Accepted Manuscript

Accepted Date:

Copper(II) and nickel(II) complexes with two new bis(thiosemicarbazone) ligands: synthesis, characterization, X-ray crystal structures and their electrochemistry behaviour

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PII: DOI:	S0020-1693(14)00749-X http://dx.doi.org/10.1016/i.ica.2014.12.011
Reference:	ICA 16337
To appear in:	Inorganica Chimica Acta
Received Date:	16 October 2014
Revised Date:	7 December 2014

14 December 2014



Please cite this article as: S.A. Hosseini-Yazdi, S. Hosseinpour, A.A. Khandar, W. Scott Kassel, N.A. Piro, Copper(II) and nickel(II) complexes with two new bis(thiosemicarbazone) ligands: synthesis, characterization, X-ray crystal structures and their electrochemistry behaviour, *Inorganica Chimica Acta* (2014), doi: http://dx.doi.org/10.1016/j.ica.2014.12.011

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1	Copper(II) and nickel(II) complexes with two new bis(thiosemicarbazone)
2	ligands: synthesis, characterization, X-ray crystal structures and their
3	electrochemistry behaviour
4	
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14

15 Abstract

16 Two new bis(thiosemicarbazone) ligands 2-[1-(2-{3-[2-({2-[(4-chloroanilino)carbothioyl]
17 hydrazono}methyl)phenoxy]propoxy}phenyl)methylidene]-N¹-(4-chlorophenyl)-1-

18 hydrazinecarbothiamide (H_2L1) and 2-[1-(2-{3-[2-({2-[(4-

19 chloroanilino)carbothioyl]hydrazono}methyl)phenoxy]-2-hydroxypropoxy}phenyl)

methylidene]- N^{1} -(4-chlorophenyl)-1-hydrazinecarbothiamide (**H**₃**L**2) were synthesized and 20 characterized by FT-IR spectroscopy, ¹HNMR spectroscopy and elemental analysis. Their 21 nickel(II) and copper(II) complexes were prepared and characterized by UV-Vis 22 spectroscopy, FT-IR spectroscopy, elemental analysis and single-crystal X-ray diffraction. 23 Both ligands lose hydrazinic hydrogen atoms upon coordination and act as dianionic 24 tetradentate donors. In [NiL1].EtOH and [CuL1].MeOH complexes metal centers are 25 coordinated by two imine nitrogen atoms and two sulfur atoms with a distorted square planar 26 coordination geometry. The geometrical distortion from square planar in the copper complex 27 is greater than in the nickel complex. Cyclic voltammetry studies of Cu(II) and Ni(II) 28 complexes in DMF show that all complexes able to stabilize low oxidation states of Cu(I) and 29 30 Ni(I).

31 Keywords: Nickel; Copper; Bis(thiosemicarbazone); Schiff base; Cyclic Voltammetry

33 1. Introduction

Metal complexes of thiosemicarbazone and bis(thiosemicarbazone) ligands have a wide range 34 of biological activities including antibacterial [1], antifungal [2], antiviral [3], antimalarial 35 [4,5] and antitumor [6-8] activities. Some reactivities of copper and nickel complexes are 36 dependent on stabilization of unusual oxidation states of metals such as potential of copper 37 complexes as radiopharmaceuticals for the specific targeting of hypoxic tissue [9-12] and as 38 superoxide dismutase-like radical scavengers [13]. Also, in nickel containing enzymes such 39 as hydrogenase unusual oxidation states of nickel are involved [14]. Therefore, model 40 complexes for stabilization of nickel and copper in lower oxidation state than its normal +241 are of interest [15-18]. Electrochemical reactivity of complexes is strongly influenced by the 42 nature and number of various types of donor atoms. Thiosemicarbazone and 43 bis(thiosemicarbazone) ligands with soft donor atoms such as N of imine and S of thiolate 44 with σ -donor and π -acceptor properties can stabilize the Ni^I and Cu^I states [15]. In this paper, 45 we report the synthesis, structure, and spectral and electrochemical properties of Cu^{II}N₂S₂ and 46 Ni^{II}N₂S₂ coordination environments. Furthermore, the subtle change of introducing hydroxyl 47 group to the coordination sphere and electrochemical behaviours of copper and nickel 48 complexes of these ligands were investigated. 49

50

51 **2. Experimental**

52 2. 1. Materials

53 2-[3-(2-formyl phenoxy)propoxy]benzaldehyde (3) and 2-[3-(2-formylphenoxy)-254 hydroxypropoxy]benzaldehyde (4) were prepared according to literature methods [19-21].
55 Other reagents and solvents were obtained from Alfa Aesar and Merck and were used as
56 received.

