

Full Paper

Preparation of Zinc (II) and Cadmium (II) Complexes of the Tetradentate Schiff Base Ligand 2-((*E*)-(2-(2-(pyridine-2-yl)ethylthio)ethylimino)methyl)-4-bromophenol (PytBrsalH)

Lotf A. Saghatforoush^{1,*}, Ali Aminkhani², Sohrab Ershad³, Ghasem Karimnezhad¹, Shahriar Ghammamy⁴ and Roya Kabiri⁵

¹ Department of Chemistry, Payame Noor University (PNU), Khoy, Iran

² Department of Chemistry, Islamic Azad University, Khoy Branch, Khoy, Iran

³ Department of Chemistry, Payame Noor University (PNU), Marand, Iran

⁴ Department of Chemistry, Imam Khomeini International University, Qazvin, Iran

⁵ Faculty of Chemistry, Tabriz University, Tabriz, Iran

* Author to whom correspondence should be addressed; E-mail: saghatforoush@yahoo.com

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Abstract: We describe the synthesis and characterization of two new zinc (II) and cadmium (II) complexes of the tetradentate dissymmetric Schiff base ligand 2-((*E*)-(2-(2-(pyridine-2-yl)ethylthio)ethylimino)methyl)-4-bromophenol (PytBrsalH), prepared from 1-(2-pyridyl)-3-thia-5-aminopentane (pyta) and 5-bromosalicylaldehyde. The complexes were synthesized by treating an ethanolic solution of the ligand with equimolar amounts of appropriate metal salts in 1 M methanolic solution of NaOH or alternatively, by a more direct route in which the two reactants are added to a solution of the ligand immediately after formation of the latter and prior to any isolation. The complexes were characterized by elemental analysis, FTIR, ¹H-NMR, electronic spectra and molar conductivity. According to obtained data, the probable coordination geometries of zinc and cadmium in these complexes with mixed N, S and O donor atoms are tetrahedral- and octahedral-like, respectively. Both complexes were found to be 1:1 electrolyte systems in acetonitrile.

Keywords: Tetradentate ligand; Schiff base; Unsymmetric; Zinc; Cadmium; Complex.

