

DNA Cleavage, Electrochemical and Magnetic Studies of Scorpionand Copper(II) complex

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Abstract: The copper(II) complex of a new scorpionand ligand with side chain 2-hydroxy-3-formyl-5-bromobenzyl group has been synthesized and characterized. The pendant arm of the ligand undergoes pH dependent complexation/decomplexation to the metal center. The precursor compound of scorpionand ligand crystallized as monoclinic in the space group $P2_1/n$. Electrochemical and magnetic properties of Cu(II) complex were studied. The copper(II) complex promote cleavage of plasmid pBR 322 DNA from the supercoiled form I to the open circular form II and show catalytic oxidation properties of catechol to o-quinone.

Keywords: Scorpionand copper(II) complex, Crystal structure, Electrochemistry, DNA cleavage studies.

Introduction

Recently chelating ligands based on polyazamacrocycles find numerous applications in various areas such as selective complexation, extraction of metallic cations, MRI contrast agent [1-3], biomimetic chemistry [4-6], as agents which cleave phosphate esters including DNA and RNA [7-9], catalysis [10,11] and molecular electronics [12]. Owing to their remarkable complexation properties, the 14 member tetraaza macrocycle and its derivatives have received considerable attention and there is a great demand for economical and efficient synthesis for new bifunctional structures. The bifunctional ligands are those with a macrocyclic ring and a chelating pendant arm which offer facile routes to heteronuclear supramolecular structures through self-assembly [13]. Different approaches have been devised for the synthesis of mono-N-alkylated tetraazamacrocycles (current

name scorpionands) [14]. Metal scorpionate complexes consist of a fixed part (the rigid tetra-aza ring) and a mobile portion (the flexible pendant arm). Taking profit from a chemical input (the addition of either H^+ or OH^-), the pendant arm can alternatively locate between two distinct positions: either axially bound to the metal center or far away from it. In this sense, the scorpionate complexes described are suitable systems for generating controlled molecular motions by repeatable movements and the pendant arms can also enhance the selectivity of the ligand for a given ion and may fine-tune the properties of the complex [15,16]. We now consider a new type of scorpionand, in which the pendant arm of the macrocyclic ligand has a phenolic group apart from a formyl group, which can be further condensed with polymers, which can be used in metal extraction processes [17] and catalytic applications or fluorescent moiety or redox active molecule which can be used as sensors

[18,19]. This paper deals with synthesis and characterization of mono-N-functionalized 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclo tetradecane (tet *a*) macrocyclic scorpionand ligand and its copper(II) complex.

Experimental

Elemental analysis was carried out on a Carlo Erba Model 1106 elemental analyzer. The copper content was analyzed using a Varian Spectra 200 atomic absorption spectrometer. Electronic spectral studies were carried out on a Hitachi 320 spectrophotometer in CH₃CN. IR spectra were recorded on a Hitachi 270-50 spectrophotometer on KBr disks in the range of 400–4000 cm⁻¹. Cyclic voltammograms were obtained on a CHI600A electrochemical analyzer using a three-electrode cell in which a glassy carbon electrode was the working electrode, a saturated Ag/AgCl electrode was the reference electrode and a platinum wire was used as an auxiliary electrode under oxygen-free conditions. Caution! Tetra(butyl)ammonium perchlorate (TBAP) is potentially explosive; hence care should be taken in handling the compound. A ferrocene/ferrocenium (1+) couple was used as an internal standard and $E_{1/2}$ of the ferrocene/ferrocenium (Fc/Fc⁺) couple under the experimental conditions was 470 mV in DMF, and ΔE_p for Fc/Fc⁺ was 70 mV. X-band EPR spectrum of the Cu(II) complex were recorded on a Varian EPR-E 112 spectrometer with diphenylpicrylhydrazine (DPPH) as the reference. The catalytic oxidation of 3,5-di-tertiarybutylcatechol to the corresponding o-quinone was studied using 10⁻³ M of the copper(II) complex in acetonitrile solution. The reaction was followed spectrophotometrically by choosing the strongest absorbance of the product, 3,5-ditertiarybutylbenzoquinone, around 390 nm and monitoring the increase in the absorbance at this wavelength over time intervals of 10 min. Initial rates (dc/dt) (<2% conversion of 3,5-ditertiarybutylcatechol) were determined by spectrophotometric determination of the released o-quinone. The initial reaction rates were also determined from the slope of the trace at 390 nm during the first 30 min of the reactions, when the absorption at 390 nm increases linearly. The DNA cleavage was monitored by agarose gel electrophoresis on plasmid pBR 322 DNA. The tests were performed under aerobic conditions with H₂O₂ as a reducing agent. The reaction was incubated at 37 °C for 2 h. After incubation, 1 µl of loading buffer (0.25% bromophenol blue, 0.25% xylene cyanol, 30% glycerol in H₂O) was added to each tube and the mixed samples were loaded on 1% agarose gel. The electrophoresis was carried out for 2 h at 50V in TBE buffer (89 mM tris-borate, pH