58 2.2. Physical Measurements

NMR spectra were recorded on Bruker Avance 400 in DMSO-d₆ solvent and chemical shifts 59 are relative to residual solvent protons as internal standard at room temperature. Elemental 60 analyses were performed on Elementar Vario EL III. FT-IR spectra were recorded on a FT-IR 61 Spectrometer Bruker Tensor 27 in the region 4000-400 cm⁻¹ using KBr pellets. Electronic 62 absorption spectra were recorded with an Analytick Jena Specord 250 in the region 230-1100 63 nm. Melting points were obtained with an Electrothermal 9100 and are uncorrected. 64 Electrochemical studies were performed using a glassy carbon as working electrode, a 65 platinum wire auxiliary electrode, and an Ag/AgCl reference electrode. 66 The ferrocene/ferrocenium couple (Fc/Fc⁺, $E_{1/2} = 0.505$ V) was used as a standard. All potentials 67 are referenced to the Ag/AgCl reference electrode. Solutions containing about 10⁻³ M 68 complexes and 0.1 M LiClO₄ as supporting electrolyte were deoxygenated by a stream of 69 high purity nitrogen for at least 10 minutes. 70

71

72 2.3 Synthesis of the ligands

73 2.3.1 Synthesis of 4-chlorophenyl thiosemicarbazide (2)

4-chlorophenyl thiosemicarbazide was prepared in a way similar to the reported methods with
minor modification [22, 23]. 4-Chlorophenylisothiocyanate (6 mmol, 1.00 g) in 10 mL of
ethanol was added dropwise to excess hydrazine hydrate (80 %) (24 mmol, 1.43 mL) under
vigorous stirring at room temperature. The white precipitate was formed immediately.
Stirring was continued for 6 h. Then the mixture was filtered and the precipitate was washed
with ethanol to give 2. The reaction conditions should be controled because the side product
will form [24].

81

83 2.3.2 Synthesis of H_2L1

2 (6.4 mmol, 1.29 g) was dissolved in 50 ml methanol. Then a methanolic solution of 84 dialdehyde 3 (3.2 mmol, 0.91 g) was added and refluxed for 5 h. The yellow precipitate was 85 formed immediately. The mixture was filtered and the yellow precipitate was washed with 86 methanol and then diethyl ether. Yield 1.86 g (92 %). m. p. 210 °C (dec.). FT-IR (KBr disc, 87 cm⁻¹): 3402 m, 3070 w, 2927 m, 2879 m, 1605 s, 1485 s, 1453 s, 1321 m, 1293 m, 1241 s, 88 1161 m, 1050 m, 856 w, 752 s. ¹H NMR (400 MHz, DMSO-d₆): δ 2.28 (quintet, 2H, 89 CH₂CH₂CH₂), 4.31 (t, 4H, CH₂CH₂CH₂), 6.99 (t, 2H, ArH), 7.13 (d, 2H. ArH), 7.40-7.42 90 (m, 6H, ArH), 7.62 (d, 4H, ArH), 8.25 (d, 2H, ArH), 8.63 (s, 2H, ArCHN), 10.10 (s, 2H, 91 MAS NH), 11.88 (s, 2H, NH) ppm. 92

93

94 2.3.3 Synthesis of H_3L2

 H_3L2 ligand was prepared by a similar procedure to that of H_2L1 except that dialdehyde 4 95 (3.2 mmol, 0.96 g) was used instead of **3** as dialdehyde. The resulting yellow-colored solid 96 product was formed, filtered, and dried. Yield 1.91 g (92 %). m. p. 220 °C. FT-IR (KBr disc, 97 cm⁻¹): 3332 s, 2926 s, 2855 s, 1611 s, 1534 m, 1485 s, 1451 s, 1293 m, 1240 s, 1161 m, 1105 98 m, 1028 s, 823 w, 750 s. ¹H NMR (400 MHz, DMSO-d₆): δ 4.27 (m, 5H, CH₂CH(OH)CH₂), 99 5.37 (s, 1H, OH), 6.99 (t, 2H, ArH), 7.14 (d, 2H. ArH), 7.40-7.43 (m, 6H, ArH), 7.64 (d, 4H, 100 ArH), 8.24 (d, 2H, ArH), 8.63 (s, 2H, ArCHN), 10.11 (s, 2H, NH), 11.87 (s, 2H, NH) ppm. 101 102

2.4. Synthesis of the complexes 103

2.4.1. General procedure 104

H₂L1 or H₃L2 (1 mmol) was dissolved in a dichloromethane-methanol mixture (10:1) under 105 reflux. To this refluxing solution was added a solution of the metal acetates of Cu²⁺ and Ni²⁺ 106 (1 mmol) dissolved in the methanol and refluxing was continued for 4 h. The solvent was 107

concentrated and products were filtered off, washed with methanol and then with diethyl
ether. The complexes were isolated as air-stable solids and soluble in chloroform, DMF and
slightly soluble in ethanol and methanol.

