

Synthesis and spectroscopic investigation of a new hexadentate Schiff base ligand with N₂O₄ donor atoms and related metal complexes

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ABSTRACT

Five new complexes [CdH₂L(NO₃)]ClO₄ (**1**), [ZnH₂L](ClO₄)₂ (**2**), [NiH₂L](ClO₄)₂ (**3**), [CuH₂L](ClO₄)₂ (**4**) and [CoH₂L](ClO₄)₂ (**5**) were prepared by reaction of a new Schiff base ligand and different metal ions in 1:1 ratios. The new Schiff base ligand H₂L was synthesized by reaction of 2-(4-(2-formylphenoxy)butoxy) benzaldehyde and ethanol amine and characterized with IR, ¹H and ¹³C NMR and elemental analysis. The synthesized complexes were also characterized by IR and elemental analysis in all cases and ¹H, ¹³C NMR and COSY in the case of [CdH₂L(NO₃)]ClO₄ and [ZnH₂L](ClO₄)₂ complexes.

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1. Introduction

Interest in macrocyclic and macroacyclic Schiff base ligands and related different complexes is growing on, due to their utility as catalysts, enzyme mimicking, radiopharmaceuticals, magnetic resonance imaging reagents and fluorescent probes [1-6]. In this work, we report synthesis and characterization of a new Schiff base ligand with N₂O₄ donor atoms and related complexes with different metal ions such as zinc(II), cadmium(II), nickel(II), copper(II) and cobalt(II) metal ions. The interaction of zinc(II) and cadmium(II) with different ligands with nitrogen and oxygen donor atoms is one of the most studied fields in coordination chemistry. Zinc(II) is the second most abundant trace metal in the human body [7,8] and can be considered as non-toxic to humans. Cadmium(II), on contrary, is a very toxic metal widely used in many industrial processes. After systematic entrance, cadmium localizes intracellular and kidney, liver, lung and pancreas [9-13] are the main organs involved in its accumulation. The toxic effect of cadmium(II) is associated with the fact that it often competes with zinc for a variety of important binding sites in cells, including sites potentially important in gene regulation. So, the coordination chemistry of cadmium in both biological and non-biological areas has attracted the interest of many

researchers. In addition, cadmium(II) has a d¹⁰ electron configuration that adapts to a wide variety of stereochemical environments. According to our previous researches in the case of preparation of cadmium (II) complexes, it has been shown, that when we used the salt of Cd(NO₃)₂, the prepared cadmium(II) complex with different hexadentate Schiff base ligand is eight-coordinated [14].

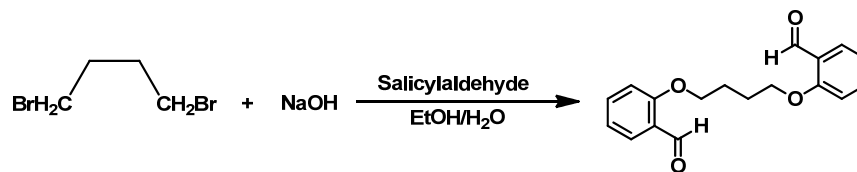
2. Experimental

2.1. General information

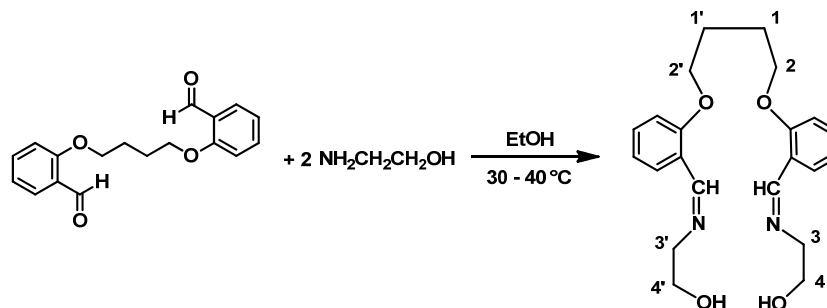
Hydrated metal salts and ethanol amine were obtained from Aldrich and were used without further purification. 2-(4-(2-Formylphenoxy)butoxy)benzaldehyde was prepared via literature method [12]. IR and NMR spectra were measured on a Perkin Elmer FT-IR GX and a Bruker DPX 300 spectrometer, respectively. Elemental analyses were performed in a Carlo-Erba EA micro analyser.