8.3, 1 mmol l⁻¹ EDTA). Gels were stained with ethidium bromide (1 µg ml⁻¹) for 30 min prior to being photographed under UV light.

Synthesis of precursor compound: The compound 1,4,8,11-tetraaza-5,5,7,12,12,14-hexamethyltricyclo [9.3.1.1^{4,8}]hexadecane (5 g, 16 mmol) was dissolved in acetonitrile (30 ml) and 3-chloromethyl-5-bromosalicylaldehyde (4 g, 16 mmol) in acetonitrile (30 ml) were added. This solution was stirred at room temperature (25 °C) for three days and the yellow precipitate formed was filtered, washed with a small quantity of CH₃CN and dried under vacuum. This crude quaternary ammonium compound was recrystallized from water to give white crystals. The resulting compound (0.5 g, 0.9 mmol) was dissolved in 100 ml of an aqueous NaOH solution (1 M) with stirring. After stirring for 4 h, the solution was extracted with CHCl₃ (5 x 30 ml). The combined CHCl₃ extracts were dried with anhydrous MgSO₄, and concentrated under vacuum to give a yellow color compound. The N-{(2-hydroxy-3-formyl-5-bromo)benzyl}-5,5,7,12,12,14-hexamethyl-4-azania bicyclo-1,4,8,11-tetraazacyclotetradecane were obtained upon recrystallization from chloroform. Yield: 0.28 g (56 %); mp: 210 °C (dec.). Analytical data for C₂₅H₄₁N₄O₂Br: Calculated (%): C, 58.95; H, 8.05; N, 11.00; Found (%): C, 58.88; H, 8.01; N, 10.97, Selected IR data (KBr)(v, cm⁻¹): 3485 (br), 3265 (s), 1672 (s), FAB mass (NBA matrix): m/z (%) = 295 (98) [C₁₇H₃₅N₄]⁺, 510 (60) [C₂₅H₄₁N₄O₂Br +1]⁺; ¹H NMR δ (ppm in CDCl₃) = 1.01 - 1.40 (s, 18H, C-CH₃), 2.01 - 2.17 (m, 4H, CH₂), 2.47 (m, 2H, CH), 2.50 - 2.90 (m, 4H, α-CH₂), 3.0 (br. s, 3H, NH), 3.29 (m, 4H, β-CH₂), 4.18 (d, 2H, N-CH₂-Ar), 5.20 (s, 2H, N-CH₂-N), 7.27 (d, 2H, Ar-H), 10.40 (s, H, Ar-CHO). ¹³C NMR δ (ppm in CDCl₃) = 12.12, 29.9, 40.47, 45.41, 55.85, 64.37, 103.10, 127.04, 139.68, 172.52 and 191.29.

Crystal data for PC: C₂₅H₄₁N₄O₂Br, M = 509.52, Monoclinic, space group P2₁/n, a = 8.605(1), b = 21.886(3), c = 13.314(2) Å, V = 2507.34(6) Å³, T = 273 (2), Z = 4, D_c = 1.350 Mg/m³, absorption coefficient = 1.668 mm⁻¹, F(000) = 1080, final R₁ = 0.0389 on I>2σ(I), wR₂ = 0.0828 (R₁ = 0.0812, wR₂ = 0.0971 for all data), GOF = 1.003.

Synthesis of ligand: The precursor compound (0.5 g, 0.9 mmol) was further hydrolyzed with 100 ml of an aqueous NaOH solution (excess) with stirring. After stirring for 4 h, the solution was extracted with CHCl₃ (5 x 30 ml). The ligand N-{(2-hydroxy-3-formyl-5-bromo)benzyl}-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclo tetradecane (L) was obtained upon recrystallization from chloroform.

