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Coordination behavior of 3,4-bis(2-pyridylmethylthio)toluene with copper(II) ions: Synthesis, structural characterization and reactivity, and DNA binding study of the dinuclear copper(II) complex

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ABSTRACT

On reaction of different copper(II) salts with 3,4-bis(2-pyridylmethylthio)toluene (L) having neutral tetradentate NSSN donor set in different chemical environments, two mononuclear copper(II), one dinuclear copper(I) and one dinuclear copper(II) complexes, formulated as $[Cu^{II}(L)(H_2O)_2](NO_3)_2$ (**1**), $[Cu^{II}(pic)_2]$ (**2**), $[Cu^{I}_2(L)_2](ClO_4)_2$ (**3**) and $[Cu^{II}_2(L)_2Cl_2](ClO_4)_2$ (**4**), respectively, were isolated in pure form [where pic = picolinate]. All the complexes were characterized by physicochemical and spectroscopic methods. The product of the reactions are dependent on the counter anion of copper(II) salts used as reactant and on the reaction medium. Complexes **1** and **4** were obtained with nitrate and perchlorate copper(II) salts, respectively. On the other hand, C–S bond cleavage was observed in the reaction of L with copper(II) chloride to form *in situ* picolinic acid and complex **2**. Dinuclear complexes **3** and **4** were separated out when copper(II) perchlorate was allowed to react with L in methanol and in acetonitrile, respectively, under aerobic condition. The X-ray diffraction analysis of the dinuclear complex **3** shows a highly distorted tetrahedral geometry about each copper ion. Complex **4** is converted to **3** in acetonitrile in presence of catechol. The spectral study of complex **4** with calf thymus DNA is indicative of a groove binding mode interaction.

1. Introduction

The coordination chemistry of dinuclear copper(I/II) complexes has received increased attention over the last decades [1–5]. This is mainly due to the potential application of these complexes their potential applications in metallosupramolecular assemblies [6–10], photosensitization reactions [5,6], bioinorganic chemistry [11], medicine [12] and catalysis [13]. Many efforts have been devoted to the design and synthesis of new multidentate ligands that are able to address the coordination geometry and the properties of copper(I/II) complexes [14–17]. With flexible polydentate ligands, the competition between bridging and chelating coordination mode is an important factor towards the synthesis of mono, di, and polynuclear metal complexes [18,19].

Considering the above facts and in continuation of our research efforts [20–22] to explore the reactivity of different organic moieties with nitrogen–sulfur donor centres with transition metal ions, we report here on the coordination behavior of a newly designed 3,4-bis(2-pyridylmethylthio)toluene ligand (L) with copper(II) ions in different chemical environments. The reaction of L with various copper(II) salts carried out in different media, two mononuclear copper(II), one dinuclear copper(I) and one dinuclear copper(II) complexes formulated as $[Cu^{II}(L)(H_2O)_2](NO_3)_2$ (**1**), $[Cu^{II}(pic)_2]$ (**2**), $[Cu^{I}_2(L)_2](ClO_4)_2$ (**3**), and $[Cu^{II}_2(L)_2Cl_2](ClO_4)_2$ (**4**), respectively, were obtained [where pic = picolinate]. It has been observed that the counter anion of copper(II) salt used as reactant and the reaction medium govern the product of the reactions. The complexes have been characterized by physicochemical and spectroscopic tools along with X-ray structural analysis of **3**. In continuation of our interest [23], DNA binding study of dinuclear copper(II) complex 4 has been performed spectroscopically.

2. Experimental

2.1. 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.

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

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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 ^1H NMR spectra were obtained on a Bruker AC300 spectrometer with chemical shifts reported relative to the residual solvent resonance of $CDCl_3$. The room temperature magnetic susceptibility measurements were performed by using a vibrating sample magnetometer PAR 155 model. Molar conductances (Λ_M) were measured in a systronics conductivity meter 304 model using $\sim 10^{-3}$ mol L^{-1} solutions in appropriate organic solvents. Thermogravimetric analysis was performed on a Perkin–Elmer Diamond TG/DTA Thermal Analyzer from room temperature to 600 °C at a heating rate of 20 °C min^{-1} using platinum crucibles. The fluorescence spectra of EB bound to DNA were obtained in the Hitachi-2000 fluorimeter.

2.2. Preparation of 3,4-bis(2-pyridylmethylthio)toluene (L)

The organic moiety, 3,4-bis(2-pyridylmethylthio)toluene (L) was prepared following our earlier report [24]. An ethanolic solution of 2-picolyl chloride, hydrochloride (1.64 g, 10.0 mmol) was added to 3,4-toluenedithiol (0.78 g, 5.0 mmol) in dry ethanol containing sodium ethoxide (0.46 g, 20.0 mmol) at low temperature (0–5 °C). Then the mixture was allowed to stir at room temperature for 0.5 h and then refluxed for 2 h. The mixture was cooled to room temperature, water was added and finally the ethanol was evaporated off by rotary evaporator. The product was extracted into dichloromethane and dried by using Na_2SO_4. Finally the product 3,4-bis(2-pyridylmethylthio)toluene was obtained as a yellow oil by removing the dichloromethane by rotary evaporator. The compound was characterized by ^1H NMR spectroscopy using $CDCl_3$. Yield: 82–85%. ^1H NMR (δ, in $CDCl_3$) ppm: 2.41(s, 3H), 4.39(s, 4H), 6.78(d, 1H, j = 7.2), 6.83(s, 1H), 7.03(d, 1H, j = 7.1), 7.27–7.31(m, 4H), 7.79–7.82(m, 2H) and 8.69(d, 2H, j = 5.1).

