

*Inorg. Chem. Res.*, Vol. 2, No. 1, 1-5, June 2019

DOI: 10.22036/icr.2017.94685.1039

## Synthesis and Characterization of Metal Complexes with New Unsymmetrical Schiff Base Ligand Derived from 2-Aminoethanethiol

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(Received 6 August 2017, Accepted 4 November 2017)

A new unsymmetric thioether diamine N-(2-(2-aminophenylthio)ethyl)benzene-1,2-diamine was prepared through the nucleophilic substitution of cysteaminium chloride with 1-chloro-2-nitrobenzene and then the nitro groups of prepared compound converted to the amine by zinc powder and ammonium chloride. Then, unsymmetric Schiff base ligand 2-(((2-((2-((2-hydroxybenzylidene)amino)phenyl)amino)ethyl)thio)phenyl)imino)methyl)phenol [H<sub>2</sub>L] was synthesized *via* [2+1] condensation of 2-hydroxybenzaldehyde with this unsymmetric thioether diamine and the corresponding Schiff base complexes of this ligand were prepared by adding metal salts of Zn(II), Cu(II), Ni(II) and Mn(II). The thioether diamine, ligand and unsymmetric Schiff base complexes are characterized by FT-IR, UV-Vis, <sup>1</sup>H NMR, <sup>13</sup>C NMR spectroscopy, molar conductivity, microanalysis and mass spectrometry.

**Keywords:** N<sub>3</sub>O<sub>2</sub>S donor, Unsymmetrical ligand, Schiff base ligand, Thioether ligand, 2-Aminoethanethiol

### INTRODUCTION

Schiff base ligands have been prepared by condensation reaction of appropriate carbonyl and primary amine precursors [1-3]. Over the decades, Schiff bases have been discussed in various fields due to different properties such as structure variety, the ability of being coordinated, temperature stability, biological activity and catalytic properties [4,5]. Schiff base complexes are used as medicine and have biochemical activities against bacteria, fungi and certain types of tumors [6-9]. Unsymmetrical Schiff base ligands containing oxygen, nitrogen and sulfur atoms are significant. They are readily coordinated with a wide range of transition metal ions due to the presence of both hard and soft donor atoms in their backbones [10-14].

For the first time, the preparation of a linear hexadentate Schiff base ligand containing hard and soft donors in its structure was reported by Dwyer and Lions in 1950 [15]. Complexes of this ligand and of this type ligands with some

metal ions have also been prepared and characterized [16]. Hexadentate Schiff base ligands containing oxygen, nitrogen and sulfur donors are very interesting compounds of the viewpoint of coordination chemistry because they have ability toward complexation and involvement in a wide range of biological and non-biological processes [17-19]. Unsymmetrical linear hexadentate Schiff base ligands that have NOS donors in their structure are very rare. Recently, we have synthesized and characterized some NOS donor Schiff base ligands (N<sub>2</sub>O<sub>2</sub>S and N<sub>2</sub>O<sub>2</sub>S<sub>2</sub> donors) and their some metal complexes [14,20,21]. In this study, a new unsymmetrical linear hexadentate Schiff base ligand (N<sub>3</sub>O<sub>2</sub>S donors) (Scheme 2) and its complexes with Zn(II), Cu(II), Ni(II) and Mn(II) ions were synthesized and characterized with appropriate spectroscopic methods.

### EXPERIMENTAL

#### Chemical and Starting Materials

Cysteaminium chloride, 1-chloro-2-nitrobenzene, 2-hydroxybenzaldehyde, MnCl<sub>2</sub>·2H<sub>2</sub>O, NiCl<sub>2</sub>·6H<sub>2</sub>O,

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ZnCl<sub>2</sub>·6H<sub>2</sub>O and CuCl<sub>2</sub>·2H<sub>2</sub>O were commercial products (from Merck, Aldrich and Fluka) and used without further purification. Other reagents and solvents were of analytical grade and purchased commercially.

### Instrumentation

Elemental analyses were performed in a CHNS-O-2400 II Perkin-Elmer. Infrared spectra were recorded in ATR, using a Bruker FT-IR Equinax-55 spectrophotometer (4000-400 cm<sup>-1</sup>). MS spectra were obtained using a QP-1100EX Shimadzu GC-MS (EI at 70 eV). Conductivity measurements were carried out in 10<sup>-3</sup> mol dm<sup>-3</sup> DMF solution at 25 °C using a Metrohm 660 conductometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were taken in CDCl<sub>3</sub> on a DPXAVANCE 500 MHz BRUKER, Jeol 90 MHz and Varian 300 MHz spectrometer using Si(CH<sub>3</sub>)<sub>4</sub> as an internal standard. The electronic spectra were taken in GBC UV-Visible Cintra 101 spectrophotometer with 1 cm quartz, in the range 200-1100 nm at 25 °C.