Introduction

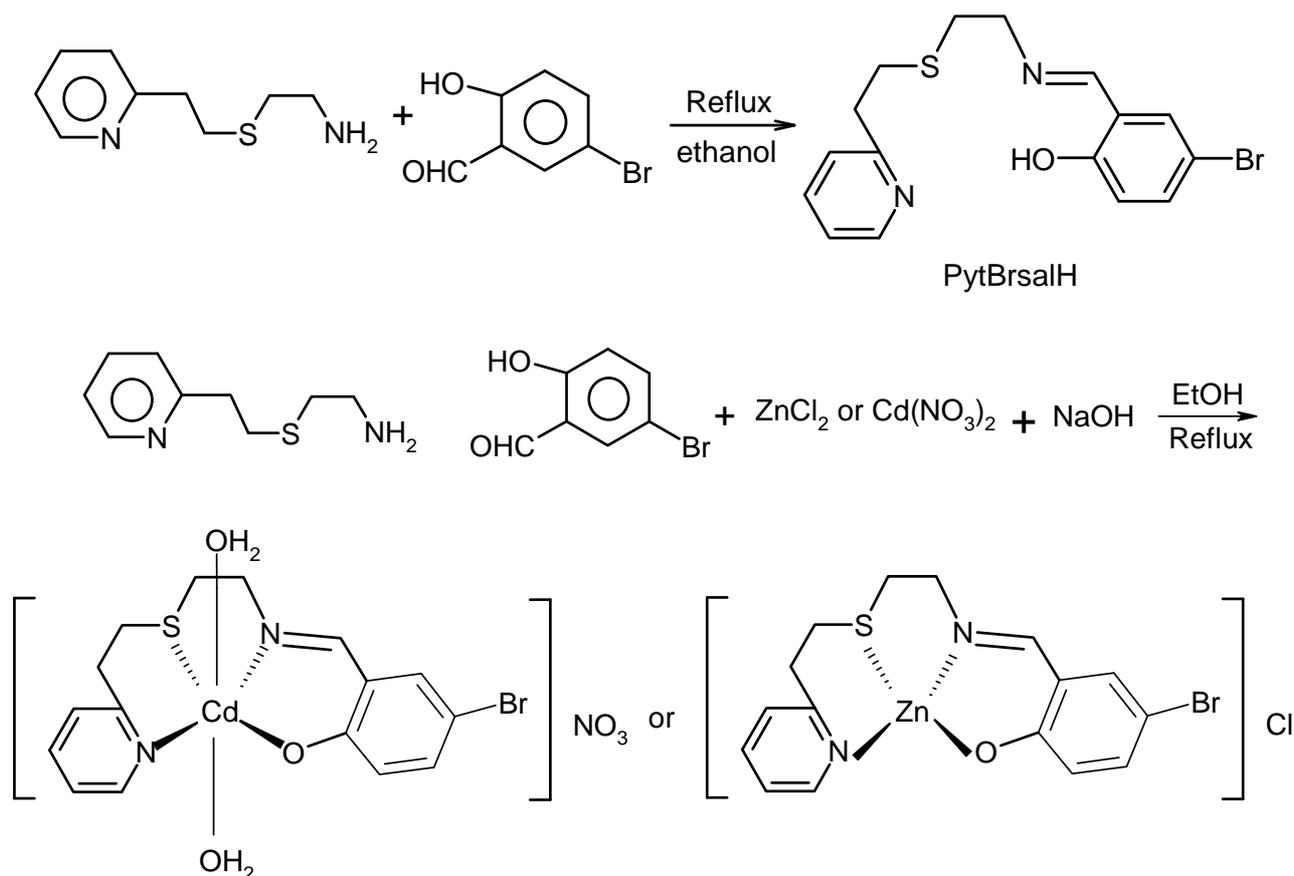
Schiff bases have often been used as chelating ligands in the field of coordination chemistry and their metal complexes are of great interest for many years. It is well known that N and S atoms play a key role in the coordination of metals at the active sites of numerous metalloproteins [1]. Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer and herbicidal applications [2-3]. They serve as models for biologically important species and find applications in biomimetic catalytic reactions. Chelating ligands containing N, S and O donor atoms show broad biological activity and are of special interest because of the variety of ways in which they are bonded to metal ions. It is known that the existence of metal ions bonded to biologically active compounds may enhance their activities [4-6]. The variety of possible Schiff base metal complexes with wide choice of ligands, and coordination environments, has prompted us to undertake research in this area [7]. Zinc can function as active site of hydrolytic enzymes, where it is ligated by hard donors (N or O). It has long been recognized as an important co-factor in biological molecules, either as a structural template in protein folding or as a Lewis acid catalyst that can readily adopt the coordination numbers 4, 5, or 6 [8-10]. The catalytic role of Zn comprises Lewis acid activation of substrate, generation of a reactive nucleophile (Zn-OH) and stabilization of the leaving group [11]. There is substantial interest in the coordination chemistry of cadmium complexes because of the toxic environmental impact of cadmium. The mobilization and immobilization of cadmium in the environment, in organisms, and in some technical processes (such as in ligand exchange chromatography) have been shown to depend significantly on the complexation of the metal center by chelating nitrogen donor ligands [12]. As a part of our continuing work on dissymmetric tetradentate Schiff base complexes containing N, S and O donor atoms [13-14] and in light of the importance of Cd and Zn ion metals, we now report the synthesis and characterization of zinc (II) and cadmium (II) complexes of the tetradentate unsymmetric Schiff base ligand 2-((E)-(2-(2-(pyridine-2-yl)ethylthio)ethylimino)methyl)-4-bromophenol and a brief study of its coordination behavior with the d^{10} group elements.

