydrazine based metal carboxylates, only very few reports are available on phenyl hydrazinium based metal complexes [9-12]. In view of the above facts, the present article embodies the spectral and thermal studies on the newly synthesized hydrated metal bis(phenylhydrazoneglyoxylato)diaqua metal(II) complexes. In addition, the interaction behaviour with CT-DNA and the cleavage efficiency have been explored.

EXPERIMENTAL SECTION

Materials

All the chemicals used were of AnalaR grade and phenyl hydrazine was distilled before use. Double distilled water was used for the preparation of the complexes. Calf thymus DNA (CT-DNA) was purchased from Merck and stored at 4°C.

Physical Measurements

The C, H and N analyses were carried out using a Perkin-Elmer model 1240 CHN analyzer. The metal contents in the complexes were determined by EDTA complexometric titrations after completely decomposing a known amount of complexes with concentrated nitric acid to eliminate the organic portion of the molecule [13]. The molar conductances of the complexes were measured at room temperature using the Systronics-303 conductivity meter in DMSO. Room temperature magnetic moments of the complexes were determined by using a Gouy balance and $Hg[Co(SCN)_4]$ as the calibration standard. UV-visible absorbance spectra were recorded in the range 800-200 nm using Systronics double beam UV-visible spectrophotometer. The infrared absorption spectra were recorded using a Perkin-Elmer 597 spectrophotometer with KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded at 298 K on Bruker FT-NMR-500 spectrometer operating at 400.13 MHz using DMSO as a solvent and tetra methyl silane as an internal standard. The simultaneous TG-DTA analyses (in N_2 and air atmosphere) were undertaken on a SWI TG/DTA 6200 thermal analyzer using 5 mg of the samples with the heating rate of 10°C per minute. The X-ray powder diffraction patterns were recorded on Philips PW 1050/70 using Cu-Kα radiation with an iron filter. The measurements were taken in the range of 2θ angles 20° to 80° and wavelength of 1.5406 Å.

DNA Binding and Cleavage Studies

Electronic absorption titration:

All the experiments involving interaction of complexes with CT-DNA were carried out in a buffer containing 5 mmol of Tris(hydroxy-methyl)aminomethane and 50 mmol of NaCl adjusted to pH 7.2 with hydrochloric acid. A solution of CT-DNA gave a ratio of UV absorbance of about 1.8–1.9 at 260 and 280 nm, indicating that the CT-DNA was sufficiently free of protein [14]. The CT-DNA concentration per nucleotide was determined by UV-spectrophotometer employing molar absorption coefficient 6600 M^{-1} cm^{-1} at 260 nm [15].

Absorption titrations were carried out at room temperature for determining the binding affinity between DNA and complexes 2, 3 and 5. An appropriate amount of metal complexes were dissolved in a solvent mixture of 1% DMSO and 99% Tris-HCl buffer. Absorption titration experiments were performed with the fixed concentration of the metal complex while gradually increasing the concentration of CT-DNA. From the absorption titration data, the binding constant (K_b) of the complexes were determined from Eq. (1), through a plot of $[DNA]/(\varepsilon_a - \varepsilon_f)$ vs. [DNA].

$$[DNA]/(\varepsilon_a - \varepsilon_f) = [DNA]/(\varepsilon_b - \varepsilon_f) + 1/K_b(\varepsilon_b - \varepsilon_f) \quad (1)$$