2.3. Preparation of $[Cu^{II}(L)(H_2O)_2](NO_3)_2$ (**1**)

To a methanolic solution of 3,4-bis(2-pyridylmethylthio)toluene (L) (0.339 g), copper(II) nitrate trihydrate (0. 242 g) in methanol was added dropwise and the resulting mixture was stirred for 4 h at ambient temperature. The green colored complex was precipitated out, filtered and washed with water, cold methanol and dried in *vacuo*. Yield: 80–82%.

$[Cu(L)(H_2O)_2](NO_3)_2$ (**1**): *Anal* Calc. for $C_{19}H_{22}CuN_4O_8S_2$: C, 40.60; H, 3.95; N, 9.97, Cu, 11.31. Found: C, 39.92; H, 4.09; N, 10.06, Cu, 11.45%. IR (cm^{-1}): $\nu_{C=N}$, 1476; ν_{C-S}, 758; ν_{NO_3}, 1379. Magnetic moment (μ, B.M.): 1.81. Conductivity (Λo, ohm^{-1} cm^2 mol^{-1}) in acetonitrile: 245.

2.4. Preparation of $[Cu^{II}(pic)_2]$ (**2**)

Complex **2** was synthesized following a similar procedure as stated in case of **1**, by using copper(II) chloride in place of copper(II) nitrate in equimolar ratio to the organic ligand L. The deep green colored complex was precipitated out and the solid complex was filtered, washed with water, cold methanol and finally dried in *vacuo*. Yield: 76–78%.

$[Cu(pic)_2]$ (**2**): *Anal* Calc. for $C_{12}H_8CuN_2O_4$: C, 46.83; H, 2.62; N, 9.10, Cu, 20.64. Found: C, 46.36; H, 2.72; N, 8.94, Cu, 20.54%. IR (cm^{-1}): $\nu_{C=N}$, 1476. Magnetic moment (μ, B.M.): 1.81. Conductivity (Λo, ohm^{-1} cm^2 mol^{-1}) in acetonitrile: 105.

2.5. Preparation of $[Cu^{I}_2(L)_2](ClO_4)_2$ (**3**)

Complex **3** was synthesized using copper(II) perchlorate hexahydrate and organic compounds in equimolar ratio. To a methanolic solution of the ligand L (0.338 g, 1.0 mmol), a solution of copper(II) perchlorate hexahydrate (1.0 mmol) in methanol was added and the reaction mixture was stirred for 4 h at room temperature. The green colored filtrate was kept at undisturbed condition in a beaker. After few days colorless crystals suitable for X-ray diffraction were collected. Yield: 84–85%.

$[Cu^{I}_2(L)_2](ClO_4)_2$ (**3**): *Anal* Calc. for $C_{38}H_{36}Cl_2Cu_2N_4O_8S_4$: C, 45.51; H, 3.62; N, 5.59, Cu, 12.67. Found: C, 45.60; H, 3.54; N, 5.51, Cu, 12.59%. IR (cm^{-1}): $\nu_{C=N}$, 1478; ν_{C-S}, 760, ν_{ClO_4}, 1088 and 622. Magnetic moment (μ, B.M.): 1.45 per Cu atom. Conductivity (Λo, ohm^{-1} cm^2 mol^{-1}) in DMF: 149.

2.6. Preparation of $[Cu^{II}_2(L)_2Cl_2](ClO_4)_2$ (**4**)

Complex **4** was synthesized following the same procedure described for **3** by taking copper(II) perchlorate hexahydrate and organic compound (L) in equimolar ratio but the reaction was carried out in acetonitrile instead of methanol followed by addition of aqueous solution of sodium chloride (0.585 g) to the reaction mixture. The resulting mixture was filtered and kept undisturbed for several days. After few days crystalline compound was obtained from this filtrate. Yield: 75–76%.

$[Cu_2(L)_2Cl_2](ClO_4)_2$ (**4**): *Anal* Calc. for $C_{38}H_{36}Cl_4Cu_2N_4O_8S_4$: C, 42.50; H, 3.38; N, 5.22, Cu, 11.83. Found: C, 42.58; H, 3.34; N, 5.29, Cu, 11.87%. IR (cm^{-1}): $\nu_{C=N}$, 1478; ν_{C-S}, 760, ν_{ClO_4}, 1088 and 622. Magnetic moment (μ, B.M.): 1.45 per Cu atom. Conductivity (Λo, ohm^{-1} cm^2 mol^{-1}) in DMF: 156.

2.7. DNA binding experiments

The Tris–HCl buffer solution (pH 8.04), used in all the experiments involving CT-DNA, was prepared using deionized and sonicated HPLC grade water (Merck). The purity of CT-DNA was verified by UV absorbance [25], while the concentration of DNA was ensured by verifying the extinction coefficient of DNA solution at 260 nm (ε_{260}) of 6600 L mol^{-1} cm^{-1} [26]. 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 was performed by keeping constant the concentration of the copper(II) complex, while varying that of CT-DNA. To detach 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 DNA solution (at saturated binding levels) [27], stored in the dark for 2 h. Then the solution of the copper(II) complex was titrated into the DNA/EB mixture and diluted in Tris–HCl buffer to 5 mL to get the solution with the appropriate copper(II) complex/CT-DNA molar ratio. Before measurements, the mixture was shaken up and incubated at room temperature for 30 min. The fluorescence spectra of EB bound to DNA, obtained at an emission wavelength of 522 nm, were followed at the Hitachi-2000 fluorimeter.

