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Synthesis, crystal structure, DNA binding and cleavage activities of oximato bridged cationic dinuclear copper(II) complex having labile ligands

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Oximato bridged dinuclear copper(II) complex $[Cu(L)(CH_3OH)]_2(ClO_4)_2$ with an oxime-Schiff base ligand, viz. 3-[2-[(dimethylamino)ethyl]imino]-2-butanoneoxime (HL), has been synthesized and structurally characterized. The dinuclear copper(II) complex crystallizes in monoclinic space group $P2_1/n$ with the unit cell parameters, a = 13.3564(9) Å, b = 12.0821(8) Å, c = 17.5045(11) Å, β = 90.097, V = 2824.8(3) Å^3, Z = 4, R = 0.0769. The complex shows quasi-reversible cyclic voltammetric response at 0.844V (ΔE_p = 276 mV) at 100 mVs^{-1}. The binding studies of the complex with calf thymus DNA has been investigated using absorption spectrophotometry. Cleavage activity of the complex has been carried out on double stranded pBR 322 plasmid DNA by using gel electrophoresis experiments in the absence and in the presence of the oxidant, viz., H_2O_2.

Keywords: Coordination chemistry, Bioinorganic chemistry, Schiff bases, Oxime-Schiff base ligands, Oximato bridged complexes, Dinuclear complexes, X-ray crystallography, DNA binding, DNA cleavage activity, Copper

Oximes have been widely used as very efficient complexing agents in analytical chemistry for isolation, separation and extraction of different metal ions[1-11]. Different oximes and their metal complexes have shown notable bioactivity as chelating therapeutics, as drugs, as inhibitors of enzymes and as intermediates in the biosynthesis of nitrogen oxides[12]. Copper(II) complexes have a wide range of biological activity and some of these complexes are known to be antitumor, antiviral and anti-inflammatory agents. In addition, since copper(II) complexes, especially with oxime-Schiff base ligands, are proposed as models for understanding physical and chemical behaviour of biological copper systems, considerable attention has been focused on these compounds[13-17].

There is also much interest in the development of artificial nucleases. Artificial metallonucleases require ligands which effectively deliver metal ions to the vicinity of DNA[18-20]. The development of inorganic DNA cleavage reagents has been an area of active research[21-23]. Studies on chemical modification of nucleic acids with transition metal complexes are of great interest in the design of chemotherapeutic drugs, regulation of expression and design of tools for molecular biology[24,25]. Copper (II) has been shown to bind the DNA bases at the N(7) of purines and N(1) of pyrimidines[26]. These ions can be reduced and then oxidized by dioxygen leading to hydroxyl radical production, close to the metal binding site, which can damage DNA in site-specific reactions. However, investigation on DNA interactions and cleavage activity of metal complexes with oxime-Schiff bases are quite limited.

In the light of the above, and as part of our ongoing research programme[27-30] concerning DNA binding and cleavage activities of di- and polynuclear transition metal complexes, herein we report the synthesis, crystal structure, DNA binding and cleavage activity of a new catioinic dinuclear copper(II) complex having the formula $[Cu(L)(CH_3OH)]_2(ClO_4)_2$ (HL = 3-[2-[(dimethylamino)ethyl]imino]-2-butanoneoxime. Moreover, oximato bridged cationic dinuclear copper(II) complex with good labile ligands is not reported so far. The complex has three favourable DNA binding features, viz., (i) It has positive charge and therefore it can bind strongly with negatively charged phosphodiester backbone of DNA via electrostatic attraction; (ii) It has labile ligands (CH_3OH, good leaving groups) which may be easily replaced by the bases of DNA to bind polynucleotide

via coordination; and, (iii) It has two metal centers, and therefore, is expected to bind DNA more strongly than the corresponding mononuclear complex.