- 111
- 112 2.4.2. [CuL1].MeOH
- 113 Dark green crystals. Yield 0.52 g (70 %). m.p. 190 °C (dec.). Anal. Calc. for 114 $C_{31}H_{26}Cl_2CuN_6O_2S_2.CH_3OH$: C, 51.58; H, 4.06; N, 11.28 %. Found: C, 51.48; H, 4.12: N,
- 115 11.20 %. FT-IR (KBr disc, cm⁻¹): 3301 m, 2927 m, 1599 s, 1487 s, 1435 s, 1296 m, 1243 s,
- 116 1161 m, 1104 m, 1027 s, 803 m, 751 s.
- 117
- 118 2.4.3. [NiL1].EtOH
- 119 Brown crystals. Yield 0.56 g (74 %). m.p. 205 °C (dec.). Anal. Calc. for 120 $C_{31}H_{26}Cl_2N_6NiO_2S_2.CH_3CH_2OH$: C, 52.54; H, 4.28; N, 11.14 %. Found: C, 52.34; H, 4.30; 121 N, 11.01 %. FT-IR (KBr disc, cm⁻¹): 3064 w, 2925 w, 1595 m, 1538 m, 1499 s, 1456 m,
- 122 1305 m, 1245 m, 1162 w, 1091 w, 1050 m, 827 m, 752 m.
- 123
- 124 2.4.4. [Cu(**HL2**)].2MeOH
- 125 Dark green precipitates. Yield 0.57 g (72 %). m.p. 175 °C (dec.). Anal. Calc. for 126 $C_{31}H_{26}Cl_2CuN_6O_3S_2.2CH_3OH$: C, 49.97; H, 4.32; N, 10.59 %. Found: C, 50.13; H, 4.34; N, 127 10.37 %. FT-IR (KBr disc, cm⁻¹): 3326 s, 2931 w, 1595 s, 1488 s, 1393 m, 1303 s, 1249 s, 1112 m, 1044 m, 947 w, 824 m, 751 m.
- 129
- 130 2.4.5 [Ni(**HL2**)].MeOH
- Brown precipitates. Yield 0.6 g (79 %). m.p. 210 °C (dec.). Anal. Calc. for
 C₃₁H₂₆Cl₂N₆NiO₃S₂.CH₃OH: C, 50.82; H, 4.00; N, 11.11 %. Found: C, 50.76; H, 4.03; N,

10.89 %. FT-IR (KBr disc, cm⁻¹): 3392 m, 3060 w, 2925 w, 1595 s, 1538 s, 1486 s, 1453 s,
134 1395 s, 1305 s, 1244 s, 1164 w, 1091 w, 1036 m, 825 m, 750 m.

- 135
- 136 2.5. Single-crystal X-ray diffraction

X-ray structural analysis for [CuL1].MeOH and [NiL1].EtOH: For each structure 137 determination a single crystal was selected and mounted using NVH immersion oil onto a 138 nylon fiber and cooled to the data collection temperature of 100(2) K. Data were collected on 139 a Bruker-AXS Kappa APEX II CCD diffractometer with Mo-Ka radiation. Unit cell 140 parameters were obtained from 60 data frames, 0.5 ° ϕ , from three different sections of the 141 Ewald sphere. A complete and redundant data set was collected using the APEX2 software 142 [25]. These data were integrated using SAINT+ and treated with SADABS [26] absorption 143 corrections based on redundant multi-scan data. The systematic absences in the data were 144 analysed with XPREP [27] and were consistent with the centrosymmetric, monoclinic space 145 group $P2_1/c$ for both crystals, whose unit cell parameters were very similar. The structures 146 were solved by intrinsic phasing methods and refined by least squares method on F^2 using the 147 SHELXTL program package [28]. Details regarding specific solution refinement for each 148 compound are provided in the following paragraphs. 149

Details for [CuL1].MeOH: Single crystals were grown by slow evaporation of dichloromethane/methanol solvent mixture. The asymmetric unit was found to contain one molecule of [CuL1] and one molecule of methanol solvent disordered over two positions. The methanol was modeled with the aid of similarity restraints on bond distances and anisotropic displacement parameters. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bound to nitrogen were located and refined isotropically, and the remaining hydrogen atoms were treated as idealized contributions.

