Polyhedron 30 (2011) 2783–2789

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Zinc(II) complexes of 1,3-bis(2-pyridylmethylthio)propane: Anion dependency, crystal structure and DNA binding study

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ARTICLE INFO

Article history:
Received 16 June 2011
Accepted 7 August 2011
Available online 31 August 2011

Keywords:
Anion dependency
Zinc(II) complex
Nitrogen–sulfur ligand
Crystal structure

ABSTRACT

Zinc(II) complexes of the formula $[Zn(L)(X)_2]$ (where $X = Cl^-$, N_3^-, NCO^- and SCN^- (**1a–d**, respectively)) and $\{[Zn(L)(ClO_4)(H_2O)](ClO_4)\}_n$ (**2**), were isolated in the pure form on the reaction of 1,3-bis(2-pyridylmethylthio)propane (L) with different zinc(II) salts. All the complexes were characterized by physicochemical and spectroscopic tools. The X-ray crystallographic analyses of the complexes **1d** and **2** showed that the former is mononuclear while complex **2** is a 1D coordination polymer, $\{[Zn(L)(ClO_4)(H_2O)](ClO_4)\}_n$, due to a different coordination mode of the tetradentate ligand L. The zinc(II) ions present an octahedral coordination geometry in both compounds, which is more distorted in the mononuclear complex **1d**. The study indicates that the counter anion of the zinc(II) salt used as reactant leads to a different type of complex when isolated as a crystalline material. A spectroscopic study of the interaction of complex, **2** with calf thymus-DNA (CT-DNA) in Tris–HCl buffer showed a significant non-intercalative interaction with a binding constant (K_b) of $4.7 \times 10^4\ M^{-1}$, and the linear Stern–Volmer quenching constant (K_{sv}) and the binding sites (n) were found to be 1.3×10^3 and 0.92 respectively, calculated from ethidium bromide (EB) fluorescence displacement experiments.

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1. Introduction

In recent years, the coordination chemistry of nitrogen–sulfur donor ligands towards transition metal ions [1,2] has attracted much attention and the interest arises in part from the fact that S-ligated transition metal complexes mimic the coordination environment of many biological systems. The structural and reactivity studies of these complexes could provide useful insight into the chemistry and biochemistry of bio-active molecules [3–6]. Moreover zinc ions play diverse roles in medicinal, chemical and biological events, and they are the second most abundant transition metal next to the iron ion in the body (human beings contain an average of ~2–3 g of zinc), being vital in many cellular processes [7], including gene expression [8], apoptosis [9], enzyme regulation [10] and neurotransmission [11]. Since zinc is an essential and one of the most bio-relevant transition metal ions, it is no surprise that its complexes have attracted particular interest as synthetic structural mimics of the active site of a range of metalloenzymes containing zinc(II) cores often seen in biological systems, such as phosphatases [12] and aminopeptidases [13,14]. In addition, some synthetic dinuclear zinc(II) complexes are found to have functions in RNA hydrolysis [15] and dephosphorylation [16]. Zinc complexes with N,S-donor sets are potential mimics of various zinc-containing metalloproteins [17].

As part of our continuous interest in nitrogen–sulfur polydentate chelators [18,19], herein we report an account on zinc(II) complexes obtained with the tetradentate ligand 1,3-bis(2-pyridylmethylthio)propane (L) (*vide* Scheme 1), having two pyridinic-N and two thioether-S donors, together with different halide and pseudohalides in the coordination sphere. Two types of zinc(II) complexes have been achieved, depending on the counter anion of the zinc(II) salt used, and the detailed structures of $[Zn(L)(SCN)_2]$ (**1d**) and $\{[Zn(L)(ClO_4)(H_2O)](ClO_4)\}_n$ (**2**), established by single crystal X-ray crystallography, show a different coordination binding mode for the ligand L.

2. Experimental

2.1. Materials and physical measurements

All chemicals and reagents were obtained from commercial sources and used as received, unless otherwise stated. Solvents were distilled from an appropriate drying agent. The organic moiety 1,3-bis(2-pyridylmethylthio)propane (L), used as the ligand, was synthesized following the procedure as stated in our earlier report [19].

The C, H, N elemental analyses were performed on a Perkin Elmer model 2400 elemental analyzer. The electronic absorption

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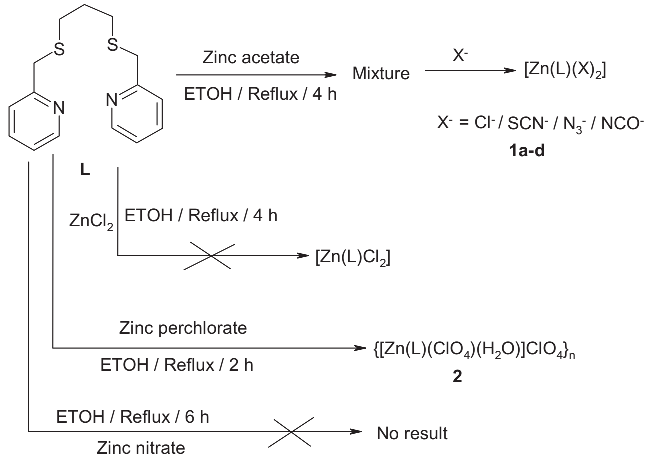
doi:10.1016/j.poly.2011.08.025