### Synthesis of the N-(2-(2-aminophenylthio)ethyl)benzene-1,2-diamine

Cysteaminium chloride (5.68 g, 50 mmol), 1-chloro-2-nitrobenzene (15.75 g, 100 mmol), and sodium carbonate (10.6 g, 100 mmol) were mixed in a round-bottomed flask, and then fused at 140 °C for 4 h and then allowed to cool to room temperature. The resulting solid was washed with 1:1 H<sub>2</sub>O/EtOH and 2-nitro-N-(2-(2-nitrophenylthio)ethyl)aniline obtained (Scheme 1). Yield: 80%. M.p.: 120 °C. IR (ATR, cm<sup>-1</sup>): 3378 ν(N-H); 735 ν(C-S); 1567 and 1343 ν(NO<sub>2</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δH 1.27 (1H, br), 3.27 (2H, t), 3.33 (2H, t), 6.44 (2H, d), 7.47 (4H, m), 8.18 (2H, t); <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): δC 31.5, 41.4, 113.3, 116.1, 116.3, 125.4, 126.2, 127.1, 127.2, 133.4, 133.5, 135.4, 136.4, 149.4.

The N-(2-(2-aminophenylthio)ethyl)benzene-1,2-diamine was prepared by reaction of 2-nitro-N-(2-(2-nitrophenylthio)ethyl)aniline and ammonium chloride with zinc dust according to the procedure of Keypour et al [22]. A mixture of 2-nitro-N-(2-(2-nitrophenylthio)ethyl)aniline (15.9 g, 50 mmol), ammonium chloride (10.7 g, 200 mmol), and water (20 ml) in ethanol (200 ml) was heated to boiling, and then zinc dust (9.8 g, 150 mmol) was added. After 24 h, the solution turned brown and was filtered. The solution

was evaporated to yield the crude product as a brown precipitate (Scheme 1). Yield: 59%. IR (ATR, cm<sup>-1</sup>) 3300-3400 ν(NH<sub>2</sub> and N-H); 740 ν(C-S); <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δH 2.98 (2H, t), 3.20 (2H, t), 3.50 (3H, br), 4.42 (2H, br), 6.60-7.39 (8H, m). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): δC 34.0, 42.8, 111.8, 114.8, 116.2, 118.3, 118.6, 119.2, 120.2, 129.7, 134.2, 135.8, 136.6, 148.2.

### Synthesis of the 2-(((2-((2-(2-Hydroxybenzylidene)amino)phenyl)amino)ethyl)thio)phenyl)imino)methyl)phenol [H<sub>2</sub>L]

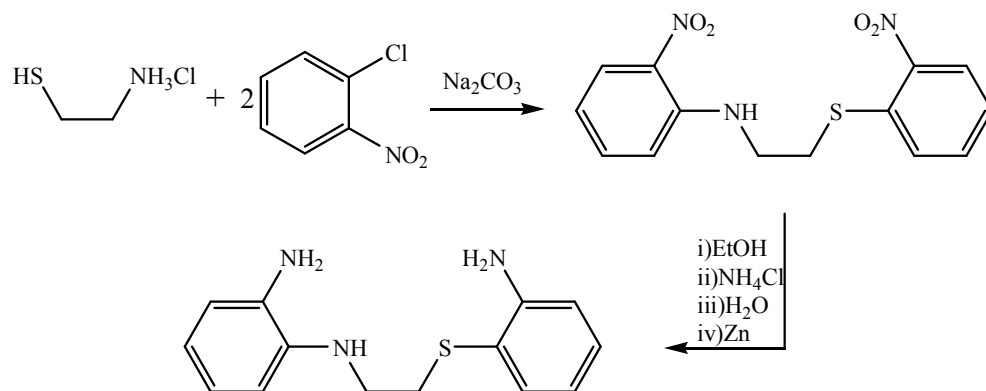
A solution of N-(2-(2-aminophenylthio)ethyl)benzene-1,2-diamine (2.59 g, 10 mmol) in ethanol was added dropwise to a refluxing solution of 2-hydroxybenzaldehyde (2.44 g, 20 mmol) in the same solvent (50 ml). After refluxing for 8 h the solution was evaporated to yield the crude product as a brown oil. A small volume of diethyl ether was added to the residue remaining in the flask and rubbed. Then liquid was decanted and residue was yellow (Scheme 2). Yield: 70%. Mp: 90 °C. IR (ATR, cm<sup>-1</sup>) 1613 ν(C=N); 742 ν(C-S); 2500-3300 ν(O-H and N-H); <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δH 1.20 (1H, br), 3.36 (2H, t), 4.68 (2H, t), 6.70-7.44 (16H, m), 8.57 (2H, s), 13.27 (2H, br). EI-MS (m/z): 466 [H<sub>2</sub>L]. UV-Vis in DMF (λ, nm) 282 (logε = 4.81), 320 (logε = 4.22), 374 (logε = 3.86); Λ<sub>m</sub> (DMF) 4.74 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>.