Details for [NiL1].EtOH: Single crystals were grown by diffusing a chloroform/ethanol 157 solution of the compound with toluene. The crystals obtained for this complex were very 158 small and weakly diffracting, with data only out 0.90 Å. The asymmetric unit was found to 159 contain one molecule of [NiL1] and one molecule of ethanol solvent that participates in a 160 hydrogen bond with an NH group of the ligand. All non-hydrogen atoms were refined with 161 anisotropic displacement parameters. Hydrogen atoms bound to nitrogen and oxygen were 162 located and refined isotropically, and the remaining hydrogen atoms were treated as idealized 163 contributions. Table 1 summarizes crystal and refinement data for [NiL1].EtOH and 164 MAN [CuL1].MeOH. 165

166

	[NiL1].EtOH	[CuL1].MeOH
Empirical formula	$C_{33}H_{32}Cl_2N_6NiO_3S_2$	$C_{32}H_{30}Cl_2CuN_6O_3S_2$
Formula weight	754.37	745.18
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	P 21/c	P 21/c
Unit cell dimensions	$a = 18.808(3) \text{ Å}, \alpha = 90^{\circ}$	a = 18.9426(15) Å, α = 90 °
	$b = 9.2333(13) \text{ Å}, \beta = 107.161(4)^{\circ}$	$b = 9.0834(8) \text{ Å}, \beta = 106.2808(19) ^{\circ}$
	$c = 19.805(3) \text{ Å}, \gamma = 90^{\circ}$	$c = 19.9463(17) \text{ Å}, \gamma = 90^{\circ}$
Volume	$3286.2(8) \text{ Å}^3$	$3294.4(5) \text{ Å}^3$
Z	4	4
Density (calculated)	1.525 Mg/m^3	1.502 Mg/m^3
Absorption coefficient	0.926 mm^{-1}	0.996 mm^{-1}
F(000)	1560	1532
Crystal size	0.120 x 0.050 x 0.020 mm ³	0.320 x 0.210 x 0.060 mm ³
Theta range for data collection	2.116 to 23.256 °	2.108 to 32.577 °
Index ranges	$-20 \le h \le 20, -10 \le k \le 10, -21 \le l \le 22$	$-28 \le h \le 28, -13 \le k \le 13, -30 \le l \le 30$
Reflections collected	33755	96509
Independent reflections	4711 [R(int) = 0.1248]	12000 [R(int) = 0.0476]
Completeness to theta = 25.242°	79.3 %	100.0 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7449 and 0.6511	0.7465 and 0.6489
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	4711 / 0 / 440	12000 / 39 / 438
Goodness-of-fit on F^2	1.005	1.070
Final R indices [I>2sigma(I)]	R1 = 0.0521, $wR2 = 0.0973$	R1 = 0.0456, $wR2 = 0.1275$
R indices (all data)	R1 = 0.1052, wR2 = 0.1157	R1 = 0.0627, wR2 = 0.1378
Largest diff. peak and hole	0.702 and $-0.411 \text{ e } \text{\AA}^3$	2.213 and $-1.202 \text{ e} \text{ Å}^3$

167 Table 1. Crystal data and structure refinement for [NiL1].EtOH and [CuL1].MeOH

168

169 **3. Results and discussions**

170 3.1. Synthesis of compounds

Scheme 1 illustrates the reaction scheme used to obtain H_2L1 and H_3L2 ligands. The 171 synthesis of 4-substituted thiosemicarbazides can be achieved in a one-pot synthesis by the 172 reaction of 4-substituted phenylisothiocyanate with hydrazine. A condensation reaction 173 between two equivalents 4-chlorophenylthiosemicarbazide and one equivalent of 3 or 4 as 174 dialdehydes gave two bis(thiosemicarbazone) ligands H₂L1 and H₃L2, respectively, in high 175 176 yield. Thiosemicarbazone ligands may exist as thione/thiol tautomeric forms owing to the intramolecular proton transfer [29] but the IR spectra of H₂L1 and H₃L2 do not display v(S-177 H) in the region 2500-2600 cm^{-1} indicating that in the solid state these ligands remain in the 178 thione form [30]. 179

The infrared spectra of H_2L1 and H_3L2 show a strong absorption band at 1605 and 1611 cm⁻¹, respectively, assigned to the C=N stretching vibration, indicating the formation of the Schiff base product. Furthermore, ¹H NMR spectra of H_2L1 and H_3L2 show singlets at 8.63 ppm assigned to the HC=N protons. The chemical Shift of NH–N and NH–Ar protons observed as singlets, respectively, at 11.88 and 10.10 ppm for H_2L1 and 11.87 and 10.11 ppm for H_3L2 .

