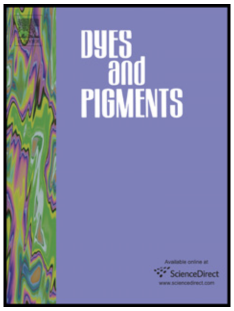

Synthesis, characterization, and electrochemical study of some novel, azo-containing Schiff bases and their Ni(II) complexes

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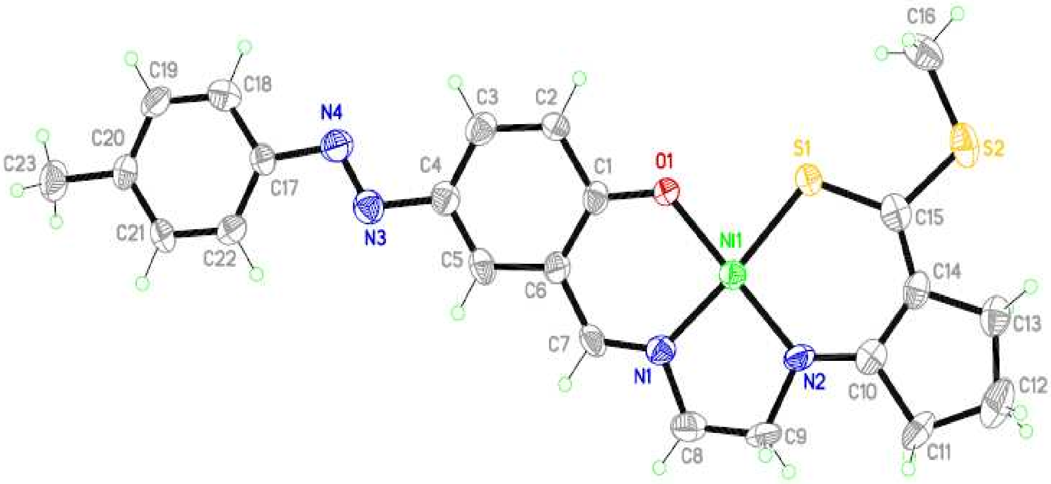

Synthesis, characterization, and electrochemical study of some novel, azo-containing Schiff bases and their Ni(II) complexes

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Abstract

Five novel azo-azomethine ligands with NN'OS coordination spheres were prepared by reaction of methyl-2-{*N*-(2'-aminoethane)}-amino-1-cyclopentenedithiocarboxylate (Hcden) with (*E*)-2-hydroxy-5-(phenyldiazenyl)benzaldehyde and its substituted derivatives and then the corresponding nickel(II) complexes were synthesized. The structures of ligands and the complexes were characterized by elemental analyses, IR, UV-Vis, ^{1}HNMR spectroscopy and cyclic voltammetry. The structures of (methyl 2-(2-((*E*)-2-hydroxy-5-((*E*)-*p*-tolyldiazenyl)benzylideneamino)ethylamino)cyclopent-1-enecarbodithioato)nickel(II) and (methyl 2-(2-((*E*)-5-((*E*)-(4-chlorophenyl)diazenyl)-2-hydroxybenzylideneamino)ethylamino)cyclopent-1-enecarbodithioato)-nickel(II) have been determined by X-ray crystallography. The X-ray results confirm that the geometry of the complexes are slightly distorted square-planar structures. The nickel(II) ions coordinate to two nitrogen atoms from the imine moiety of the ligand, a sulfur atom from the methyl dithiocarboxylate moiety and a phenolic oxygen atom.

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Keyword: Schiff base complexes; Azo dyes; Azo-azomethine compounds; X-ray crystal structure ; Nickel(II) complexes: Asymmetry Schiff bases.

1. Introduction

Azo compounds are the oldest and largest class of industrial synthesized organic dyes due to their versatile application in various fields, such as biomedical studies, advanced application in organic synthesis, dyeing textile fibers and high technology areas such as electro-optical devices, liquid crystalline displays, laser and ink-jet printers[1-3]. The great majority of azo dyes are monoazo compounds, which have the common structure unit of the azo chromophore, -N=N-, linking two aromatic systems. The textile industry is the largest consumer of dyestuffs. Although some azo dyes have been reported to be toxic, dozens of additional monoazo dyes are permitted in drugs and cosmetics [4]. The oxidation-reduction behaviours of these compounds play an important role in its biological activity [5]. The pharmaceutical importance of compounds including an arylazo group has been extensively reported in the literature [6,7].