### General Synthesis of the Complexes

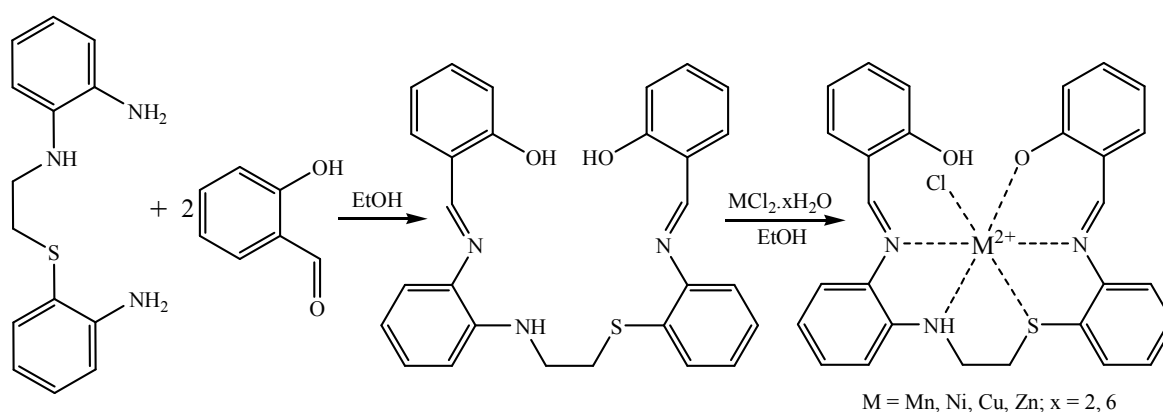
A solution of metal ion (MCl<sub>2</sub>·xH<sub>2</sub>O, M = Zn, Cu, Ni, Mn; x = 2, 6) (1 mmol) in ethanol (20 mL) was added to a refluxing solution of [H<sub>2</sub>L] (0.466 g, 1 mmol) in ethanol and the reaction mixture was refluxed for 3h. Then, a solution of triethylamine (2 mmol) in ethanol was added and reaction mixture was refluxed for 1 h. The solution was then concentrated in a rotary evaporator to 5-10 ml and a small volume of diethyl ether was slowly added. The complexes were filtered off and air-dried (Scheme 2).

**[Mn(HL)Cl]·3H<sub>2</sub>O.** Yield: 73%. IR (ATR, cm<sup>-1</sup>) 1605 ν(C=N); 1154 ν(C-O); 744 ν(C-S). Anal. Calcd. for C<sub>28</sub>H<sub>27</sub>Cl<sub>2</sub>N<sub>3</sub>O<sub>3</sub>SMn: C, 55.04; H, 4.95; N, 6.88. Found: C, 54.36; H, 4.34; N, 7.81%. EI-MS (m/z): 524 [Mn(HL)+H]. UV-Vis in DMF (λ, nm) 281 (logε = 4.68), 328 (logε = 4.02), 453 (logε = 3.24), 560 (logε = 2.75); Λ<sub>m</sub> (DMF) 12.92 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>.