The reaction of nickel(II) and copper(II) acetates with ligands yielded corresponding 186 complexes in high yields. On the basis of their elemental analysis and X-ray analysis (only 187 for two complexes) the complexes were formulated as [CuL1].MeOH, [NiL1].EtOH, 188 [Cu(HL2)].2MeOH, and [Ni(HL2)].MeOH. In all complexes both ligands act as doubly 189 negatively charge anions in complexation through deprotonation of the hydrazinic hydrogen 190 atoms. In ¹H nmr of nickel complexes in CDCl₃, signals of NH–N protons at 11.88 ppm for 191 H_2L1 and at 11.87 ppm for H_3L2 at free ligands are omitted upon coordination to the nickel. 192 But signals of NH-Ar protons appear as two distinct signals at 10.07 and 10.15 ppm for 193 [NiL1].EtOH and at 10.05 and 10.16 ppm for [Ni(HL2)].MeOH. The frequency of the imine 194 bond, v(C=N), observed above 1600 cm⁻¹ in the free ligands, shifts to lower wavenumbers 195 upon coordination to the metal in all complexes. Distinguishing between v(C=C) and v(C=N)196 in the complexes is difficult. Therefore, the v(C=C) of the phenyl rings and v(C=N) of the 197 imine in the complexes are assigned, without distinguishing them, to the peaks observed 198 between 1400 to 1600 cm^{-1} [31]. 199



200

201

Scheme1. Preparation steps of H_2L1 and H_3L2 and corresponding complexes

202

203 *3.2. Crystal structure of compounds*

An ORTEP view of the nickel complex [NiL1].EtOH is given in Fig. 1 and selected bond 204 distances and angles are given in Table 2. In this complex ligand H_2L1 has lost hydrazinic 205 hydrogen atoms and therefore acts as a dianion. Two thiosemicarbazone moieties act as 206 convergent to form a mononuclear complex. The ligand is tetradentate and nickel is 207 coordinated by two imine nitrogen atoms (N13 and N43) and two sulfur atoms (S1 and S2). 208 The metal center has a distorted square planar NiN₂S₂ coordination environment according to 209 the geometrical parameter τ_4 , defined as $[360 - (\alpha + \beta)]/141$, where α , β are the two largest 210 coordination angles (166.02(14) and 161.85(14) °). The τ_4 values are zero and one for perfect 211 square planar and tetrahedral geometry, respectively [32]. The calculated τ_4 index is 0.23 for 212 Ni1 showing that nickel has a distorted square planar. The Ni–N_{imine} bond distances (1.902(4) 213 and 1.904(4) Å) and Ni–S bond distances (2.1645(14) and 2.1651(15) Å) are comparable to 214 corresponding distances in related complexes [33]. N12-C10 and N42-C40 bond distances 215 1.298(6) and 1.300(6) Å, respectively, are consistent with C=N double bond and similar to 216 217 bond distances of C=N double bonds N43-C50 and N13-C20 with 1.293(7) and 1.310(6) Å distances, respectively. Also C-S distances are not in the range of double bond character and 218 are comparable to corresponding distances in other thiosemicarbazone complexes [34-36]. 219

- 220 These observations are consistent to lossing of hydrazinic hydrogens and producing negative
- 221 charges on sulfur atoms that are coordinated to nickel cation.



- 222
- . . .

223

Fig. 1. Molecular structure of [NiL1].EtOH complex. Solvent molecule is omitted

224

The molecular structure of the copper complex [CuL1].MeOH is given in Fig. 2 with selected 225 distances and angles listed in the Table 2. The molecular structure of [CuL1].MeOH is 226 similar to [NiL1].EtOH. The ligand acts as an N₂S₂ donor set around the copper, giving a 227 distorted square planar geometry and τ_4 index is 0.36 for Cu1. Distortion of square planar for 228 the [CuL1].MeOH is greater than for the [NiL1].EtOH. The angles around the nickel are 229 closer to the 90° preferred at the square planar geometry. In copper complex deviation from 230 90° for N3–Cu1–N6 (99.26(7) °) and S1–Cu1–S2 (100.42(2) °) angles are greater. However, 231 N6-Cu1-S2 and N3-Cu1-S1 angles are, respectively, 85.18(5) ° and 86.16(5) ° and are 232 similar to N13-Ni1-S1 and N43-Ni1-S2 angles with values 85.71(12) ° and 86.52(14) °, 233 respectively. The Cu-N_{imine} distances (1.9915(16) and (1.9964(17) Å) and Cu-S distances 234 (2.2303(5) and 2.2381(6) Å) are longer than the Ni–N_{imine} distances (1.902(4) and 1.904(4) 235