Results and Discussion

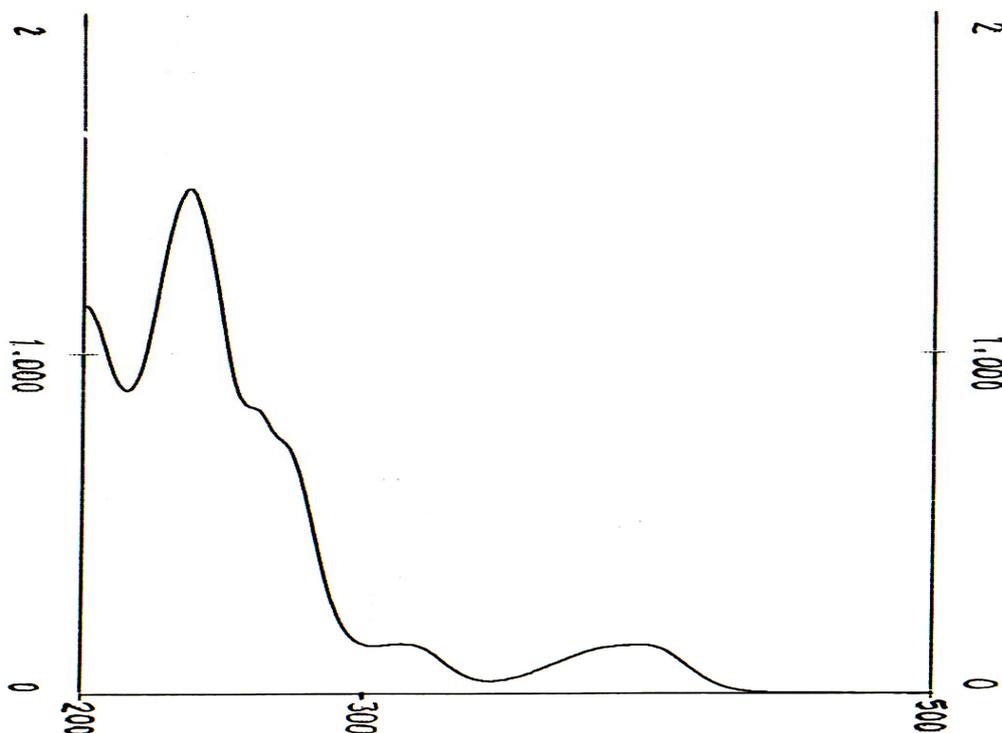
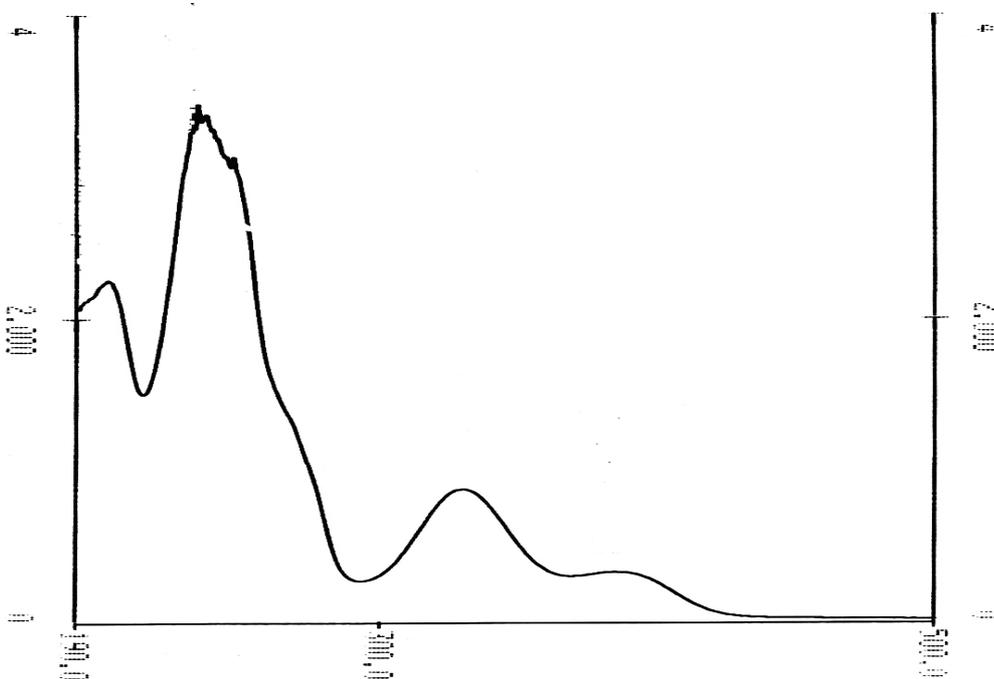
The ligand (PytBrsalH) was prepared as reported in the literature [14] by the condensation in ethanol of 1-(2-pyridyl)-3-thia-5-aminopentane (pyta) with 5-bromosalicylaldehyde. It was characterized by elemental analysis, IR, ^1H - and ^{13}C -NMR spectral data. The corresponding cadmium and zinc complexes were prepared by treating an ethanolic solution of the ligand with equimolar amounts of ZnCl_2 or $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and methanolic NaOH, or alternatively, by a more direct route in which the two reactants are added to a solution of the ligand immediately after formation of the latter and prior to any isolation (Scheme 1). The same products are obtained by both routes, but the latter was less time consuming and gave higher yields. These complexes were stable in the solid state at ambient conditions, and were characterized by the usual methods: elemental analysis, FTIR, ^1H -NMR, molar conductivity and absorption electronic spectroscopy. The characteristic IR bands of Zn(II) and Cd(II) complexes are: 1622 and 1639 cm^{-1} ($\nu_{\text{C=N}}$ iminic), 1285 and 1298 cm^{-1} ($\nu_{\text{C-O}}$ phenolic), respectively, [14,17-18]. The latter are shifted from the 1243-1275 cm^{-1} range seen for the free Schiff