2.8. X-ray crystal structure analysis

The intensity data on a suitable crystal of **3** were collected at 173 K on a Stoe Mark II-Image Plate Diffraction System [28] equipped with a two-circle goniometer using Mo Kα graphite monochromated radiation. Image plate distance 100 mm, ω rotation scans 0–180° at φ = 0°, step $\Delta\omega$ = 1.0°, exposures of 3 min per image, 2θ range 2.29–59.53°, d_{min}–d_{max} = 17.779–0.716 Å. The structure was solved by direct methods, the refinement and all further calculations were carried out using SHELX-97 [29]. The H-atoms were included at calculated positions and treated as riding atoms

using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. An absorption correction was applied using the MULscanABS routine in PLATON [30]; transmission factors: T_{min}/T_{max} = 0.675/0.865. The crystallographic data and the ORTEP [31] drawing of the molecular structure with atom numbering scheme are illustrated in Table 1 and Fig. 1 respectively.

3. Results and discussion

3.1. Ligands and complexes

The ligand 3,4-bis(2-pyridylmethylthio)toluene (L) was synthesized by refluxing the reaction mixture of toluene-3,4-dithiol with 2-picolyl chloride in dry ethanol medium in presence of sodium ethoxide. The organic product was extracted into dichloromethane and the pure compound was obtained as yellow viscous liquid by evaporating the organic solvent. This organic product was characterized using spectroscopic tools. The ^{1}HNMR spectrum of this viscous liquid in $CDCl_3$ showed the characteristic peaks of the protons. The signals of the three aromatic dithiol toluene protons of L are at different δ values, 6.78 (d, 1H), 6.83(s, 1H), 7.03(d, 1H) due to the methyl group. But a singlet signal for the four protons of the two methylene groups was observed at δ 4.39. One doublet signal in the lowest region (δ = 8.69) is attributable to the protons in *ortho* position of the two pyridine rings.

The copper(I/II) complexes $[Cu^{II}(L)(H_2O)_2](NO_3)_2$ (**1**), $[Cu^{II}(pic)_2]$ (**2**), $[Cu^{I}_2(L)_2](ClO_4)_2$ (**3**) and $[Cu^{II}_2(L)_2Cl_2](ClO_4)_2$ (**4**) were obtained in good yield from the reaction mixture of 3,4-bis(2-pyridylmethylthio)toluene (L) with the correspondent $Cu^{II}X_2$ salt (X = nitrate, chloride and perchlorate) in equimolar ratio and in different solvents as indicated in Scheme 1. Complex **1** was obtained by reacting L with copper(II) nitrate in methanol medium, whereas **2** was isolated from the *in situ* formed picolinate through the C–S bond cleavage of L during the reaction with cupric chloride. Complex **2** has been already reported and it was obtained by oxidative dealkylation of diethyl 2-pyridylmethyl-phosphonate and diethyl 2-quinolylmethylphosphonate (2-qmpe) ligands when reacting with $CuCl_2$ [32]. Here and in the cited ref. [31] the counter anion of the reactant copper(II) salt plays a key role to help different products.

The present observations might be explained on the basis of HSAB principle [33] And it might be taken into account that chlorides are more strongly bound in the coordination sphere of copper(II) with respect to nitrate ions. Assuming that the pyridinic-N atoms, being border line donors, formerly coordinate the metal ion by substituting two monodentate ligands, the soft thioether-S donors in the second step, cannot substitute two other monodentate ligands from the coordination sphere due to the less bonding affinity of soft thioether-S with borderline copper(II) in the presence of chlorides. Thus in case of chloride salt the process of L coordination is too slow. By this time, substituted chloride ion/aquo molecule might attack the methylene centre, being this group slightly positive due to the bonding of pyridinic-N to copper(II) ion and as a result, the C–S bond cleavage is taking place. But, in case of nitrate salt, the rate of coordination process is little bit faster than that in chloride and the nitrate ion is not good nucleophile as chloride. Consequently, the C–S bond cleavage was not observed and the formation of the expected mononuclear copper(II) complex of L can occur.

Table 1
Crystal data and details of refinement data for complex **3**.

Empirical formula	$C_{38}H_{36}Cl_2Cu_2N_4O_8S_4$
Formula weight	1002.99
Crystal system	orthorhombic
Space group	*F* dd2
a (Å)	19.272(2)
b (Å)	36.886(4)
c (Å)	11.4258(17)
V (Å^3)	8122.2(17)
Z	8
ρ_{calc} (g/cm^3)	1.640
F(0 0 0)	4096
θ range(deg)	2.1–25.7
μ (Mo Kα) (mm^{-1})	1.442
Collected reflections	10198
Independent reflections	3822
Observed data [$I > 2.0\sigma(I)$]	2537
R_1 [$I > 2.0\sigma(I)$]	0.0506
wR_2 [$I > 2.0\sigma(I)$]	0.1096
Goodness-of-fit	0.888
Residuals (e Å^{-3})	0.637, −0.477