- 236 Å) and Ni–S distances (2.1645(14) and 2.1651(15) Å). The Cu–S thiolate and Cu–N imine bond
- distances are similar to other compounds with $S_{thiolate}$ and N_{imine} coordination [12, 36].

bond distances	[NiL1].EtOH	bond distances	[CuL1].MeOH
Ni1–S1	2.1645(14)	Cu1–S1	2.2381(6)
Ni1–S2	2.1651(15)	Cu1–S2	2.2303(5)
Ni1-N13	1.902(4)	Cu1–N3	1.9915(16)
Ni1-N43	1.904(4)	Cu1–N6	1.9964(17)
S1-C10	1.761(5)	S1C1	1.750(2)
S2-C40	1.756(5)	S2-C3	1.759(2)
N11-C10	1.370(6)	N1C1	1.372(3)
N41–C40	1.365(6)	N4-C3	1.368(2)
N12-C10	1.298(6)	C1-N2	1.309(3)
N42-C40	1.300(6)	C3-N5	1.302(3)
N13-N12	1.415(5)	N2-N3	1.395(2)
N42-N43	1.407(5)	N5-N6	1.397(2)
N13-C20	1.310(6)	C2-N3	1.296(2)
N43-C50	1.293(7)	C4-N6	1.293(3)
C21–C20	1.443(7)	C4–C41	1.460(3)
C50–C51	1.447(7)	C2-C21	1.457(3)
Bond angles	[NiL1].EtOH	Bond angles	[CuL1].MeOH
N13-Ni1-N43	96.62(17)	N3–Cu1–N6	99.26(7)
N13–Ni1–S1	85.71(12)	N3–Cu1–S2	156.51(5)
N43-Ni1-S1	166.02(14)	N6-Cu1-S2	85.18(5)
N13-Ni1-S2	161.85(14)	N3-Cu1-S1	86.16(5)
N43-Ni1-S2	86.52(14)	N6–Cu1–S1	152.87(5)
S1-Ni1-S2	95.56(6)	S2-Cu1-S1	100.42(2)

238	Table 2. Selected bond distances (A	Å) and ang	gles (°) for	[NiL1].EtOI	H and [CuL1].MeOF
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239



Fig. 2. Molecular structure of [CuL1].MeOH complex. Solvent molecule is omitted

242 Hydrogen bonds and short contacts in [NiL1].EtOH and [CuL1].MeOH complexes are similar. The unit cell of [NiL1].EtOH complex consists of four units of [NiL1] and four 243 ethanol molecules, held together in the crystal packing by intermolecular bonds such as 244 hydrogen bonds, O–H... π , and C–H... π interactions (Fig. S1 and Fig. S2). The uncoordinated 245 ethanol molecules in [NiL1].EtOH act as hydrogen acceptor from N41-H41 and C46-H46 246 with distances O1S...H41 = 2.24(6) Å and O1S...H46 = 2.51 Å and as a hydrogen donor 247 toward π -ring (C_g5 = C41, C42, C43, C44, C45, and C46) of other complex unit through 248 O1S-H1S... $C_g 5 = 2.47$ Å. In [CuL1].MeOH complex the uncoordinated methanols act as 249 hydrogen acceptor from N1–H1 and C16–H16 with distances O1S...H1 = 2.14(3) Å and 250 O1S...H16 = 2.44 Å and as a hydrogen donor toward N1 atom (H1S...N1 = 2.58 Å). In both 251 complexes uncoordinated imine nitrogen atoms (N12 and N42 in [NiL1].EtOH and N2 and 252 N5 in [CuL1].MeOH) are involved in intramolecular hydrogen bonds with hydrogen atoms 253 of 4-chloro substituted phenyl rings (see Table 3). 254

