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Copper(II) complexes with neutral Schiff bases: Syntheses, crystal structures and DNA interactions

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This work is our tribute to Sir P.C. Rây on the eve of his 150th birth anniversary

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ABSTRACT

The synthesis and X-ray structural characterisation of a new Cu(II) complex, $[Cu(L^1)Cl](ClO_4)\cdot CH_3OH$ (**1**) [L^1 = *N*,*N′*-bis((pyridine-2-yl)phenylidene)-1,3-diaminopropan-2-ol], has been described in this work. The structural study reveals that the Cu(II) centre in **1** has a square pyramidal geometry with a trigonality index $\tau = 0.43$, being coordinated by the organic ligand and a chloro group. The interaction of complex **1** and another complex previously reported by our group, $[Cu(L^2)](ClO_4)_2$ (**2**) [L^2 = *N*-(1-pyridin-2-yl-phenylidene)-*N′*-[2-({2-[(1-pyridin-2-ylphenylidene)amino]ethyl}amino)ethyl]ethane-1,2diamine], with calf thymus DNA (CT-DNA) has been investigated using absorption and emission spectral studies. The binding constant (K_b) and the linear Stern–Volmer quenching constant (K_{sv}) have been determined.

1. Introduction

The design and synthesis of new cationic complexes that interact with DNA are of considerable interest nowadays as the affinity and selectivity of molecules in binding to nucleic acids are valuable for the rational design of new diagnostic and therapeutic agents [1–5]. These metal complexes are known to bind to DNA through a series of interactions, such as π-stacking interactions associated with intercalation of aromatic heterocyclic groups between the base pairs, hydrogen-bonding and van der Waals interactions in the case of binding to the groove of the DNA helix [6]. Copper, with its relevant oxidation states +1 and +2, has been extensively used in metal mediated DNA cleavage [2–5]. Copper(II) complexes under certain ligand environments have also been shown to bring about photocleavage of DNA as well as RNA [2–4]. In this present report, we determine the binding constants (K_b) and the linear Stern–Volmer quenching constants (K_{sv}) for the interaction of the new Cu(II) complex $[Cu(L^1)Cl](ClO_4)\cdot CH_3OH$ (**1**) [L^1 = *N*,*N′*-bis((pyridine-2-yl)phe nylidene)-1,3-diaminopropan-2-ol, Scheme 1] and a previously reported complex, $[Cu(L^2)](ClO_4)_2$ (**2**) [L^2 = *N*-(1-pyridin-2-yl-phenylidene)-*N′*-[2-({2-[(1-pyridin-2-ylphenylidene)amino]ethyl}amino) ethyl] ethane-1,2diamine, Scheme 1] [7] with CT-DNA by absorption and emission spectral studies.

2. Experimental

2.1. Materials

High purity 2-benzoylpyridine (Fluka, Germany), copper(II) chloride dihydrate (E. Merck, India), sodium perchlorate (Alfa Aesar, Germany) and 1,3-diaminopropan-2-ol (Aldrich, UK) were purchased from the respective concerns and used as received. The calf thymus (CT) DNA and ethidium bromide (EB) were obtained from Sigma.

Caution! Perchlorate salts of metal ions are potentially explosive, especially in the presence of organic ligands. Only a small amount of material should be prepared and handled with care.

2.2. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed on a Perkin-Elmer 2400 CHNS/O elemental analyzer. IR spectra (KBr discs, 4000–300 cm^{-1}) were recorded using a Perkin-Elmer FT-IR model RX1 spectrometer. Ground-state absorption and steady-state fluorescence measurements were made with a

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[1] These two authors have made an equal contribution to this work.

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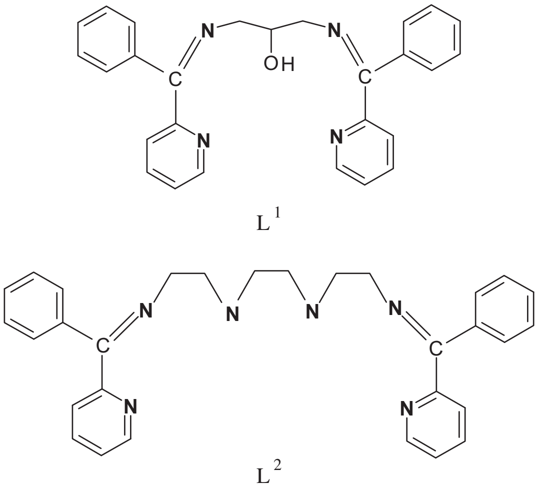

Scheme 1.

Jasco model V-530 UV–Vis spectrophotometer and a Hitachi model F-4010 spectrofluorimeter, respectively.

2.3. Preparation of the Schiff bases and the complexes

The Schiff base L^1 was prepared following a reported method [8] with a little modification. The details are given below:

2-Benzoylpyridine (0.366 g, 2 mmol) was refluxed with 1,3-diaminopropan-2-ol (0.086 g, 1 mmol) in 30 ml dehydrated alcohol. After 10 h the reaction solution was evaporated under reduced pressure to yield a gummy mass, which was dried and stored *in vacuo* over $CaCl_2$ for subsequent use. Yield, 0.469 g (72%). *Anal.* Calc. for $C_{27}H_{23}N_4O$ (L^1): C, 77.23; H, 5.52; N, 13.34. Found: C, 76.52; H, 4.90; N, 12.92%. IR (KBr, cm^{-1}): 1632 (s), 3375 (s).