Materials and Methods

Diacetylmonoxime (AR grade) was purchased from Merck. N,N-dimethyl ethylenediamine (AR grade) was purchased from Sigma-Aldrich. All other chemicals were of AR grade and used as supplied. The solvents used for synthesis of the complex were distilled before use. Calf thymus DNA (CT-DNA) and plasmid pBR-322 were purchased from Genie Bio Labs, Bangalore, India. Single crystal X-ray diffraction data was collected at 298 K on a Bruker AXS Kappa Apex CCD diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073Å). Magnetic measurements of the complex were recorded at 298 K on a Faraday's magnetic susceptibility balance (Sherwood Scientific, Cambridge, UK). High purity penta $CuSO_4.5H_2O$ was used as a standard. The conductivity measurements at 298±2 in dry and purified DMF were carried out on a CM (model 162) conductivity cell (Elico). Electronic spectra of the complex were recorded in DMF with Perkin-Elmer (UV lamda 50) spectrophotometer. IR spectra were recorded in the range 4000-400 cm^{-1} with Perkin-Elmer (spectrum 100) spectrometer as KBr discs. ESR spectra were recorded on a Varian E-112 X-band spectrophotometer at room temperature and at liquid nitrogen temperature (LNT) in both solution (DMF) as well as solid state. Cyclic voltammetric measurements were made on a BAS CV-27 assembly equipped with an X-Y recorder. The measurements were made on degassed (N_2 bubbling for 5 min) solutions in (10^{-3} *M*) containing 0.1 *M* Bu_4NPF_6 as the supporting electrolyte. The three-electrode system consisted of glassy carbon (working), platinum wire (auxiliary) and Ag/AgCl (reference) electrodes. DNA cleavage activities were performed on UVI-tech-UK gel documentation system.

Synthesis of 3-[2-[(dimethyl amino)ethyl]imino]-2-butanone-oxime (HL)

The ligand was prepared by refluxing N,N-dimethylethylenediamine (0.55 mL, 5 mmol) and diacetylmonoxime (0.505 g, 5 mmol) in 30 mL of methanol for one hour. On cooling the reaction mixture, a reddish-yellow coloured viscous liquid (HL) was obtained. It was subsequently used in the preparation of complex.

Synthesis of complex $[Cu(L)(CH_3OH)]_2.2ClO_4$

A 10 mL of methanolic solution of $Cu(ClO_4)_2.6H_2O$ (1.853 g, 5 mmol) was added to a solution of the oxime-Schiff base ligand HL (5 mmol in 10 mL methanol), and the resulting solution was stirred well. Triethylamine (0.85 mL, 5 mmol) was added dropwise to the resulting solution with constant stirring. The resultant solution was filtered and evaporated at room temperature. The green coloured complex was collected and recrystallised from acetonitrile solution. Deep green single crystals of complex suitable for X-ray diffraction were grown by slow evaporation of the acetonitrile-hexane solvent mixture.

Yield: 1.68 g (76%), Anal. (%): Found (Calc.) C 29.38 (29.91); H 4.14 (4.43); N 11.26 (11.63). IR (KBr pellet, cm^{-1}): 1655, 1516 cm^{-1} for *ν*(C=N), 3501 cm^{-1} for *ν* (OH), 1087 cm^{-1} for *ν* (ClO_4). λ_{max}: 577 nm.

X-ray crystallography

Single crystal X-ray diffraction measurements were made on a Bruker AXS Kappa Smart Apex CCD diffractometer. The unit cell parameters were determined and the data collections were performed using graphite-monochromated Mo Kα radiation (λ = 0.71073) radiation. The crystal was found to be tetragonal with a $P2_1/n$ space group. Least square refinements of 12032 reflections were done for the complex. The data collected were reduced using the SAINT program[31]. The structure was obtained by direct method[32] using SHELXS-86, which revealed the position of all non-hydrogen atoms, and, refined by full-matrix least squares on F^2 (SHELXS-97)[33]. The graphic tool used was MERCURY for windows[34]. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were treated with a mixture of independent and constrained refinements.