**[Zn(HL)Cl]·H<sub>2</sub>O.** Yield: 61%. IR (ATR, cm<sup>-1</sup>) 1607



Scheme 1. Synthesis of the N-(2-(2-aminophenylthio)ethyl)benzene-1,2-diamine



Scheme 2. Synthesis of the H<sub>2</sub>L and related complexes

$\nu(\text{C}=\text{N})$ ; 1154  $\nu(\text{C}-\text{O})$ ; 748  $\nu(\text{C}-\text{S})$ . Anal. Calcd. for  $\text{C}_{28}\text{H}_{26}\text{ClN}_3\text{O}_3\text{SZn}$ : C, 57.45; H, 4.48; N, 7.18. Found: C, 57.54; H, 4.41; N, 8.28%. EI-MS ( $m/z$ ): 532 [ $\text{Zn}(\text{HL})$ ]. UV-Vis in DMF ( $\lambda$ , nm) 280 ( $\log \epsilon = 5.02$ ), 358 ( $\log \epsilon = 3.83$ );  $\Lambda_m$  (DMF)  $5.77 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ .

**[Ni(HL)Cl]·H<sub>2</sub>O**. Yield: 72%. IR (ATR,  $\text{cm}^{-1}$ ) 1605  $\nu(\text{C}=\text{N})$ ; 1151  $\nu(\text{C}-\text{O})$ ; 743  $\nu(\text{C}-\text{S})$ . Anal. Calcd. for  $\text{C}_{28}\text{H}_{26}\text{ClN}_3\text{NiO}_3\text{S}$ : C, 58.01; H, 4.69; N, 7.25. Found: C, 57.56; H, 4.47; N, 7.99%. EI-MS ( $m/z$ ): 524 [ $\text{Ni}(\text{HL})$ ]. UV-Vis in DMF ( $\lambda$ , nm) 280 ( $\log \epsilon = 4.72$ ), 332 ( $\log \epsilon = 3.98$ ), 463 ( $\log \epsilon = 4.07$ ), 565 ( $\log \epsilon = 2.41$ ), 750 ( $\log \epsilon = 2.07$ );  $\Lambda_m$  (DMF)  $12.96 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ .

**[Cu(HL)Cl]·0.5H<sub>2</sub>O**. Yield: 69%. IR (ATR,  $\text{cm}^{-1}$ ) 1609  $\nu(\text{C}=\text{N})$ ; 1148  $\nu(\text{C}-\text{O})$ ; 746  $\nu(\text{C}-\text{S})$ . Anal. Calcd. for  $\text{C}_{28}\text{H}_{25}\text{ClN}_3\text{NiO}_{2.5}\text{S}$ : C, 58.53; H, 4.39; N, 7.31. Found: C, 58.35; H, 4.39; N, 8.41%. EI-MS ( $m/z$ ): 529 [ $\text{Cu}(\text{HL})$ ]. UV-

Vis in DMF ( $\lambda$ , nm) 281 ( $\log \epsilon = 4.66$ ), 368 ( $\log \epsilon = 4.08$ ), 465 ( $\log \epsilon = 3.28$ );  $\Lambda_m$  (DMF)  $11.85 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ .

## RESULTS AND DISCUSSION

The IR spectrum for the 2-nitro-N-(2-(2-nitrophenylthio)ethyl)aniline shows a band at  $3378 \text{ cm}^{-1}$  assignable to N-H stretch and a band at  $735 \text{ cm}^{-1}$  due to the thioethers stretch. In the IR spectrum of the N-(2-(2-aminophenylthio)ethyl)benzene-1,2-diamine, the broad band observed in the region of  $3300\text{-}3400 \text{ cm}^{-1}$  can be assigned to N-H and  $\text{NH}_2$  groups (due to the interaction of the two groups together, broad peak is observed). The vibration peak of C-S is observed in  $740 \text{ cm}^{-1}$ . The IR spectrum for the ligand (H<sub>2</sub>L) confirms the presence of imines ( $1613 \text{ cm}^{-1}$ ) and the absence of carbonyl and amine

functional groups of the starting materials. The absence of  $\nu(\text{C}=\text{O})$  absorption in the IR spectrum of the ligand together with the appearance of new  $\nu(\text{C}=\text{N})$  absorption in  $1613\text{ cm}^{-1}$  clearly indicated that a new Schiff base ligand is formed. In addition, the vibration peak of C-S is observed in  $742\text{ cm}^{-1}$ . The broad band observed in the spectrum of ligand in the region of  $2500\text{-}3300\text{ cm}^{-1}$  can be assigned to the  $\nu(\text{O}-\text{H})$  and  $\nu(\text{N}-\text{H})$  groups (due to the interaction of the two groups together, broad peak is observed). The IR spectra of Zn(II), Cu(II), Ni(II) and Mn(II) complexes of this unsymmetrical Schiff base ligand show strong band at  $1605\text{-}1609\text{ cm}^{-1}$  assigned to the C=N stretching mode. These bands are shifted relative to the similar band of the ligand that show the imines nitrogen atoms coordinated to the metal ions. In the all complexes, the vibration peaks of C-S are observed in  $743\text{-}748\text{ cm}^{-1}$ . In the event that the vibration peak of C-S is not shifted relative to the similar band of the ligand shows the thioether sulfur atom is not coordinated to the metal ion [21-26].

