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Structural effects of potentially hexadentate Schiff base ligands involving pyrrolic, etheric or thioetheric donors towards zinc(II) cation: Synthesis, characterization and crystal structures

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ABSTRACT

The three new zinc (II) complexes (ZnL^m, m = 1–3) of potentially hexadentate Schiff base ligands containing N_4O_2 and N_4S_2 donors with pyrrole terminal binding groups H_2L^1:[(1Z)-1H-pyrrole-2-ylmethylene]{2-[2-(2-{[(1Z)-1H-pyrrole-2-ylmethylene]amino}phenoxy)ethoxy]phenyl}amine, H_2L^2:[(1Z)-1H-pyrrole-2-ylmethylene]{2-[4-(2-{[(1Z)-1H-pyrrole-2-ylmethylene]amino}phenoxy)butoxy]phenyl}amine and H_2L^3:[1*H*-pyrrole-2-ylmethylene][2-({2-[(2-{[1*H*-pyrrole-2-ylmethylene] amino}phenyl)thio]ethyl}thio)phenyl]amine, were synthesized and physicochemically characterized. Cyclic voltammetry data indicate that the complexes are electrochemically inactive. The molecular structures of the complexes were determined by single crystal X-ray diffraction. The Zn(II) is five coordinated by N_4O donor set of the ligands in the ZnL^1 and ZnL^2 and six coordinated by N_4S_2 donor set in the ZnL^3.

1. Introduction

Schiff bases form an interesting class of chelating ligands that have enjoyed popular use in the coordination chemistry of transition, inner-transition and main group elements [1–5]. The chemistry of metal complexes with chelate ligands containing nitrogen, sulfur or oxygen donors has been extensively studied in order to gain an understanding of the following processes: (i) the redox function of various metalloenzymes in living systems; (ii) the formation and reactivity of dioxygen in synthetic, industrial and biological processes. In enzymes metal ions have several functions: (i) redox as in superoxide dismutase-like activity [6–10], (ii) structural and catalytical functions [11–15]. The complexation sites of these proteins are N, S or O donors coming from histidine, tyrosine, aspartic or glutamic acids and cysteine[16–20].

Zinc atom has either a structural or catalytic role in several proteins. It has also been recognized as an important cofactor in biological molecules, either as a structural template in protein folding or as a Lewis acid catalyst that can readily adopt 4-, 5- or 6-coordination [21].

Mononuclear zinc complexes may serve as model compounds for zinc enzymes such as phospholipase C, bovine lens leucineaminopeptidase, ATPases, carbonic anhydrases and peptide deformylase. Binuclear cores are present at the active sites of many metalloenzymes and play an essential role in many biological systems. The zinc(II) ion is known to have a high affinity towards nitrogen and sulfur donors. Dowling and Parkin investigated Zn(II) complexes with mixed N, O and S coordination to understand the reactivity of the pseudotetrahedral zinc center in proteins [22]. In order to elucidate the effects of the distinctive structural features of the ligands on the properties of their complexes, we recently described [23] the coordination of copper and nickel atoms with a series of potentially hexadentate Schiff base ligands containing N_4O_2 and N_4S_2 donors with pyrrole terminal binding groups, H_2L^m (m = 1–4) (Scheme 1).

As a continuation of our interest to provide a better understanding of the physicochemical and coordination properties of complexes, and as models for the active sites in metalloproteins, we present herein the synthesis, spectroscopic characterization and electrochemical behavior of the three zinc(II) complexes of H_2L^m (m = 1–3) ligands. The complexes were also characterized by single crystal X-ray crystallography.

2. Experimental

2.1. Materials

The solvents and reagents used in these studies were obtained from commercial sources and were used as received.

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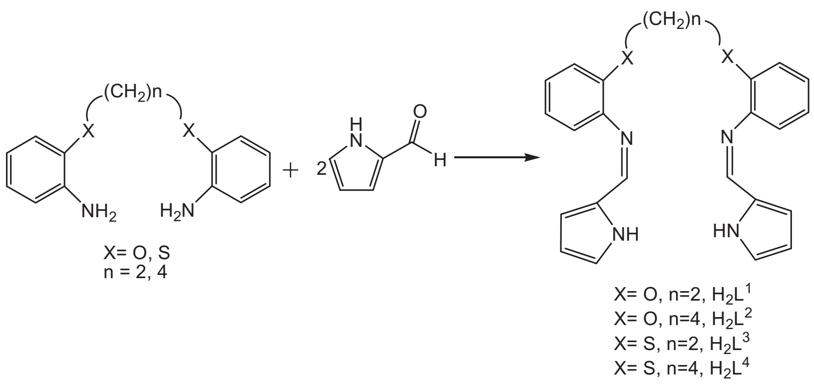

Scheme 1. Synthesis and structure representation of Schiff base ligands (H_2L^m, m = 1–4).