DNA binding experiments

Interaction of the complexes with calf thymus DNA was studied by electronic absorption spectra. A solution of CT-DNA in 5 m*M* Tris-HCl/50 m*M* NaCl (*p*H 7.0) gave a ratio of UV absorbance at 260 and 280 nm (A_{260}/A_{270}) 0f 1.8-1.9, indicating that the DNA is sufficiently free of proteins [35]. A concentrated stock solution of DNA was prepared in 5 m*M* Tris-HCl/ 50 m*M* NaCl in water at *p*H 7.0 and the concentration of CT-DNA was determined per nucleotide from the absorption coefficient (6600 dm^3 mol^{-1} cm^{-1}) at

260 nm[36]. Stock solutions were stored at 4 °C and were used after no more than 4 days. Doubly distilled water was used to prepare the buffer solutions. The solutions were prepared by mixing the complex and CT-DNA in DMF medium. After equilibrium was reached (*ca*. 5 min), the spectra were recorded against an analogous blank solution containing the same concentration of DNA.

UV-spectral data were fitted into Eq. 1 to obtain the intrinsic binding constant (K_b),

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

where [DNA] is the concentration of DNA in base pairs, ε_a, ε_b and ε_f are ***apparent*** extinction coefficient, extinction coefficient for the metal complex in the fully ***bound*** form and the extinction coefficient for ***free*** metal respectively. A linear plot of [DNA]/(ε_a-ε_f) versus [DNA] gave a slope of 1/(ε_b-ε_f) and Y-intercept equal to 1/K_b(ε_b-ε_f); K_b is the ratio of the intercept.

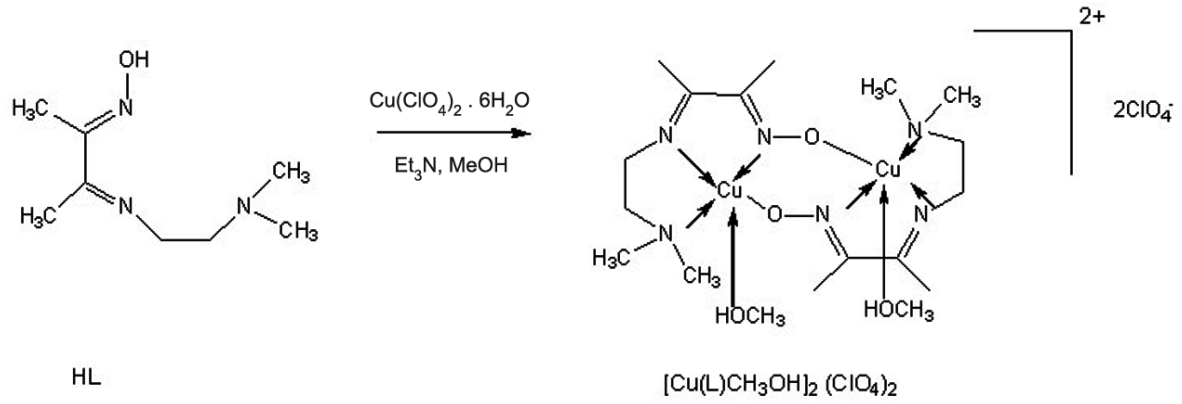
Assay of nuclease activity

The extent of cleavage of DNA by the copper(II) complexes was monitored by agarose gel electrophoresis using pBR 322 DNA. The samples after incubation for 30 min at 37 °C were added to the buffer containing 0.25% bromophenol blue + 0.25% xylene cynaol + 30% glycerol and the resulting solutions were loaded on 0.8% agarose gel containg 100 µg of ethidium bromide. Electrophoresis was performed at 75 V in TBE buffer until the bromophenol blue reached up to 3/4th length of the gel. The bands were visualized by UV-transilluminator and photographed. The efficiency of DNA cleavage was measured by determining the ability of the complex to form open circular (OC) or nicked circular (NC) DNA from its super coiled (SC) form. The reactions were carried out under oxidative and/or hydrolytic conditions. Control experiments were carried out in the presence of the hydroxyl radical scavenger, DMSO (4 µL).

