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Synthesis, Reactivity and CT-DNA Study of Copper(II) Complexes with 1,2-bis(3-pyridylmethylthio)ethane

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ABSTRACT: On reaction of 1,2-bis(3-pyridylmethylthio)ethane (L^1)containing nitrogen-sulphur donor sets with copper(II) perchlorate, hexahydrate,copper(II) nitrate, trihydrate and copper(II) chloride, dihydratein alcoholic medium, three different color copper(II) complexes of L^1 were synthesized and isolated in pure form. The complexes were characterized by physicochemical and spectroscopic methods. From characterization it has been proposed that the three complexes may be $[Cu(L^1)(H_2O)_2](ClO_4)_2$ (1), $[Cu(L^1)(H_2O)_2](NO_3)_2$ (2), $[Cu(L^1)Cl]Cl$ (3).Reactivity of complexes 1 and 2 towards pseudo-halide ions in acetonitrile at ambient temperature has been studied. These copper(II) complexes have been isolated from the reaction mixtures and characterized by physico-chemical and spectroscopic tools. Biological activity of complex (1) towards calf thymus DNA has been examined systematically and groove binding behaviour of the copper(II) complex 1 with calf thymus DNA has been observed from the spectral study.

Keywords: copper complex, Nitrogen-Sulphur ligand, Reactivity, DNA binding

INTRODUCTION

Copper(II) is a plastic metal ion[1]which displays a variety of coordination numbers and geometries forms compounds of different coordination numbers with many kinds of irregular coordination geometries such as octahedral six-coordinate, square pyramidal or trigonal-bipyramidal five-coordinate, and tetrahedral or square planar four-coordinate Cu(II) complexes [2-6]. These structural changes have been associated with the large reorganization effects observed for Cu^I/Cu^{II} transitions and the energy associated with this charge has been utilized by the majority of biochemical systems in copper-containing metallo-enzymes [4-7]. It is well known that thioether donors destabilize the copper(II) state[8-11] and that structural flexibility is more pronounced in copper (II) complexes. The interesting spectroscopic, electrochemical, magnetic and biological properties have been influenced by the structural variability in penta-coordinated complexes[12-14] as the molecular structures of five coordinated copper(II) complexes show an extensive range from trigonalbipyramidal to square pyramidal depending on the ligands,co-ligands, and counterions[15-22]. The redox nature of the complexes are two important properties which control the nuclease activity of the complexes [19, 20].

In continuation of our research work on copper complex [21, 22], here, we report copper(II) complexes ofbis (3-pyridyl-methylthio) alkanetetradentate N2S2 donor. In previouswork [21] 2-picolyl chloride was used for synthesizing the organic moiety.Here,the hexa-coordinated complexes formulated as $[Cu(L^1)(H_2O)_2](ClO_4)_2$ (**1**), $[Cu(L^1)(H_2O)_2](NO_3)_2$ (**2**), and penta-coordinatedcomplex ($[Cu(L^1)Cl]Cl$ (**3**)) are mononuclear which have been characterized by spectroscopic studies. The complexes **1-3** changed to penta-coordinated copper(II) complexes formulated as $[Cu(L^1)X]Y$(**1a, 1b, 2a & 2b**) [where X = azide/thiocyanate] on reaction with pseudohalides at room temperature in acetonitrile. As a result, two types of copper(II) complexes in terms of their coordination geometry have been obtained due to the absence (for **1** and **2**) or presence (for **3**, **1a, 1b, 2a & 2b**) of co-ligand pseudohalide ions in the same regulated chemical

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environment of N2S2 donor sets. CT-DNA and protein binding study have been done on complexes **1**, **2** and **3**.

EXPERIMENTAL

Materials and Physical Measurements

All chemicals and reagents were obtained from commercial sources and used as received. Solvents were distilled from an appropriate drying agent [21, 22].