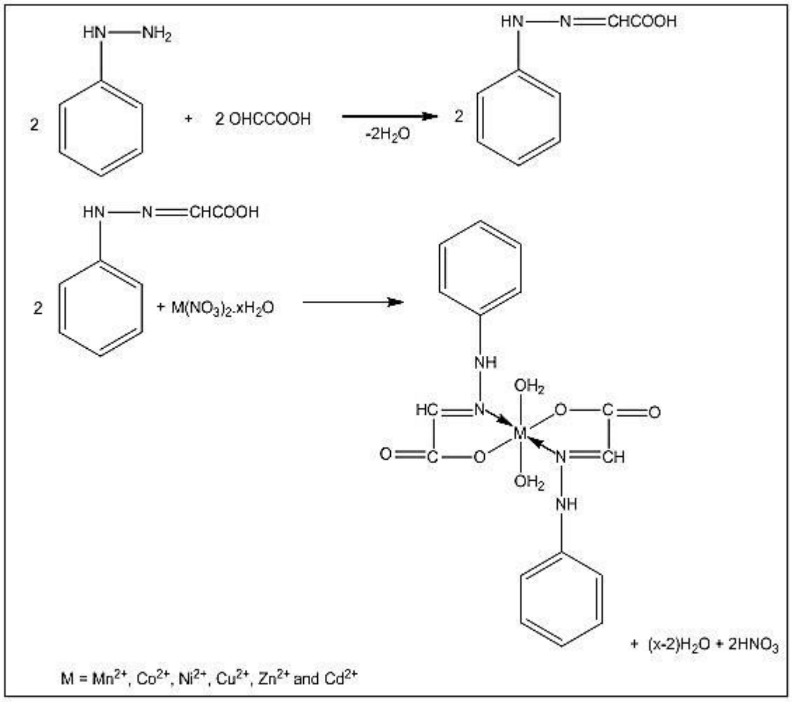
Where, [DNA] is the concentration of DNA, and ε_a, ε_f and ε_b the apparent extinction coefficient ($A_{obs}/[M]$), the extinction coefficient for free metal complex (M), and the extinction coefficient for the free metal complex (M) in the fully bound form, respectively. In plots of $[DNA]/(\varepsilon_a - \varepsilon_f)$ vs. [DNA], K_b is given by the ratio of slope to intercept [16].

Gel electrophoresis:

The cleavage experiment of CT-DNA in (5 mmol Tris-HCl, 50 mmol NaCl) buffer at pH 7.2 was carried out using agarose gel electrophoresis. In this experiment, 8 μL CT-DNA was mixed with different concentrations of complexes (25, 50, 75 and 100 μM) dissolved in DMSO) to determine cleavage activity. The gel was run at 80 V for 2 h in TAE buffer and photographed under UV light.

Preparation of the complexes 1-6:

To an aqueous solution (50 mL) containing a mixture of phenyl hydrazine (2.2 mL, 0.02 mol) and glyoxylic acid (1.84 g, 0.02 mol) an aqueous solution of respective metal nitrate hydrate (0.01 mol) was added with stirring. The clear solution thus obtained was allowed to stand at room temperature. The complexes precipitated from the solution after 24 h were filtered, washed with water and dried in air. The chemical reactions for the formation of the complexes are given in Scheme 1.



Scheme 1: Synthesis and proposed structure of bis(phenylhydrazoneglyoxylato)diaqua metal(II) complex

Physical Data

$MnC_{16}H_{18}N_4O_6$(1): Yield: 66%. Anal. Calc.: C, 45.17; H, 4.26; N, 15.05; Metal, 12.92%. Found: C, 44.47; H, 4.08; N, 14.95; Metal, 11.98%. Molar conductance, Λ_M(DMSO): 0.17 Ω^{-1} cm^2 mol^{-1} (non-electrolyte). Magnetic moment, μ_{eff}: 5.64 BM. IR (KBr): ν = 3299 (O–H), 3396 (N–H), 981 (N–N), 1649 (C=N), 1591 $(COO^-)_{asym}$, 1396 $(COO)_{sym}$$cm^{-1}$. ^{1}H NMR(400.23 MHz, [D_6]DMSO, 25 °C, TMS): δ = 10.4 (s, 1 H, NH), 7.6 (s, 1 H, N=CH), 7.95-7.2 (m, Ar-H), 6.97, 7.1 (2 × d, 4 H, OH_2). ^{13}C NMR (400.23 MHz, [D_6]DMSO):δ = 166.5 (COO^-), 144.5 (N=CH), 128.9-137.3 (Ar-C).