2.2. Synthesis

2.2.1. Preparation of 2-(4-(2-formylphenoxy)butoxy) benzaldehyde



Scheme 1



Scheme 2

1,4-Dibromo butane (0.1 mol) and NaOH (0.2 mol) were mixed and heated under reflux in 500 mL ethanolic solution. Salicylaldehyde (0.2 mol) in 30 mL EtOH was added and heated under reflux for 4 days. After cooling the resulting yellow crystals were filtered, washed and recrystallized [15] (Scheme 1). IR (KBr, cm^{-1}): 1678 ($\nu\text{C}=\text{O}$, Aldehyde).

2.2.2. Preparation of ligand H_2L

2-(4-(2-Formylphenoxy)butoxy)benzaldehyde (0.27 g, 1 mmol) and ethanol amine (0.122 g, 2 mmol) were mixed and heated in the 40 °C for 30 min in EtOH (30mL). The solution was filtered and the filtrate was reduced to ca 10 mL. Yellow crystalline compound was obtained, washed with cooled ethanol and dried (Scheme 2). Color: Yellow. Yield: 54%. IR (KBr, v, cm^{-1}): 3186 (OH), 1635 (C=N Schiff base), 1490 (C=C). $^1\text{H NMR}$ (300 MHz, DMSO- d_6 , δ , ppm): 2.03 (m, 4H, 1,1'-H), 3.68 (t, 4H, 3,3'-H), 3.85 (t, 4H, 4,4'-H), 4.09 (t, 4H, 2,2'-H), 6.88 (m, 2H, Ar-H), 7.34 (m, 2H, Ar-H) 7.92 (m, 2H, Ar-H), 7.94 (m, 2H, Ar-H), 8.74 (s, 2H, Imines-H, Schiff base), 10.54 (br, 2H, OH). $^{13}\text{C NMR}$ (75 MHz, DMSO- d_6 , δ , ppm): 26.11 (C-1), 62.27 (C-2), 63.73 (C-3), 67.78 (C-4), 111.86, 120.79, 127.32, 132.10 (Aromatic Rings), 159.05 (Schiff base). Anal. calcd. for $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_4$: C, 68.73; H, 7.34; N, 7.29. Found: C, 68.44; H, 6.72; N, 7.74.

2.2.3. Preparation of complex $[\text{CdH}_2\text{L}(\text{NO}_3)]\text{ClO}_4$ (1)

This complex was prepared by reaction of ligand H_2L and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. Ligand H_2L (0.368 g, 1 mmol) was solved in 10 mL methanol and the solution was stirred at 30-40 °C. $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.308 g, 1 mmol) dissolved in MeOH (5 mL) was subsequently added. The mixture was stirred at 50-60 °C for 24 h, then NaClO_4 (0.28 g, 2 mmol) was added. The solution was filtered and the filtrate was reduced to ca. 10 cm^3 . A crystalline compound was obtained by slow diffusion of Et_2O vapor into this solution. Complex 1: Color: White. Yield: 75%. IR (KBr, v, cm^{-1}): 3330 (OH), 1644 (C=N Schiff base), 1492 (C=C), 1356 (N-O), 1079 (ClO_4). $^1\text{H NMR}$ (300 MHz, DMSO- d_6 , δ , ppm): 1.95 (t, 2H, 1- H_α), 2.08 (t, 2H, 1- H_β), 3.37 (t, 2H, 4- H_α), 3.60 (t, 2H, 4- H_β), 3.62 (t, 2H, 3- H_α), 4.14 (t, 2H, 3- H_β), 4.22 (t, 2H, 2- H_α), 4.52 (t, 2H, 2- H_β), 6.94 (m, 2H, Ar-H), 7.00 (m, 2H, Ar-H), 7.02 (m, 2H, Ar-H) 7.38 (m, 2H, Ar-H), 8.63 (s, 2H, CH=N). COSY (300 MHz, DMSO- d_6 , δ , ppm): 1.95/2.08 (1- H_α /1-

H_β), 1.95/4.22 (1- H_α /2- H_α), 1.95/4.52 (1- H_α /2- H_β), 2.08/4.22 (1- H_β /2- H_α), 2.08/4.52 (1- H_β /2- H_β), 3.62/4.14 (3- H_α /3- H_β), 3.62/3.37 (3- H_α /4- H_α), 3.62/3.60 (3- H_α /4- H_β), 4.14/3.37 (3- H_β /4- H_α), 4.14/3.60 (3- H_β /4- H_β). $^{13}\text{C NMR}$ (75 MHz, DMSO- d_6 , δ , ppm): 25.43 (C-1), 60.78 (C-4), 63.81 (C-3), 67.64 (C-2), 112.64, 113.46, 120.38, 120.45, 124.02, 126.63, 127.61, 131.94, 136.43, 156.67 (Aromatic rings) and 157.66 (Schiff base). Anal. calcd. for $\text{C}_{22}\text{H}_{28}\text{CdClN}_3\text{O}_{11}$: C, 42.70; H, 4.23; N, 9.05. Found: C, 42.34; H, 4.11; N, 9.03%.