The elemental (C, H, N) analyses were performed on a Perkin Elmer model 2400 elemental analyzer. Copper analysis was carried out by Varian atomic absorption spectrophotometer (AAS) model-AA55B, GTA using graphite furnace. Electronic absorption spectra were recorded on a JASCO UV-Vis/NIR spectrophotometer model V-570. IR spectra (KBr discs, 4000–300 cm^{-1}) were recorded using a Perkin-Elmer FTIR model RX1 spectrometer.the fluorescence spectra on a Fluorometer Hitachi-2000. The room temperature magnetic susceptibility measurements were performed by using a vibrating sample magnetometer PAR 155 model. Electrochemical measurements were recorded on a com-puter controlled EG&G PAR model 270 VERSTAT electrochemical instruments with TEAP as supporting electrolyte, a Pt-disk as working electrode and a Pt-wire as auxiliary electrode. All the measurements were made at 298 K with acetonitrile as solvent. Molar conductances (L_M) were measured in a systronics conductivity meter 304 model using ~10^{-3} $mol.L^{-1}$ solutions in appropriate organic solvents. Thermal analyses of the complexes (**1, 2** and **3**) were carried out using Perkin-Elmer Diamond TG/DT analyzer.

DNA Binding Experiments

Tris-(hydroxymethyl)aminomethane-HCl (Tris–HCl) buffer solution (pH=7.30) was used in all the experiments involving CT-DNA. The CT-DNA used in the experiments was sufficiently free from protein as the ratio of UV absorbance of the solutions of DNA in tris–HCl at 260 and 280 nm (A_{260}/A_{280}) was almost ≈ 1.9 [23]. The concentration of DNA was determined with the help of the extinction coefficient (ε_{260}= 6600 L $mol^{-1}cm^{-1}$) of DNA solution[24]. Stock solution of DNA was always stored at 4 °C and used within 4 days. Stock solution of the copper(II) complex was prepared by dissolving the complex in DMSO and suitably diluted with tris–HCl buffer to the required concentration for all the experiments. Absorption spectral titration experiment was performed by keeping constant the concentration of the copper(II) complex and varying the CT-DNA concentration. To eliminate the absorbance of DNA itself, equal solution of CT-DNA was added both to the copper(II) complex solution and to the reference solution.

In the ethidium bromide (EB) fluorescence displacement experiment, 5 µL of the EB tris–HCl solution (1 mmol L^{-1}) was added to 1 mL of CT-DNA solution (at saturated binding levels)[25], stored in the dark for 2 h. Then the solution of the copper(II) complex was titrated into the CT-DNA/EB mixture and diluted in tris–HCl buffer to 5 mL to get the solution with the appropriate copper(II) complex/CT-DNA mole ratio. Before measurements, the mixture was shaken up and incubated at room temperature for 30 min. The fluorescence spectra of EB bound to DNA were obtained at an emission wavelength of 522 nm in the Fluorimeter (Hitachi-2000).

For the viscosity measurements, CT-DNA samples approximately 200 base pairs in length were prepared by sonication in order to minimize complexities arising from DNA flexibility[26]. Each sample was measured three times, and an average flow time was calculated. Relative viscosities for CT-DNA in the presence and absence of the complex were calculated from the relation $\eta = (t - t_0)/t_0$, wheret is the observed flow time of DNA-containing solution, and t_0 is that of Tris–HCl buffer alone.

Preparation of the Ligand

The preparation of 1,2-bis(3-pyridylmethylthio) ethane (L^1) has been carried out following common procedure with slight modification[21]. The procedure for the preparation of 1,2-bis(3-pyridylmethylthio) ethane, (L^1) is here described. An ethanolic solution of 3-picolyl chloride, hydrochloride (1.64 g, 10.0 mmol) was added to 1,2-ethandithiol (0.47 g, 5.0 mmol) in dry ethanol containing sodium ethoxide (0.46 g 20.0 mmol) at low temperature (0°-5 °C). Then this mixture was allowed to stir at room temperature for 0.5 h and then it was refluxed for 2 h. The mixture was cooled to room temperature, water was added and finally the ethanol was off by rotary evaporator.

The product was extracted into dichloromethane and dried by using $NaHSO_3$. The product, 1,2-bis(3-pyridylmethylthio)ethane (L) was obtained as a yellow oil by removing the dichloromethane by rotary evaporator. The other products were also obtained as liquids. Finally the products were verified by ^1H NMR spectroscopy.