$CoC_{16}H_{18}N_4O_6$ (2): Yield: 81%. Anal. Calc.: C, 44.75; H, 4.22; N, 14.91; Metal, 13.73%. Found: C, 43.57; H, 4.13; N, 14.07; Metal, 14.18%. Molar conductance, Λ_M(DMSO): 0.19 Ω^{-1} cm^2 mol^{-1} (non-electrolyte). Magnetic moment, μ_{eff}: 4.86 BM. IR (KBr): ν = 3304 (O–H), 3392 (N–H), 986 (N–N), 1642 (C=N), 1596 $(COO^-)_{asym}$, 1398 $(COO)_{sym}$$cm^{-1}$.^{1}H NMR (400.23 MHz, [D_6]DMSO, 25 °C, TMS): δ = 10.38 (s, 1 H, NH), 7.63 (s, 1 H, N=CH), 7.96-7.26 (m, Ar-H), 6.97, 7.13 (2 × d, 4 H, OH_2).^{13}C NMR (400.23 MHz, [D_6]DMSO):δ = 166 (COO^-), 144.2 (N=CH), 128.6-140.3 (Ar-C).

$NiC_{16}H_{18}N_4O_6$ (3): Yield: 86%. Anal. Calc.: C, 44.77; H, 4.23; N, 14.92; Metal, 14.68%. Found: C, 44.14; H, 4.13; N, 14.87; Metal, 12.84%. Molar conductance, Λ_M(DMSO): 0.12 Ω^{-1} cm^2 mol^{-1} (non-electrolyte).–Magnetic moment, μ_{eff}: 3.1 BM. IR (KBr): ν = 3316 (O–H), 3397 (N–H), 985 (N–N), 1645 (C=N), 1598 $(COO^-)_{asym}$, 1391 $(COO)_{sym}$$cm^{-1}$.^{1}H NMR (400.23 MHz, [D_6]DMSO, 25 °C, TMS): δ = 10.3 (s, 1 H, NH), 7.66 (s, 1 H, N=CH), 6.88-7.29 (m, ArH), 6.90, 7.14 (2 × d, 4 H, OH_2). ^{13}C NMR (400.23 MHz, [D_6]DMSO):δ = 166.1 (COO^-), 146.1 (N=CH), 129.6-140.3 (Ar-C).

$CuC_{16}H_{18}N_4O_6$ (4): Yield: 72%. Anal. Calc.: C, 44.27; H, 4.18; N, 14.75; Metal, 15.80%. Found: C, 43.98; H, 4.05; N, 13.97; Metal, 14.87%. Molar conductance, Λ_M(DMSO): 0.15 Ω^{-1} cm^2 mol^{-1} (non-electrolyte).–Magnetic moment, μ_{eff}: 1.84 BM.–IR (KBr): ν = 3278 (O–H), 3395 (N–H), 982 (N–N), 1642 (C=N), 1596 $(COO^-)_{asym}$, 1396 $(COO)_{sym}$$cm^{-1}$. ^{1}H NMR (400.23 MHz, [D_6]DMSO, 25 °C, TMS): δ = 10.56 (s, 1 H, NH), 7.41 (s, 1 H, N=CH), 6.98-7.31 (m, Ar-H), 6.86, 7.1 (2 × d, 4 H, OH_2).^{13}C NMR (400.23 MHz, [D_6]DMSO): δ = 165.6 (COO^-), 145.9 (N=CH), 128.6-139.6 (Ar-C).

$ZnC_{16}H_{18}N_4O_6$ (5): Yield: 90%. Anal. Calc.: C, 44.08; H, 4.16; N, 14.69; Metal, 15.01%. Found: C, 42.76; H, 4.02; N, 14.07; Metal, 14.36%. Molar conductance, Λ_M(DMSO): 0.19 Ω^{-1} cm^2 mol^{-1} (non-electrolyte).–Magnetic moment, μ_{eff}: diamagnetic. IR (KBr): ν = 3302 (O–H), 3396 (N–H), 986 (N–N), 1648 (C=N), 1591 $(COO^-)_{asym}$, 1394 $(COO)_{sym}$$cm^{-1}$. ^{1}H NMR (400.23 MHz, [D_6]DMSO, 25 °C, TMS): δ = 10.2 (s, 1 H, NH), 7.62 (s, 1 H, N=CH), 6.85-7.36 (m, Ar-H), 6.89, 7.15 (2 × d, 4 H, OH_2). ^{13}C NMR (400.23 MHz, [D_6]DMSO): δ = 164.1 (COO^-), 144.7 (N=CH), 128.7-139.2 (Ar-C).