2.2. Physical measurements and methods

FT-IR spectra were recorded using KBr discs on a Bruker Tensor 27 instrument. The electronic spectra in the 220–500 nm range were obtained on a Shimadzu UV-1650 PC spectrophotometer using 1.0 cm quartz cells and solutions with the concentration of 5×10^{-5} M in CH_2Cl_2. Elemental analyses were carried out using an Elementar Vario EL III instrument. Melting points were taken using an electrothermal IA 9100 apparatus in open capillary tubes. Cyclic voltammograms were obtained using 1×10^{-3} M solutions of the complexes in DMF using an Auto lab potentiostat PGSTAT 302 ECO CHEMIE. All solutions were deoxygenated by passing a stream of argon into the solution for at least 10 min prior to recording the voltammogram. All potentials were measured at room temperature and referenced to the saturated Ag/AgCl electrode with ferrocene as an internal standard. A glassy carbon disc with a diameter of 3 mm was used as the working electrode and a platinum wire was used as the counter electrode. Before each experiment the working electrode was polished with alumina and rinsed thoroughly with distilled water and acetone. The electrolytic medium consisted of 0.1 M $LiClO_4$ in DMF. Conductivity data were measured in DMF on a Metrohem 712 conductometer instrument.

2.3. X-ray crystallography

Single crystals of the complex ZnL^1 were obtained from ethanol/dichloromethane (1:4, v/v), and those of ZnL^2 and ZnL^3 from acetonitrile/dichloromethane (1:4, v/v) by slow evaporation at room temperature. The data sets for ZnL^1 and ZnL^3 were collected on an Oxford Diffraction Super Nova diffractometer, using Enhance (Mo) X-ray structure, mirror-mono chromatized Mo Kα radiation λ = 0.7107 Å at 130 K. The data for ZnL^2 were collected on an Oxford Diffraction Xalibur, Sapphire 3 diffractometer with graphite-monochromatized Mo Kα at 293 K. Data were reduced and corrected for absorption using the CrysAlisPro software [24]. The structures were solved using direct methods and refined on F^2 by full-matrix least-squares procedures using the SHELXL-97 program package [25]. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were located to carbon in geometric positions refined by using a riding model. A summary of crystallographic data for the complexes is given in Table 1.

2.4. Synthesis

2.4.1. Diamines and ligands

The Schiff base ligands, H_2L^1, H_2L^2 and H_2L^3 (Scheme 1) and their related diamines were prepared according to published procedures [23,26,27] but with an extension of the reflux time to 48 h in the case of H_2L^3.

2.4.2. Zinc(II) complexes

All zinc (II) complexes of the ligands were prepared by addition of a solution of zinc acetate dihydrate (0.5 mmol, 0.1097 g) in ethanol (20 ml) to a solution of H_2L^1, H_2L^2 and H_2L^3 (0.5 mmol) in absolute ethanol. In each case, the reaction mixtures were refluxed for 4 h, and the precipitate was filtered and recrystallized from CH_3CH_2OH/CH_2Cl_2 (1:4, v/v)

ZnL^1: color: brown, Yield: 47.63% (0.11 g), M.P > 280 °C (dec), Selected FT-IR data ν (cm^{-1}); 3066 w (CH_{arom}), 2925–2857 w (CH_{aliph}), 1562 s (C═N), 1296s $(C–O–C)_{asym}$, 1028 s $(C–O–C)_{sym}$, 741 m (δ $CH_{aromatic}$). *Anal.* Calc. for $C_{24}H_{20}ZnN_4O_2$: C, 62.41; H, 4.36; N, 12.13. Found: C, 62.37; H, 4.261; N, 12.04%. Λ_m = 1.6 Ω^{-1} - cm^2 mol^{-1} in DMF. UV–Vis [λ_{max}/nm (ε/M^{-1} cm^{-1})]: 396(28620), 299(4640), 248(6720), 224(7720) in CH_2Cl_2

ZnL^2: color: yellow, Yield: 57.15% (0.14 g), M.P > 215 °C (dec), Selected FT-IR data ν (cm^{-1}): 3066 w (CH_{arom}), 2933 w (CH_{aliph}), 1561 s (C═N), 1285 s $(C–O–C)_{asym}$, 1030 s $(C–O–C)_{sym}$, 745 m (δ $CH_{aromatic}$). *Anal.* Calc. for $C_{28}H_{27}ZnN_5O_2$: C, 63.74; H, 4.94; N, 11.44. Found: C, 63.69; H, 4.846; N, 11.44%. Λ_m = 1.8 Ω^{-1} cm^2 - mol^{-1} in DMF. UV–Vis [λ_{max}/nm (ε/M^{-1} cm^{-1})]: 388(30420), 299(4640), 247(6740), 227(6880) in CH_2Cl_2