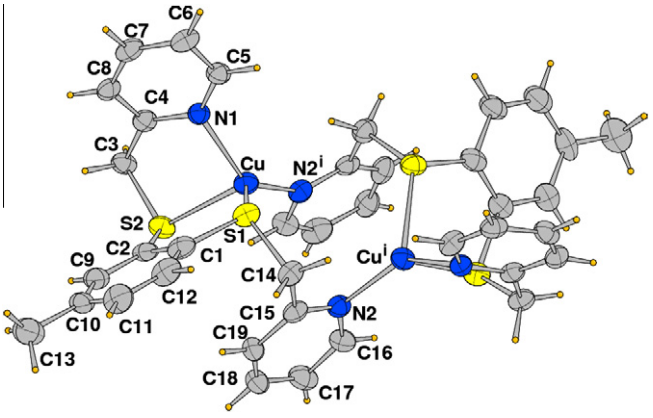


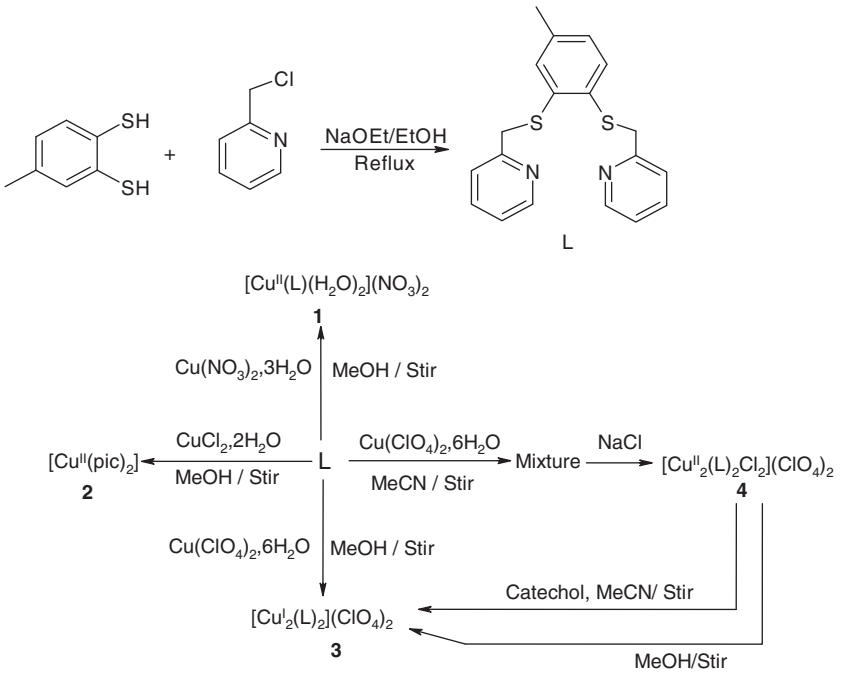
Fig. 1. ORTEP view (50% probability ellipsoid) of only the cation of the complex **3** with atom labeling scheme of crystallographic independent atoms.

Colorless dinuclear copper(I) complex **3** was obtained upon reaction of L with copper(II) perchlorate hexahydrate at ambient temperature and under aerobic conditions in methanol, while green colored dinuclear copper(II) complex **4** was isolated in good yield under same conditions in acetonitrile medium after the addition of chloride ions to the reaction medium. Here, the variation of the reaction medium from methanol to acetonitrile revealed to be crucial since complex **3** did not form in the latter solvent. Thus methanol favors the reduction of copper(II) to copper(I), a reaction usually not observed at aerobic condition. The process for the synthesis of **3** is slow but faster than that observed with $CuCl_2$ salt where C–S bond cleavage was observed. However the addition of chloride ions in the reaction medium of **3** and **4** did not induce C–S bond cleavage of L.

The purity and formulation of all the complexes were checked by elemental analyses. The characterization of complex **2** was performed by elemental analyses and X-ray crystallography, the latter corresponding to the structure already reported [32]. Complex **1** is soluble either in acetonitrile and DMF, while both dinuclear copper(I/II) complexes **3** and **4** are soluble in DMF only. At room temperature the magnetic moment (μ) of **1** is 1.80 B.M., that of **4** is 1.44 B.M. per copper atom. The conductivity measurement of complex **1** in acetonitrile shows a conductance of 145 Λo mol^{-1} cm^{-1}, the values of **3** and **4** in DMF are 145 and 150 Λo mol^{-1} cm^{-1}, respectively, at 300 K, suggesting that complexes **1**, **3** and **4** behave in solution as 1:2 electrolytes.

3.2. Thermal analysis

The thermal behavior of the complexes **1** and **4** was followed up to 650 °C in a flowing atmosphere of dinitrogen. For complex **1**,



Scheme 1. Ligand structure and synthetic route of the complexes.

TGA studies indicate that the first weight loss (7.1%) in the temperature range of 84–105 °C is attributed to the removal of two coordinated water molecules (Calc. 6.4%) [34]. Stable framework of molecular formula has formed in the temperature range of 105–312 °C with the weight of complex hardly loss. The second stage has weight loss of 62.59% (calc. 62.92%) in the range of 312–400 °C, corresponding to the loss of organic moiety. Further heating, the mass remains unchanged with a residual mass of 14.45% corresponding to CuO percentage (Calc. 14.15%).