The synthetic procedure for complex **2** is described elsewhere [7]. Complex **1** was synthesized from the chloride salt of copper(II) using a 1:1 molar ratio of the metal salt and L^1 in MeOH at room temperature. X-ray quality single crystals of **1** separated out within a week.

2.3.1. Preparation of **1**

A methanolic solution (5 cm^3) of L^1 (0.419 g, 1 mmol) was added dropwise to a solution of $CuCl_2 \cdot 2H_2O$ (0.170 g, 1 mmol) in the same solvent (10 cm^3). $NaClO_4$ (0.122 g, 1 mmol) was then mixed in the reaction mixture. The deep green solution was filtered and the supernatant liquid was kept in air for slow evaporation.

Yield: 0.469 g (72% based on metal salt). *Anal.* Calc. for $C_{28}H_{28}N_4O_6Cl_2Cu$ (**1**): C, 51.66; H, 4.33; N, 8.60. Found: C, 51.30; H, 4.17; N, 8.06%. IR (KBr, cm^{-1}): 1618, 1593 ($\nu_{C=N}$), 472 (ν_{Cl}), 3224 (ν_{OH}), 1286, 1117, 1084, 625 (ν_{ClO_4}); UV–Vis (λ_{max}, nm): 268.

2.4. X-ray diffraction studies

Single crystal data of **1** were collected on a Bruker AXS KAPPA APEX II diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å) at 295(2) K. Systematically absent reflections led to the identification of space group *P*212121 for **1**. Of the 26 597 total reflections for the complex, 7037 with $[I > 2\sigma(I)]$ were used for structure solutions. The structures were solved by direct methods, and the structure solution and refinement were based on $|F^2|$. All non-hydrogen atoms were refined with anisotropic displacement parameters whereas hydrogen atoms were placed in calculated positions were possible and given isotropic *U* values 1.2 times that of the atom to which they are bonded. The final differences Fourier map showed the maximum and minimum peak heights at 0.775 and -0.680 e Å^{-3} for **1** with no chemical significance. All calculations were carried out using SHELXL-97 [9] and ORTEP-32 [10]. The crystal data and data collection parameters are listed in Table 1.

Table 1
Crystal data and structure refinement parameters for **1**.

Empirical formula	$C_{28}H_{28}N_4O_6Cl_2Cu$
Formula weight	650.98
T (K)	295(2)
Wavelength (Å)	0.71073
Crystal system	orthorhombic
Space group	*P*212121
Unit cell dimensions	
a (Å)	8.3120(2)
b (Å)	9.8493(2)
c (Å)	34.7109(7)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	2841.69(11)
Z	4
D_{calc} (mg/m^3)	1.522
Absorption coefficient (mm^{-1})	1.006
F(000)	1340
Crystal size (mm^3)	0.45 × 0.35 × 0.32
Theta range for data collection (°)	2.15–28.33
Index ranges	$-11 \leqslant h \leqslant 11$, $-13 \leqslant k \leqslant 13$, $-45 \leqslant l \leqslant 39$
Reflections collected	26 597
Independent reflections	7037 [$R_{int} = 0.0570$]
Completeness to theta = 28.33°	99.4%
Absorption correction	semi-empirical from equivalents
T_{max} and T_{min}	0.725 and 0.662
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	7037/1/371
Goodness-of-fit (GOF) on F^2	1.047
Final *R* indices $[I > 2\sigma(I)]$	$R_1 = 0.0584$, $wR_2 = 0.1555$
R indices (all data)	$R_1 = 0.0875$, $wR_2 = 0.1691$
Absolute structure parameter	0.013(19)
Largest difference in peak and hole (e Å^{-3})	0.775 and -0.680

3. Results and discussion

3.1. Synthesis and formulation

The ligand L^1 was synthesized by refluxing 1,3-diaminopropan-2-ol with 2-benzoylpyridine in 1:2 molar ratio in dehydrated alcohol. Compound **1** was prepared using the chloride salt of copper(II) and L^1 in a proper molar ratio as appeared in the compound. The compound was recrystallised from a methanol–water mixture. It was characterised using microanalytical, spectroscopic and other physicochemical results. The exact coordination sphere was determined by single crystal X-ray crystallography. In the IR spectrum the well resolved peak at 1592 cm^{-1} is attributed to ν(C=N) [11]. The compound shows weak bands in the range 2980–2900 cm^{-1} that are assignable to the aliphatic C–H stretching frequency.

3.2. X-ray structures

Oak Ridge Thermal Ellipsoid Plots (ORTEP) of **1** and **2** are represented in Figs. 1 and 2. The structure of **2** is described in our previous report [7]. Bond angles and distances for the structure of **1** are listed in Table 2. The coordination geometry at the copper(II) centre of **1** is best described as a square pyramid, as exemplified by its τ value (τ = 0.43) [12][2] with a CuN_4Cl chromophore. The imine

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[2] $\tau = (\alpha - \beta)/60$; α = largest L–M–L bond angle, β = second largest bond angle; If the τ value is in between 0 and 0.5, then the geometry is square pyramid (Sq py) and if the value is in between 0.5 and 1.0, then the geometry is trigonal bipyramid (TBP).