Results & Discussion

The reaction of $Cu(ClO_4)_2.\ 6H_2O$ with HL to the formation of $[Cu(L)(CH_3OH)]_2.2ClO_4$ is shown in Scheme. 1. The complex is a green coloured solid and insoluble in common organic solvents, but soluble in acetonitrile, dimethyl formamide and dimethyl sulfoxide. The molar conductivity (163 Ω^{-1} cm^{-2} mol^{-1}) value indicates the ionic nature of complex. The electronic spectrum of the complex in DMF solution shows a single absorption at 577 nm. The position of this band is consistent with the observed square based geometry around copper centre[37]. In the infrared spectrum of the Cu(II) complex**,** a broad band at 3501 cm^{-1} is assigned to ν(OH) of the coordinated CH_3OH. The other characteristic bands are easily located at 1655 cm^{-1} ν(C=N) and 1516 cm^{-1} oxime ν(C=N) for the complex. There is a broad band at 1087 due to the ν_3 mode of perchlorate ions group in T_d symmetry. The DMF solution of complex in 0.1 *M* tetrabutyl ammonium hexafluorophosphate ($TBAPF_6$) shows quasi-reversible cyclic voltammetric response due to Cu(II)/Cu(I) reduction with $E_{1/2}$ value of 0.982 vs Ag/AgCl reference electrode with i_c/i_a = 0.104 V and ΔE_p value of 276 mV at a scan rate 100 mV/s. The ΔG^0 (700 kcal) value indicates that the complex is stable in solution state.

The complex has been characterized by single crystal X-ray diffraction. Crystal data and structure refinement parameters are shown in Table 1. A ORTEP view of $[Cu(L)(CH_3OH)]_2^{2+}$ with the atomic



HL

[Cu(L)CH3OH]2 (ClO4)2

Scheme 1

Table 1 – Crystal data, data collection and structure refinement parameters for $[Cu(L)CH_3OH]_2(ClO_4)_2$

Formula	$C_{18}H_{32}Cl_2Cu_2N_6O_{12}$
Formula weight (M)	722.48
Temp. (K)	293(2)
Wavelength (Mo-Kα) (Å)	0.71073
Crystal system	Monoclinic
Lattice constants	
a (Å)	13.3564(9)
b (Å)	12.0821(8)
c (Å)	17.5045(11)
α (°)	90
β (°)	90.0970(10)
γ (°)	90
Vol. (Å^3)	2824.8(3)
Z	4
Calcd density (mg m^{-3})	1.699
Abs. coeff (mm^{-1})	1.763
F (0 0 0)	1480
Crystal size	0.15 X 0.09 X 0.04
θ range for data collection	1.92-27.7
Limiting indices	$-16\leq h\leq17$, $-15\leq k\leq15$, $-23\leq l\leq23$
Reflections collected	24019
Unique reflections	6646[R_{int}=0.0575]
Completeness to θ (%)	100
Max. and min. transmission	0.9328 and 0.7779
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	6646/2/367
Goodness-of-fit on F^2	1.048
Final R indices [$I > 2\sigma(I)$]	[a]R_1 = 0.0769, [b,c] wR_2 = 0.1828
R indices (all data)	[a]R_1 = 0.1286, [b,c] wR_2 = 0.2141
Largest diff. peak and hole (e.Å^{-3})	1.012 and –0.690

[a]$R_1 = \sum(\left|F_O\right| - \left|F_C\right| / \sum \left|F_O\right|$. [b]$wR_2 = \{\sum [w (F_O^2 - F_C^2)^2] / \sum [w(F_O^2)^2]\}^{1/2}$

[c]$w=1/[\sigma^2(F_O^2)+(aP)^2+bP]$ with $P=[F_o^2+2F_c^2]/3$, a=0.0612 and b =0.24.

number scheme is depicted in Fig. 1. Selected bond distances and angles are given in Table 2. The structure shows, a dinuclear copper(II) complex with each copper having a square pyramidal geometry formed by oxime, imine and amine nitrogen atoms at the base of the pyramid and the solvent (CH_3OH) oxygen atom occupying the axial position. The basal plane is completed by the oxime oxygen of the second ligand of the dimer. The central six-membered ring in the structure formed by two copper atoms and two oxime N-O bridges is non-planar and adopts a chair conformation. The Cu-O bond distances were found to be Cu(1)-O(1) = 1.892Å and Cu(2)-O(2) = 1.886Å