256	Table 3. Hydrogen bonds and X-	H π interactions for [NiL]	1].EtOH and [CuL1].MeOH
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		Hydroge	n bonds		
compound	D–HA	d(D–H)	d(HA)	d(DA)	< (D–H…A)
[NiL1].EtOH	N41–H41…O1S ⁱ	0.75(6)	2.24(6)	2.960(6)	162(6)
	C12–H12…N12	0.95	2.23	2.847(7)	122
	C42–H12…N42	0.95	2.22	2.839(7)	122
	C46–H46… O1S ⁱ	0.95	2.51	3.310(7)	142
[CuL1].MeOH	N1–H1…O1S ⁱⁱ	0.83(3)	2.14(3)	2.952(11)	166(3)
	O1S-H1SN1	0.84	2.58	2.952(11)	108
	N4–H4…S2 ⁱⁱⁱ	0.75(3)	2.80(3)	3.5118(19)	159(3)
	C12-H12N2	0.95	2.20	2.820(4)	122
	C16–H16… O1S ⁱⁱ	0.95	2.44	3.251(13)	144
	C36–H36…N5	0.95	2.27	2.888(3)	122
Symmetry codes (i	i) –x + 2, -y, -z + 2 (ii) x	, −y − 1/2, z +	1/2 (iii) -x - 1, -y	/−1, -z + 1	
		X–H \dots π in	teractions		
compound	X–H…C _g		$d(HC_g)$	d(X	.C _g)
[NiL1].EtOH	$O1S-H1SC_{g}(5)$		2.47(6)	3.311(4)	
	$C13-H13C_{g}(6)$		2.97	3.726(6)	
	C32–H32…C _g (3)		2.66	3.515(6)	
[CuL1].MeOH	C35–H35…C _g (4)		2.92	3.655(2)	
	C50–H50A…C _g (5)	5) 2.68 3.518(3)		8(3)	
	O2S-H2SC _g (3)		2.64	3.06(3)
	C2S-H2S2 $C_g(6)$		2.82	3.504	(8)

258 *3.3 UV-Vis spectroscopy*

The spectra of H₂L1 and H₃L2 exhibit similar patterns in the 230-700 nm region (Fig. S3). 259 The UV-Vis spectra of the metal-free ligands are dominated by intra-ligand transitions 260 261 associated with the phenyl rings, imines, and thione portions of the ligands. The electronic spectra taken in CH₂Cl₂ of copper(II) and nickel(II) complexes are shown in Fig. 3 and Fig. 262 4, respectively, and the spectral data are tabulated in Table 4. Coordination of 263 bis(thiosemicarbazone) ligands to the Cu(II) and Ni(II) leads to changes in the UV region 264 (230-400 nm). This is presumably because of the change in the ligand conjugation caused by 265 the deprotonation of the ligands upon coordination. Also, upon coordination new bands (two 266 bands for copper(II) complexes and one band for nickel(II) complexes) above 400 nm appear 267 which correspond to square planar thiosemicarbazone Cu(II) and Ni(II) complexes [9, 12]. 268 The spectra of the nickel and copper complexes of the two ligands are very similar. 269 Therefore, based on the above spectral evidences, it is confirmed that the ligands H_2L1 and 270 H_3L2 are coordinated via the azomethine nitrogen and thiolate sulphur atoms with the same 271 coordination mode (Structure of Cu(II) and Ni(II) complexes of H₂L1 ligand have been 272 confirmed by X-ray single-crystal structure analysis). 273

274



Fig. 3 UV-Vis absorption spectra of 3×10^{-5} M of [CuL1].MeOH and [Cu(HL2)].2MeOH and 4×10^{-4} M (inset)







Compound	λ , nm (ε , M ⁻¹ cm ⁻¹)
H ₂ L1	312 (42005) sh, 339 (51503)
H_3L2	313 (43699) sh, 335 (58182)
[CuL1].MeOH	245 (46054), 332 (50620), 421 (3445) sh, 569(1143)
[Cu(HL2)].2MeOH	249 (39884), 334 (46093), 425 (2844) sh, 587 (1005)
[NiL1].EtOH	269 (51759), 337 (38206), 498 (316) sh
[Ni(HL2)].MeOH	269 (49114), 336 (36642), 498 (301) sh

Table 4. Electronic spectral data of compounds in CH_2Cl_2

286

287 *3.4 Cyclic voltammetry*

To investigate the redox properties of the complexes, the cyclic voltammograms were recorded for all the complexes in DMF using the same cell set up. Results are summarized in Table 5 and in Fig. 5 and Fig. 6. Bis(thiosemicarbazone) Schiff base ligands, H₂L1 and H₃L2, have imine and thiolate donor sites which have π -acceptor property, therefore, they are expected to stabilize the lower oxidation states of copper and nickel. Neither ligands were electroactive in the range of -1.25 to +1 V.

[CuL1].MeOH and [Cu(HL2)].2MeOH complexes exhibit a reversible one electron reduction process assigned to the metal-centered Cu^{II}/Cu^I redox couple at $E_{1/2} = 0.023$ and -0.099 V vs an Ag/AgCl reference electrode in DMF, respectively. Reduction in [CuL1].MeOH is easier than [Cu(HL2)].2MeOH, also reversibility in [CuL1].MeOH ($\Delta E_p = 70$ mV, $i_{pc}/i_{pa}=1.001$) is higher than in [Cu(HL2)].2MeOH ($\Delta E_p = 71$ mV, $i_{pc}/i_{pa}= 0.878$). Redox potentials of Cu^{II} complexes lie within a range accessible to cellular oxidants and reductants [18].