The complex **4** is stable up to 230 °C and then begins to decompose. The TG curve indicates that the complex shows three-stage decomposition process. The first one occurs in the temperature range of 230–280 °C while the second stage is sharp endothermic process in the range of 280–336 °C. The third and final stage leads to the formation of cupric oxide upto 550 °C with the total mass loss of 84.48% agrees well with the calculated mass loss of 85.19% and then the mass loss remains unchanged.

3.3. Conversion of complex *4* to complex *3*

By stirring for 12 h, the green colored methanolic solution of complex **4** became fade, and after several days the colorless crystalline complex **3** was obtained. On the other hand, in acetonitrile the green solution of **4** changed to almost colorless within 1–2 h after the addition of a catalytic amount of catechol, obtaining the colorless precipitate of copper(I) complex **3** as indicated in the following equation.

$$[Cu^{II}_2(L)_2Cl_2](ClO_4)_2(\mathbf{4}) \xrightarrow[\text{or Chatechol/CH}_3\text{CN/Stir}]{\text{Stir in MeOH}} [\mathbf{Cu^{I}_2(L)_2}](\mathbf{ClO_4})_2(\mathbf{3})$$

The above observations indicate that the solvent methanol plays a key role for the reduction of copper(II) to copper(I) species in presence of the ligand L. It is worth noting that the reduction process was observed in aerobic condition and not under inert atmosphere. In the control experiment the solvent methanol did not convert copper(II) perchlorate into its corresponding copper(I) species in absence of 3,4-bis(2-pyridylmethylthio)toluene. Therefore the reduction of the metal is ligand assisted, similarly to that already reported [35].

3.4. Structure description of Cu(I) complex *3*

A perspective view of the molecular structure of complex **3** with the atom numbering schemes is shown in Fig. 1, while selected bond lengths and angles are reported in Table 2. The dinuclear complex **3** resides about a two-fold axis and the crystallographic independent Cu(I) ion presents an irregular pseudo-tetrahedral geometry arising from the restricted bite angles of the chelating ligand (Table 2) that bridges the two metal ions in such a way that the thioether-S atoms and one pyridyl-N donors chelate one copper ion, the other pyridyl-N donor being connected to the other metal.

The Cu–S bond distances are almost comparable in length (2.302(2), 2.355(2) Å), while the Cu–N ones differ by ca. 0.13 Å (2.107(5) 1.974(5) Å), and the shorter distance refers to the py ring that appears conformationally more free (Cu–N2). This feature, indicative of a strain of L upon coordination, is also reflected by the coordination bond angles that are close to 90° between the chelating donors, and in the range 113.26(15)–131.16(15)° for the angles involving N2. The Cu–Cu separation is of 4.331 Å excludes any interaction between the metals.

Two mononuclear copper(II) complexes have been reported containing a py-C-S-$(CH_2)_2$-S-C-py fragment, namely the tetrachelating ligand [Cu^{I}(1,2-bis(2′-quinolylmethylthio)ethane)$_2$] [35] and [Cu^{II}(1,2-bis(2-pyridylmethylthio)ethane)$_2$Cl] [20]. Although the S-$(CH_2)_2$-S moiety is expected to be more flexible than the S-toluene-S chelating fragment of **3**, the Cu–S bond distances are slightly

Table 2
Selected coordination bond distances (Å) and angles (°) for **3**.

Bond lengths			
Cu–S(1)	2.302(2)	Cu–N(1)	2.107(5)
Cu–S(2)	2.355(2)	Cu–N(2^i)	1.974(5)
Bond angles			
S(2)–Cu–(1)	86.35(16)	S(2)–Cu–N(2^i)	113.26(15)
S(1)–Cu–(1)	92.83(14)	N(1)–Cu–N(2^i)	128.1(2)
S(1)–Cu–(2)	92.02(7)	S(1)–Cu–sN(2^i)	131.16(15)

Symmetry code (i) $-x + 1/2, -y + 1/2, z$.

longer (mean value 2.372 and 2.436 Å, respectively) while the Cu–N ones (mean values 1.988, 2.000 Å) are close to the short value observed in **3** (Cu–N2). Moreover copper(II) complexes containing 1,2-bis(benzimidazol-2-ylmethylthio)benzene [36] and 3,4-bis(2-aminoethylthio)toluene [37] have been also reported. The coordination geometry around the metal is trigonal bipyramidal in the former case, and distorted octahedral and distorted square pyramidal in the two independent ions of other, while N donors are always located in trans positions. In these cases the Cu-S bond distances are even longer (range 2.445–2.609 Å) than those measured in **3**, indicative of steric constraints inside the tetrachelating ligand upon coordination.

3.5. Spectral studies

In the IR spectrum of **1** a broad band around at 3480 cm^{-1} and an intense band centered at 1380 cm^{-1} are attributable to the coordinated water and to the to ν_{NO_3} strectching frequency, respectively. In the infrared spectra of **3** and **4** a strong absorption at *ca.* 1080 cm^{-1} along with a weak absorption band at *ca.* 624 cm^{-1} are due to the symmetric and asymmetric stretching frequency, respectively, for perchlorate ion. In the IR spectra of all the complexes, bands at 1469–1478 cm^{-1} for asymmetric $\nu_{C=N}$ and 758–761 cm^{-1} for ν_{C-S} stretching were detected. Differently from the spectra of the other complexes, it is noteworthy the intense band at 1645 cm^{-1} attributable to ν_{COO^-} observed in the IR spectrum of **2**.