Preparation of Cu(II) Complexes (1)

To prepare these copper(II) complexes (**1,2** and **3** with L) a common procedure were followed as described below, using copper(II) salts and the respective organic compounds(L) in equimolar ratio. For complex **1**, L^1 (276.0 mg, 1.0 mmol) and copper perchlorate, hexahydrate, for complex **2**, L^1 (276.0 mg, 1.0 mmol) and copper nitrate, trihydrate and for complex **3**, L^1 (276.0 mg, 1.0 mmol) and copper chloride, dihydrate were mixed with 1.0 mmol of copper(II) salts, and the mixtures were stirred for 4 h in methanol. Then the precipitates from respective resulting mixture were collected at room temperature. Precipitates were washed by water, methanol and recrystalized by acetonitrile solvent and dried in *vacuo*. Yield: 80-85%.

Preparation of Cu(II) Complexes (1a &1b) and (2a &2b)

To the suspension of the complex $[Cu(L^1)(H_2O)_2](ClO_4)_2$ (1)or $[Cu(L^1)(H_2O)_2](NO_3)_2$ (2) (1.0 mmol) in acetonitrile (30 mL), the solution of sodium sodiumazide (65 mg) (for a) or potassium thiocyanate (97.1 mg) (for b) in methanol-water was added dropwise during a period of 15 min. The mixture was stirred for 4 h at room temperature. Then the clear filtrate was collected from the resulting solution. The crystalline products were obtained from the filtrates by allowing slow evaporation of the solvent at room temperature. Yield: 70-80%.

RESULTS AND DISCUSSION

Ligands and Complexes

The copper(II) complexes were obtained in good yield from the reaction of different copper(II) saltswith equimolar amounts of the respective organic moieties in the methanol medium. The organic moieties (L^1)(depicted in Scheme 1) act as tetradentate neutral ligands with four NSSN donor centers in these complexes.

Microanalytical data (**Table S1**) confirm the composition of the complexes. Monomericcomplexes (**1, 2, 3**) are soluble in DMF but sparingly soluble in acetonitrile and methanol.The conductivity measurement of complexes **1, 2** and **3** in DMF shows conductance of 145, 140 and 115Λo mol^{-1} cm^{-1}, respectively,The values suggest that the complexes **1**and **2** exist as 1:2 electrolyte while complex **3** shows 1:1 electrolyte. Form AAS study it reveals that one copper atom is present in the proposed chemical formula of the complexes. The results of TGA of the complex **1** and **2** showed an initial mass loss between 150-180 °C corresponding to the loss of two coordinated water molecules due to the presence of the intermolecular H-bonding with nitrate molecules.

Reactivity of Complexes 1, 2 and 3

Reactivity of complexes **1**and **2** towards pseudo-halide ions in actenotrile at ambient temperature has been studied. On reaction of complexes **1** and **2** with sodium azide (NaN_3) and potassium thiocyanate (KSCN), **1**and **2** were converted to $[Cu(L^1)(N_3)]ClO_4$ (**1a**) and $[Cu(L^1)(SCN)]ClO_4$ (**1b**), $[Cu(L^1)(N_3)]NO_3$ (**2a**) and $[Cu(L^1)(SCN)]NO_3$ (**2b**) respectively. Here all the complexes formed after adding pseudohalide ions are converted from hexa-coordinated complex to peta-coodinated complex. Two water molecules are replaced by one pseudohalide ions.

Microanalytical data of complexes 1, 2 are tabulated in Table S1. The complexes are soluble in both acetonitrile and DMF. The conductivity measurement of complexes in DMF are in the range of 110 - 125 Λo mol^{-1} cm^{-1} at 300 K. and behave as 1:1 electrolytes in solution. At room temperature the magnetic moment (m) of all the complexes are in the range of 1.78 to 1.83 B.M. which are equivalent to one unpaired electron, as expected, in each case. But complexes 1a, 1b, 2a, 2b and 3 don't show any initial mass between 150 and 180°C and from these data it may be concluded that two water molecules of complexes 1 and 2 have been substituted by one pseudohalide ions.