Scheme 1. Synthetic procedure of the Zn(II) complexes (**1** and **2**).

spectra were recorded on a JASCO UV–Vis/NIR spectrophotometer model V-570. IR spectra were obtained by a JASCO FT-IR spectrometer model 460 plus using KBr disks. Room temperature magnetic susceptibilities were recorded using a vibrating sample magnetometer PAR 155 model. Molar conductances (Λ_M) were measured in a Systronics conductivity meter 304 model in dimethylformamide with a complex concentration of $\sim 10^{-3}$ mol L^{-1}.

2.2. Preparation of the zinc(II) complexes

2.2.1. [Zn(L)(X)$_2$] (**1a–d**)

For the syntheses of the zinc complexes (**1a–d**), a common procedure was carried out using zinc(II) acetate dihydrate and the organic ligand 1,3-bis(2-pyridylmethylthio)propane (L) in an equimolar ratio, as described below.

An ethanolic solution of L (292.0 mg, 1.0 mmol) was mixed with an ethanolic solution containing 1.0 mmol (219.5 mg) of zinc(II) acetate dihydrate under stirring conditions, and the mixture was refluxed for 4 h. The resulting mixture was filtered to collect the clear filtrate, which in turn was allowed to react with different coordinating halide/pseudohalides anions for the synthesis of the different complexes as follows.

To the filtrate, a solution of sodium chloride for **1a** (58.5 mg), [sodium azide (65.0 mg), sodium cyanate (65.0 mg), potassium thiocyanate (97.1 mg) were used for **1b–d**] in an ethanol–water mixture was added dropwise over a period of 15 min. The mixture was stirred for 4 h at room temperature. A clear filtrate was then collected from the resulting solution and kept aside at room temperature. After a few days, crystalline complexes were collected by filtration, followed by washing with water and methanol, and then drying *in vacuo*. Single crystals of **1d** suitable for X-ray diffraction were obtained by this procedure, while attempts to obtain crystals of **1a**, **1b** and **1c** were unsuccessful. Yield: 70–75%.

*2.2.1.1. [Zn(L)(Cl$_2$)] (**1a**). Anal.* Calc. for $C_{15}H_{18}Cl_2ZnN_2S_2$: C, 42.22; H, 4.25; N, 6.56. Found: C, 42.16; H, 4.51; N, 6.74%. IR (cm^{-1}): $\nu_{C{=}N}$ 1477; ν_{C-S} 758. Conductivity (Λ_o, ohm^{-1} cm^2 mol^{-1}) in DMF: 46.

*2.2.1.2. [Zn(L)(N$_3$)$_2$] (**1b**). Anal.* Calc. for $C_{15}H_{18}ZnN_8S_2$: C, 40.96; H, 4.12; N, 25.56. Found: C, 40.86; H, 4.21; N, 25.74%. IR (cm^{-1}): $\nu_{C{=}N}$ 1477; ν_{C-S} 762; ν_{N3} 2037. Conductivity (Λ_o, ohm^{-1} cm^2 mol^{-1}) in DMF: 41.

*2.2.1.3. [Zn(L)(NCO)$_2$] (**1c**). Anal.* Calc. for $C_{17}H_{18}O_2ZnN_4S_2$: C, 42.42; H, 4.12; N, 12.74. Found: C, 42.46; H, 4.25; N, 12.84%. IR (cm^{-1}): $\nu_{C{=}N}$ 1477; ν_{C-S} 759; ν_{NCO} 2167. Conductivity (Λ_o, ohm^{-1} cm^2 mol^{-1}) in DMF: 33.

*2.2.1.4. [Zn(L)(NCS)$_2$] (**1d**). Anal.* Calc. for $C_{17}H_{18}ZnN_4S_4$: C, 43.26; H, 3.84; N, 11.87. Found: C, 42.16; H, 3.75; N, 11.94%. IR (cm^{-1}): $\nu_{C{=}N}$ 1477; ν_{C-S} 761; ν_{NCS} 2083. Conductivity (Λ_o, ohm^{-1} cm^2 mol^{-1}) in DMF: 37.

2.3. {[Zn(L)(ClO$_4$)(H$_2$O)](ClO$_4$)}$_n$ (2)

The zinc(II) complex **2** was prepared following a similar procedure as described above. One millimolar of the organic ligand L (292.0 mg) dissolved in ethanol was added to an ethanolic solution containing 1.0 mmol (372.4 mg) of zinc(II) perchlorate hexahydrate under stirring conditions, and the mixture was refluxed for 2.0 h. The clear filtrate was then collected from the resulting solution. The crystallized product, along with single crystals suitable for X-ray diffraction analysis, was obtained from the filtrate by allowing slow evaporation of the solvent at room temperature. Yield: 75–80%.