The electronic absorption spectra of complexes **1**, **3** and **4** were recorded at room temperature using DMF as solvent and the data are tabulated in Table 3. Each complex shows an absorption in the range from 360 to 450 nm, which is not observed for the corresponding free ligand. This suggests that the absorption bands of all complexes are assignable to the LMCT transition from the copper center to the pyridyl-N of organic moiety [38]. Transition at high energy region corresponds to intramolecular $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions [39]. The characteristic d–d absorption band have been also observed at *ca.* 650 nm for **1** and *ca.* 682 nm for **4**. For complex **3** no broad d-d absorption band was observed in the range 600–680 nm, due to the tetrahedral geometry of copper (I) present also in solution for this complex [40,41].

3.6. DNA binding studies

The binding mode of complex **4** with CT-DNA was examined by using absorption and emission spectra. The absorption spectra of the copper(II) complex **4**, were recorded during the titration with calf thymas DNA. As shown in Fig. 2, the titration indicated a significant hyperchromism effect of the absorption spectra, suggesting that there exists a interaction between the copper(II) complex and DNA. From this spectral change it can be said that the binding mode of copper(II) complex is groove binding [42].

The spectral titration data allows determining the intrinsic binding constant K_b of **4** with CT-DNA by using the following equation [43]:

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

where [DNA] is the DNA concentration, ε_f and ε_b represent the extinction coefficients for the free and fully bound copper(II) complex, respectively, and ε_a the copper(II) complex extinction coefficient during each addition of DNA. The $[DNA]/(\varepsilon_a - \varepsilon_f)$ plot against [DNA] gave a linear relationship (Fig. 3), from the slope of which the intrinsic binding constant K_b for the complex **4** was calculated to be 2.21×10^5 M^{-1} ($R = 0.99338$ for five points). This value is comparable well with that of the well-established groove binding rather than classical intercalator agent [44].

Table 3
UV–Vis spectral data in DMF.

Compds	λ nm (ε) (ε, dm^3 mol^{-1} cm^{-1})
1	273 (s, 8,442), 362 (s, 3,076), 650 (br, 238)
3	263 (s, 8,302), 378 (s, 3,045),
4	266(s, 8,532), 364 (s, 3,474), 682 (br, 218),

s for strong; br for broad.

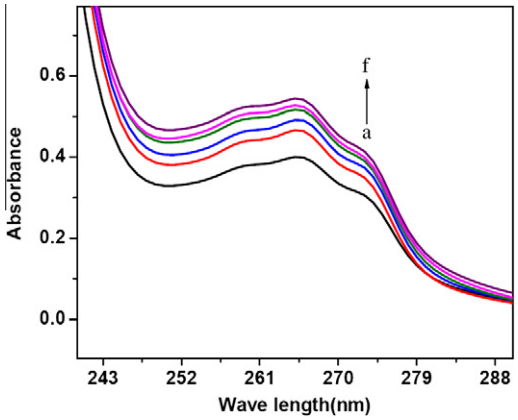


Fig. 2. Electronic spectral titration of complex **4** with CT-DNA at 266 nm in Tris–HCl buffer; [complex] = 1.3×10^{-5}; [DNA]: (a) 0.0, (b) 2.0×10^{-6}, (c) 4.0×10^{-6}, (d) 6.0×10^{-6}, (e) 8.0×10^{-6}, (f) 1.0×10^{-5} mol L^{-1}. Arrow indicates the increase of DNA concentration.

Ethidium bromide (EB) fluorescence displacement experiments were also performed in order to investigate the interaction mode of **4** with CT-DNA. EB has been used as probe the interaction of the complex with DNA. In fact the EB fluorescence intensity will be enhanced in the presence of DNA because of its intercalation into the helix, and it is quenched by the addition of another molecule that displaces EB from DNA [45]. Here, a significant decrease of the fluorescence intensity of EB bound to DNA at 522 nm was recorded by increasing the concentration of **4** (Fig. 4).

This observation of EB fluorescence quenching leads us to deduce that the copper(II) complex may interact with DNA through the groove binding mode, releasing some EB molecules from the EB-DNA system [46]. The quenching of EB bound to DNA by the copper(II) complex is in agreement with the linear Stern–Volmer equation:

$$I_0/I = 1 + K_{sv}[\text{complex}]$$

where I_0 and I represent the fluorescence intensities in the absence and presence of quencher, respectively. K_{sv} is the linear Stern–Volmer quenching constant and [complex] the concentration of the

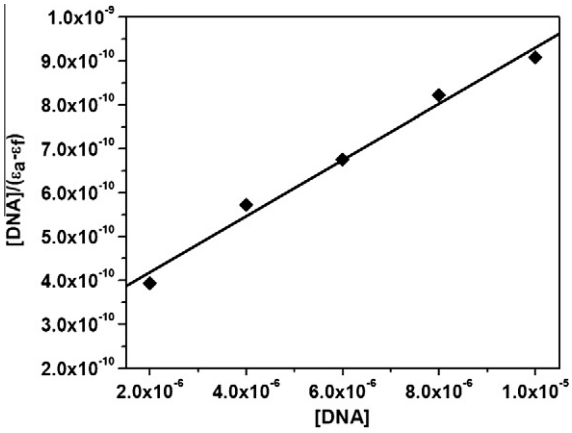


Fig. 3. Plot of $[DNA]/(\varepsilon_a - \varepsilon_f)$ vs. [DNA] for the absorption titration of CT-DNA with complex **4** in Tris–HCl buffer.