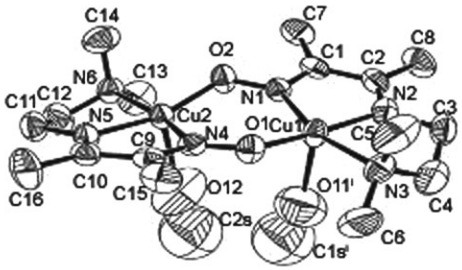


Fig. 1 – ORTEP view of $[Cu(L)(CH_3OH)_2]^{2+}$. [Hydrogen atoms and ClO_4^- anions are omitted for clarity].

Table 2 – Selected bond lengths and bond angles of $[Cu(L_1)(CH_3OH)]_2(ClO_4)_2$

Bond lengths (Å)	
Cu(1)-O(1)	1.892(4)
Cu(2)-O(2)	1.886(4)
Cu(1)-N(1)	2.006(5)
Cu(1)-N(2)	1.933(5)
Cu(1)-N(3)	2.064(5)
Cu(2)-N(4)	2.010(5)
Cu(2)-N(5)	1.931(5)
Cu(2)-N(6)	2.053(5)
Bond angles (deg.)	
O(1)-Cu(1)-N(2)	168.8(2)
O(1)-Cu(1)-N(1)	104.3(2)
N(2)-Cu(1)-N(1)	80.4(2)
O(1)-Cu(1)-N(3)	90.9(2)
N(2)-Cu(1)-N(3)	83.1(2)
N(1)-Cu(1)-N(3)	162.6(2)
N(4)-O(1)-Cu(1)	122.7(3)
O(2)-N(1)-Cu(1)	129.3(4)
O(1)-Cu(1)-O(11)	94.8(3)
O(2)-Cu(2)-N(5)	162.4(2)
O(2)-Cu(2)-N(4)	103.6(2)
N(5)-Cu(2)-N(4)	80.5(2)
O(2)-Cu(2)-N(6)	90.7(2)
N(5)-Cu(2)-N(6)	83.3(2)
N(4)-Cu(2)-N(6)	163.2(2)
N(1)-O(2)-Cu(2)	121.7(3)
O(1)-N(4)-Cu(2)	129.4(3)
O(2)-Cu(2)-O(12)	100.9(3)

and whilst Cu-N bond distances were Cu(1)-N(1) = 2.006Å, Cu(1)-N(2) = 1.933Å, Cu(1)-N(3) = 2.064Å, Cu(2)-N(4) = 2.010Å, Cu(2)-N(5) = 1.931Å, Cu(2)-N(6) = 2.053Å. In this case, terminal amine nitrogen (N(3) and N(6)) atoms form a significantly longer Cu-N bond.

In solid state, the oxygen atom of the coordinated solvent group (CH_3OH**)** on Cu(1) forms a intramolecular

hydrogen bond with the other coordinated -OH group of the solvent group present on Cu(2). The –OH group of coordinated solvent ligand on Cu(1) forms a intermolecular hydrogen bond with oxygen atom of the perchlorate group of the another molecule.

The magnetic moment of complex is found to be 0.58 BM. The magnetic moment of copper(II) complex at room temperature is sub-normal due to the spin-coupling interaction between copper(II) ions. Figure 2 shows X-band ESR spectra of complex. The spin Hamiltonian and orbital reduction parameters of complex are given in Table 3. The $g_{\|}$ and $g_{\perp}$ values are computed from the spectrum using tetracyanoethylene (TCNE) free radical as '*g*' marker. From the observed values of complexes at 300 K and 77 K in the solid state spectrum, it is clear that $g_{\|} > g_{\perp} > 2.00$, which suggests that the unpaired electrons lie predominantly in the d_{x2-y2} orbital[38] characteristic of square pyramidal or octahedral geometry in copper(II) complex. The g_{av} value for the complex is greater than 2, indicating covalent nature of the metal-ligand bond. The solid state spectra of the complexes at 77 K and 300 K indicates that the geometry around copper(II) is unaffected on cooling to liquid nitrogen temperature. In these conditions, *G* values were found to be < 4 for these complexes. According to Hathaway[39], if *G* value is greater than 4, the exchange interaction is negligible whereas *G* value less than 4 indicates considerable exchange interaction between metal ions in the solid complex. In the present case the G values indicate considerable exchange interaction between Cu(II) ions. The solution ESR spectra recorded in DMF shows four hyperfine signals for the complex (g_{iso} = 2.114, A_{iso} = 80 G) which were not observed in DMF at 77 K. The appearance of a four line pattern in solution at room temperature may be due to a slight loss of magnetic coupling between the two copper ions. At the same time, disappearance of the four hyperfine signals in ESR spectrum at 77 K can be attributed to the recombination of the monomers to dimers due to an increase in the viscosity of the solvent[30].