$CdC_{16}H_{18}N_4O_6$(6): Yield: 84%. Anal.Calc.: C, 39.79; H, 3.75; N, 13.26; Metal, 23.69%. Found: C, 39.06; H, 3.51; N, 12.18; Metal, 22.65%. Molar conductance, Λ_M(DMSO): 0.16 Ω^{-1} cm^2 mol^{-1} (non-electrolyte).–Magnetic moment, μ_{eff}: diamagnetic. IR (KBr): ν = 3352 (O–H), 3397 (N–H), 985 (N–N), 1643 (C=N), 1599 $(COO^-)_{asym}$, 1395 $(COO)_{sym}cm^{-1}$. ^{1}H NMR (400.23 MHz, [D_6]DMSO, 25 °C, TMS): δ = 10.3 (s, 1 H, NH), 7.63 (s, 1 H, N=CH), 6.88-7.27 (m, Ar-H), 6.96, 7.1 (2 × d, 4 H, OH_2). ^{13}C NMR (400.23 MHz, [D_6]DMSO): δ = 166.1 (COO^-), 146.2 (N=CH), 129.1-140.3 (Ar-C).

RESULTS AND DISCUSSION

Phenylhydrazoneglyoxylic acid formed in situ by the aqueous condensation between phenyl hydrazine and glyoxylic acid reacts with metal(II) nitrate hydrates to yield phenylhydrazoneglyoxylato metal(II) complexes. These complexes are stable in air, insoluble in water and soluble in DMSO. The analytical data of the complexes are in accordance with the assigned composition $M(OOCCH{=}NNHC_6H_5)_2(H_2O)_2$. The conductivity measurements of 0.01 molar solutions of the complexes in DMSO were found to be around 0.2 Ω^{-1} cm^2 mol^{-1} which indicates that these complexes are non-electrolytes [17]. The magnetic moment values reveal their high-spin nature [18].

Electronic Absorption Spectra

The electronic spectra of cobalt complex show a band at 23,500 cm^{-1} which is assigned to $^4T_{1g(F)} \rightarrow {}^4T_{1g(P)}$ transition. The nickel complex shows two bands at 14,300 cm^{-1} and 20,400 cm^{-1} which are assigned to $^3A_{2g} \rightarrow {}^3T_{1g(F)}$) and $^3A_{2g} \rightarrow {}^3T_{1g(P)}$ transitions respectively. The copper complex shows a band at 16,700 cm^{-1} due to the $^2E_{2g} \rightarrow {}^2T_{2g}$ transition. All these observations suggest octahedral geometry around the metal ions [19].

Infrared Spectra

The infrared spectra of the complexes are almost similar. Sharp bands at 3400, 3310 and 3250 cm^{-1} are assigned to the N–H stretching of the ligand and O–H stretching of coordinated water molecules. A sharp band observed in 1640–1650 cm^{-1} is due to the –HC=N– stretching of hydrazine moiety. The monodentate nature of carboxylate ion is proposed on the basis of ν_{asy} and ν_{sym} stretching for carboxylate ion seen in the range 1590–1600 cm^{-1} and 1390–1400 cm^{-1} respectively. The N–N stretching was observed at 980–990 cm^{-1} which is higher than the values reported for hydrazine and phenyl hydrazine. This shift could be due to the presence of the electron withdrawing phenyl group in the nitrogen atom [20,21] and coordination of the nitrogen of phenyl hydrazine.

