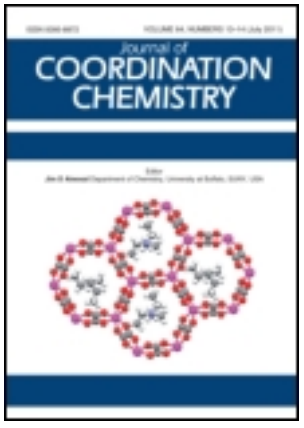

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A Schiff base N-(2-hydroxylacetophenone)-3-oxapentane-1,5-diamine and its copper(II) coordination polymer: synthesis, crystal structure, antioxidation, and DNA-binding properties

Huilu Wu [a], Fei Jia [a], Fan Kou [a], Bin Liu [a], Jingkun Yuan [a] & Ying Bai [a]

[a] School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou, China

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A Schiff base *N*-(2-hydroxylacetophenone)-3-oxapentane-1, 5-diamine and its copper(II) coordination polymer: synthesis, crystal structure, antioxidation, and DNA-binding properties

HUILU WU*, FEI JIA, FAN KOU, BIN LIU, JINGKUN YUAN and YING BAI

School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou, China

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A Schiff base, *N*-(2-hydroxylacetophenone)-3-oxapentane-1,5-diamine (HL) and its Cu(II) coordination polymer, $[Cu(L)(NO_3)]_n$, have been synthesized and characterized. $[Cu(L)(NO_3)]_n$ is a 1 : 1 (Cu : L) polymer, in which copper is six-coordinate with distorted octahedral geometry. The polymer has a 1-D infinite chain structure in which coppers are bridged by a single nitrate. The interaction of HL and complex with calf thymus DNA (CT-DNA) has been investigated; the linear Stern–Volmer quenching constants (K_{SV}) suggest that the two compounds bind to DNA via intercalation. The binding affinity of complex was higher than HL. Antioxidant assay *in vitro* shows that the Cu(II) complex possesses significant antioxidant activities.

Keywords: *N*-(2-hydroxylacetophenone)-3-oxapentane-1,5-diamine; Copper(II) complex; Crystal structure; DNA-binding; Antioxidant

1. Introduction

Self-assembly synthetic routes have been developed in the field of metal–organic complexes or supramolecular architectures [1]. Metal–organic complexes offer the possibility of new functional materials, in which pore size, coordination forms, and functionality could be varied [2, 3]. Schiff bases constitute an important class of ligands studied in coordination chemistry mainly due to their facile synthesis and easily tunable steric, electronic, and catalytic properties [4]. Schiff bases are also important in medicinal and pharmaceutical fields [5, 6]. Recently, Schiff-base complexes were investigated as inhibitors in prostate cancer cells [7], tumor cells [8], and some Schiff-base complexes were reported to possess inhibitory activities against xanthine oxidase and excellent antibacterial activities [9–11].

Interactions of molecules with DNA have attracted attention because of their interference with events in cells of living organisms [12–15]. DNA binding is the critical step for DNA activity. To design effective chemotherapeutic agents and better anticancer drugs, it is essential to explore the interactions of metal complexes with

*Corresponding author. Email: wuhuilu@163.com

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DNA [16, 17]. Understanding of how small molecules bind to DNA will be potentially useful in the design of new drugs, sensitive spectroscopic, or diagnostic probes and reactive agents, which can recognize specific sites or conformation of DNA [18–21]. Metal complexes such as Schiff-base derivatives and their transition metal complexes have been extensively investigated in interactions between complexes and DNA. In addition, the antioxidant activities of the complex were determined by hydroxyl radical ($HO^{\bullet}$) scavenging methods *in vitro*.

2. Experimental

2.1. *Measurements and methods*

The C, H, and N elemental analyses were determined using a Carlo Erba 1106 elemental analyzer. IR spectra were recorded from 4000 to 400 cm^{-1} with a Nicolet FT-VERTEX 70 spectrometer using KBr pellets. Fluorescence spectra were recorded on an LS-45 spectrofluorophotometer. Electronic spectra were taken on a Lab-Tech UV Bluestar spectrophotometer. Antioxidant activities containing the hydroxyl radical ($OH^{\bullet}$) were performed in a water-bath with a 722sp spectrophotometer.