2.2.4. Preparation of complex $[\text{ZnH}_2\text{L}](\text{ClO}_4)_2$ (2)

Compound 2 was prepared in an analogous method to compound 1. Complex 2: Color: White. Yield: 67%. IR (KBr, v, cm^{-1}): 3456 (OH), 1641 (C=N Schiff base), 1488 (C=C), 1118 (ClO_4). $^1\text{H NMR}$ (300 MHz, DMSO- d_6 , δ , ppm): 1.98 (t, 2H, 1- H_α), 1.99 (t, 2H, 1- H_β), 2.05 (t, 2H, 4- H_α), 2.51 (t, 2H, 4- H_β), 4.16 (t, 2H, 3- H_α), 4.22 (t, 2H, 3- H_β), 4.23 (t, 2H, 2- H_α), 5.15 (t, 2H, 2- H_β), 6.98-7.85 (m, 8H, Ar-H), 8.65 (s, 2H, Schiff base). COSY (300 MHz, DMSO- d_6 , δ , ppm): 1.98/1.99 (1- H_α /1- H_β), 1.98/4.23 (1- H_α /2- H_α), 1.98/5.15 (1- H_α /2- H_β), 1.99/4.23 (1- H_β /2- H_α), 1.99/5.15 (1- H_β /2- H_β), 4.16/4.22 (3- H_α /3- H_β), 4.16/2.05 (3- H_α /4- H_α), 4.16/2.51 (3- H_α /4- H_β), 4.22/2.05 (3- H_β /4- H_α), 4.22/2.51 (3- H_β /4- H_β). $^{13}\text{C NMR}$ (75 MHz, DMSO- d_6 , δ , ppm): 25.43 (C-1), 60.78 (C-4), 63.81 (C-3), 67.64 (C-2), 112.64, 113.46, 120.38, 120.45, 124.02, 126.63, 127.61, 131.94, 136.43, 156.67 (aromatic rings) and 157.66 (Schiff base). Anal. calcd. for $\text{C}_{22}\text{H}_{28}\text{ZnCl}_2\text{N}_2\text{O}_{12}$: C, 58.74; H, 6.27; N, 6.23. Found: C, 58.21; H, 6.14; N, 6.16%.

2.2.5. Preparation of complex $[\text{NiH}_2\text{L}](\text{ClO}_4)_2$ (3)

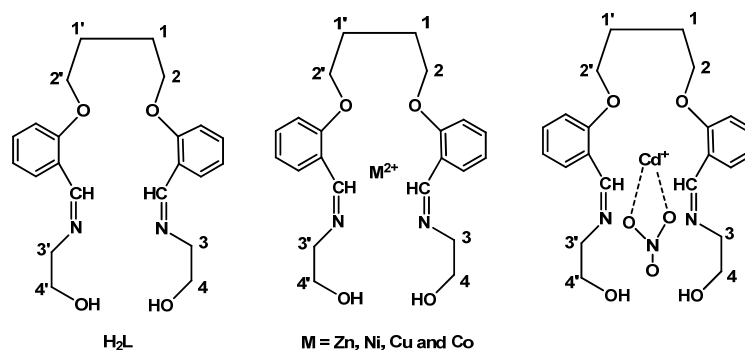
Compound 3 was prepared in an analogous method to compound 1. Complex 3: Color: Green. Yield: 63%. IR (KBr, v, cm^{-1}): 3336 (OH), 1644 (C=N Schiff base), 1112 (ClO_4). Anal. calcd. for $\text{C}_{22}\text{H}_{28}\text{NiCl}_2\text{N}_2\text{O}_{12}$: C, 59.62; H, 6.37; N, 6.32. Found: C, 59.31; H, 6.12; N, 6.09%.

2.2.6. Preparation of complex $[\text{CuH}_2\text{L}](\text{ClO}_4)_2$ (4)

Compound 4 was prepared in an analogous method to compound 1. Complex 4: Color: Blue. Yield: 67%. IR (KBr, v, cm^{-1}): 3435 (OH), 1637 (C=N Schiff base), 1488 (C=C), 1098 (ClO_4).

Table 1. Stretching activities of a number of functional groups of synthesized compounds.