ZnL^3: color: yellow, Yield: 52.63% (0.13 g), M.P > 285 °C (dec), Selected FT-IR data ν (cm^{-1}): 3067 w (CH_{arom}), 2909–2845 w (CH_{aliph}), 1547 s (C═N), 1179 s $(C–S–C)_{asym}$, 1034 s $(C–S–C)_{asym}$, 744 m (δ $CH_{aromatic}$). *Anal.* Calc. for $C_{24}H_{20}ZnN_4S_2$: C, 58.35; H, 4.08; N, 11.34. Found: C, 58.32; H, 3.986; N, 11.29%. Λ_m = 2.1 Ω^{-1} - cm^2 mol^{-1} in DMF. UV–Vis [λ_{max}/nm (ε/M^{-1} cm^{-1})]: 427(19440)(sh), 407(28140), 308(4540), 259(4760), 225(9260) in CH_2Cl_2.

3. Results and discussion

The ZnL^m (m = 1–3) complexes were prepared by the reaction of the ligands, H_2L^m, with zinc acetate dihydrate in a 1:1 ratio in ethanol (Scheme 1). Unfortunately all attempts using a range of different procedures failed to synthesize ZnL^4. All elemental analyses are consistent with the proposed molecular formulae which had a ratio of 1:1 metal:ligand in all cases. The low molar conductivity of the complexes in ca. 10^{-3} M solutions in DMF at room temperature [28], on the one hand, and the absence of pyrrole N–H stretches in the FT-IR spectra of the complexes, on the other hand, indicate that the complexes are all neutral and that the ligands act as doubly negatively charged anions in complexation by deprotonation of the pyrrole groups, prior to complexation. The zinc ions are also bound to the ligands through the azomethine nitrogens. This can

Table 1
Crystallographic data for ZnL^1, ZnL^2 and ZnL^3.

	ZnL^1	ZnL^2	ZnL^3
Formula	$C_{24}H_{20}N_4O_2Zn$	$C_{28}H_{27}N_5O_2Zn$	$C_{24}H_{20}N_4S_2Zn$
Formula weight	461.81	530.92	493.93
T (K)	130.0	293(2)	130.0
Crystal color	brown	yellow	yellow
Crystal size (mm)	0.34 × 0.23 × 0.20	0.54 × 0.19 × 0.10	0.53 × 0.36 × 0.21
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$C2$	$P2_1/n$	$P2_1/c$
a (Å)	20.7753(4)	14.0530(10)	14.2936(3)
b (Å)	10.6096(2)	22.5538(13)	10.6233(2)
c (Å)	20.0017(4)	17.2518(13)	15.3449(3)
β (°)	109.329(2)	110.235(8)	109.423(2)
V (Å^3)	4160.22(14)	5130.5(6)	2197.44(8)
Z	8	8	4
μ (mm^{-1})	1.210	0.992	1.327
D_{calc} (Mg/m^3)	1.475	1.375	1.493
Radiation (λ, Å)	0.7107	0.7107	0.7107
Reflections collected/unique	5652/5371	9371/4850	3865/3618
$F(000)$	1904	2208	1016
θ (°)	3.2105–28.0752	2.9228–29.2060	3.0162–29.2362
Index ranges	$-24 \leqslant h \leqslant 18$, $-12 \leqslant k \leqslant 11$, $-23 \leqslant l \leqslant 20$	$-18 \leqslant h \leqslant 18$, $-31 \leqslant k \leqslant 23$, $-22 \leqslant l \leqslant 20$	$-16 \leqslant h \leqslant 16$, $-12 \leqslant k \leqslant 11$, $-18 \leqslant l \leqslant 18$
Data/restraints/parameters	5652/1/559	9371/0/651	3865/0/281
Goodness-of-fit (GOF) on F^2	0.957	1.025	1.052
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0272$, $wR_2 = 0.0516$	$R_1 = 0.0648$, $wR_2 = 0.1792$	$R_1 = 0.0222$, $wR_2 = 0.0571$
R indices (all data)	$R_1 = 0.0295$, $wR_2 = 0.0493$	$R_1 = 0.1288$, $wR_2 = 0.1621$	$R_1 = 0.0244$, $wR_2 = 0.0560$
Largest difference in peak and hole (e/Å^3)	0.293 and −0.291	0.536 and −0.590	0.276 and −0.247

$R_1 = [\sum - ||F_o| - |F_c||]/\sum|F_o|$ (based on F), $wR_2 = \{[\sum w(|F_o{}^2 - F_c{}^2|)^2]/[\sum w(F_o{}^2)^2]\}^{1/2}$ (based on F^2).