Calf thymus DNA (CT-DNA) and ethidium bromide (EB) were purchased from Sigma. Other reagents and solvents of reagent grade were obtained from commercial sources and used without purification. Tris-HCl buffer and EDTA-Fe(II) solution were prepared using twice-distilled water. The stock solution of complex was dissolved in DMF at 3×10^{-3} mol L^{-1}. All chemicals were of analytical grade. The experiments involving interaction of the ligand and the complex with CT-DNA were carried out in doubly-distilled water buffer containing 5 m mol L^{-1} Tris and 50 m mol L^{-1} NaCl and adjusted to pH 7.2 with hydrochloric acid.

2.2. *Preparation of HL and its complex*

2.2.1. Preparation of 3-oxapentane-1,5-diamine. 3-Oxapentane-1,5-diamine was synthesized following the reported procedure [22]. (Found (%): C, 45.98; H, 11.50; N, 26.76. Calcd. (%): C, 46.25; H, 11.54; N, 26.90). Selected IR data: (KBr ν (cm^{-1})), 1120(ν_{C-O-C}), 3340(ν_{-NH2}).

2.2.2. *N*-(2-hydroxyl acetophenone)-3-oxapentane-1,5-diamine (HL). For the synthesis of HL, 2-hydroxylacetophenone (10 mmol, 1.36 g) in EtOH (5 mL) was added dropwise to a 5 mL EtOH solution of 3-oxapentane-1,5-diamine (10 mmol, 1.04 g). After completion of the addition, the solution was stirred for an additional 4 h at 78°C. After cooling to room temperature, the precipitate was filtered, the product was dried *in vacuo*, and a yellow green crystalline solid was obtained. Yield: 1.5 g (62.5%). (Found (%): C, 64.72; H, 8.25; N, 12.46. Calcd. (%): C, 64.84; H, 8.16; N, 12.60). Selected IR data (KBr ν (cm^{-1})), 1622($\nu_{C=N}$), 1282(ν_{C-O-C}), 3213(ν_{OH}). UV-Vis (DMF): $\lambda = 280, 380$ nm.

2.2.3. $[Cu(L)(NO_3)]_n$. To a stirred solution of HL (0.22 g, 0.1 mmol) in MeOH (5 mL), $Cu(NO_3)_2(H_2O)_3$ (0.241 g, 0.1 mmol) in MeOH (5 mL) was added. Blue sediment formed rapidly was filtered off, washed with MeOH and absolute Et_2O, and dried *in vacuo*. The dried precipitate was dissolved in DMF to form a blue solution, and blue block crystals of $[Cu(L)(NO_3)]$ suitable for X-ray diffraction studies were obtained by vapor diffusion of diethyl ether into the solution for 3 weeks at room temperature. Yield: 0.193 g (41.8%). (Found (%): C, 41.46; H, 5.01; N, 11.95. Calcd. (%): C, 41.56; H, 4.94; N, 12.12). Selected IR data: (KBr ν (cm^{-1})), 1228(ν_{C-O-C}), 1440(ν_{OH}), 1600($\nu_{C=N}$), 1440($\nu_{N=O}$), 1329(ν_{aNO2}), 1062(ν_{sNO2}). UV-Vis (DMF): λ = 278, 376 nm.

2.3. *X-ray structure determination of $[Cu(L)(NO_3)]_n$*

A suitable single crystal was mounted on a glass fiber and intensity data were collected on a Bruker SMART APEX diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 296 K. Data reduction and cell refinement were performed using SAINT [23]. Absorption corrections were carried out by the empirical method. The structure was solved by direct methods and refined by full-matrix least-squares against F^2 using SHELXTL [24, 25].

All hydrogen atoms were found in difference electron maps and subsequently refined in a riding-model approximation with C–H distances ranging from 0.93 to 0.97 Å and $U_{iso}(H) = 1.2\ U_{eq}(C)$ or $U_{iso}(H) = 1.5\ U_{eq}(C)$. Hydrogen atoms bonded to nitrogen were refined independently with the distance constraint of N–H = 0.9 Å. A summary of parameters for data collection and refinement are given in table 1.