The binding interaction of the complexes with CT-DNA was monitored by comparing their absorption spectra with and without CT-DNA. Addition of increasing amounts of CT-DNA to all the complexes shows a decrease in molar absorptivity of the π- π* absorption band as well as a red shift of a few nm (~1 nm), indicating the binding of the complex to DNA in different modes and to different extents. Figure 3 shows absorption spectra of complex in the absence and presence of increasing amounts of

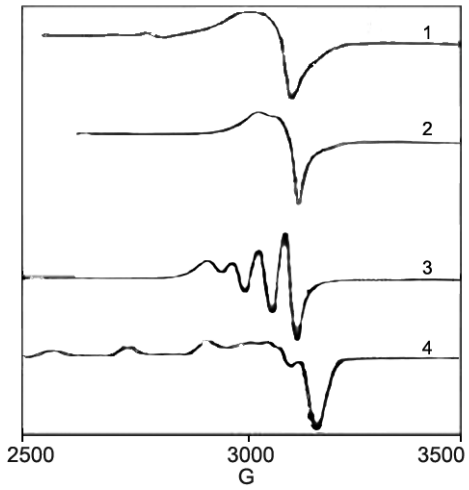


Fig. 2 – X-band ESR spectrum of $[Cu(L)(CH_3OH)_2]$ $(ClO_4^-)_2$. [Solid state: 1, at 300 K; 2, at liquid N_2 temperature; In DMF solution: 3, at 300 K; 4, at liquid N_2 temperature].

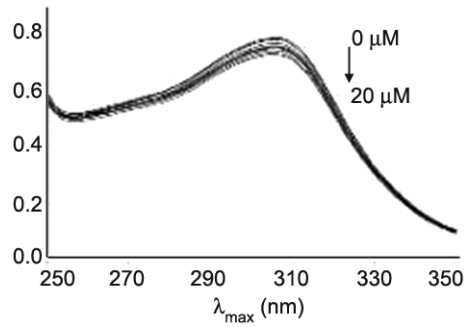


Fig. 3 – Absorption spectra of $[Cu(L)(CH_3OH)_2]$ $(ClO_4^-)_2$ in absence and presence of DNA. [Arrows show the decrease in absorbance upon increasing concentration of DNA from 0-20 μ*M*].

Table 3 – Spin Hamiltanian and orbital reduction parameters for $[Cu(L_1)(CH_3OH)]_2.(ClO_4)_2$

	$g_{\|}$	$g_{\perp}$	g_{av}	G	g_{iso}	A_{iso} G (10^{-3}cm^{-1})	$A_{\|}$ G (10^{-2}cm^{-1})	$A_{\perp}$ G (10^{-3}cm^{-1})
At 300 K and 77 K in solid state	2.074	2.061	2.065	1.223	-	-	-	-
At 300 K in DMF	-	-	-	-	2.114	80 (7.9)	-	-
At 77 K in DMF	2.219	2.060	-	3.778	-	-	185 (1.92)	27.5 (2.64)