^{1}H and ^{13}C NMR Spectra

The ^{1}H NMR of the complexes are similar and show N–H proton at δ 10.4 and 11 ppm is probably due to free rotation of the phenyl group and distorted structure. The C-H proton of –N=CH– is observed at 7.6 ppm. Aromatic protons appear in the region 7.26 to 6.95 ppm. The O–H protons of water are observed as two doublets in the region 6.79 and 7.1 ppm. In the ^{13}C NMR spectra the carboxylate carbon appears at 166.5 ppm and the –N=CH– carbon is seen at 144.5 ppm. The aromatic carbons are found in the region 140–112 ppm.

Thermal Degradation Studies

The simultaneous TG-DTA traces of the complexes in air and nitrogen atmosphere were recorded to understand the presence and nature of a water molecule (coordinated/non-coordinated) and the ligand pyrolysis patterns. The traces clearly reveal multistep degradation behaviours. The first step is endothermic dehydration as expected which takes place in the temperature range 145-220°C could be due to the elimination of coordinated water molecules. This is followed by the ligand pyrolysis yielding the respective metal oxide as the final residue below 600 °C. The TG-DTA traces of the complexes 2 and 6 are given in Figures 1 and 2 respectively.

X-ray Powder Diffraction Studies

The X-ray powder patterns of the complexes are almost super-imposable reflecting their structural similarity. The powder diffraction patterns of the complexes 5 and 6 complexes are shown in Figures 3 and 4 respectively.