SPECTRAL STUDIES

IR Spectra

Infrared spectral data of all the complexes **1, 2** and **3** has been tabulated in the Table S2. Complex

1showsanintense band at approximately 1090 cm^{-1} along with a weak band at 624 cm^{-1}, which have been assigned to $\nu_{s(ClO4)}$ and $\nu_{as(ClO4)}$ respectively (Fig. 1). Complex **2** exhibits an intense band at *ca.* 1380 cm^{-1} which has been assigned to ν_{NO3}. In IR spectra of all the complexes, the bands at 1469-1478 cm^{-1} for $\nu_{C=N}$ at 758-761 cm^{-1} forn$_{C-S}$ were observed. In addition to these, the characteristic intense band *ca.* 2035 cm^{-1} in complex **1a** and **2a** (Fig. 3) and the strong band *ca.* 2085 cm^{-1} and a weak band *ca.* 776 cm^{-1} in complex **1b** and **2b** (Fig. 2) confirm the presence of terminal end-on azide [27] and the N-bonded SCN [28], respectively. The presence of water molecules is confirmed by a broad band (3500 – 3200 cm^{-1}). The IR spectra also show bands corresponding-rr (H_2O) (729 cm^{-1}) and ρ_w (H_2O) (631 cm^{-1}) which indicate the presence of coordinated water molecules.

Figure 1: IR spectrum of complex **2**

Figure 2: IR spectrum of **2b**

Figure 3: IR spectrum of **2a**

UV-Vis Spectra

The electronic absorption spectra of the complexes **1**,**2** and **3** were recorded at room temperature using DMF as solvent and the data are tabulated in Table S3. All the spectra exhibit a band above 320 nm assignable to theS(σ) $\rightarrow$ Cu(II) transition[29] along with the transition at high energy region corresponding to intramolecular $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions[30]. A characteristic d-d absorption band above 650 nm in the electronic spectra of all the complexes has been also observed. This result may be assignable to the existence of the trigonalbypyramidal geometry of the complexes (**a** and**b** of **1** and **2**, and **3**) in solution [31-33]. UV-Vis spectrum of complex **1a** is represented in Fig. 4.

Figure 4: A representative UV-Vis spectrum of **1a** in DMF

Electrochemistry

Redox properties of complexes **1**, **2** and **3** were examined by cyclic voltametry using a Pt-disk working electrode and a Pt-wire auxiliary electrode in dry MeOH and in presence of [*n*-$Bu_4N]ClO_4$ as supporting electrolyte. In solution all compounds displayed a quasi-reversible voltammogram in the range of -287 to -373 mV for Cu(II)/Cu(I) redox couple with ΔE = 106-182 mV. The potentials are expressed with reference to Ag/AgCl electrodes and the values have been tabulated in Table S3. Arepresentative cyclic voltammogram of **1a** has been shown in Fig. 5.

Figure 5: Arepresentative CV diagram of copper complex **1a** in dimethylformamide (DMF) at scan rate of 100 mVs^{-1}

Voltammetric parameters are studied in the scan rate interval of 50-400 mVs^{-1}. The ratio between the cathodic peak current and the square root of the scan rate ($i_{pc}/v^{1/2}$) is approximately constant. The peak potential shows a small dependence with the scan rate. The ratio i_{pc} to i_{pa} is close to unity. From these data, it can be deduced that the redox couple is related to a quasi-reversible one-electron transfer process controlled by diffusion.

DNA-binding Studies

The interaction of copper(II) complex1 with calf thymus DNA (CT-DNA) has been investigated by absorption and emission spectral studies in fig. 6.

Figure 6: Electronic spectral titration of complex **1**with CT-DNA at 271 nm in tris-HCl buffer. Arrow indicates the direction of change upon the increase of DNA concentration

Electronic absorption spectroscopy is an effective method to examine the binding modes of metal complexes with DNA. In general, binding of the metal complex to the DNA helix is testified by an increase of the CT band of copper(II) complex due to the involvement of strong interactions between an aromatic chromophore of complex and the base pairs of DNA[34].