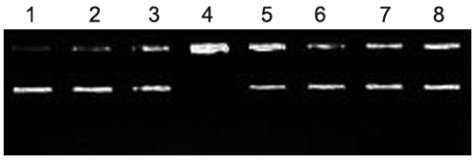


Fig. 4 – Electrophoresis of pBR 322 plsmid DNA (1 μL) in agarose gel (0.8%). [Tris-HCl/NaCl (50 m*M*/5m*M*); buffer (pH 7) (4 μL); $[Cu(L)(CH_3OH)_2]$ $(ClO_4^-)_2$ complex (2 μL) in DMF(1×10^{-3}*M*); sterilized water (11 μL); H_2O_2 (2 μL) (total 20 μL) incubated at 37 ^oC (30 min.). Lane 1: DNA control; Lane 2: DNA control + H_2O_2; Lane 3: complex + DNA; Lane 4: Complex + DNA + H_2O_2; Lane 5: Complex + DNA + DTT; Lane 6: Complex + DNA Na N_3; Lane 7: Complex + DNA + DMSO (4 μL); Lane 8: Complex + DNA + EDTA].

DNA. The change in the absorbance values with increasing amounts of CT-DNA were used to evaluate the intrinsic binding constant (K_b), for the complex has a highest binding constant (6.06×10^6 M^{-1}) which may be due to strong electrostatic attraction between the positively charged complex and negatively charged phophodiester backbone of DNA[40] or due to coordinatively unsaturated copper sites in the complex.

Nuclease activity of complex has been studied by agarose gel electrophoresis using pBR 322 DNA in Tris-HCl/NaCl (50 m*M*/ 5 m*M*) buffer (*p*H-7) in the presence/absence of H_2O_2 (Fig. 4). The complex cleaves all supercoiled DNA (Form I) into nicked DNA (Form II) in the presence of the oxidant, H_2O_2. Cleavage activity increases in the presence of a reducing agent (DTT) due to the formation copper (I) complex by catalytic reaction (lane 5). The chelating agent EDTA efficiently inhibits the complex activity, similar to that for nuclease activity. As shown in Fig. 4 (lane 7) nuclease activity of complexes is decreased in the presence of DMSO which acts as a scavenger of free radicals. This is indicative of involvement of the hydroxyl radical in the cleavage process, suggesting that cleavage of DNA takes place by oxidative mechanism.

Supplementary Data

Crystallographic data for $[Cu(L)CH_3OH]_2(ClO_4)_2$ has been deposited with the Cambridge Crystallographic Data Centre, under CCDC reference number 827006. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK, (Fax: +44-1223-336-033; Email: deposit@ccdc.cam.ac.uk of; website http://www.ccdc.cam.ac.uk). Other supplementary data associated with this article, viz., Fig. S1, is available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_52A(03)327-333_SupplData.pdf.

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References

1 G H Jeffery , J Bassett , J Mendham & R C Dennney, *Vogel's Textbook of Quantitative Chemical Analysis*, 5th Edn, (Longman UK) 1989.

2 Ray M S, Mukhopadhyay G, Bhattacharya R, Chaudhuri S, Righi L, Bocelli G & Ghosh A, *Polyhedron*, 22 (2003) 617.

3 Chattopadhyay S, Ray M S, Chaudhuri S, Mukhopadhyay G, Bocelli G, Cantoni A & Ghosh A, *Inorg Chim Acta*, 359 (2006) 1367.

4 Ray M S, Ghosh A, Bhattacharya R, Mukhopadhyay G, Drew M G B & Ribas J, *Dalton Trans*, (2004) 252.

5 Ray M S, Mukhopadhyay G, Drew M G B, Lu T-H, Chaudhuri S & Ghosh A, *Inorg Chem Commun*, 6 (2003) 961.

6 Ray M S, Ghosh A, Chaudhuri S, Drew M G B & Ribas J, *Eur J Inorg Chem*, 15 (2004) 3110.

7 (a) Akbar M A & Livingstone S F, *Coord Chem Rev*, 13 (1974) 101 (b) Chakravorthy A, *Coord Chem Rev*, 13 (1974) 1

8 (a) Sambasiva Reddy P & Hussain Reddy K , *Polyherdron*, 19 (2000) 168; (b) Surendra Babu M S, Krishna P G, Hussain Reddy K, Philip G H, *Indian J Chem*, 47A (2008) 1661