2.4. *DNA binding experiments*

EB emits intense fluorescence in the presence of CT-DNA, due to its strong intercalation between adjacent CT-DNA base pairs. Enhanced fluorescence can be quenched by the addition of a second molecule [26, 27]. The extent of fluorescence quenching of EB bound to CT-DNA can be used to determine the extent of binding between the second molecule and CT-DNA. Competitive binding experiments were carried out in buffer by keeping [DNA]/[EB] = 1.13 and varying the concentrations of the compounds. Fluorescence spectra of EB were measured using an excitation wavelength of 520 nm and the emission range was set between 550 and 750 nm. The spectra were analyzed according to the classical Stern–Volmer equation [28]:

$$I_0/I = 1 + K_{SV}[Q]$$

where I_0 and I are the fluorescence intensities at 599 nm in the absence and presence of the quencher, respectively, K_{SV} is the linear Stern–Volmer quenching constant, $[Q]$ is the concentration of the quencher. In these experiments [CT-DNA] = 2.5×10^{-3} mol L^{-1}, [EB] = 2.2×10^{-3} mol L^{-1}.

Viscosity experiments were conducted on an Ubbelodhe viscometer, immersed in a water bath maintained at 25.0 ± 0.1°C. Titrations were performed for the complexes (3 μM), and each compound was introduced into CT-DNA solution (50 μM) present in the viscometer. Data were presented as $(\eta/\eta_0)^{1/3}$ *versus* the ratio of the concentration of the compound to CT-DNA, where η is the viscosity of CT-DNA in the presence of the

compound and η_0 is the viscosity of CT-DNA alone. Viscosity values were calculated from the observed flow time of CT-DNA containing solutions corrected from the flow time of buffer alone (t_0), $\eta = (t - t_0)$ [29].

2.5. *Antioxidation study methods*

Hydroxyl radicals in aqueous media were generated through the Fenton-type reaction [30, 31]. The 3 mL reaction mixtures contained 1.0 mL of 40 μg mL^{-1} aqueous safranin, 1 mL of 1.0 mmol aqueous EDTA-Fe(II), 1 mL of 3% aqueous H_2O_2, and a series of solutions of the tested compound. The sample without the tested compound was used as the control. The reaction mixtures were incubated at 37°C for 30 min in a water-bath. Absorbance at 520 nm was measured and the solvent effect was corrected throughout. The scavenging effect for OH$^{\bullet}$ was calculated from the following expression:

$$\text{Scavenging effect}\% = (A_{\text{sample}} - A_r)/(A_o - A_r) \times 100\%$$

where A_{sample} is the absorbance of the sample in the presence of the tested compound, A_r is the absorbance of the blank in the absence of the tested compound, and A_o is the absorbance in the absence of the tested compound and EDTA–Fe(II).

Table 1. Crystallographic data and data collection parameters for $[Cu(L)(NO_3)]_n$.

Formula	$CuC_{12}H_{17}N_3O_5$
Molecular weight (gm^{-1})	346.83
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	7.172(2)
b	9.887(3)
c	10.202(3)
α	103.611(3)
β	101.587(3)
γ	90.322(3)
Volume (Å^3), Z	687.7(3), 2
Temperature (K)	296(2) K
Calculated density (g cm^{-3})	1.675
Absorption coefficient (mm^{-1})	1.614
$F(000)$	358
Crystal size (mm^3)	0.38 × 0.30 × 0.28
θ range for data collection (°)	2.10–25.00
Reflections collected	4846
Independent reflection	2409 [R(int) = 0.0277]
Index ranges	$-8 \le h \le 8$, $-11 \le k \le 11$, $-12 \le l \le 12$
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2409/0/191
Goodness-of-fit on F^2	1.069
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0362$, $wR_2 = 0.0843$
R indices (all data)	$R_1 = 0.0455$, $wR_2 = 0.0876$
Largest difference peak and hole (e Å^{-3})	0.287 and −0.389

3. Results and discussion

The ligand and Cu(II) complex are stable under the ambient condition. They are remarkably soluble in polar aprotic solvents such as DMF and DMSO; slightly soluble in ethanol, methanol, and chloroform, and insoluble in water.