In order to further illustrate the binding strength of the copper(II) complexes with CT-DNA, the intrinsic binding constant Kb was determined from the spectral titration data using the following equation [35]:

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

where [DNA] is the concentration of DNA, ε_f, ε_a and ε_b correspond to the extinction coefficient, respectively, for the free copper(II) complex, for each addition of DNA to the copper(II) complex and for the copper(II) complex in the fully bound form. A plot of $[DNA]/(\varepsilon_a - \varepsilon_f)$ versus [DNA], gives K_b, the intrinsic binding constant as the ratio of slope to the intercept. From the $[DNA]/(\varepsilon_a - \varepsilon_f)$ versus [DNA] plot (Fig. 7), the binding constant K_b for the copper (II) complex 4 was estimated to be 1.5 x 10^5 M^{-1} (R^2 = 0.93964 for five points).

Figure 7: Plot of $[DNA]/(\varepsilon_a - \varepsilon_f)$ vs .[DNA] for the absorption titration of CT-DNA with the copper (II) complex**1** in Tris-HCl buffer

Fluorescence intensity of EB bound to DNA at 522 nm shows a decreasing trend with the increasing concentration of the copper (II) complex (Fig. 8). Pink colored spectrum indicates the maximum binding with copper(II) complex replacing EB. The quenching of EB bound to DNA by the copper(II) complexes are in agreement with the linear Stern–Volmer equation[36]:

Figure 8: Emission spectra of the CT-DNA–EB system in tris–HCl buffer upon the titrationof the copper(II) complex **1**. λex = 522 nm. Arrow shows the intensity change upon the increase of the complex concentration.

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

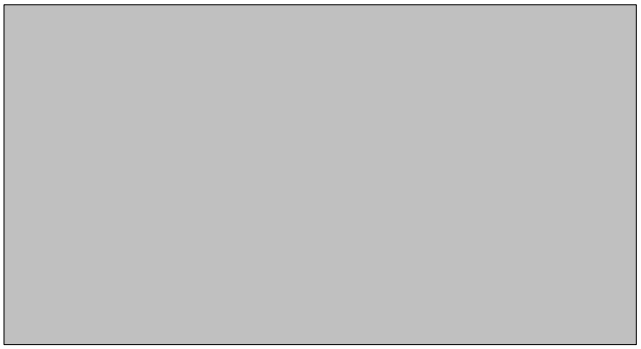
where I_0 and I represent the fluorescence intensities in the absence and presence of quencher, respectively. K_{sv} is a linear Stern–Volmer quenching constant, Q is the concentration of quencher. In the quenching plot (Fig. 9) of I_0/I versus [complex], K_{sv} value is given by the ratio of the slope to intercept. The K_{sv} value for the copper (II) complex is 0.13×10^4 (R^2 = 0.96561for five points), suggesting a strong affinity of the copper (II) complex to CT-DNA.

Figure 9: plot of I_0/I vs. [complex] for the titration of nickel (II) complex **3** with CT-DNA-EB system in Tris-HCl buffer

Thermogravimetric Analysis

The powder samples of complexes **1-2** was analysed using a TGA apparatus under 20 mL min^{-1} flowing nitrogen (Fig. 10).

Figure 10: TGA-DTA curve of the complex **1a** at the rate of 20 °C/min.



Scheme 1: Ligand's structure andsynthetic route of the complexes

The temperature was increased at a rate of 20°C min^{-1} from 40 to 500°C. The intermediate stages of decomposition were readily assigned for these complexes. The results of TGA of the complex **1**and **2** showed an initial mass loss between 150-180°C corresponding to the loss of two coordinated water molecules due to the presence of the intermolecular H-bonding with nitrate molecules This loss process above 180°C for all the complexes lead to the decomposition of the complexes. DTA curve showed the exothermic peak at 179°C. But complexes **1a**, **1b**, **2a**, **2b** and **3** don't show any initial mass between 150 and 180°C and from these data it may be concluded that two water