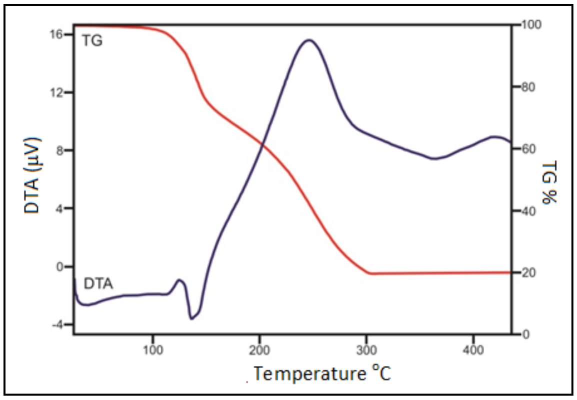


Figure 1: Simultaneous TG-DTA pattern of complex 2

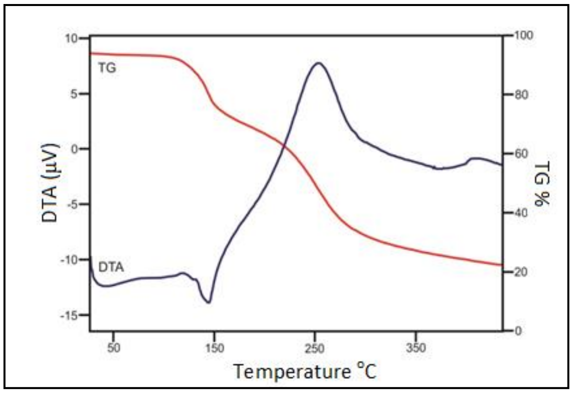


Figure 2: Simultaneous TG-DTA pattern of complex 6

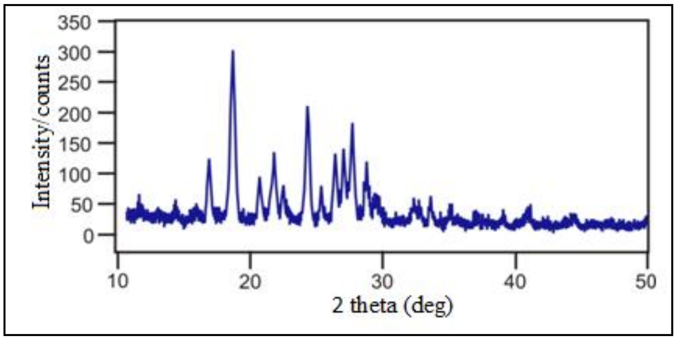


Figure 3: X-ray powder diffraction pattern of 5

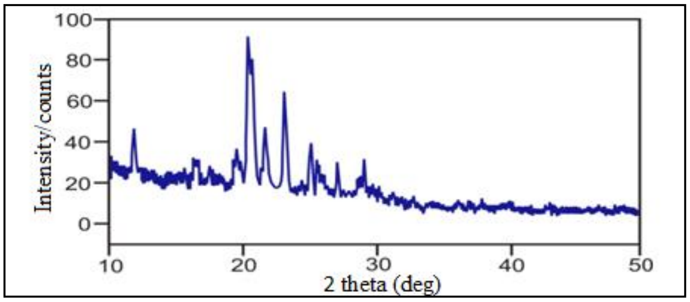


Figure 4: X-ray powder diffraction pattern of 6

DNA Binding Studies

Electronic absorption titration:

The electronic absorption spectrum of the complexes 2, 3 and 5 in DMSO buffer shows intense bands at 267, 286 and 291 nm respectively. All the complexes show hyperchromic effect with blue shift (about 1 nm) indicates that these complexes bind to DNA by external contact possibly via electrostatic interaction [22,23]. The hyperchromic effect is also due to the electrostatic interaction between positively charged cation and the negatively charged phosphate backbone at the periphery of the double helix-CT-DNA [24]. These spectral characteristics indicate that hyperchromism results in the slight change in conformation of DNA due to the cleavage of its secondary structure. The binding constant K_b for complexes 2, 3 and 5 were determined from a plot of [DNA] /($\varepsilon_a - \varepsilon_f$) vs. [DNA] and was found to be 1.85×10^4 M^{-1}, 4.97×10^3 M^{-1} and 2.1×10^4 M^{-1} respectively. The binding constant of the complex 5 is greater than that of 2 and 3.The absorption spectral traces of 2, 3 and 5 at room temperature are shown in Figures 5A-5C respectively. Arrows indicate the change in absorption upon increasing DNA concentration.