2.3.1. {[Zn(L)(ClO$_4$)(H$_2$O)](ClO$_4$)}$_n$ (**2**)

Anal. Calc. for $C_{15}H_{20}Cl_2O_9ZnN_2S_2$: C, 31.46; H, 3.52; N, 4.89. Found: C, 31.26; H, 3.43; N, 4.93%. IR (cm^{-1}): $\nu_{C{=}N}$ 1479; ν_{C-S} 758; ν_{ClO_4} 1092 and 623. Conductivity (Λ_o, ohm^{-1} cm^2 mol^{-1}) in DMF: 61.

Caution: Perchlorate compounds of metal ions are potentially explosive, especially in the presence of organic ligands. The preparation should be handled with care.

2.4. X-ray crystal structure analysis

Crystal data and details of the data collection and refinement for complexes **1d** and **2** are summarized in Table 1. Diffraction data of **1d** and **2** were collected at room temperature on a Cu rotating anode (λ = 1.54178 Å, graphite monochromatized), equipped with a Brucker CCD2000 detector, and on a Nonius DIP-1030H system (Mo Kα radiation, λ = 0.71073 Å), respectively. Cell refinement, indexing and scaling of the data sets were performed using the programs DENZO and SCALEPACK [20]. The structures were solved by

Table 1
Crystal data and details of refinement data for complexes **1d** and **2**.

	1d	**2**
Empirical formula	$C_{17}H_{18}N_4S_4Zn$	$C_{15}H_{20}Cl_2N_2O_9S_2Zn$
Formula weight	471.96	572.72
Wavelength (Å)	1.54178	0.71073
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	7.948(3)	8.762(3)
b (Å)	14.092(3)	10.216(3)
c (Å)	18.851(3)	12.869(4)
α (°)	90.00	82.39(3)
β (°)	92.03(3)	74.85(3)
γ (°)	90.00	84.15(2)
V (Å^3)	2110.0(10)	1099.4(6)
Z	4	2
ρ_{calc} (g/cm^3)	1.486	1.730
F(0 0 0)	968	584
θ Range (°)	3.92–56.83	3.25–26.36
μ (mm^{-1})	5.384	1.600
Collected reflections	18 833	12 849
Independent reflections	2692	4156
Observed data [$I > 2.0\sigma(I)$]	1667	1989
R_1 [$I > 2.0\sigma(I)$]	0.0445	0.0555
wR_2 [$I > 2.0\sigma(I)$]	0.1161	0.1447
Goodness-of-fit (GOF)	1.045	0.886
Residuals (e Å^{-3})	0.252, −0.272	0.643, −0.507

direct methods and subsequent Fourier analyses, and refined by the full-matrix least-squares method based on F^2 with all observed reflections [21]. The contribution of hydrogen atoms at calculated positions (except those of the aqua ligand in **2** detected in the ΔF map) were included in the final cycles of refinement. All the calculations were performed using WinGX System, Ver. 1.80.05 [22].

2.5. DNA binding experiments

Tris–HCl buffer solution was used in all the experiments involving CT-DNA. This Tris–HCl buffer (pH 7.2) was prepared using deionized and sonicated HPLC grade water (Merck). 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 approximately 1.9 [23]. The concentration of DNA was estimated with the help of the extinction coefficient (6600 M^{-1} cm^{-1}) of the DNA solution at 260 nm [24] and the stock solution of DNA was always stored at 4 °C. The stock solution of the zinc(II) complex was prepared by adding 2 mL DMSO for dissolving and it was diluted with Tris–HCl buffer to get the required concentration for all the experiments. The absorption spectral titration experiment was performed by keeping the concentration of the zinc(II) complex constant and varying the CT-DNA concentration. To eliminate the absorbance of DNA itself, an equal solution of CT-DNA was added 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 the DNA solution (at saturated binding levels) [25], stored in the dark for 2 h. Then a solution of the zinc(II) complex was titrated into the DNA/EB mixture and diluted in Tris–HCl buffer to 5 mL to get a solution with the appropriate 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 with the emission wavelength of 610 nm (λ_{ex} = 522 nm) in the Fluorimeter (Hitachi-2000).

3. Results and discussion

3.1. Synthesis and characterization

The organic ligand 1,3-bis(2-pyridylmethylthio)propane (L) was prepared by the reaction of the propane dithiol compound with 2-picolyl chloride in the presence of sodium ethoxide. In the complexes, the organic molecule L acts as a tetradentate neutral ligand through N_2S_2 donor centers. The complexes **1a–d** were obtained in good yield from the reaction of zinc(II) acetate with an equimolar amount of the organic moiety in the ethanol medium under refluxing conditions, followed by the addition of an ethanol–water solution of sodium chloride, sodium cyanate or potassium thiocyanate to the reaction mixture under cold conditions (viz. Scheme 1). In this context it is worth mentioning that complex **1a** could not be obtained by using zinc(II) chloride in place of the acetate salt in the first step, and no significant reaction of L with zinc(II) nitrate was observed in this study. On the contrary, complex $[Zn(L)(ClO_4)(H_2O)](ClO_4)$ (**2**), was obtained only when zinc(II) perchlorate was allowed to react with L. The crystal structure of **2** shows the ligand L acting as a bridging ligand, giving origin to a 1D coordination polymer.