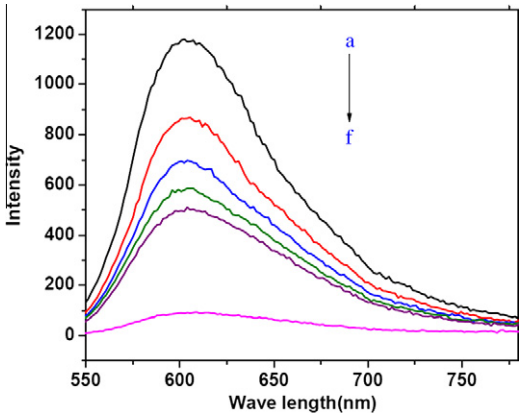


Fig. 4. Emission spectra of the CT-DNA–EB system in Tris–HCl buffer upon the titration of complex **4**. k_{ex} = 522 nm; [EB] = 0.96×10^{-5} mol L^{-1}; [DNA] = 1.0×10^{-5}; [complex]: (a) 0.0, (b) 6.50×10^{-6}, (c) 1.30×10^{-5}, (d) 1.95×10^{-5}, (e) 2.60×10^{-5}, (f) 3.25×10^{-5} mol L^{-1}. The arrow shows the intensity change upon the increase of the complex concentration.

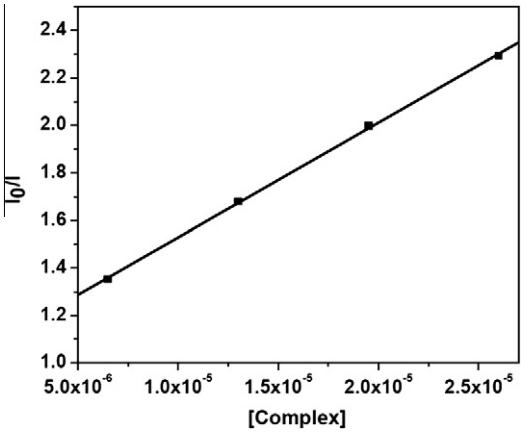


Fig. 5. Plot of I_0/I *vs* [complex] for the titration of complex **4** to CT-DNA–EB system.

quencher. From the slope of the regression line in the derived plot of I_0/I *versus* [complex] (Fig. 5), the K_{sv} value for the copper(II) complex was found to be 4.62×10^4 (R = 0.99977 for four points), indicating a strong affinity of the copper(II) complex to CT-DNA.

4. Conclusion

The tetradentate N_2S_2 ligand 3,4-bis(2-pyridylmethylthio)toluene L, has been synthesized and its coordination with different copper(II) salts has been studied. The resulting complexes are dependent on the counter anion of copper(II) salts used as reactant and on the reaction medium. Mononuclear $[Cu^{II}(L)(H_2O)_2](NO_3)_2$ complex is formed with copper(II) nitrate, while C–S bond cleavage of L formed *in situ* is observed with $CuCl_2$ yielding neutral $[Cu^{II}(picolinate)_2]$ species. This behavior is tentatively rationalized through HSAB principle. On the other hand, copper(II) perchlorate leads to the formation of a dinuclear copper(II) complex (**4**) in acetonitrile but a dinuclear copper(I) complex (**3**) in methanol. In the latter case the solvent behaves as a reducing agent for the metal through a ligand assisted reduction. In methanol it was observed the slowly conversion of the dinuclear copper(II) species to copper(I), whereas the process proceeds faster in acetonitrile in presence of catechol. The dinuclear Cu(II) complex (**4**) showed to be a good groove binding agent by studying its interaction with calf thymus DNA (CT-DNA).

5. Supporting data

Crystallographic data for compound **3** have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 778243. Copies of this information is available on request at free of charge from CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.ac.uk or http://www.ccdc.cam.ac.uk).

