



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 N₄O₂ and N₄S₂ donors with pyrrole terminal binding groups H₂L¹:[(1Z)-1H-pyrrole-2-ylmethylene][2-[2-(2-[(1Z)-1H-pyrrole-2-ylmethylene]amino)phenoxy]ethoxy]phenyl]amine, H₂L²:[(1Z)-1H-pyrrole-2-ylmethylene][2-[4-(2-[(1Z)-1H-pyrrole-2-ylmethylene]amino)phenoxy]butoxy]phenyl]amine and H₂L³:[1H-pyrrole-2-ylmethylene][2-[(2-[(1H-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 N₄O donor set of the ligands in the ZnL¹ and ZnL² and six coordinated by N₄S₂ donor set in the ZnL³.

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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 catalytic 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 N₄O₂ and N₄S₂ donors with pyrrole terminal binding groups, H₂L^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 H₂L^m (m = 1–3) ligands. The complexes were also characterized by single crystal X-ray crystallography.

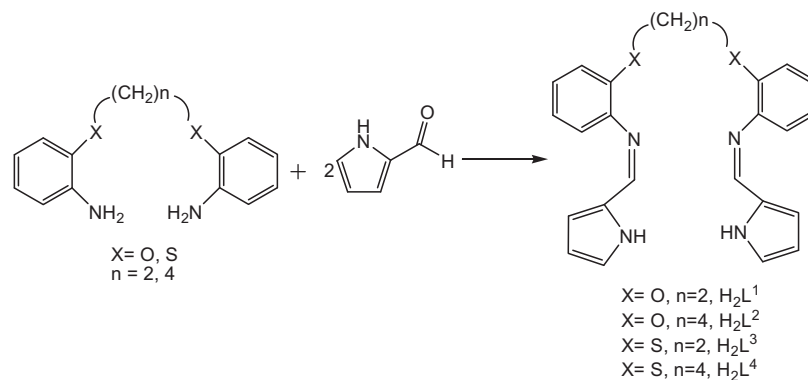
2. Experimental

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 $\text{K}\alpha$ radiation $\lambda = 0.7107 \text{ \AA}$ at 130 K. The data for ZnL^2 were collected on an Oxford Diffraction Xalibur, Sapphire 3 diffractometer with graphite-monochromatized Mo $\text{K}\alpha$ 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 pro-

cedures [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 $\text{CH}_3\text{CH}_2\text{OH}/\text{CH}_2\text{Cl}_2$ (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 $\text{CH}_{\text{aromatic}}$). Anal. Calc. for $\text{C}_{24}\text{H}_{20}\text{ZnN}_4\text{O}_2$: C, 62.41; H, 4.36; N, 12.13. Found: C, 62.37; H, 4.261; N, 12.04%. $\Lambda_m = 1.6 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ in DMF. UV-Vis [$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1} \text{ cm}^{-1}$)]: 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 $\text{CH}_{\text{aromatic}}$). Anal. Calc. for $\text{C}_{28}\text{H}_{27}\text{ZnN}_5\text{O}_2$: C, 63.74; H, 4.94; N, 11.44. Found: C, 63.69; H, 4.846; N, 11.44%. $\Lambda_m = 1.8 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ in DMF. UV-Vis [$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1} \text{ cm}^{-1}$)]: 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 $\text{CH}_{\text{aromatic}}$). Anal. Calc. for $\text{C}_{24}\text{H}_{20}\text{ZnN}_4\text{S}_2$: C, 58.35; H, 4.08; N, 11.34. Found: C, 58.32; H, 3.986; N, 11.29%. $\Lambda_m = 2.1 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ in DMF. UV-Vis [$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1} \text{ cm}^{-1}$)]: 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

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