The neutral complexes **1a–d** are soluble in DMF, but are only sparingly soluble in acetonitrile and methanol, while the monocationic complex **2** is soluble both in acetonitrile and DMF. The conductivity measurements in DMF showed that the conductance of the complexes **1a–d** were in the range 32–46 Λ_o mol^{-1} cm^{-1}, while that of **2** was 61 Λ_o mol^{-1} cm^{-1} at 300 K. These values suggest that all the complexes (**1** and **2**) exist as non-electrolytes. The observation of the non-electrolytic nature of the complexes **1a–d** are comparable with the reported neutral $[Ni(L)(ONO_2)_2]$ derivative [26].

3.2. Structure of complexes **1d** and **2**

The ORTEP views of **1d** and **2**, with the atom numbering schemes, are illustrated in Figs. 1 and 2, respectively, and a selection of bond distances and angles are listed in Table 2.

In the mononuclear complex **1d** the organic moiety L behaves as a tetradentate ligand, chelating the metal in such a way as to locate the pyridine rings in trans positions, and the metal ion completes the highly distorted octahedral coordination sphere with two cis located isothiocyanato anions. The configuration is similar to the complexes $[Fe(L)Cl_2]$ and $[Ni(L)Cl_2]$ reported by these laboratories [19].

The Zn–N(py) and Zn–NCS bond lengths are comparable within their e.s.d.'s (mean values 2.142(5) and 2.040(5) Å, respectively), while the Zn–S distances differ by ca. 0.02 Å, being of 2.6500(18) and 2.6990(17) Å. The bond angles subtended at the metal deviate considerably from the ideal octahedral values and the N(1)–Zn–N(2) and N(2)–Zn–S(2) angles of 161.28(17)° and 77.57(13)°, respectively show the highest deviation. In fact the pyridine rings of the ligand are bent with respect to the S_2N_2 plane, forming a dihedral angle of 82.3(1)°, induced by ligand constraints upon coordination, while the dihedral angle made by the trans located pyridine mean planes is 52.2(2)°.

The Zn–N–C coordination bond angles involving the thiocyanate are slightly different, with values of 159.4(5)° and 165.7(5)°, the difference might likely be adopted to favor sulfur···π interactions. In fact the crystal packing of complex **1d** shows a 1D polymeric arrangement built by S(4)···π interactions along the *a*-axis (Fig. 3). Labeling Cg as the centroid of the pyridine N(1) at $-1 + x$, y, z, the S···Cg distance is 3.902(4) Å, with a C(17–S(4)···Cg angle of 108.0(2)°.

The solid state structure of complex **2** demonstrates that the organic moiety L behaves as bridging ligand between two zinc ions,

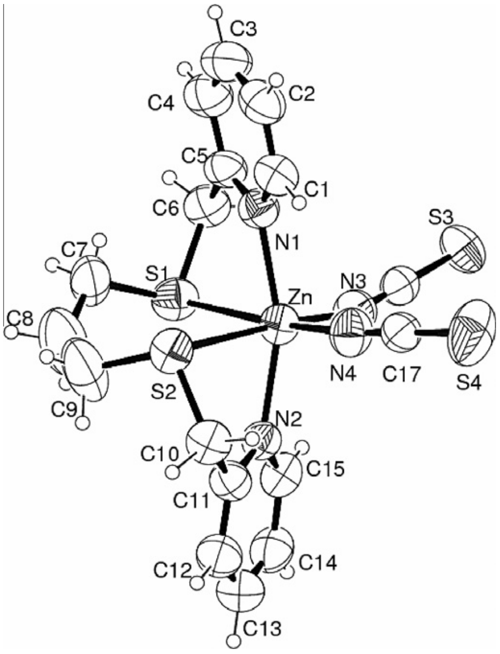


Fig. 1. An ORTEP diagram of the complex $[Zn(L)(SCN)_2]$ (**1d**) with the atom numbering scheme.