The CV of [NiL1].EtOH in DMF displays a reversible reductive response at $E_{1/2} = -0.797$ V vs Ag/AgCl ($E_{pc} = -0.832$ V, $E_{pa} = -0.761$ V and $\Delta E_p = 71$ mV) that has been shown in Fig. 6. The value of $i_{pc}/i_{pa} = 1.081$ clearly indicates the reversibility of Ni^{II}/Ni^I couple. [Ni(**HL2**)].MeOH complex also exhibits a reversible reductive response at $E_{1/2} = -0.870$ V ($E_{pc} = -0.921$ V, $E_{pa} = -0.821$ V) but with a greater ΔE_p value (100 mV) than [NiL1].EtOH complex. Therefore, in [CuL1].MeOH and [NiL1].EtOH complexes without a hydroxyl

306 group reduction is easier and reversibility is higher than in the corresponding
307 [Cu(HL2)].2MeOH and [Ni(HL2)].MeOH complexes with an OH group.

308

Table 5. Cyclic voltammetry data for complexes in DMF solutions at 100 mVs^{-1} scan rate

Complex	$E_{pc}(V)$	E _{pa} (V)	$\Delta E_{p} (mV)$	E _{1/2} (V)	$ \mathbf{i}_{\mathrm{pc}} / \mathbf{i}_{\mathrm{pa}} $
[CuL1].MeOH	-0.013	0.058	70	0.023	1.001
[Cu(HL2)].2MeOH	-0.134	-0.063	71	-0.099	0.878
[Ni L1].EtOH	-0.832	-0.761	71	-0.797	1.081
[Ni(HL2)].MeOH	-0.921	-0.821	100	-0.871	1.291

The ferrocenium-ferrocene couple shows a peak separation of 110 mV under the same experimental conditions. $\Delta E_p = E_{pa} - E_{pc}$ and $E_{1/2} = (E_{pc} + E_{pa})/2$





311

Fig 5. Cyclic voltammograms of [CuL1].MeOH (solid line) and [Cu(HL2)].2MeOH (dashed

313

С

line) in DMF solution containing 0.1 M LiClO₄ at 100 mVs⁻¹



314

Fig. 6. Cyclic voltammograms of [NiL1].EtOH (solid line) and [Ni(HL2)].MeOH (dashed



line) in DMF solution containing 0.1 M LiClO₄ at 100 mVs⁻¹

317 Conclusions

318	Two new bis(thiosemicarbazone) Schiff base ligands were prepared in good yields. Both
319	ligands lose hydrazinic hydrogen atoms upon coordination and act as doubly negative anions
320	when react with Ni(II) and Cu(II) acetates. These ligands act as N_2S_2 donor set in all
321	complexes and hydroxyl group has no effect on coordination geometry but has influence on
322	electrochemical potentials and reversibility of M^{II}/M^{I} couples. Redox properties of these
323	complexes clearly revealed that imine N and thiolate S donor set able to stabilize the +1
324	oxidation state of nickel and copper.
325	
326	Acknowledgements
327	We would like to thank University of Tabriz for supporting this work.
328	
329	Appendix A. Supplementary material
330	CCDC 1028265 and 1028266 contain the supplementary crystallographic data for
331	[CuL1].MeOH and [NiL1].EtOH complexes, respectively. These data can be obtained free of
332	charge from The Cambridge Crystallographic Data Centre via
333	www.ccdc.cam.ac.uk/data_request/cif. Supplementary material contains hydrogen bonds, O-
334	H π , and C-H π interactions for [NiL1].EtOH and UV-Vis spectra of H ₂ L1 and H ₃ L2
335	ligands.

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- ✓ Ni(II) and Cu(II) complexes of new bis(thiosemicarbazone) ligands were prepared
- $\checkmark~$ ligands act as N_2S_2 donor set and OH group has no effect on coordination geometry
- ✓ New ligands can stabilize low oxidation state (+1) of nickel and copper
- Accepter \checkmark OH group has effect on redox potentials and reversibility of M^{II}/M^I couples

Two new bis(thiosemicarbazone) Schiff base ligands and their metal complexes with Cu(II) and Ni(II) were prepared and characterized by NMR, FT-IR, UV-Vis absorption spectroscopy, single crystal X-ray diffraction, CHN elemental analysis and cyclic voltammetry.