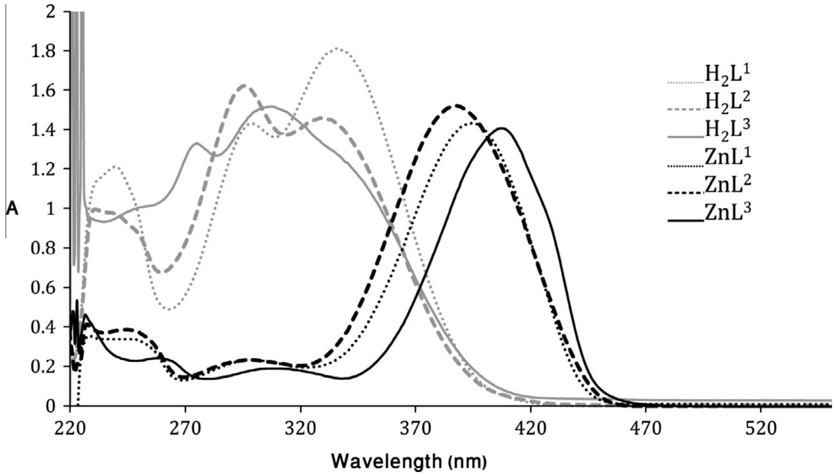

Fig. 1. UV–Vis spectra of the free ligands and their corrosponding zinc complexes.

be deduced from the observed decreases of 55, 62 and 74 cm^{-1} in C=N stretching frequencies in comparison with those of corresponding free ligands, H_2L^m (m = 1–3, 1617, 1623 and 1621 cm^{-1}, respectively). It seems that the C=N frequency in the complex is affected by the coordination geometry of the complex but the length of the aliphatic linkage has relatively little impact. ZnL^1 and ZnL^2 with five coordinated X-ray structures have equivalent $\nu_{C=N}$ values of 1562 and 1561 cm^{-1}. In contrast, ZnL^3 with a six-coordinated X-ray structure has a quite different $\nu_{C=N}$, of 1547 cm^{-1}. Compared to these complexes, NiL^3 and CuL^2 analogs [23] with six- and four-coordination geometries, respectively, show comparable C=N stretching frequencies of 1540 cm^{-1} for NiL^3 and 1558 cm^{-1} CuL^2. The UV–Vis spectra of the complexes were studied in dichloromethane at 5×10^{-5} M concentration in the region of 220–500 nm. All the complexes have similar spectral features with only one broad and intense transition in 330–450 nm region, centered at 396, 388 and 407 nm for ZnL^1, ZnL^2 and ZnL^3, respectively, are corresponding to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions [23]. In contrast the electronic transitions of the free ligands are intense and blue shifted with respect to the complexes, Fig. 1. It seems that the dipole moments in the complexes are quite different from the free ligands.

4. Structural studies

X-ray analyses reveal that the compounds ZnL^1, ZnL^2 and ZnL^3 crystalize in the monoclinic space groups $C2$, $P2_1/n$ and $P2_1/c$, respectively. The ORTEP diagrams of the compounds along with atomic numbering schemes are in Figs. 2,3 and 4 and selected bond lengths and angles are given in Tables 2,3 and 4, respectively.

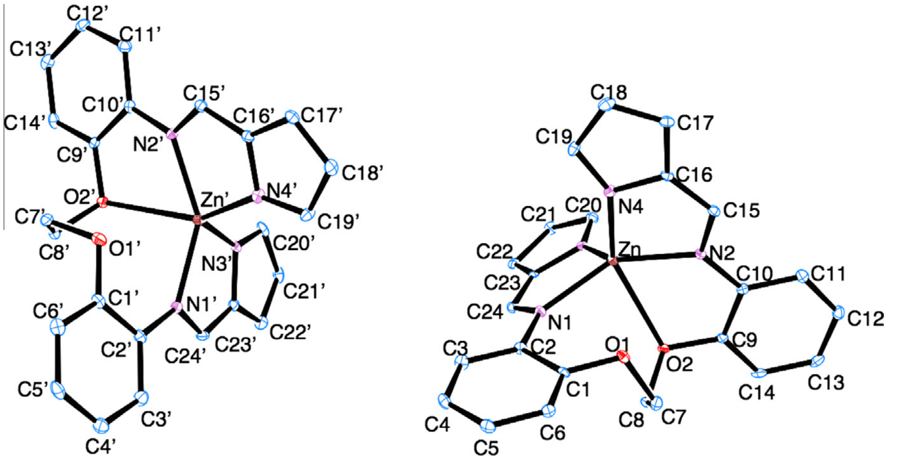

Fig. 2. Crystal structure of the ZnL^1. Hydrogen atoms are omitted for clarity.