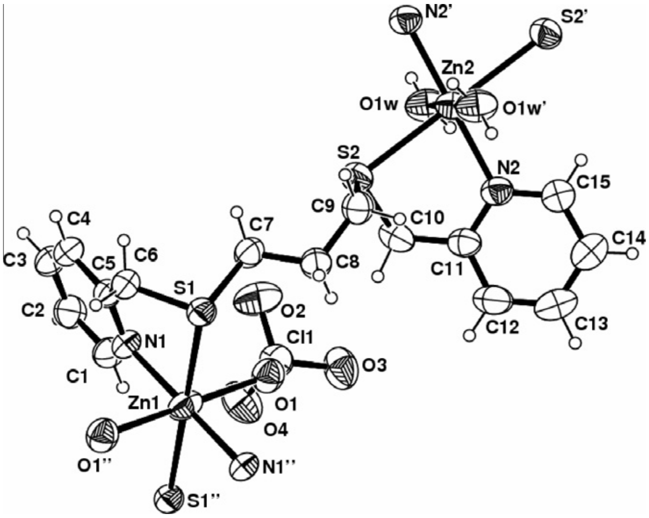


Fig. 2. Details (ORTEP drawing, 35% probability ellipsoid) of the coordination polymeric chain of $\{[Zn(L)(ClO_4)(H_2O)](ClO_4)\}_n$ (**2**) with the atom labeling scheme (the second perchlorate anion is not shown).

Table 2
Selected bond distances (Å) and bond angles (°) for complexes **1d** and **2**.

1d		**2**	
Bond lengths (Å)			
Zn–N(1)	2.141(5)	Zn(1)–N(1)	2.066(4)
Zn–N(2)	2.144(4)	Zn(1)–S(1)	2.5792(16)
Zn–N(3)	2.039(5)	Zn(1)–O(1)	2.308(5)
Zn–N(4)	2.041(5)	Zn(2)–N(2)	2.111(5)
Zn–S(1)	2.6500(18)	Zn(2)–S(2)	2.5779(19)
Zn–S(2)	2.6990(17)	Zn(2)–O(1w)	2.124(5)
Bond angles (°)			
N(1)–Zn–N(2)	161.28(17)	N(1)–Zn(1)–S(1)	82.08(13)
N(1)–Zn–N(3)	95.56(19)	N(1)–Zn(1)–S(1′)	97.92(13)
N(1)–Zn–N(4)	95.5(2)	N(1)–Zn(1)–O(1)	92.22(17)
N(1)–Zn–S(1)	77.63(15)	N(1)–Zn(1)–O(1′)	87.78(17)
N(1)–Zn–S(2)	88.51(12)	O(1)–Zn(1)–S(1)	91.04(12)
N(2)–Zn–N(3)	97.4(2)	O(1)–Zn(1)–S(1′)	88.96(12)
N(2)–Zn–N(4)	95.90(19)		
N(2)–Zn–S(1)	89.40(12)	N(2)–Zn(2)–S(2)	81.52(16)
N(2)–Zn–S(2)	77.57(13)	N(2)–Zn(2)–S(2″)	98.48(16)
N(3)–Zn–N(4)	98.7(2)	N(2)–Zn(2)–O(1w)	90.88(19)
N(3)–Zn–S(1)	87.63(15)	N(2)–Zn(2)–O(1w″)	89.12(19)
N(3)–Zn–S(2)	173.61(15)	O(1w)–Zn(2)–S(2)	83.53(16)
N(4)–Zn–S(1)	171.15(15)	O(1w)–Zn(2)–S(2″)	96.47(16)
N(4)–Zn–S(2)	85.81(15)		
S(1)–Zn–S(2)	88.43(6)		
C(16)–N(3)–Zn	159.4(5)		
C(17)–N(4)–Zn	165.7(5)		

Symmetry codes: (′) $-x+1, -y+1, -z+1$; (″) $-x+1, -y, -z$.

giving origin to 1D coordination polymers running parallel to the (0 1 1) crystallographic planes. Actually the flexible NSSN ligand acts as a bis chelating agent through one thioether-S and one pyridyl-N atom towards the two crystallographically independent metal ions, positioned on centers of symmetry, separated by 8.729(3) Å. The two ions have similar $N_2S_2O_2$ octahedral coordination spheres and are doubly chelated by two different (symmetry related) L ligands, completing the octahedral coordination geometry through two perchlorate oxygens (Zn(1)) and two water molecules (Zn(2)). The Zn–N bond distances (2.066(4) and 2.111(5) Å) manifest a slight difference, while the Zn–S ones have comparable values (2.5792(16) and 2.5779(19) Å) [27], but all these are shorter than those measured in **1d**, likely indicating a reduced strain upon bridging coordination. This feature is supported by the coordination bond angles being closer to the ideal values (Table 2), the chelating N–Zn–S angles (82.08(13)° and 81.52(16)°) being those most deviated (Table 3). Finally the Zn(1)–O(1)ClO_3 bond length of 2.308(5) Å is significantly longer than that of Zn(2)–O(1w) (2.124(5) Å), most likely due to the more bulky perchlorate anion, though packing effects and H-bond formation cannot be ruled out. The polynuclear chains are connected to each other by H-bonds (Fig. 4 and Table 3) occurring between the aquo ligand with the oxygens atoms of the perchlorate anions to form a 2D layered arrangement.