Table 1
Microanalytical[a] and Physicochemical data of 1 - 4

Compds.	*Elemental analyses[a] %*					
	C	*H*	*N*	*Cu*	*Magnetic moment[b] μ, B. M.*	*Conductance Λo, mho. mol^{-1}cm^{-1}*
1	31.21 (31.10)	3.67 (3.73)	5.23 (5.18)	11.87 (11.94)	1.82	231[d]
1a	34.94 (34.85)	3.27 (3.35)	14.48 (14.52)	13.31 (13.38)	1.83	82[c]
1b	36.20 (36.14)	3.29 (3.24)	8.47 (8.43)	12.89 (12.95)	1.81	85[c]
2	33.61 (33.56)	4.10 (4.02)	11.23 (11.19)	12.81 (12.88)	1.82	232[d]
2a	37.81 (37.78)	3.67 (3.63)	18.99 (18.90)	14.41 (14.51)	1.78	130[d]
2b	39.16 (39.08)	3.46 (3.50)	12.21 (12.16)	13.81 (14.00)	1.79	125[d]
3	40.89 (40.81)	3.96 (3.92)	6.78 (6.80)	15.61 (15.67)	1.76	145[d]

[a]Calculated values are in parenthesis; [b]at room temperature; [c]in DMF; [d]in acetonitrile

Table 2
IR data of Cu(II) complexes

Compds.	*IR data (cm^{-1})*							
	$\nu_{(C=N)}$	$\nu_{(NO3^-)}$	$\nu_{(C-S)}$	$\nu_{(NCS)}$	$\nu_{(N3)}$	$\nu_{(Cu-Cl)}$	$\nu_{(ClO4^-)}$	$\nu_{(H2O)}$
1	1472	-	761	-	-	-	1090, 624	3367
1a	1472	-	760	-	2037	-	1088, 626	-
1b	1469	-	759	2085	-	-	1089, 625	-
2	1472	1381	762	-	-	-	-	3356
2a	1477	1384	760	-	2035	-	-	-
2b	1478	1382	759	2084	-	-	-	-
3	1478	-	759	-	-	321	-	-

Table 3
Electronic spectra and cyclic voltammetry data for the copper complexes

Compds.	*λnm (ε)[a] (ε, dm^3 mol^{-1} cm^{-1})*	*Electrochemical data[b] E°', mV(ΔE$_p$, mV) [E$_{pa}$ mV E$_{pc}$ mV]*
1a	272 (s, 9,512), 360 (s, 3,012), 657(b, 112)	-435 (124) [-373, -497]
1b	281 (s, 9,711), 361 (s, 2,905),658 (b, 117)	-387 (132) [-321, -453]
2a	230(s,10,157),261 (s, 9,859), 328 (s, 2,562), 652 (b, 167)	-378 (182) [-287, -469]
2b	231 (s, 9,805), 261 (s, 9,435), 326 (s, 2,612), 648 (b, 165)	-398 (106) [-345, -451]

[b]scan rate of 100 mVs^{-1}

molecules of complexes 1 and 2 have been substituted by one pseudohalide ions.

CONCLUSION

Two copper (II) complexes with tetradentate N2S2 donor ligand (L^1) formulated as $Cu(L^1)(H_2O)_2](ClO_4)_2$ (**1**) and $[Cu(L^1)(H_2O)_2](NO_3)_2$(**2**) were obtained from the reaction mixture of the ligands and copper(II) salts where complex **3** was formed from the reaction with copper chloride and organic moiety (L^1). On reaction with pseudohalides (azideand thiocyanate ions) in acetonitrile at room

temperature, the complexes, **1** and **2** are changed to pseudo-halide containingcopper(II) complexes. From this study it may be mentioned that pseudo-halide containing copper(II) complexes could be obtained by replacing two aquo molecules selectively due to the plasticity of the coordination zone of copper (II) ion depending upon the coordinated ligand. DNA binding study was performed using copper **1** and **2** complexes. It has been shown that copper complexes (**1** and **2**) similar binding affinity with CT-DNA. From the binding study it reveals that copper complexes have good binding affinitywith CT-DNA.

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