3.1. *IR and electronic spectra*

In HL, a strong band is found at 1622 cm−^{1} along with a weak band at 1282 cm^{-1}. The former can be attributed to $\nu_{(C=N)}$, while the latter can be attributed to $\nu_{(C-O-C)}$. These bands shift to lower frequency, *ca.* 22–60 cm^{-1}, in the complex, which implies direct coordination of nitrogen and oxygen to copper. Bands at 1440, 1329, and 1062 cm^{-1} indicate that nitrate is bidentate [32], in agreement with X-ray diffraction.

Electronic spectra of the ligands and the metal complexes were recorded in DMF solution at room temperature. The UV bands of L (280, 380 nm) are marginally shifted in complexes, providing evidence for nitrogen and oxygen coordination. Two absorption bands are assigned to $\pi \rightarrow \pi^*$ (benzene) and $n \rightarrow \pi^*$ (C=N) transitions.

3.2. *X-ray structure of complexes*

Selected bond lengths and angles of the Cu complex are listed in table 2. The ORTEP structure of the complex with atom labeling is shown in figure 1. The polymer unit consists of a divalent copper, one fully deprotonated ligand, and one nitrate. The Cu(II) is N_2O_2-chelated by L and is further coordinated by two nitrates. The polymer is $[Cu(L)(NO_3)]_n$ units linked into polymeric chains, where one nitrate connects adjacent copper(II) ions of the symmetry-related unit in an end-to-end bridging mode. The coordination environment at copper is best described as distorted octahedral. An equatorial plane is formed by N1, N2, O1, and O2, where the maximum deviation (O1, N1) by 0.009 Å and the Cu(II) is out of this plane by 0.113 Å. Axial positions are occupied by nitrate O5 and another nitrate O3. The distance between axial O5 and the equatorial plane is 2.450 Å, but the distance between axial O3 and the equatorial plane is 2.536 Å. The bond angle of O3 and O5 is 171.39°, reflecting a relatively distorted octahedral coordination around Cu(II).

N–H $\cdots$ O hydrogen-bonding interactions play important roles in crystal packing in the complex (figure 2); selected hydrogen bonds are listed in table 3. Intermolecular N–H $\cdots$ O hydrogen bonds interlink two adjacent chains into a two-dimensional network.

Table 2. Selected atomic distances (Å) and angles (°) for the complex.

Cu(1)–O(2)	1.874(2)	Cu(1)–N(1)	1.942(3)
Cu(1)–N(2)	1.982(3)	Cu(1)–O(1)	2.015(2)
Cu(1)–O(3)	2.655(2)		
O(2)–Cu(1)–N(1)	94.22(10)	O(2)–Cu(1)–N(2)	97.76(10)
N(1)–Cu(1)–N(2)	165.69(11)	O(2)–Cu(1)–O(1)	173.44(10)
N(1)–Cu(1)–O(1)	83.13(10)	N(2)–Cu(1)–O(1)	84.12(9)
O(2)–Cu(1)–O(3)	87.80(9)	N(1)–Cu(1)–O(3)	90.03(9)
N(2)–Cu(1)–O(3)	82.66(10)	O(1)–Cu(1)–O(3)	86.21(8)