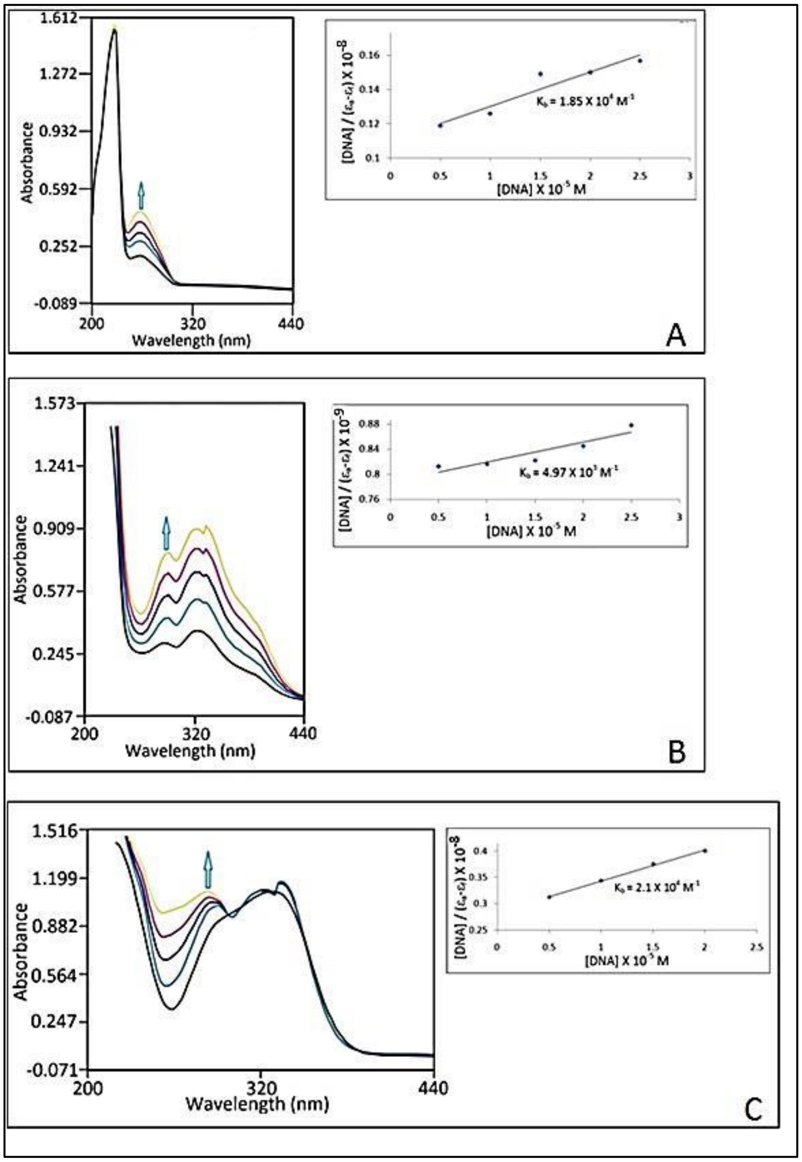


Figure 5: Absorption spectral traces of the complexes 2(A), 3 (B) and 5 (C)

DNA Cleavage Studies

Gel electrophoresis:

The complexes 2 and 5 exhibit maximum binding affinity with CT-DNA, therefore, the cleavage activity has been evaluated for those complexes. Upon increasing the concentration of the complexes (25, 50, 75, 100 μM) Form I of

CT-DNA converted into Form II as shown in Figure 6. These cleavage efficiencies depend on the concentration of the complexes. The cleavage magnitude of 2 and 5 were evaluated (Figure 7) and complex 5 is found to exhibit greater cleavage efficiency than complex 2.

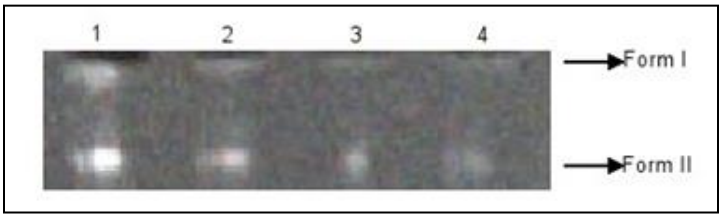


Figure 6: The cleavage patterns of the agarose gel electrophoresis for CT-DNA by Lane 1: 100 µM complex 5 + DNA; Lane 2: 75 µM complex 5 + DNA; Lane 3: 50 µM complex 5 + DNA; Lane 4: 25 µM complex 5 + DNA

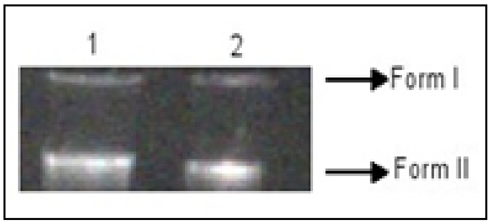


Figure 7: The cleavage patterns of the agarose gel electrophoresis for CT-DNA by Lane 1: complex 5 (100 µM) + DNA; Lane 2: complex 2 (100 µM) + DNA

CONCLUSION

Phenyl hydrazine interestingly condenses with glyoxylic acid in aqueous medium in the presence of metal(II) ions to yield bis(phenylhydrazoneglyoxylato) metal(II) dihydrates. Attempts to isolate simple phenylhydrazoneglyoxalic acid were not successful and resulted in the formation of oily liquid. However, the formation of ligand is confirmed by the isolation of solid complexes in the presence of metal ions. Hence, it is proposed that the ligand was generated 'in situ' which further reacts with metal ions to yielded desired complexes. Since the reactions were carried out in aqueous medium the formation of hydrated complexes is quite expected and indeed the spectral and thermal studies confirm the presence of two coordinated water molecules.