Schiff bases are an important class of ligands in coordination chemistry and find extensive applications in different fields. There is a continuing interest in transition metal complexes of asymmetrical Schiff bases because of the presence of soft sulphur, hard nitrogen and oxygen donor atoms in the backbones of these ligands. Some of these complexes exhibit interesting physical and chemical properties [8] and potentially useful biological activities [9]. Also, these transition metal complexes are used in analytical fields [10] and as model molecules for biological oxygen carrier systems [11]. Tetradentate Schiff base complexes are well known to form stable complexes, where the coordination takes place through the NN'OS donor set [12]. The number of the Schiff bases derived from condensation of various aldehyds with methyl-2-{*N*-(2'-

aminoethane)}-amino-1-cyclopentenedithiocarboxylate (Hcden) and their transition metal complexes with Ni(II) have been reported in the literature [13-17].

We reported herein the syntheses and structural characterization of some novel, azo-containing Schiff bases derivatives ligands (H_2L) [(6a=methyl 2-(2-((*E*)-2-hydroxy-5-((*E*)-phenyldiazenyl)benzylideneamino)ethylamino)cyclopent-1-enecarbodithioate); (6b=methyl 2-(2-((*E*)-2-hydroxy-5-((*E*)-*p*-tolyldiazenyl)benzylideneamino)ethylamino)cyclopent-1-enecarbodithioate); (6c=methyl 2-(2-((*E*)-5-((*E*)-(4-ethylphenyl)diazenyl)-2-hydroxybenzylideneamino)ethylamino)cyclopent-1-enecarbodithioate); (6d=methyl 2-(2-((*E*)-5-((*E*)-(4-chlorophenyl)diazenyl)-2-hydroxybenzylidenamino)ethylamino)cyclopent-1-enecarbodithioate); (6e=methyl 2-(2-((*E*)-5-((*E*)-(4-nitrophenyl)diazenyl)-2-hydroxybenzylidenamino)ethylamino)cyclopent-1-enecarbodithioate); (Scheme 1) and their nickel(II) complexes (Scheme 2). Elemental analyses, IR, UV-Vis ^{1}HNMR spectra and cyclic voltammetry were obtained to determine the structure of the ligands derived from condensation of azo-containing aldehyde with Hcden and their complexes with Nickel(II). In addition the complexes 7b= (methyl 2-(2-((*E*)-2-hydroxy-5-((*E*)-*p*-tolyldiazenyl)benzylideneamino)ethylamino)cyclopent-1-enecarbodithioato)nickel(II) and 7d= (methyl 2-(2-((*E*)-5-((*E*)-(4-chlorophenyl)-diazenyl)-2-hydroxybenzylideneamino)ethylamino)cyclopent-1-enecarbodithioato)nickel(II) were characterized in the solid state by X-ray diffractometry in order to elucidate their molecular and crystal structures and to evaluate their degree of tetrahedral distortion to the square planar geometry.

2. Experimental

2.1. Reagents and solvents

All solvents were purchased commercially. 1,2-ethylendiamine, aniline, 4-chloroaniline, 4-nitroaniline, 4-methylanilin, 4-ethylanilin, sodium carbonate, sodium nitrite, carbon disulfide, cyclopentanone, dimethylsulfate, nickel(II) chloride hexahydrate and salicylaldehyde were obtained from Merck and were used without further purification.

2.2. Instrumentation

Elemental analyses (C, H and N) were measured with a Termo Fininngan-Flash 1200 analyzer and UV-Vis measurements were recorded on a Jenus 5606 UV-Vis spectrophotometer. The NMR spectra were obtained in a Brucker Avance DPZ-500 MHz spectrometer. IR spectra were recorded by Perkin Elmer RX1 FT-IR infrared spectrophotometer. Electrochemical experiments were performed using an Autolab modular electrochemical system (Eco Chem. Utrecht, The Netherlands) equipped with PSTA 20 model and driven by GPES software (Eco Chem.). A conventional three-electrode cell was used with a saturated Ag|AgCl as reference electrode, a Pt wire as counter electrode and a modified carbon paste as working electrode. All experiments were carried out at ambient temperature of 20 ± 1 °C. A Metrohm pH-meter (model 691) was also applied for the pH measurements

2.3. Synthesis

2.3.1. Synthesis of methyl-2-{N-(2-aminoethane)}-amino-1-cyclopentenedithiocarboxylate(Hcden)

Hcden was prepared by published method [18,19].