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the 2-nitro-N-(2-(2-nitrophenylthio)ethyl)aniline, N-(2-(2-aminophenylthio)ethyl)benzene-1,2-diamine and the ligand ( $\text{H}_2\text{L}$ ) indicate that these compounds have synthesized. The broad signals in the  $^1\text{H}$  NMR spectrum of the 2-nitro-N-(2-(2-nitrophenylthio)ethyl) aniline at 1.27 ppm and in the  $^1\text{H}$  NMR spectrum of the ligand ( $\text{H}_2\text{L}$ ) at 1.20 ppm are assigned to the NH proton. The broad signals at 3.50 ppm ( $\text{NH}_2$  and NH) and 4.42 ppm ( $\text{NH}_2$ ) in the  $^1\text{H}$  NMR spectrum of N-(2-(2-aminophenylthio)ethyl)benzene-1,2-diamine are assigned to the  $\text{NH}_2$  and NH protons. The aliphatic protons appear as two triplet resonance at 3.27 ppm and 3.33 ppm for the 2-nitro-N-(2-(2-nitrophenylthio)ethyl)aniline, at 2.98 ppm and 3.20 ppm for the N-(2-(2-aminophenylthio)ethyl)benzene-1,2-diamine and at 3.36 ppm and 4.68 ppm for the ligand ( $\text{H}_2\text{L}$ ). The signals for aromatic protons observed at 6.44-8.18 ppm. The  $^1\text{H}$  NMR spectrum of ligand, shows peaks at 8.57 ppm corresponding to the imine protons and 13.27 ppm corresponding to the OH protons and these indicates that the condensation have occurred. The  $^{13}\text{C}$  NMR spectra of 2-nitro-N-(2-(2-nitrophenylthio)ethyl)aniline and N-(2-(2-aminophenylthio)ethyl) benzene-1,2-diamine features 16 signals, as expected for these compounds.

The EI mass spectra of the unsymmetrical Schiff base

ligand and the complexes, provide strong evidence for the formation of these compounds and exhibit peaks at higher molecular weights. The molecular weight peak and some fragments in the spectrum of the ligand are observed at  $m/z$  466, 197, 270, 210, 256, 228, 237. The peaks in spectra of the Mn(II), Ni(II), Cu(II) and Zn(II) complexes are observed at  $m/z$  524, 524, 529 and 532, respectively, confirming the presence of metal unit in the complexes.

The absorption spectra for 0.001 M solutions of ligand and complexes in DMF show bands at 279 to 374 nm. These bands can be attributed to  $\pi\rightarrow\pi^*$  and  $n\rightarrow\pi^*$  (and/or charge transfer) transitions within the Schiff base molecule and bands at 441 to 665 nm can be attributed to charge transfer and d-d transition within the complexes [26,27]. The elemental analyses of the complexes indicated that there are the chlorine atoms in the formula. Electrical conductivities of the ligand in DMF (0.001M) ( $4.74\text{ }\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$ ) and the complexes in DMF (0.001M) ( $5.77\text{-}12.96\text{ }\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$ ) indicating that they are non-electrolytes [28]. According to the elemental analyses and electrical conductivities of the complexes indicated that the chlorine atoms has coordinated in the structures.

## CONCLUSIONS

We report the successful synthesis of the unsymmetrical diamine and then unsymmetrical potential hexadentate ligand  $\text{H}_2\text{L}$ . Then, four complexes of zinc, manganese, copper and nickel from ligand have been synthesized and specify that this ligand can coordinate to the metal ions. According to the elemental analyses and electrical conductivities of the complexes indicated that the chlorine atoms are coordinated in the structures. Although, appropriate spectroscopic methods used in this study confirming the formation of these complexes, but there are no X-ray data which confirm the proposed structures of the complexes.

## ACKNOWLEDGMENTS

We are grateful to the Faculty of Chemistry of Yazd University and Ministry of Science, Research and Technology of Iran, for financial support.

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