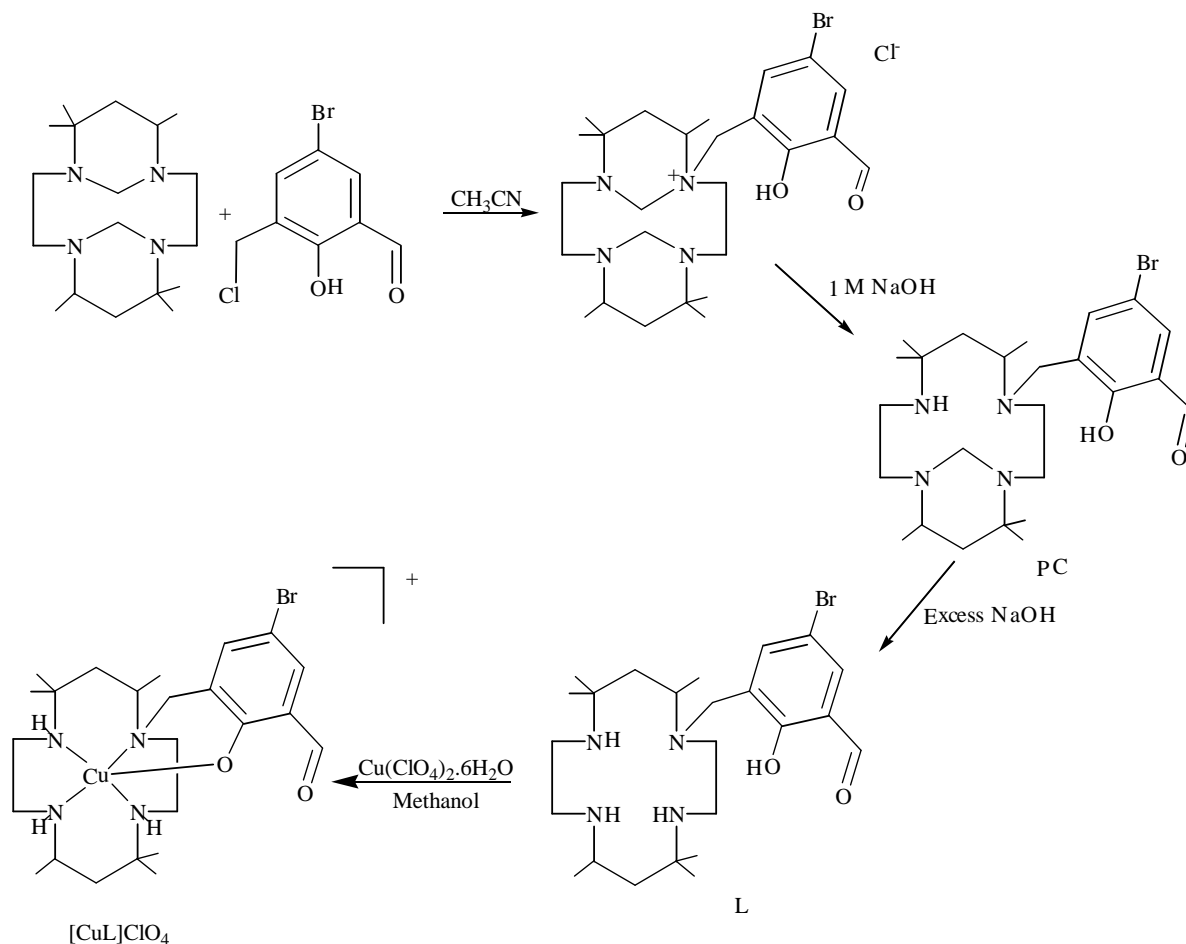
Yield: 0.28 g (56 %); mp: 225 °C (dec.) Analytical data for $C_{25}H_{42}N_4O_2BrCl_3$: Calculated (%): C, 48.68; H, 6.81; N, 9.08, Found (%): C, 48.62; H, 6.75; N, 9.02, Selected IR data (KBr)(ν , cm^{-1}): 3437 (br), 3241 (s), 1667 (s); 1H NMR δ (ppm in $CDCl_3$) = 1.01 - 1.40 (s, 18H, C- CH_3), 2.01 - 2.17 (m, 4H, CH_2), 2.47 (m, 2H, CH), 2.50 - 2.90 (m, 4H, α - CH_2), 3.0 (br. s, 3H, NH), 3.29 (m, 4H, β - CH_2), 4.02 (d, 2H, N- CH_2 -Ar), 7.26 (d, 2H, Ar-H), 10.40 (s, H, Ar-CHO), 12.94 (br. s, H, Ar-OH).