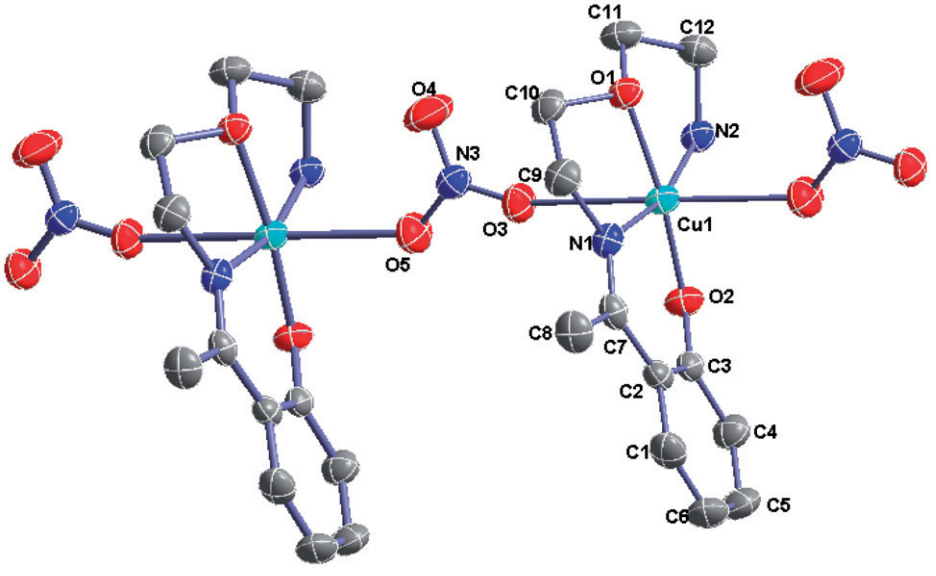

Figure 1. Molecular structure and atom numberings of $[Cu(L)(NO_3)]_n$ with hydrogens omitted for clarity.

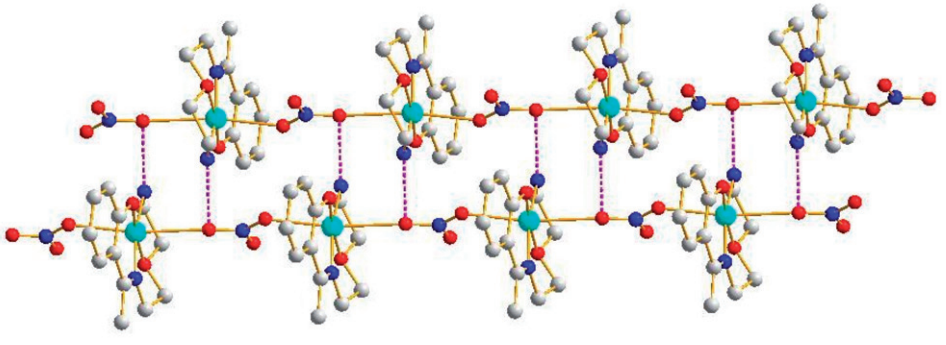

Figure 2. View of N–H–O hydrogen bonds in the complex.

Table 3. Selected hydrogen bonding distances (Å) and angles (°).

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
C(10)–H(13A)···O(3)#1	0.97	2.55	3.200(4)	124.8
C(10)–H(13B)···O(4)#2	0.97	2.53	3.302(4)	136.1
N(2)–H(2A)···O(5)#3	0.90	2.30	3.180(4)	164.1
N(2)–H(2B)···O(2)#3	0.90	2.26	3.152(4)	168.6
N(2)–H(2A)···O(3)#3	0.90	2.50	3.020(4)	117.2

Symmetry transformations used to generate equivalent atoms: $1 = x, y, z$; $\#2 = -x+1, -y+1, -z+1$; $\#3 = -x+1, -y+1, -z$.

The NH_2 groups in the frameworks assemble these chains by intermolecular hydrogen bonds, as illustrated in figure 2.

3.3. *Fluorescence spectroscopic studies*

In general, measurement of the ability of a complex to affect the EB fluorescence intensity in the EB-DNA adduct allows determination of the affinity of the complex for DNA, whatever the binding mode may be. If a complex can replace EB from DNA-bound EB, the fluorescence of the solution will be quenched due to the fact that free EB molecules are readily quenched by surrounding waters [33]. For the ligand and the complex, no emission was observed either alone or in the presence of CT-DNA in the buffer.

The fluorescence intensity of the EB-DNA system greatly decreases upon gradual addition of the compounds. Fluorescence quenching of EB-DNA is shown in figure 3. The Stern–Volmer constant K_{SV} is obtained as the slope of I_0/I *versus* [complex] linear plot. From the inset in figure 3, K_{SV} values are $2.6 \times 10^3\,M^{-1}$ ($R^2 = 0.952$ for 11 points) and $3.3 \times 10^3\,(mol\,L^{-1})^{-1}$ ($R^2 = 0.992$ for 16 points). Compared with DNA-intercalative