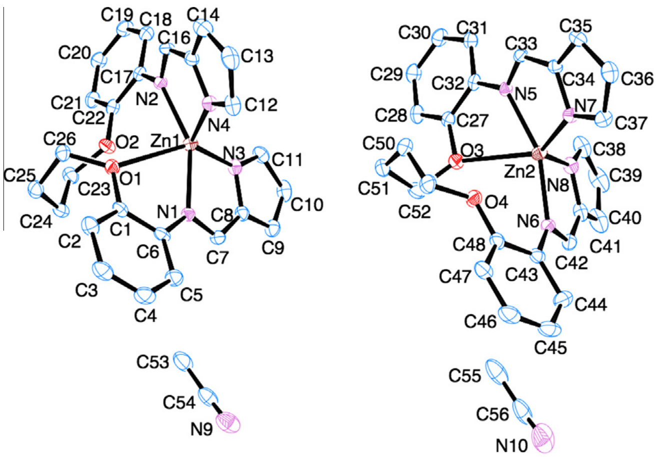

Fig. 3. Crystal structure of the ZnL^2. Hydrogen atoms are omitted for clarity.

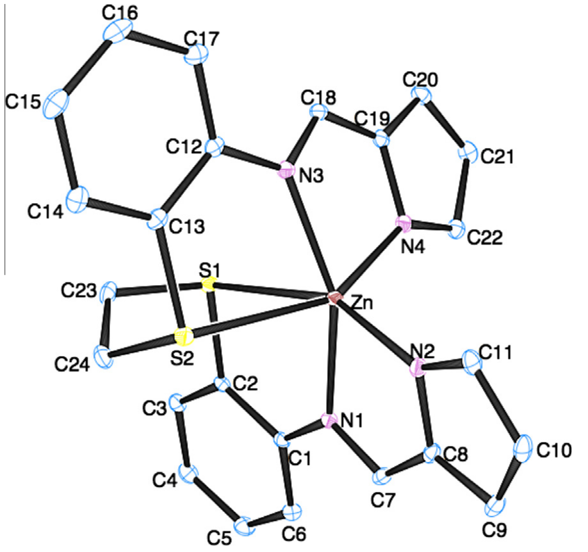

Fig. 4. Crystal structure of the ZnL^3. Hydrogen atoms are omitted for clarity.

Table 2
Selected bond lengths (Å) and bond angles (°) for ZnL^1.

Bond lengths			
Zn–N(1)	2.062(3)	Zn′–N′(1)	2.073(3)
Zn–N(2)	2.049(3)	Zn′–N′(2)	2.050(3)
Zn–N(3)	2.007(3)	Zn′–N′(3)	1.996(3)
Zn–N(4)	2.027(3)	Zn′–N′(4)	2.028(3)
Zn–O(2)	2.559(2)	Zn′–O′(2)	2.574(2)
Bond angles			
N(1)–Zn–N(2)	145.27(10)	N′(1)–Zn′–N′(2)	146.00(11)
N(2)–Zn–N(3)	120.47(11)	N′(2)–Zn′–N′(3)	122.01(11)
N(3)–Zn–N(1)	82.72(11)	N′(3)–Zn′–N′(1)	82.97(11)
O(2)–Zn–N(4)	149.25(9)	O′(2)–Zn′–N′(4)	149.10(9)
N(4)–Zn–N(1)	111.82(11)	N′(4)–Zn′–N′(1)	110.29(11)
N(4)–Zn–N(2)	82.12(11)	N′(4)–Zn′–N′(2)	81.93(11)
N(4)–Zn–N(3)	116.75(10)	N′(4)–Zn′–N′(3)	114.07(10)
O(2)–Zn–N(1)	86.27(8)	O′(2)–Zn′–N′(1)	88.91(8)
O(2)–Zn–N(2)	69.95(9)	O′(2)–Zn′–N′(2)	69.12(9)
O(2)–Zn–N(3)	89.21(9)	O′(2)–Zn′–N′(3)	91.15(9)

Table 3
Selected bond lengths (Å) and bond angles (°) for ZnL^2.