$[CuL](ClO_4) \cdot H_2O$: The complex was prepared by methanolic solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.73g, 2 mmol) was added to a hot solution of L (1.0g, 2 mmol) in methanol. The solution was refluxed on a water bath for 24 h, and filtered while hot. The crude product was precipitated by slow evaporation of the solvent at room temperature. The complex was obtained as a dark-green compound upon recrystallization of the crude product from CH_3CN . Yield: 1.10 g (68 %). Analytical data for $C_{24}H_{42}N_4O_7ClBrCu$: Calculated (%): C, 42.54; H,

6.20; N, 8.27; Cu, 9.38, Found (%) : C, 42.49; H, 6.18; N, 8.30; Cu, 9.34, Conductance (Λ_m , $S\ cm^2\ mol^{-1}$) in CH_3CN : 110, Selected IR data (KBr)(ν , cm^{-1}): 3405 (br), 3241 (m), 1658 (s), 1085, 628, λ_{max} , nm(ϵ , $M^{-1}cm^{-1}$) in CH_3CN : 774 (40), 528 (75), 396 (6310), 268 (12300), $g = 2.29$, $g_{\perp} = 2.09$; μ_{eff} : 1.72 B.M.

DNA cleavage was analyzed by monitoring the reaction mixture contained 1 μ g of supercoiled pBR 322 DNA, 10^{-4} to 10^{-6} M of complexes, 2 μ l of DMSO (1 %) and 5 μ l of hydrogen peroxide (40 $mmol\ l^{-1}$). The reaction was incubated at 37 °C for 2 hours. After incubation, 1 μ l of loading buffer (0.25 % bromophenol blue, 0.25 % xylene cyanol, 30 % glycerol in H_2O) was added to each tube and the mixed samples were loaded on 1 % agarose gel. The electrophoresis was carried out for 2 h at 50 V in TBE buffer (89 mM tris-borate, pH 8.3, 1 $mmol\ l^{-1}$ EDTA). Gels were stained with ethidium bromide (1 μ g ml^{-1}) for 30 min prior to being photographed under UV light.

Scheme



Results and discussion

Synthesis

Mono-N-alkylated tetraazamacrocyclic precursor compound [20, 21] was prepared by reacting equimolar amount of 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraaza [9.3.1.1^{4,8}]hexadecane [22] with 3-chloromethyl-5-bromosalicylaldehyde [23] in acetonitrile and the resulting compound was hydrolyzed with aqueous 1 M NaOH solution. The ligand L was obtained as yellow color compound by further hydrolysis of precursor compound with 2 M NaOH. The copper(II) complex was prepared in 68 % yield by reacting equimolar amounts of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with an equimolar amount of L in methanol. The synthetic route for the preparation of complex is shown in the **Scheme**.

X-ray Structural Study of the precursor compound

The ORTEP plot of the precursor compound is shown in **Fig. 1**. For C-N, the distance varies between 1.439Å and 1.51Å. No anomalous bond distances and bond angles were found in the structure and all the bond distances and bond angles agree well with the reported literature [24, 25]. The phenyl ring is essentially planar. The cyclam unit is more buckled compared to the unsubstituted cyclam due to the attachment of a bulkier group in the ring. The final R-factor converged to 0.0389, maximum and minimum values of the electron densities in the final electron density map were 0.46 & -0.58 $\text{e} \cdot \text{Å}^{-3}$. There is a C-H...O type intermolecular interaction between C23C (x,y,z) and O1 (1/2+x, 1/2-y, -1/2+z) with distance of D-A = 3.505 (3) Å, D-H...A = 158°. Apart from the interaction, packing of the molecules is stabilized by Vander Waals interaction.