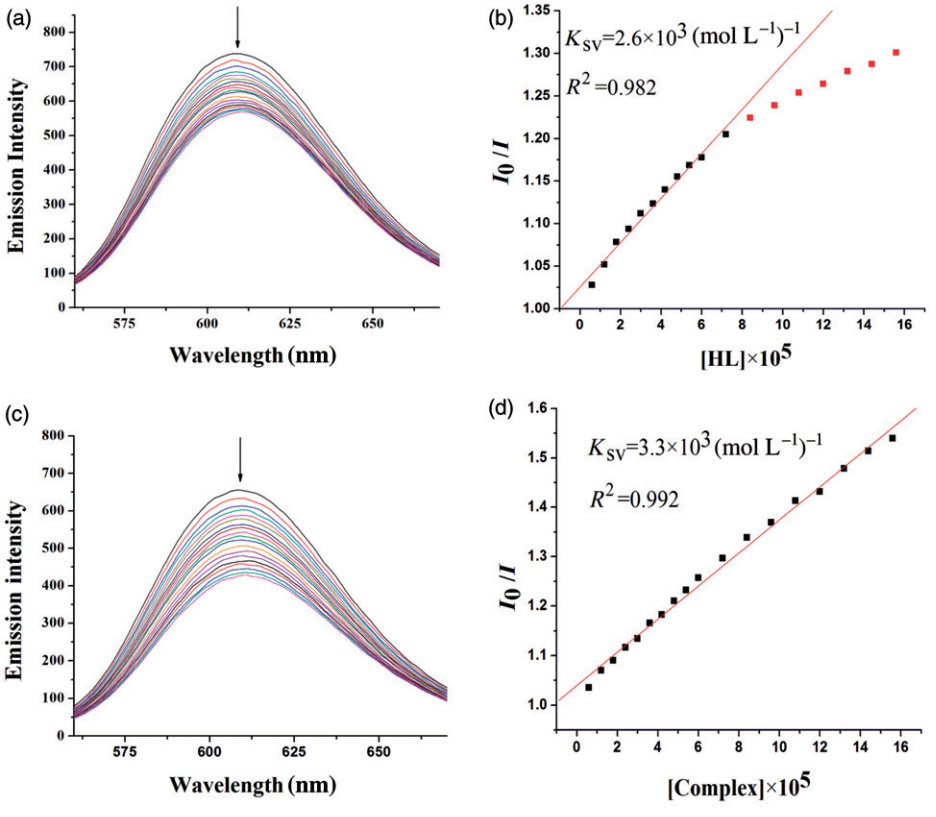

Figure 3. Emission spectra of EB bound to CT-DNA in the presence of free HL (a) and complex Cu(II) (c), $\lambda_{ex} = 520$ nm. The arrows show the intensity changes upon increasing concentrations of the complexes. Fluorescence quenching curves of EB bound to CT-DNA by the free HL (b) and complex Cu(II) (d). (Plots of I_0/I *vs.* [complex].)

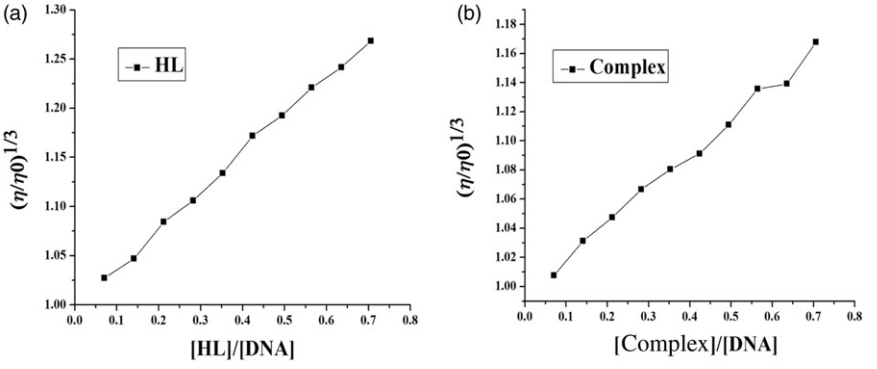

Figure 4. Effect of increasing amounts of the compounds on the relative viscosity at 25.0 ± 0.1°C.

copper complexes of Schiff bases [34–37], the K_{SV} of Schiff base and the Cu(II) complex suggest that the complex probably binds to DNA by intercalation. The ligand and complex can compete for DNA-binding sites with EB and displace EB from the EB-DNA system, which is usually the characteristic of intercalative interaction of compounds with DNA [38]. The binding strength of Cu(II) complex is greater than the free ligand [39].