3.3. Spectral characterization

The infrared spectra of all the complexes exhibit characteristic strong to medium intensity bands in the regions 1468–1472 and 758–762 cm^{-1}, which are assignable to stretching $\nu_{C=N}$ and ν_{C-S}, respectively, in addition to the other characteristic bands of the organic moieties. These observations support the presence of the ligand frame containing the pyridine ring and the C–S bond in the complex, ν_{C-S} generally being observed in the free ligand in the range 780–790 cm^{-1}. In addition, the characteristic intense band at 2035 cm^{-1} in **1b**, intense band at 2167 cm^{-1} in **1c** and the strong band at 2085 cm^{-1} in **1d** confirms the presence of terminal end-on azide [28], terminal N-bonded NCO [29] and N-bonded SCN [30], respectively.

The electronic absorption spectra of the complexes were recorded at room temperature using DMF as the solvent, and the results are given in Table 4. The spectra of the complexes exhibit transitions lower than 400 nm. The absorption bands at lower than 275 nm correspond to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi$ transitions and the weak band at around 300 nm is due to a charge transfer d(Zn) → π* transition (MLCT).

3.4. DNA-binding studies

The binding mode of complex **2** with calf thymus DNA was examined by electronic absorption titrations (Figs. 5 and 6) and ethidium bromide (EB) fluorescence displacement experiments (Figs. 7 and 8). The absorption and emission spectra were studied to investigate the interaction of the zinc(II) complex **2** to calf thymus DNA (CT-DNA). The binding phenomenon of the metal complex with DNA was investigated by the electronic absorption spectral technique. In general, an intercalative interaction between an aromatic chromophore of a complex and the DNA helix is reflected by hypochromism and a red shift of the charge transfer band due to strong stacking interactions between the aromatic chromophore of the complex and the base pairs of DNA [31]. The absorption spectra of complex **2** in the absence and presence of CT-DNA, given in Fig. 5, show a significant hyperchromism which suggests that there is a strong non-intercalative interaction. The spectral changes of complex **2** observed in the presence of CT-DNA can be illustrated in terms of groove binding. It is reported that if the aromatic ring of the molecule closely matches with the helical turn of the CT-DNA groove, the aromatic rings of the ligand interact with DNA in Tris–HCl buffer through the formation of the van der Waal's contacts or hydrogen bonds in the DNA grooves.

The binding strength and also the type of binding of complex **2** with CT-DNA were examined by the determination of the apparent association constant, K_b from the spectral titration data using the following equation [32]:

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

where [DNA] is the concentration of DNA, ε_f, ε_a and ε_b correspond to the extinction coefficients, respectively, for the free complex **2**, for each addition of DNA to complex **2** and for complex **2** in the fully bound form. The apparent association constant (K_b) for complex **2**, estimated to be 4.7×10^4 M^{-1} (R^2 = 0.97122 for seven points) from

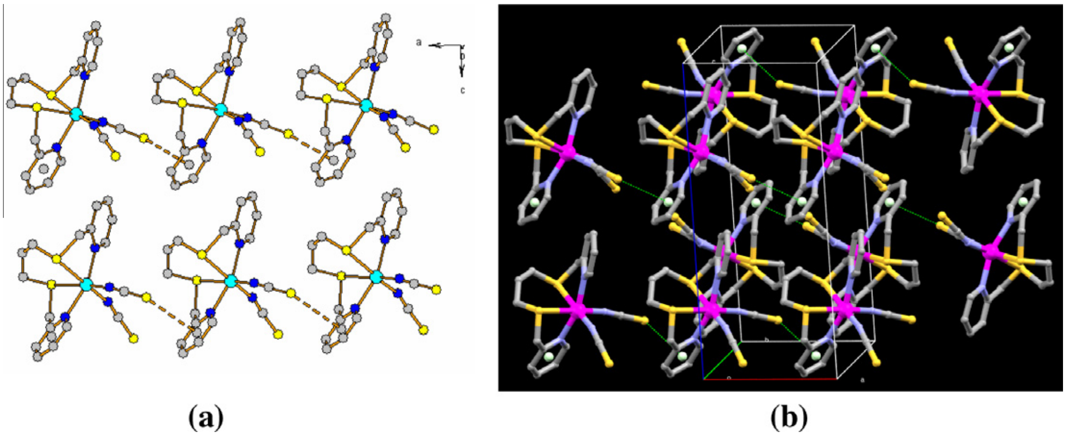


Fig. 3. (a) 1D arrangement of **1d** formed by S···π interactions extended along the *a*-axis. (b) Packing view of **1d**.

Table 3
Intermolecular hydrogen bond parameter (Å/°) of **2**.