9 Mandal D & Gupta B D, *Organometallics*, 24 (2005) 1501

10 Vijaikanth V, Gupta B D, Mandal D & Shekar S, *Organometallics*, 24 (2005) 4454

11 Gupta B D, Vijakanth V & Singh V, *Organometallics*, 23 (2004) 2069

12 Georgieva I, Tredafilova N & Bauer G, *Spectrochim Acta*, A63 (2006) 403

13 Dhar S, Nethaji M & Chakravarty A R, *Inorg Chim Acta*, 358 (2005) 2437

14 Reddy K H, Reddy P S & Babu P R, *Trans Met Chem*, 25 (2000) 505

15 Saglam N, Çolak A, Serbest K, Dulger S, Güner S, Karabocek S & Belduz A O, *Bio Metals* 15 (2002) 357.

16 Li L Z, Zhao C, Xu T, Ji H W, Yu Y H, Guo G Q & Chao H J, *Inorg Biochem*, 99 (2005) 1076

17 Babu M S, Reddy K & Krishna P G, *Polyhedron*, 26 (2007) 572.

18 Ranganathan D, Patel B K & Mishra R K, *J Chem Soc Chem Commun*, (1994) 107.

19 Magada D, Miller R A, Sessler J L & Ivenrson , *J Am Chem Soc*, 116 (1994) 7439.

20 Marumura K, Endo M & Komiyama M, *J Chem Soc Chem Commun*, (1994) 2019

21 Dhar S, Reddy P A N, Nethaji M, Mahadevan S, Saha M K & Chakravarty A R, *Inorg Chem*, 41 (2002) 3469

22 Cowan J A, *Curr Opin Chem Biol*, 5 (2001) 634.

23 Liu C, Wang M, Zhang T & Sun H, *Coord Chem Rev*, 248 (2004) 147

24 Pyle A M & Barton J K, *Inorg Chem*, 38 (1990) 413

25 O' Halloran, in Metal ions in Biological Systems, Vol 25, edited by H sigel 1989, (Marcel Dekker, New York) p. 105.

26 Martin R B & Marriam Y H, Metal ions in Biological Systems, Vol. 21, edited by H Sigel, (Marcel Dekker, New York) 1987, p. 57.

27 Hussain Reddy K, Surendrababu M, Suresh Babu P & Dayananda S, *Indian J Chem*, 43A (2004) 1233

28 Murali Krishna P, Hussain Reddy K, Pandeya J P & Siddavattam D, *Trans Met Chem* 33 (2006) 661

29 Haribabu P & Hussain Reddy K, *Indian J Chem* 50A (2011) 996

30 Haribabu P, Patil Y P, Hussain Reddy K & Nethaji M, *Trans Met Chem*, 36 (2011) 867; *Inorg Chim Acta*, 392 (2012) 478

31 *SMART and SAINT, Area Detector Control and Integration Software*, (Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA) 1996.

32 Sheldrick G M, *Acta Cryst*, A 46 (1990) 467

33 Sheldrick G M, *SHELXS-97 Program for the Solution of Crystal Structures*, (University of Gottingen, Germany), 1997

34 Brandenburg K & Putz H, *DIAMOND Ver. 3.0 Crystal Impact*, (GbR, Germany) 2004.

35 Tu C, Wu X, Liu Q, Wang X, Xu Q & Guo Z, *Inorg Chem Acta*, 357 (2004) 95

36 Wu B-Y, Gao L-H, Duan Z–M & Wang K-Z, *J Inorg Biochem*, 99 (2005) 1685

37 Sarkar B, Ray M S, Drew M G B, Figuerola A, Diaz C, Gosh A, *Polyhedron*, 25 (2006) 3084.

38 Singh B, Yadav B P & Agrwal R C, *Indian J Chem*, 23A (1984) 441.

39 Kannappan R, Mahalakshmy R, Rajendian T M, Venkatesan R & Sambasiva Rao P, *Proc Indian Acad Sci (Chem. Sci)*, 115 (2003) 1.

40 Wang Y & Okabe N, *Inorg Chim Acta* 358 (2005) 3407.