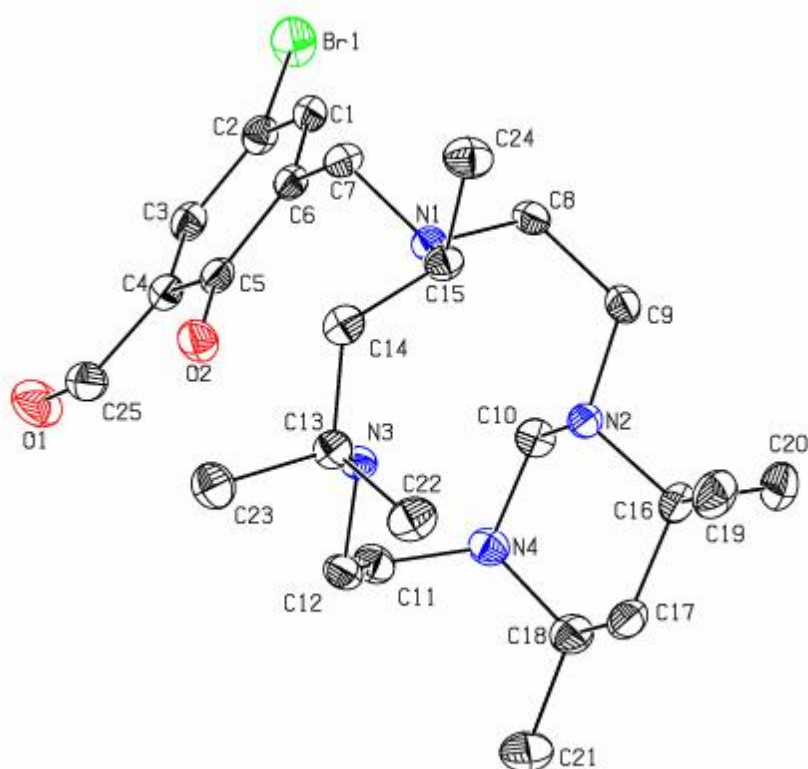


Fig.1: ORTEP diagram of precursor compound with atom labels and numbering scheme (Hydrogen atoms are omitted for clarity) Selected bond lengths (Å) and angles (°)

Analysis of spectra

The infrared spectrum of the precursor compound showed $\nu(\text{C}=\text{O})$ peak at 1672 cm^{-1} , N-H peak at 3265 cm^{-1} and $\nu(\text{OH})$ peak at 3485 cm^{-1} . The infrared spectrum of the ligand showed $\nu(\text{C}=\text{O})$ peak at 1667 cm^{-1} , N-H peak at 3241 cm^{-1} and $\nu(\text{OH})$ peak at 3437 cm^{-1} . The copper(II) complex shows $\nu(\text{N-H})$, $\nu(\text{C}=\text{O})$ peaks at 3241 cm^{-1} , 1658 cm^{-1} respectively. The complex also shows peaks at 1085 and 628 cm^{-1} characteristic of perchlorate anion. The peak at 1085 cm^{-1} is broad and there is no splitting indicates that the perchlorate is not coordinated with the metal ion [26]. The precursor compound showed the molecular ion peak at $m/z = 510$, which is assignable to the $[\text{M}+1]^+$ fragment in addition to peaks at $m/z = 285, 295, 341, 391$ for other fragments.

The copper(II) complex $[\text{CuL}](\text{ClO}_4)$ showed a visible absorption band maximum at 528 nm ($\epsilon \sim 75\text{ M}^{-1}\text{ cm}^{-1}$) and a low-energy shoulder at 774 nm ($\epsilon \sim 40\text{ M}^{-1}\text{ cm}^{-1}$). Generally five coordinated copper(II) complexes fall into two categories. [27,28] Trigonal bipyramidal complexes have a low-energy absorption band ($\sim 1000\text{ nm}$) with a high-energy shoulder ($\sim 660\text{ nm}$) in the visible region. In contrast, square pyramid complexes show high-energy absorption band ($\sim 525\text{ nm}$) with low energy shoulder ($\sim 625\text{ nm}$) in the visible region. The electronic spectral data of copper(II) complex indicate that the geometry around copper ion in solution is distorted square-pyramid. A moderate intense band observed at 396 nm ($\epsilon \sim 6310\text{ M}^{-1}\text{ cm}^{-1}$) is due to ligand to metal charge transfer transition and the strong band observed in the range 268 nm ($\epsilon \sim 12300\text{ M}^{-1}\text{ cm}^{-1}$) is due to intraligand charge transfer transition.