2.3.2. Preparation of Azo compounds (4a-e).

Azo dyes (4a-e) were synthesized according to the well-known literature procedure [20]. A mixture of aniline (10 mmol) or its derivatives in hydrochloric acid (36 mL), and water (16 mL) were heated to 70 ˚C. The clear solutions were poured into an ice-water mixture, and were diazotized between 0 ˚C and 5 ˚C with sodium nitrite (10 mmol) dissolved in water (5 mL). The cold diazo solutions were added to a solution of salicylaldehyde (10 mmol) in water (19 mL) containing sodium hydroxide (10 mmol) and sodium carbonate (40 mmol) during the period of 30 min at 0 ˚C. during the adding process, the diazo solutions were vigorously stirred. The products were collected by filtration and washed with 100 mL of NaCl solution (10%) under vacuum. Then, the solids were dried under vacuum at 80 ˚C overnight. The purity of the compounds were controlled by TLC (n-hexane:ethylacetate/60:40).

2.3.2.1 (E)-2-hydroxy-5-(phenyldiazenyl)benzaldehyde (4a)

Yield: 91%. m.p 120 ˚C. IR (KBr, cm^{-1}): 3200 ν(O-H)，1667 ν(C=O)，1620 ν(C=C)，1569 and 1478 ν(-N=N-, *cis* and *trans*)，1285 ν(C-O)，1171, 1106, 849, 764. ^{1}H NMR δ (500MHz; CDCl$_3$): 11.36 (OH, s), 10.05 (s, CHO), 8.23 (d, 1H, *J*=8.87 Hz), 8.21 (d, 1H, *J*=7.91 Hz), 7.93 (d, 1H, *J*=7.58 Hz), 7.92 (d, 1H, *J*=7.01 Hz), 7.55 (t, 2H, *J*=8.00 Hz), 7.51 (t, 1H, *J*=7.78 Hz), 7.15 (d, 1H, *J*=8.80 Hz). *Anal*. Calc. for $C_{13}H_{10}O_2N_2$: C, 69.02; H, 4.42; N, 12.39. Found: C, 69.24; H, 4.71; N, 11.99%

2.3.2.2 (E)-2-hydroxy-5-(paratolyldiazenyl)benzaldehyde (4b)

Yield: 75%. m.p 150 ˚C . IR (KBr, cm^{-1}): 3182 ν(O-H)，1656 ν(C=O)，1619 ν(C=C)，1573 and 1479 ν(-N=N-, *cis* and *trans*)，1278 ν(C-O)，1171, 1106, 849, 764. ^{1}H NMR δ (500MHz; CDCl$_3$): 11.33 (s, OH), 10.03 (s, CHO), 8.19 (s, 1H), 8.17 (d, 1H, *J*=8.68 Hz), 7.83 (d, 2H, *J*=8.22 Hz), 7.35 (d, 2H, *J*=8.12 Hz), 7.13 (d, 1H, *J*=8.52 Hz), 2.46 (s, CH$_3$). *Anal*. Calc. for $C_{14}H_{12}O_2N_2$: C, 73.13; H, 4.48; N, 10.45. Found: C, 72.55; H, 4.86; N, 10.73%.

2.3.2.3 (E)-5-((4-ethylpheny)ldiazenyl)-2-hydroxybenzaldehyde (4c)

Yield: 60%. m.p 90 ˚C . IR (KBr, cm^{-1}): 3036 ν(O-H)，1651 ν(C=O)，1622 ν(C=C)，1578 and 1478 ν(-N=N-, *cis* and *trans*)，1275 ν(C-O)，1171, 1106, 849, 764. ^{1}H NMR δ (500MHz; CDCl$_3$): 11.33 (s, OH), 10.02 (s, CHO), 8.19 (s, 1H), 8.17 (d, 1H, *J*=8.48 Hz), 7.85 (d, 2H, *J*=8.24 Hz), 7.36 (d, 2H, *J*=8.21 Hz), 7.13 (d, 1H, *J*=8.52 Hz), 2.76 (q, CH_2, *J*=7.59 Hz). 1.32 (t, CH_3, *J*=7.60 Hz). *Anal*. Calc. for $C_{15}H_{14}O_2N_2$: C, 73.94; H, 4.93; N, 9.86 Found: C, 74.21; H, 5.28; N, 9.64%.