base ligand, thus indicating coordination of the phenolic oxygen [19]. The presence of coordinated water molecules in the cadmium complex is supported by a broad IR band in the 3530-3150 cm^{-1} region and its elemental analysis data [1]. The measurement of molar conductivities at 10^{-3} M concentration carried out in acetonitrile, the obtained Λ_M values for monocationic complexes, indicating a behavior attributable to 1:1 electrolytes [21].

Scheme 1: Schematic representation of ligand and metal complex formation.



In NMR spectra of the complexes we observed an electron density shift from the ligand to the metal. The signals of the azomethine protons appear deshielded at 8.31 and 8.35 ppm in the zinc and cadmium complexes, respectively, as compared to 8.26 ppm in the Schiff base, inferring coordination through the azomethine nitrogen atom of the ligand [7, 20]. Disappearance of the $-\text{OH}$ protons in the spectra of the complexes supported the deprotonation of the phenolic group [7]. The cadmium and zinc complexes show only the charge transfer transitions which can be assigned to charge transfer from the ligand to the metal and vice versa, no d-d transition are expected for d^{10} $\text{Zn}(\text{II})$ and $\text{Cd}(\text{II})$ complexes [7]. In the electronic spectra of both complexes, recorded in acetonitrile solution (Figures 1 and 2), an absorption band in the range 320-397 nm was observed, which may be associated with a $\pi \rightarrow \pi^*$ transition originating mainly in the azomethine chromophore (imine $\pi \rightarrow \pi^*$ transition). In the UV region, the complexes show one strong absorption band at 235 – 238 nm which may be assigned to benzene ring $\pi \rightarrow \pi^*$ transition [22-25].

Figure 1. Electronic spectrum of $[\text{Zn}(\text{PytBrsal})]\text{Cl}$.**Figure 2.** Electronic spectrum of $[\text{Cd}(\text{PytBrsal})]\text{NO}_3$.

The present study of the title complexes continues our structural study of the corresponding copper complex of the ligand [13], which included the determination of its crystal structure by X-ray crystallography. The crystallographic data revealed one mode of complexation through the nitrogen atoms of the azomethine and pyridine groups, the oxygen atom of the deprotonated phenolic group and the thioether sulfur atom. On the basis of the spectral data, elemental analysis and comparison with our

previous data it is suggested that the zinc complex probably has a tetrahedral structure, with coordination number 4 and the cadmium one has an octahedral structure with coordination number 6, that includes two molecules of coordinated water coming from the hydrated salt used in its preparation. This would be consistent with the elemental analysis data and the water peaks observed in the FTIR spectrum [7, 26-27].

Experimental

General

All the chemicals and solvents used for the syntheses were of reagent grade and were obtained commercially from Merck Company with the exception of the cadmium nitrate, which was obtained from Aldrich. The solvents were purified by standard methods [15]. The ligand (PytBrsalH) was synthesized and characterized according to a published method [14] from 1-(2-pyridyl)-3-thia-5-aminopentane (pyta) [14-16] and 2-vinyl pyridine distilled in vacuum before use.

Physical measurements

The infrared spectra of the ligand and complexes were recorded on a Shimadzu Prestige 21 FT-IR spectrometer as KBr disks. Elemental CHN analyses were performed using a Heraeus CHN-O-RAPID elemental analyzer. ^1H NMR and spectral measurements were carried out on a Bruker Spectrospin Avance 400 MHz ultrashield spectrometer with TMS as an internal reference. The conductivity measurements were carried out in acetonitrile at room temperature using a Hanna HI 8828N conductometer. The electronic spectra of the compounds were recorded in acetonitrile on a Perkin-Elmer Lambda 25 (UV-Vis) spectrophotometer.