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References

[1] M. Gennari, M. Lanfranchi, R. Cammi, M.A. Pellinghelli, L. Marchio, Inorg. Chem. 46 (2007) 10143.
[2] C.-H. Chou, W.-Y. Yeh, G.-H. Lee, S.-M. Peng, Inorg. Chim. Acta 359 (2006) 4139.
[3] M. Glockle, K. Hubler, H.-J. Kummerer, G. Denninger, W. Kaim, Inorg. Chem. 40 (2001) 2263.
[4] S. Panja, S. Chowdhury, M.G.B. Drew, D. Datta, Inorg. Chem. Commun. 5 (2002) 304.
[5] W.L. Jia, T. McCormick, Y. Tao, J.-P. Lu, S. Wang, Inorg. Chem. 44 (2005) 5706.
[6] X.-H. Zhou, T. Wu, D. Li, Inorg. Chim. Acta 359 (2006) 1442.
[7] Z.R. Bell, L.P. Harding, M.D. Ward, Chem. Commun. (2003) 2432.
[8] R.I. Paul, S.P. Argent, J.C. Jeffery, L.P. Harding, J.M. Lynam, M.D. Ward, Dalton Trans. (2004) 3453.
[9] T.K. Ronson, H. Adams, M.D. Ward, Eur. J. Inorg. Chem. (2005) 4533.
[10] S. Tavacoli, T.A. Miller, R.L. Paul, J.C. Jeffery, M.D. Ward, Polyhedron 22 (2003) 507.
[11] R.M. Kretzer, R.A. Ghiladi, E.L. Lebeau, H.-C. Liang, K.D. Karlin, Inorg. Chem. 42 (2003) 3016.
[12] C. Marzano, M. Pellei, D. Colavito, S. Alidori, G.G. Lobbia, V. Gandin, F. Tisato, C. Santini, J. Med. Chem. 49 (2006) 7317.
[13] E.I. Solomon, P.M. Jones, J.A. Maj, Chem. Rev. 93 (1993) 2623.
[14] S.-M. Kuang, D.G. Cuttell, D.R. McMillin, P.E. Fanwick, R.A. Walton, Inorg. Chem. 41 (2002) 3313.
[15] Y.-C. Liu, C.-I. Li, W.-Y. Yeh, G.-H. Lee, S.-M. Peng, Inorg. Chim. Acta 359 (2006) 2361.
[16] E. Cariati, D. Roberto, R. Ugo, P.C. Foed, S. Galli, A. Sironi, Inorg. Chem. 44 (2005) 4077.
[17] C.-C. Chou, C.-C. Su, A. Yeh, Inorg. Chem. 44 (2005) 6122.
[18] H. Wang, M.-X. Li, M. Shao, X. He, Polyhedron 26 (2007) 5171.
[19] C. Ganesamoorthy, M.S. Balakrishna, P.P. George, J.T. Mague, Inorg. Chem. 46 (2007) 848.
[20] S. Sarkar, A. Patra, M.G.B. Drew, E. Zangrando, P. Chattopadhyay, Polyhedron 28 (2009) 1. and refs. therein.
[21] S. Sarkar, M.G.B. Drew, E. Zangrando, P. Chattopadhyay, J. Mol. Struct. 933 (2009) 126.
[22] A. Patra, S. Sarkar, M.G.B. Drew, E. Zangrando, P. Chattopadhyay, Polyhedron 28 (2009) 1261.
[23] S. Dey, S. Sarkar, H. Paul, E. Zangrando, P. Chattopadhyay, Polyhedron 29 (2010) 1583.
[24] B. Das, S. Sarkar, E. Zangrando, P. Chattopadhyay, Inorg. Chem. Commun. 12 (2009) 1112.
[25] J. Marmur, J. Mol. Biol. 3 (1961) 208.
[26] M.E. Reichmann, S.A. Rice, C.A. Thomas, P.J. Doty, J. Am. Chem. Soc. 76 (1954) 3047.
[27] J.K. Barton, J.M. Goldberg, C.V. Kumar, N.J. Turro, J. Am. Chem. Soc. 108 (1986) 2081.
[28] Stoe and Cie, X-Area V1.35 and X-RED32 V1.31 Software. Stoe and Cie GmbH, Darmstadt, Germany, 2006.
[29] G. Sheldrick, Acta Crystallogr., Sect. A64 (2008) 112.
[30] A.L. Spek, J. Appl. Crystallogr. 36 (2003) 7.
[31] L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.
[32] B. Zurowska, J. Ochocki, J. Mrozinski, Z. Ciunik, J. Reedijk, Inorg. Chim. Acta 357 (2004) 755.
[33] R.G. Pearson, J. Am. Chem. Soc. 85 (1963) 3533.
[34] R. Carballo, B. Covelo, F. -Hermida, E.G. -Martínez, A.B. Lago, E.M.V. -López, Polyhedron 27 (2008) 3247.
[35] S. Banthia, A. Samanta, Inorg. Chem. 43 (2004) 6890.
[36] F.J. Rietmeijer, P.J.M.W.L. Birker, S. Gorter, J. Reedijk, J. Chem. Soc., Dalton Trans. (1982) 1191.
[37] A.C. Braithwaite, Clifton E.F. Rickard, T. Neil Waters, J. Chem. Soc., Dalton Trans. (1975) 1817.
[38] J. Zubieta, K.D. Karlin, J.C. Hayes, in: K.D. Karlin, J. Zubieta (Eds.), In Copper Coordination Chemistry: Biochemical and Inorganic Perspectives, Adenine Press, Albany, NY, 1983, p. 97.

[39] Y. Nakao, M. Onoda, T. Sakurai, A. Nakahara, I. Kinoshita, S. Ooi, Inorg. Chim. Acta. 151 (1988) 55.
[40] K.D. Karlin, J.C. Hayes, S. Juen, J.P. Hutchinson, J. Zubieta, Inorg. Chem. 21 (1982) 4106.
[41] V.A. Bloomfield, D.M. Crothers, I. Tinoco, Physical Chemistry of Nucleic Acids, Harper and Row, New York, 1974. p. 432–434.
[42] R. Vijayalakshmi, M. Kanthimathi, V. Subramanian, B.U. Nair, Biochem. Biophys. Acta 1475 (2000) 157.
[43] A.M. Pyle, J.P. Rehmann, R. Meshoyrer, C.V. Kumar, N.J. Turro, J.K. Barton, J. Am. Chem. Soc. 111 (1989) 3051.
[44] L. Strekowski, D.B. Harden, R.L. Wydra, K.D. Stewart, W.D. Wilson, J. Mol. Recognit. 2 (1989) 158.
[45] R. Indumathy, S. Radhika, M. Kanthimathi, T. Weyhermuller, B.U. Nair, J. Inorg. Biochem. 101 (2007) 434.
[46] D.L. Boger, B.E. Fink, S.R. Brunette, W.C. Tse, M.P. Hedrick, J. Am. Chem. Soc. 123 (2001) 5878.