A solution of the $[\text{CuL}]\text{ClO}_4$ complex acidified with standard acid to pH 2 and made 0.05 M in NaClO_4 was titrated with standard NaOH . Titration with base induces decolorisation of light yellow to green solution and a drastic change of the absorption spectrum. The color and spectral changes are associated to the deprotonation process. It is suggested that deprotonation involves the phenolic oxygen atom of the pendant arm. Therefore the $[\text{CuL}]\text{ClO}_4$ species should be considered as a scorpionate complex, with deprotonated phenolic oxygen group coordinated to one of the axial positions of the Cu^{II} center while increasing the pH. The occurrence of a drastic geometrical change is substantiated by spectrophotometric investigations. It is seen that, on increasing pH, the absorption spectrum changes in the $325 - 550\text{ nm}$ range. In an

acidic solution of the complex (pH 2) is light yellow and shows a d-d absorption band centered at 510 nm . On increasing pH the color of the solution changes from yellow to green, while the intensity of the band at 510 nm decreases and new bands develop at 390 and 545 nm . The two bands are those expected for a square-pyramid complex. Figure 2 displays the spectra of an aqueous solution of $[\text{CuL}]\text{ClO}_4$ recorded over the $2 - 12\text{ pH}$ range.

EPR Spectrum

The EPR spectrum of the copper(II) complex showed four lines with nuclear hyperfine spin $3/2$ due to hyperfine splitting. The observed g value falls at 2.29 and g_{\perp} value at 2.09 . For the complex $[\text{CuL}](\text{ClO}_4)$ the g value is greater than g_{\perp} value ($g (2.29) > g_{\perp} (2.09) > 2.00$, $A = 176 \times 10^4\text{ cm}^{-1}$) and this indicates that geometry around copper ion in solution is distorted square-pyramid. The magnetic moment value μ_{eff} for $[\text{CuL}](\text{ClO}_4)$ is 1.72 B.M. , which is very close to that of spin only value (1.73 B.M.) expected for complexes having one copper(II) ion with single unpaired electron sited in an essentially $d_{x^2-y^2}$ orbital.

Electrochemical Properties of the Complex

Conductivity measurements of copper(II) complex in acetonitrile indicates that the complex is 1:1 electrolyte type ($110\text{ }\Lambda_{\text{m}}/\text{Scm}^2\text{mol}^{-1}$) [29]. Cyclic voltammetric studies of the complex (10^{-3} M) were carried out in acetonitrile containing 0.1 M tetra-n-butylammonium perchlorate as a supporting electrolyte with a scan range of 0 to -1.2 V vs Ag/AgCl . The cyclic voltammogram (Fig. 3) of $[\text{CuL}]$ show one irreversible reduction wave in the cathodic potential region at $E_p^c = -0.94\text{ V}$ corresponding to the $\text{Cu}^{\text{II/I}}$ couple. The corresponding reduction potential for $[\text{Cu}(\text{tet } a)]^{2+}$ complex is -1.08 V [30]. The easy reduction of the reported complex may be due to one of the nitrogen change from secondary to tertiary nitrogen atom. This agrees with the widely observed trend that the substitution of coordinated secondary amine by tertiary ones in the polyazamacrocyclic copper(II) complexes makes the reduction easier [31]. The distortion in geometry may also be one of the reasons for the anodic shift of the reduction potential [32].