Bond lengths			
Zn(1)–N(1)	2.052(4)	Zn(2)–N(6)	2.050(4)
Zn(1)–N(2)	2.060(4)	Zn(2)–N(5)	2.056(4)
Zn(1)–N(3)	2.007(4)	Zn(2)–N(8)	2.010(4)
Zn(1)–N(4)	2.009(4)	Zn(2)–N(7)	2.010(4)
Zn(1)–O(1)	2.603(3)	Zn(2)–O(3)	2.633(4)
Bond angles			
N(1)–Zn(1)–N(3)	82.73(19)	N(6)–Zn(2)–N(8)	83.14(19)
N(3)–Zn(1)–N(2)	110.51(18)	N(8)–Zn(2)–N(5)	103.53(18)
N(2)–Zn(1)–N(4)	82.50(17)	N(5)–Zn(2)–N(7)	81.60(16)
N(4)–Zn(1)–N(1)	109.96(17)	N(7)–Zn(2)–N(6)	110.96(16)
N(1)–Zn(1)–N(2)	153.57(15)	N(6)–Zn(2)–N(5)	159.51(15)
N(4)–Zn(1)–N(3)	123.24(17)	N(7)–Zn(2)–N(8)	124.27(17)
O(1)–Zn(1)–N(1)	66.89(14)	O(3)–Zn(2)–N(5)	66.63(14)
O(1)–Zn(1)–N(2)	91.07(14)	O(3)–Zn(2)–N(6)	94.26(14)
O(1)–Zn(1)–N(3)	142.89(15)	O(3)–Zn(2)–N(7)	137.98(13)
O(1)–Zn(1)–N(4)	88.22(13)	O(3)–Zn(2)–N(8)	90.69(17)

The asymmetric units of the crystals of ZnL^1 and ZnL^2 contain two independent molecules, which are essentially identical; therefore herein after the values for one molecule the values for the other are presented in brackets. The crystal structure of ZnL^2 also contains two acetonitrile molecules in each asymmetric unit.

In the ZnL^{1}and ZnL^2 compounds, Zn(II) is five-coordinated having strong interactions with two imine and two pyrrole nitrogens and a weaker interaction with an etheric oxygen atom. These interactions are characterized by the following bond distances (Å); Zn–N(1) 2.062(3)[2.073(3)], Zn–N(2) 2.049(3)[2.050(3)], Zn–N(3)

Table 4
Selected bond lengths (Å) and bond angles (°) for ZnL^3.

Bond lengths			
Zn–N(1)	2.124(1)	Zn–S(1)	2.731(1)
Zn–N(2)	2.031(1)	Zn–N(4)	2.046(1)
Zn–N(3)	2.133(1)	Zn–S(2)	2.717(1)
Bond angles			
S(1)–Zn–N(1)	75.24(4)	S(2)–Zn–N(1)	92.19(4)
S(1)–Zn–N(2)	154.49(4)	S(2)–Zn–N(2)	91.63(4)
N(1)–Zn–N(2)	81.61(5)	S(2)–Zn–N(3)	75.53(4)
N(1)–Zn–N(3)	156.36(5)	N(4)–Zn–S(1)	86.09(4)
N(2)–Zn–N(3)	118.25(5)	N(4)–Zn–N(1)	105.24(5)
N(3)–Zn–S(1)	82.51(4)	N(4)–Zn–N(2)	110.58(5)
S(2)–Zn–N(4)	153.27(4)	N(4)–Zn–N(3)	80.75(6)
S(2)–Zn–S(1)	78.84(1)		

2.007(3)[1.997(3)] and Zn–N(4) 2.027(3)[2.028(3)] in the ZnL^1 and the corresponding mean values (Å) in the ZnL^2 are Zn(1)–N$_{imine}$ 2.056[2.054], Zn(1)–N$_{pyrrole}$ 2.009[2.010] and Zn(1)–O(1) 2.602[2.633].

The bond angles around the metal ions in those two complexes are in the range 145.27(10)–159.51(15)° for N$_{imine}$–Zn–N$_{imine}$, 114.07(10)–124.27(17)° for N$_{pyrrole}$–Zn–N$_{pyrrole}$, 81.60(16)–83(14)° for *cis* N$_{imine}$–Zn–N$_{pyrrole}$, 103.53(18)–122.01(11)° for *trans* N$_{imine}$–Zn–N$_{pyrrole}$, 88.22(13)–149.25(9)° for O–Zn–N$_{pyrrole}$, and 66.63(14)–94.26(14)° for O–Zn–N$_{imine}$.