Compound	$\nu(\text{C-O})$	$\nu(\text{OH})$	$\nu(\text{C=N})$	$\nu(\text{C-H})$
Schiff base (H ₂ L)	1161	3186	1635	2825-2926
1	1175	3333	1644	2765-2948
2	1162	3456	1641	2941-2851
3	1112	3336	1644	2956
4	1164	3435	1637	2879-2942
5	1148	3427	1636	2924

**Scheme 3**

Anal. calcd. for C₂₂H₂₈CuCl₂N₂O₁₂: C, 51.12; H, 5.07; N, 5.42.
 Found: C, 50.78; H, 4.81; N, 5.13%.

2.2.7. Perpetration of complex [CoH₂L](ClO₄)₂ (5)

Compound **5** was prepared in an analogous method to compound **1**. Complex **5**: Color: Brown. Yield: 68%. IR (KBr, ν , cm⁻¹): 3427 (OH), 1636 (C=N Schiff base), 1487 (C=C), 1114 (ClO₄). Anal. calcd. for C₂₂H₂₈CoCl₂N₂O₁₂: C, 59.59; H, 9.36; N, 6.32. Found: C, 59.36; H, 9.12; N, 6.11%.

3. Result and discussion

3.1. Synthesis and characterization

All complexes were readily synthesized by the reaction of a new Schiff base ligand, H₂L and different metal ions (Scheme 3). These compounds are quite stable in air and can be stored in a desiccator for long periods of time without decomposition. The resulting compounds were characterized by IR, elemental analysis in all cases and ¹H and ¹³C NMR spectroscopy in the case of compound **1** and **2**. Condensation of all the primary amino group is confirmed by the lack of N-H stretching bands in the IR region (3150-3450 cm⁻¹) and the presence of strong C=N (Schiff base) stretching bands at 1635 cm⁻¹ for Schiff base ligand H₂L and 1644, 1641, 1644, 1637 and 1636 cm⁻¹ for complexes **1**, **2**, **3**, **4** and **5**, respectively. As it can be seen the bands related to the imine groups in Schiff bases have been shifted in the IR for all complexes and it can show that the donor atoms in ligands have been coordinated to the metal ions and the complexes have been formed. The band observed at 1356 cm⁻¹ in the IR spectrum of complex **1** can be assigned to the bidentate nitrate group [12,14]. A broad intense band at ca. 1100 cm⁻¹ due to ClO₄⁻ shows no splitting, indicating the absence of coordination of ClO₄⁻ for all complexes. Another broad band at ca. 3150-1450 cm⁻¹ is related to the OH group. Table 1 shows a number of stretching bands activities of above compounds. The result of spectroscopic studying and X-ray crystal structure of our previous works has showed that the hydroxyl group in all compounds has been coordinated as OH. The NMR studies of Schiff base ligands and synthesized complexes are completely consistent with their formulation.

3.2. NMR spectra

The NMR spectra of the cadmium(II) and zinc(II) complexes confirm that formation of a fully condensed Schiff base ligand and cadmium and zinc complexes. For complex **1** the peaks appeared at 1.95-4.52 ppm in ¹H NMR are related to the aliphatic protons that in compare to the same region in ligand they have been shifted and the peaks appeared at the 6.94-7.38 ppm are related to the aromatic protons. In both aromatic and aliphatic regions the chemical shifts and coupling constant are confirmed with the number of protons and the coupling between them. Also, as can be seen in the ¹H NMR of complex **2** the peaks appeared in both aliphatic and aromatic region are confirmed with the protons in this compound. The peaks appeared at 8.74, 8.63 and 8.65 ppm are related to the protons of imins (Schiff base) group in ligand H₂L, complex **1** and **2**, respectively. In addition, the ¹³C NMR of Schiff base ligand and both complexes confirm with the number of peaks appeared in these compounds. Also the appeared peaks in ¹³C NMR of complexes completely shifted in compare with the ¹³C NMR of ligand. The ¹³C NMR of the ligands and complexes show four distinct methylene carbons in the aliphatic region. It is interesting that the ¹H NMR spectrum of this complex show two kinds of protons for the methylene group. The COSY spectrum confirms the geminal coupling between the latter protons, indicating that the protons are diastereotopic in the rigid five-membered rings. It is clear from the COSY spectrum that both diastereotopic protons of C(1) display coupling to protons of C(2).

4. Conclusion

In summary, we report the successful synthesis of a new N₂O₄ macrocyclic Schiff base ligand, derived from a known dialdehyde and ethanolamine, and related Cd(II), Zn(II), Ni(II), Cu(II) and Co(II) complexes. The ligand and their complexes were characterized by a variety of spectroscopic methods such as IR and elemental analysis in all cases and ¹H and ¹³C NMR and COSY in the case of ligand and Cd(II) and Zn(II) compounds.

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