General procedure for the synthesis of metal complexes

A solution of the ligand was prepared by either dissolving the required amount of the ligand (1 mmol) in absolute ethanol (10 mL) or by preparing the ligand *in situ* from its precursors as follows: a solution of pyta (1 mmol) in absolute ethanol (5 mL) was added to solution of 2-hydroxy-5-bromobenzaldehyde (1 mmol) in absolute ethanol (5 mL) and the mixture was refluxed for 40 min and then 1 M methanolic NaOH (1 mL) was added and reflux and stirring were continued for a further 3 min. Then $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ or ZnCl_2 (1 mmol) in absolute ethanol (5 mL) was added to the ligand solution with stirring and the reaction mixture was further stirred under reflux for 30 min. The obtained colored solution was left standing at room temperature to crystallize. The product was removed by filtration, washed with cooled absolute ethanol, recrystallized from acetonitrile or methanol and dried under vacuum. The analytical and physical data of the complexes are:

$[\text{Zn}(\text{PytBrsal})]\text{Cl}$ - Empirical formula: $\text{C}_{16}\text{H}_{16}\text{BrClN}_2\text{OSZn}$; formula weight: 465.13 g mol^{-1} ; yield: 66%; appearance: yellowish microcrystals; m.p. = 165-166 °C (decomposed); Elem. analysis: calc. C, 41.32 %; H, 3.47 %; N, 6.02 %; found: C, 41.45 %; H, 3.49 %; N, 6.13%; FTIR: 3049 cm^{-1} $\nu_{(\text{C-H})}$ aromatic, 2860-2916 cm^{-1} $\nu_{(\text{C-H})}$ aliphatic, 1622 cm^{-1} $\nu_{(\text{C=N})}$ iminic, 1285 cm^{-1} $\nu_{(\text{C-O})}$ phenolic. $^1\text{H-NMR}$

(ppm): 8.96 (d, 1H, pyridinic), 8.31 (s, 1H, iminic), 7.89 (t, 1H, pyridinic), 7.72- 7.51 (m, 4H, aromatic), 7.24 (d, 1H, aromatic), 3.91 (t, 2H, CH₂ aliphatic), 3.25 (t, 2H, CH₂ aliphatic), 3.05 (t, 2H, CH₂ aliphatic), 2.93 (t, 2H, CH₂ aliphatic); mol. conductivity: 143 μ S; electronic spectrum: 238 nm (37,150 mol⁻¹Lcm⁻¹), 314 nm (9,646 mol⁻¹Lcm⁻¹), 397 nm (2,741 mol⁻¹Lcm⁻¹).

[Cd(PytBrsal)]NO₃·2H₂O - Empirical formula: C₁₆H₂₀CdBrN₃O₆S; formula weight: 574.462 gmol⁻¹; yield: 72 % ; appearance: light yellow microcrystals; m.p. = 210-211°C (decomposed); Elem. analysis: calc. C, 33.45 %; H, 3.51 %; N, 7.31 %; found: C, 33.31 %; H, 3.50 %; N, 7.19%; FTIR: 3530-3150 cm⁻¹ $\nu_{(O-H)}$ H₂O coordinated, 3035-3050 cm⁻¹ $\nu_{(C-H)}$ aromatic, 2910 cm⁻¹ $\nu_{(C-H)}$ aliphatic, 1639 cm⁻¹ $\nu_{(C=N)}$ iminic, 1379 cm⁻¹ $\nu_{(NO_3^-)}$, 1298 cm⁻¹ $\nu_{(C-O)}$ phenolic, 820 cm⁻¹ $\nu_{(NO_3^-)}$; ¹H-NMR (ppm): 8.94 (d, 1H, pyridinic), 8.35 (s, 1H, iminic), 7.90 (t, 1H, pyridinic), 7.70- 7.45 (m, 4H, aromatic), 7.27 (d, 1H, aromatic), 3.94 (t, 2H, CH₂ aliphatic), 3.30 (t, 2H, CH₂ aliphatic), 3.07 (t, 2H, CH₂ aliphatic), 2.91 (t, 2H, CH₂ aliphatic); mol. conductivity 137 μ S; electronic spectrum: 235 nm (42,970 mol⁻¹Lcm⁻¹), 330 nm (10,935 mol⁻¹Lcm⁻¹), 385 nm (4,106 mol⁻¹Lcm⁻¹).

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