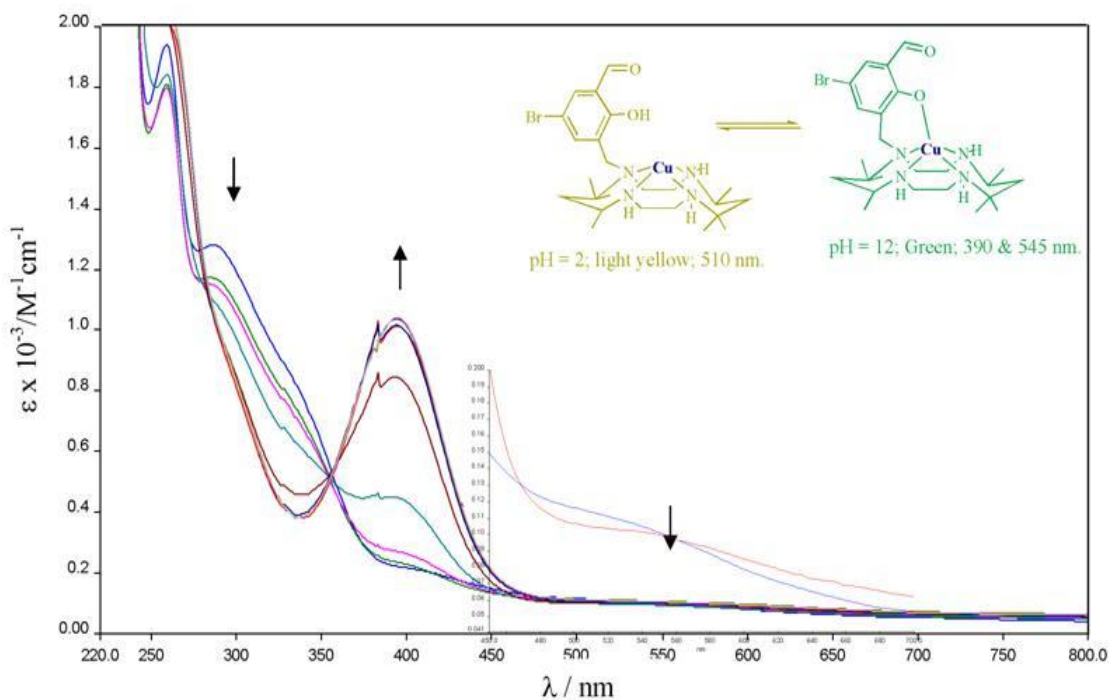


Fig. 2: Absorption spectra of $[\text{CuL}](\text{ClO}_4)$ measured during a titration with NaOH (pH range: 2-12). While increasing the pH, the color and spectral changes are associated to the deprotonation of the phenolic oxygen atom of the pendant arm which is coordinated to one of the axial positions of the CuII center.

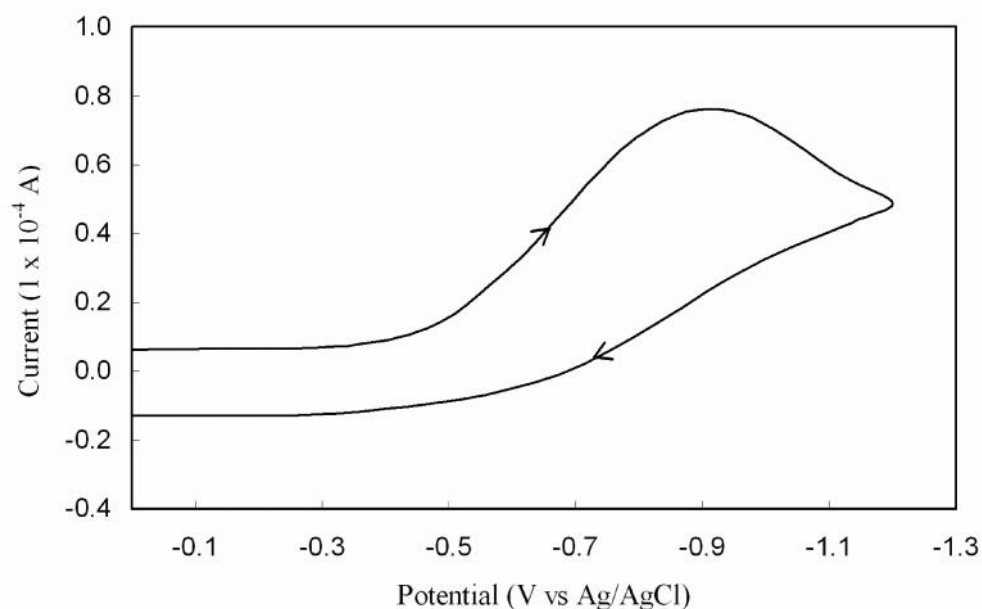


Fig. 3: Cyclic voltammogram of $[\text{CuL}](\text{ClO}_4)$ using a three-electrode cell in which a glassy carbon electrode was used as a working electrode, a saturated Ag/AgCl electrode as a reference electrode and a platinum wire was used as an auxiliary electrode in acetonitrile at 25°C (scan rate, 100 mVs^{-1})

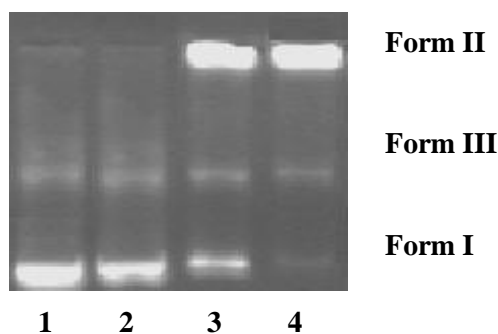


Fig. 4: Cleavage of pBR322 DNA by copper(II) complex

Lane 1. DNA control; Lane 2. DNA + H₂O₂; Lane 3. DNA + H₂O₂ + complex [CuL](ClO₄) 20 μ mol l⁻¹;
Lane 4. DNA + H₂O₂ + complex [CuL](ClO₄) 100 μ mol l⁻¹;