The coordination geometry around Zn(II) is better described as a distorted tetragonal pyramidal geometry, according to Addison and Reedijk's angular structural parameter, $\tau_5 = 0.07[0.05]$ for ZnL^1 and 0.18[0.36] for ZnL^2. In five-coordinated geometry, τ_5 is defined as $(\beta - \alpha)/60$, where α and β are the two largest coordination angles [29]. The values of τ_5 are zero and unity for perfect tetragonal pyramidal and trigonal bipyramidal geometry, respectively. In the present case β = N(4)–Zn–O(2) = 149.25° [149.09°] and α = N(1)–Zn–N(2) = 145.27° [146.00°] in the ZnL^1 and β and α in ZnL^2 are 153.57° [159.51°] and 142.89° [137.98°], respectively.

The Zn–O bond distances in ZnL^1 and ZnL^2 (2.559(2) Å [2.574(2) Å] and (2.602(3) Å [2.633(4) Å], respectively) are significantly longer than normal Zn–O bond distances, which are generally around 2 Å [30–32], but nevertheless, it may be considered normal, when compared with the values of 2.550–2.711 Å cited in the literatures [33–41].

These long Zn–O distances indicate a relatively weak interaction, which can be considered to be secondary coordination. The distance between Zn and uncoordinated oxygen atoms O(1) and O(1)′ in ZnL^1 and O(2) and O(4) in ZnL^2 (2.845 Å [2.755 Å] and 2.965 Å [2.771 Å], respectively) are distinctly longer than the bonded Zn–O distances.

Ignoring the weak Zn–O bonds in the ZnL^1 and ZnL^2, both complexes become four coordinated by two imine and two pyrrole nitrogen atoms as CuL^2 analog [23]. This assumption probably could be supported by the C=N frequencies of these three complexes 1562(ZnL^1), 1561(ZnL^2) and 1558 cm^{-1} (CuL^2). The four Zn–N primary coordinate bonds have seesaw geometry according to the geometrical parameters τ_4, defined as $[360-(\alpha+\beta)]/141$, where α and β are the two largest coordination angles [42]. τ_4 Values are zero and unity for perfect square planar and tetrahedral geometry, respectively. The calculated τ_4 indexes are 0.67[0.65] and 0.59[.054] for ZnL^1 and ZnL^2, respectively. The angle between the N$_{imine}$–Zn–N$_{imine}$ and N$_{pyrrole}$–Zn–N$_{pyrrole}$ mean planes is 70.35° [70.94°] in ZnL^1 and 73.91° [76.79°] in ZnL^2. It seems that the lengths of aliphatic linkage do not affect the coordination mode in ZnL^1 and ZnL^2 complexes.

In the complex ZnL^3, Zn(II) is located in a very distorted octahedral environment, judged from the spread in its observed *cis* and *trans* angles of [75.24(4)–118.25(5)°] and [153.27(4)–156.36(5)°], respectively. The Zn(II) ion is bound through the N$_4$S$_2$ atoms where both imine nitrogens are disposed *trans* to each other with a bond angle of 156.36(5)° and both thioether sulfur atoms and the two pyrrole nitrogen atoms occupy *cis* coordination sites with bond angles of 78.84(1)° and 110.58(5)°, respectively. The Zn–N$_{pyrrole}$ bond distances [Zn–N(2) 2.031(1) Å and Zn–N(4) 2.046(1) Å] are comparable to corresponding distances in ZnL^1 and ZnL^2, but the Zn–N$_{imine}$ distances [Zn–N(1)2.124(1) Å and Zn–N(3)2.133(1) Å] are slightly longer than corresponding distances in ZnL^1 and ZnL^2.

In all of these complexes, the Zn–N$_{pyrrole}$ bond distances are shorter than the Zn–N$_{imine}$ bond lengths, leading to rather strong Zn–N$_{pyrrole}$ bonding, because the N$_{pyrrole}$'s participate in bonding with metal center as anionic nitrogens and could donate more electron density to the metal ion [23].

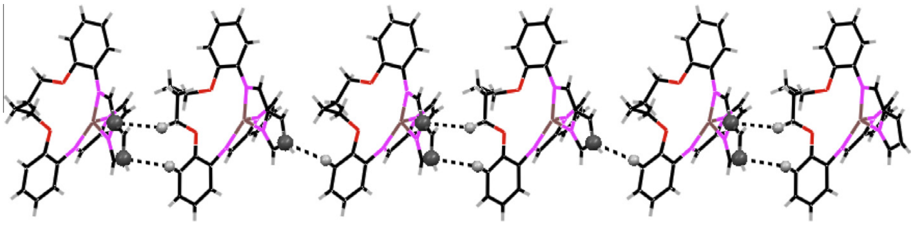

Fig. 5. The 1D coordination structure of the ZnL^2 complex.