D—H	d(D—H)	d(H···A)	∠DHA	d(D···A)	A/symmetry code
O1w–H1w	0.847	2.291	132.49	2.931	O3 [$-x+1, -y+1, -z$]
O1w–H2w	0.838	1.848	163.69	2.663	O8 [$-x+2, -y+1, -z$]

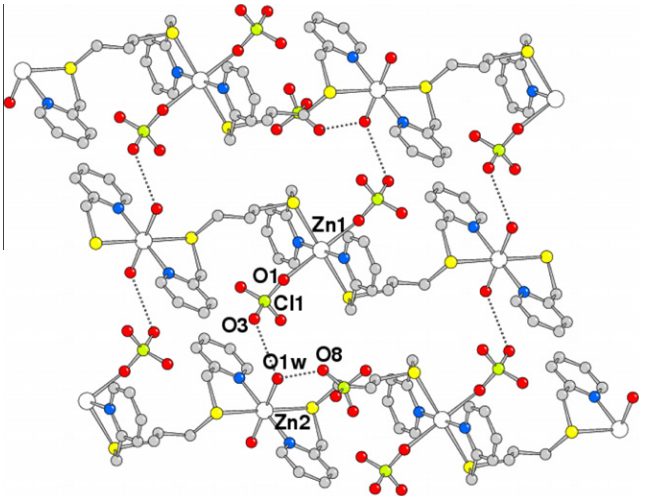


Fig. 4. 2D arrangement of **2** built up by H-bonds involving the aquo ligand with the oxygen atoms of perchlorate anions.

Table 4
UV–Vis spectral data of the zinc(II) complexes (**1** and **2**).[a]

Compounds	λ nm (ε) (ε, dm^3 mol^{-1} cm^{-1})
1a	221(6231), 246(8976), 268(10 103), 300(2987)
1b	235(3455), 250(8534), 266(9965), 296(3216)
1c	226(3660), 248(9643), 268(10 989), 298(3128)
1d	232(3448), 252(9456), 268(9889), 311(2986)
2	244(3205), 266(7943), 313(1214), 366(424)

[a] In DMF.

the [DNA]/($\varepsilon_a - \varepsilon_f$) versus [DNA] plot (Fig. 6), also establishes the presence of a groove binding interaction of the zinc(II) complex with CT-DNA, which is comparable with the well-established binding agent spermine [33].

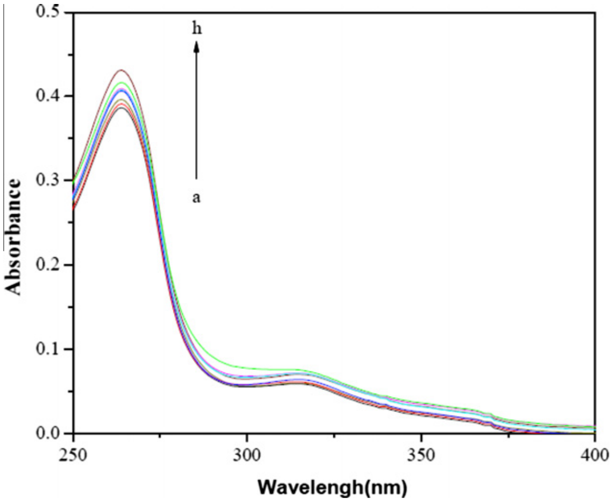


Fig. 5. Electronic spectral titration of complex **2** with CT-DNA at 266 nm in Tris–HCl buffer. Arrow indicates the direction of change upon increasing the DNA concentration.

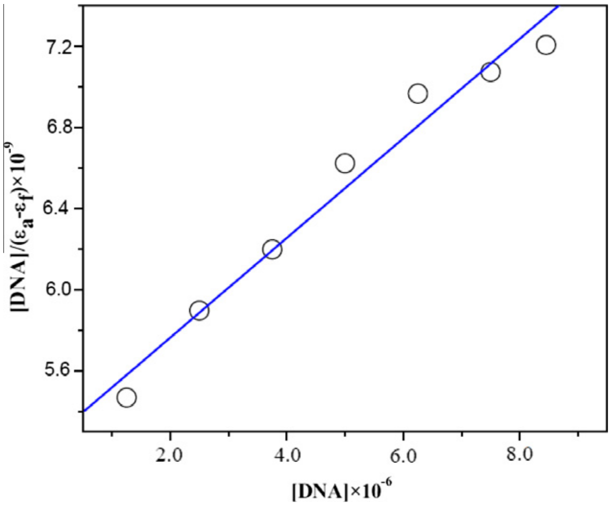


Fig. 6. Plot of [DNA]/($\varepsilon_a - \varepsilon_f$) vs. [DNA] for the absorption titration of CT-DNA with the zinc(II) complex **2** in Tris–HCl buffer.