3.4. *Viscosity measurements*

Optical photophysical techniques are widely used to study the binding model of the ligand, metal complexes, and DNA, but do not give sufficient clues to support a binding model. Therefore, viscosity measurements were carried out to further clarify the interaction of metal complexes and DNA. Hydrodynamic measurements that are sensitive to the length change (i.e., viscosity and sedimentation) are regarded as the least ambiguous and the most critical tests of a binding model in solution in the absence of crystallographic structural data [40, 41]. For increasing ligand and Cu(II) complex amounts, the viscosity of DNA increases steadily. The values of $(\eta/\eta_0)^{1/3}$ were plotted against [complex]/[DNA] (figure 4). In classical intercalation, the DNA helix lengthens as base pairs are separated to accommodate the bound ligand leading to increased DNA viscosity whereas a partial, non-classical intercalation causes a bend (or kink) in DNA helix reducing its effective length, and thereby its viscosity [42].

The effects of the ligand and the Cu(II) complex on the viscosity of CT-DNA are shown in figure 4. The viscosity of CT-DNA is increased steadily with increasing ligand and Cu(II) complex, suggesting that HL and the Cu(II) complex intercalate with CT-DNA. The results from the viscosity experiments confirm the mode of these compounds intercalating into DNA base pairs and already established through absorption spectroscopic studies and fluorescence spectroscopic studies.

3.5. *Antioxidant activity*

Figure 5 depicts the inhibitory effect of the compounds on $OH^{\cdot}$ radicals. The inhibitory activity of the compounds is marked and the suppression ratio for $OH^{\cdot}$ increases with the increase of compound concentration. Usually, mannitol and vitamin C are used as

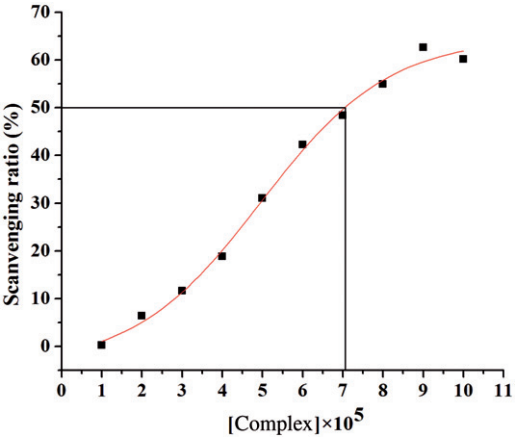

Figure 5. A plot of scavenging percentage (%) *vs.* concentration of the Cu(II) complex (■) on hydroxyl radical.

the standard antioxidant to assess other compounds' antioxidant activities [43]. The 50% inhibitory concentration (IC_{50}) value of mannitol is about 9.6 μM. According to the antioxidant experiments, the IC_{50} of Cu(II) complex is 7.1 μM (figure 5) and HL does not have antioxidant activity, which implies that the Cu(II) complex exhibits better scavenging activity than HL, mannitol, and vitamin C. We suggest that the mechanism of action of Cu(II) complex involves the redox process of the Cu(II) complex [44, 45].

4. Conclusion

N-(2-hydroxylacetophenone)-3-oxapentane-1,5-diamine (HL) and its Cu(II) complex were synthesized and characterized based on the X-ray diffraction and other structural methods. The coordination geometry can best be described as distorted octahedral. The asymmetric unit of the complex is characterized by $[Cu(L)(NO_3)]^-$ units linked into polymeric chains, where one nitrate connects adjacent copper(II)'s of the symmetry-related unit in an end-to-end bridging mode. The DNA-binding experimental results suggest that the Cu(II) complex may bind to DNA in an intercalation mode. In addition, the Cu(II) complex possesses significant antioxidant activities.

Supplementary material

Crystallographic data (excluding structure factors) for the structure in this article have been deposited with the Cambridge Crystallographic Data Center as supplementary publication CCDC 835709. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

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