The compositions and the structure of the complexes were assigned on the basis of chemical analyses, conductivity measurements and spectral, thermal and X-ray diffraction studies. An octahedral geometry around the metal ions was assigned on the basis of the above studies. The phenylhydrazoneglyoxylato ion coordinated to the metal ion as a bidentate chelating ligand and two such molecules satisfy four coordination while two molecules in the primary coordination sphere complete the octahedral geometry. DNA binding property of the complexes 2, 3 and 5 were investigated by electronic absorption experiment. The experimental results show that the complex 5 exhibit excellent binding affinity with CT-DNA. The DNA cleavage activities of the complexes were determined by gel electrophoresis method and cleavage efficiency of the complex was found to be concentration dependent.

ACKNOWLEDGEMENT

The authors sincerely acknowledge University Grants Commission-SERO, Hyderabad for the financial assistance in the form of minor research project (Ref. No. FMRP-4964/14 (SERO/UGC). One of the authors (R.Pradeep) expresses his gratitude to University Grants Commission, New Delhi for the award of RGNFD fellowship (Ref. No. F/2014-15/RGNF-2014-15D-OBC-TAM-84300).

REFERENCES

[1] R Selvakumar; T Premkumar; V Manivannan; K Saravanan; S Govindarajan. *Afr J Chem*. **2014**, 67, 52-55.
[2] T Premkumar; R Selvakumar; NP Rath; S Govindarajan. *Afr J Chem*. **2014**, 67, 85-90.
[3] S Yasodhai; T Sivakumar; S Govindrajan. *Thermochim Acta*. **1999**, 338, 57-65.
[4] K Kuppusamy; BN Sivasankar; S Govindrajan. *Thermochim Acta.* **1995**, 259, 251-262.
[5] S Yasodhai; S Govindrajan. *J Therm Anal Cal.* **2000**, 62, 737-745.
[6] W Starosta; L Wicz. *Open Crystallogr J.* **2013**, 6, 1-6.

[7] C Sonia; BN Sivasankar. *Synth React Inorg Met Org Nano Met Chem*. **2014**, 44, 1119-1127.
[8] R Ragul; L Vikram; BN Sivasankar. *Synth React Inorg Met Org Nano Met Chem*. **2015**, 45, 1069-1079.
[9] BN Sivasankar; S Govindrajan. *J Therm Anal Cal*. **1997**, 48, 1401-1413.
[10] BN Sivasankar; S Govindrajan, *SRIMOC*. **1995**, 31, 1-6.
[11] L Vikram; BN Sivasankar. *Indian J Chem*. **2006**, 45A, 864-871.
[12] D Nicholls; M Rowly; R Swindells. *J Chem Soc*. **1966**, 62A, 950-952.
[13] AI Vogels. A Text Book of Quantitative Inorganic Analysis, 3rd edition, Longmans, London, **1962**.
[14] J Marmur *J Mol Biol*. **1961**, 3, 208-218.
[15] CV Kumar; EH Asuncion. *J Am Chem Soc*. **1993**, 115, 8547-8553.
[16] PR Reddy; KS Rao; B Satyanarayana. *Tetrahedron Lett*. **2006**, 47, 7311-7315.
[17] WI Geary. *Coord Chem Rev*. **1971**, 7, 81-86.
[18] BN Figgis; J Lewis. The Magnetochemistry of Complex Compounds in Morden Coordination Chemistry, J Lewis and RG Wilkins Interscience, New York, **1996**.
[19] APB Lever. Inorganic Electronic Spectroscopy, 2nd edition, Elsevier, Amsterdam, **1984**.
[20] K Nakamoto. Infrared Spectra of Inorganic and Coordination Compounds, Wiley, New York, **1978**.
[21] A Braibanti; F Dallavalle; MA Pellinghelli; E Leporati. *Inorg Chem*. **1968**, 7, 1430-1433.
[22] S Arjmand; S Parveen. *RSC Adv*. **2012**, 2, 6354-6362.
[23] MSS Babu; KH Reddy; PG Krishna. *Polyhedron*. **2007**, 26, 572-580.
[24] N Shahabadi; S Kashanian; M Mahdavi; N Sourinejad. *Bioinorganic Chem Appl*. **2011**, 10, 525-794.