The fluorescence intensity of EB bound to CT-DNA at the excitation wavelength of 522 nm shows a decreasing trend with an

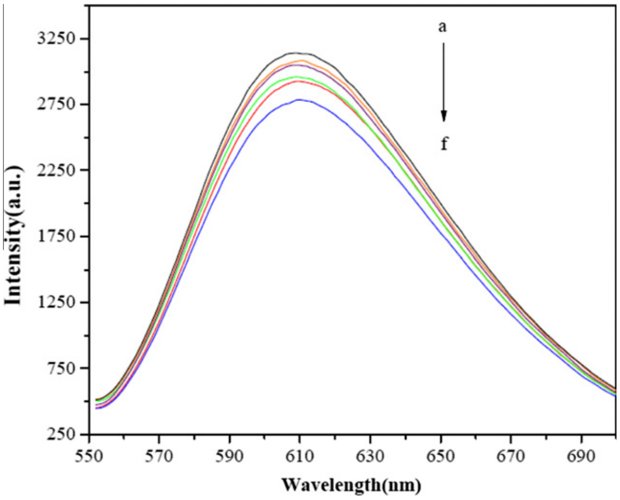


Fig. 7. Emission spectra of the CT-DNA–EB system in Tris–HCl buffer upon titration of the zinc(II) complex **2**, $\lambda_{ex} = 522$ nm. Arrow shows the intensity change upon increasing the complex concentration.

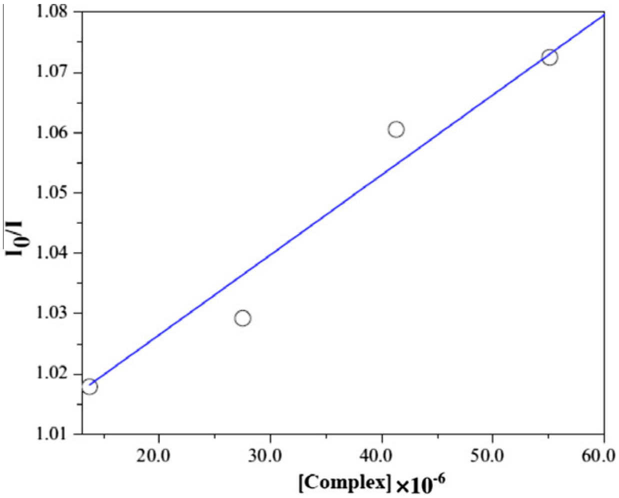


Fig. 8. Plot of I_0/I vs. [complex] for the titration of the zinc(II) complex **2** with the CT-DNA–EB system.

increasing concentration of complex **2** (Fig. 7) where the blue colored spectrum indicates the maximum binding with complex **2** replacing EB. The quenching of EB bound to DNA by complex **2** is in agreement with the linear Stern–Volmer equation [34]:

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

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. The K_{sv} value calculated from the plot (Fig. 8) of I_0/I versus [complex] for complex **2** is 1.3×10^3 ($R = 0.95648$ for four points), suggesting a strong affinity of the complex **2** to CT-DNA.

The number of binding sites can be calculated from the fluorescence titration data using the following equation [35]:

$$\log[(I_0 - I)/I] = \log K + n\log[Q]$$

K and n are the binding constant and binding site of complex **2** to CT-DNA respectively. The number of binding sites (n) determined from the intercept of $\log[(I_0 - I)/I]$ versus $\log[Q]$ is 0.92, which indicates less association of complex **2** to the number of DNA bases, and also suggests a strong affinity of complex **2** through surface or groove binding.

4. Conclusion

The synthesis and characterization of four new mononuclear complexes (**1**) and a polymeric coordination zinc(II) complex (**2**) with a N_2S_2 donor set have been performed. On reaction with chloride ions or pseudohalides (azide, cyanate and thiocyanate ions) in ethanol at refluxing temperature, the reaction mixture of the organic molecule L and zinc(II) acetate gave hexa-coordinated mononuclear zinc(II) complexes of the general formula $[Zn(L)(X_2)]$ ($X = Cl^-$, N_3^-, NCO^- and SCN^-). Complexes with similar or different coordination could not be isolated with zinc(II) nitrate or zinc(II) chloride. On the other hand, on reaction of the organic ligand L with the zinc(II) perchlorate salt, a coordination polymeric complex formulated as $\{[ZnL(ClO_4)(H_2O)](ClO_4)\}_n$ (**2**) was separated in the solid state. The study indicates that different counter anions of the zinc(II) salts used as the reactant lead to the isolation of complexes of different configurations. The electronic spectral titration of the coordination polymer $\{[Zn(L)(ClO_4)(H_2O)](ClO_4)\}_n$ (**2**) with CT-DNA in Tris–HCl buffer showed a significant non-intercalative interaction due to stacking between the aromatic chromophore of **2** and the base pairs of DNA, with the apparent estimated association constant (K_b) of 4.7×10^4 M^{-1}. The linear Stern–Volmer quenching constant (K_{sv}) of 1.3×10^3 and the binding sites (n) of 0.92, determined from ethidium bromide (EB) fluorescence displacement experiments, suggest a good affinity of complex **2** to CT-DNA through a groove binding mode.

Acknowledgments

Financial support from the Department of Science and Technology (DST), New Delhi, India is gratefully acknowledged. E. Zangrando thanks MIUR-Rome, PRIN 2007HMTJWP_002 for financial support.

Appendix A. Supplementary data

CCDC 829057 and 829058 contain the supplementary crystallographic data for compounds **2** and **1d**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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