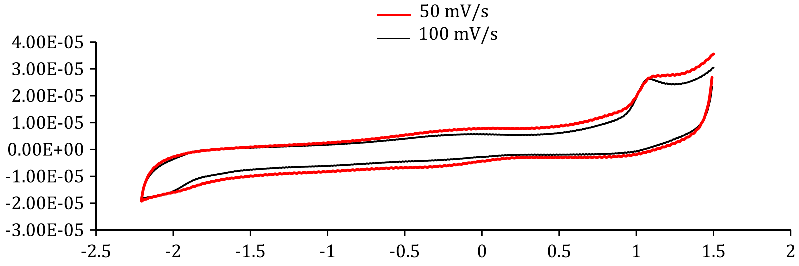

Fig. 6. Cyclic voltammogram of ZnL^2 in DMF at scan rates of 50 and 100 mV s^{-1}.

The Zn–S bond distances (average 2.724 Å) are comparable to those in references [43–46], but however seem rather longer than to those of comparable complex (average 2.617 Å) [47]. According to Brand and Vahrenkamp, the octahedral zinc complexes with Zn–S coordination are rare and that Zn–S bonding may be weak in such complexes [48].

The Zn–O bond distances in ZnL^1 and ZnL^2 (2.559–2.965 Å) are comparable with $Zn–O_{Glu}$ or $Zn–O_{Tyr}$ bond distances (2.5 and 3.0 Å respectively) reported for bacillolysin [36] and protease enzymes [37,38]. Thus it seems that the H_2L^1, H_2L^2 and H_2L^3 ligands are good platforms with which to model the structure or reactivity of zinc metalloproteins [49]. Although, the Zn–S bond distances in ZnL^3 (2.717, 2.731 Å) are longer than those reported for zinc proteins such as cobalamin with Zn–S bond distances of 2.32 Å [21].

The crystal structures of ZnL^1 and ZnL^3 show no significant interactions between the adjacent molecules. But in the ZnL^2 crystals each molecule has three H-bonding interactions with two different adjacent molecules (Table S1). One of the interactions is between the adjacent molecules in the same asymmetric unit ($C(10)_{\text{pyrrole ring}}\cdots HC(28)_{\text{phenol ring}}$) and two others are between the adjacent molecules from adjacent asymmetric units (CH(21) phenol ring···C(39) pyrrole ring) and CH(23) aliphatic linkage···C(41) pyrrole ring) and build up a one dimensional polymer along the *b* axis (see Fig. 5). Acetonitrile molecules in the ZnL^2 crystal are also H-bonded to different adjacent complex molecules. One is involved with two adjacent complex molecules (N(10)···HC(16), CH(55)B···C(31)) and the other one is engaged with three molecules(N(9)···HC(33), CH(53B)···C(17) and C(22), and CH(55C)···N(7)) (Fig. S1). The short contacts are 3D in nature and not easy to describe in any simple way. Structurally comparison between the ZnL^1 and ZnL^2, reveals that the length of aliphatic linkage has a significant effect on the crystal structures of these two compounds.

5. Cyclic voltammetry

The cyclic voltammograms of the complexes have been recorded in the potential range from 1.5 to −2.2 V, the range in which free ligands show independent anodic and cathodic peaks [23]. Upon complexation of the ligands to Zn(II), the anodic and cathodic peaks show positive and negative potential shifts, respectively, as has been observed in complexation of the ligands to Ni^{+2} [23]. But however no redox peaks can be assigned to the zinc centers in the complexes. These results suggest that the Zn^{+2} ions are becoming electrochemically inactive following complexation to the ligands. For example, cyclic voltammograms for ZnL^2 in 50 and 100 $mV\,s^{-1}$ scan rates are shown in Fig. 6.

6. Conclusion

In the present work, we have synthesized and characterized three Zn(II) complexes, ZnL^1, ZnL^2 and ZnL^3, and emphasis has been given to the structural effects of the ligands. All the complexes are neutral and electrochemically inactive. X-ray crystal structures indicate that the ZnL^3 has a distorted octahedral geometry while ZnL^1 and ZnL^2 have distorted square pyramidal coordination geometries, respectively. Due to participation of pyrrolic nitrogens as anionic nitrogens the $Zn–N_{pyrrole}$ bond lengths are shorter than the $Zn–N_{imine}$ bond distances, leading to rather strong $Zn–N_{pyrrole}$ bonding. The comparison of the C=N frequencies in the complexes indicates that the C=N frequencies is affected by the coordination geometry of the complex and the aliphatic linkage has relatively little impact. But however the length of aliphatic linkage has a significant effect on the crystal structure and no effect on the coordination mode of complexes.

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Appendix A. Supplementary material

CCDC 880929, 880930, and 880931 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2013.02.035.

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