Kinetic Studies

Catecholase Activity

It has been of great interest to investigate the catecholase activity of copper(II) complex using 3,5-ditertiarybutyl catechol as a convenient model substrate for the identification of functional models for the metalloenzymes. [33] The mononuclear copper(II) complex synthesized was subjected to catecholase activity. The product *o*-quinone is considerably stable and has a strong absorbance around 390 nm. For the oxidation studies 10⁻³ M solution of complexes in acetonitrile were treated with 3,5-ditertiarybutyl catechol (10⁻¹ M) (100 fold excess than the complex) in the presence of air. The course of the reaction was followed spectrophotometrically at 390 nm nearly for 90 minutes. The DTBQ formed with respect to time. The initial rate (V_{in}) of the oxidation of catechol to quinone was determined from the slope of the trace at 390 nm during the first 30 minutes of the reaction. The average of three values of the initial rate of copper(II) complex of ligand L is 1.5 x 10⁻⁵ Ms⁻¹. The catecholase activity of “tet *a*” copper(II) complex has a initial rate value of 1.2 x 10⁻⁵ Ms⁻¹. This higher catalytic activity may be due to a greater distortion in the geometry of the substituted macrocyclic complex than the unsubstituted macrocyclic complexes. This may be due to steric effects of the N-substitution of the macrocycle, which causes a distortion of the geometry of the Cu(II) complexes (due to macrocyclic ring distortion) and also due to the increased number of tertiary nitrogen atoms which stabilize the low valent Cu(I) ion. [34].

DNA cleavage studies

In order to ascertain, the ability of complex to serve as metalonuclease, DNA cleavage was

monitored by agarose gel electrophoresis on plasmid pBR 322 DNA. [35] The test was performed under aerobic conditions with H₂O₂ as a reducing agent. Incubation of plasmid DNA pBR 322 with the Cu(II) complex for 2 h at 37 °C results in extensive cleavage of DNA as shown in Figure 4. No cleavage occurs in the absence of H₂O₂ and the complex. As shown in Fig. 4, the supercoiled form I is first degraded to form II (relaxed circular) and then to form III (linear) in the presence of 100 μ mol l⁻¹ Cu(II) complex. When the concentration of complex [CuL](ClO₄) increased from 20 to 100 μ mol l⁻¹ the conversion of Form I to Form II also increases. (Fig. 3. Lane 3,4). It is inferred that most of the cleavage are caused by copper ions reacting with H₂O₂ to produce diffusible hydroxyl radicals ([•]OH) or molecular oxygen, which may damage DNA through Fenton type chemistry [36, 37]. It is assumed that a copper–oxygen species might be responsible for DNA cleavage. Yan Jin et al [38] studied variety of metal complex mediated DNA cleavage reactions, which shows a regulated cleavage pattern. Sigman et al [39] also postulated that the copper-oxygen species might be formed in their DNA cleavage reaction in the presence or absence of H₂O₂. Further studies on the macrocyclic ring size effect on DNA molecules as well as on the sequence selectivity of the copper(II) complexes are in progress.

In summary, a new N-functionalised tetraaza macrocyclic copper(II) complex of ligand (L) in which the pendant arm has been equipped with phenolate oxygen and formyl moiety. The spectroscopic results of copper(II) complex are consistent with a distorted square pyramid geometry. The electrochemical studies indicate that the complex undergoes one electron irreversible reduction process. This work will be of much value in terms of factors that as the complex finds its use as a potential candidate for the DNA cleavage

activity and this activity remarkably increases with the concentration of copper(II) complex.

Acknowledgement

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Supplementary material

Full crystal data and structure refinement details of the atomic coordinates, equivalent isotropic displacement parameters, full interatomic distances and angles anisotropic displacement

parameters, hydrogen coordinates and isotropic displacement parameters for precursor compound are available from the Cambridge Crystallographic Data Centre CCDC No. **282436**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk[or] www.http/www.ccdc.cam.ac.uk.).

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