2.3.2.4 (E)-5-((4-chloropheny)ldiazenyl)-2-hydroxybenzaldehyde (4d)

Yield: 80%. m.p 204 ˚C . IR (KBr, cm^{-1}): 3208 ν(O-H)，1633 ν(C=O)，1613 ν(C=C)，1581 and 1479 ν(-N=N-, *cis* and *trans*)，1283 ν(C-O)，1171, 1106, 849, 764. ^{1}H NMR δ (500MHz; $CDCl_3$): 11.38 (s, OH), 10.06 (s, CHO), 8.22 (s, 1H), 8.19 (d, 1H, *J*=9.00 Hz), 7.87 (d, 2H, *J*=8.73 Hz), 7.51 (d, 2H, *J*=8.72 Hz), 7.15 (d, 1H, *J*=8.88 Hz). *Anal*. Calc. for $C_{13}H_9O_2N_2$: C, 72.51; H, 3.59; N, 11.16. Found: C, 72.85; H, 3.21; N, 11.33%.

2.3.2.5 (E)-2-hydroxy-5-((4-nitrophenyl)diazenylbenzaldehyde (4e)

Yield: 90%. m.p 184 ˚C . IR (KBr, cm^{-1}): 3103 ν(O-H)，1657 ν(C=O)，1620 ν(C=C)，1577 and 1478 ν(-N=N-, *cis* and *trans*)，1342 ν(NO_2)，1284 ν(C-O), 1171, 1106, 849, 764. ^{1}H NMR δ (500MHz; $CDCl_3$): 11.48 (s, OH), 10.08 (s, CHO), 8.41 (d, 2H, *J*=9.00 Hz), 8.31 (s, 1H), 8.24 (d, 1H, *J*=8.95 Hz), 8.04 (d, 2H, *J*=8.97 Hz), 7.19 (d, 1H, *J*=8.94 Hz). *Anal*. Calc. for $C_{13}H_9O_4N_3$: C, 57.56; H, 3.32; N, 15.50. Found: C, 57.28; H, 3.67; N, 15.18%.

2.3.3 Synthesis of azo-containing Schiff bases(6a-e)

Schiff bases (6a-e) were prepared by addition of (4a-e) compounds (1 mmol) in methanol (10 mL) to a methanolic solution of Hcden (1 mmol). The mixtures were stirred for about 30 min and allowed to react at room temperature for about 24 h. The colour powders were recrystallized from chloroform/methanol (1:1) v/v solution.

2.3.3.1. Methyl 2-(2-((E)-2-hydroxy-5-((E)-phenyldiazenyl)benzyledeneamino)ethyleamino)cyclo-pent-1-ene-carbodithioate (6a)

Yield: 93%. m.p: 145 ˚C. IR (KBr, cm^{-1}): 1628 ν(C=N), 1587 ν(N=N), 1479 (Phenol ring), 1272 ν(C-O), 1109, 841, 603. ^{1}H NMR δ (500 MHz; $CDCl_3$): 13.42 (s, 1H, OH), 12.40 (s, 1H, NH), 8.51 (s, 1H, CH=N), 7-7.9 (Phenol ring), 3.85 (t, 2H, *J*=8.23 Hz), 3.73 (t, 2H, *J*=8.18 Hz), 2.73 (m, 6H), 2.53 (s, -SCH$_3$). *Anal*. Calc. for $C_{22}H_{24}N_4OS_2$: C, 62.23; H, 5.69; N, 13.19. Found: C, 62.34; H, 5.37; N, 13.29 %.

2.3.3.2. Methyl 2-(2-((E)-2-hydroxy-5-((E)-para-tolyldiazenyl)benzyledeneamino)ethyleamino)cyclopent-1-ene-carbodithioate (6b)

Yield: 70%. m.p: 170 ˚C. IR (KBr, cm^{-1}): 1630 ν(C=N), 1584 ν(N=N), 1486 (Phenol ring), 1270 ν(C-O), 1107, 844, 601. ^{1}H NMR δ (500 MHz; CDCl$_3$): 13.39 (s, 1H, OH), 12.40 (s, 1H, NH), 8.51 (s, 1H, CH=N), 7-7.9 (Phenol ring), 3.87 (t, 2H, *J*=8.19 Hz), 3.76 (t, 2H, *J*=8.16 Hz), 2.73 (m, 6H), 2.56 (s, -SCH$_3$), 2.43 (s, -CH$_3$). *Anal*. Calc. for $C_{23}H_{26}N_4OS_2$: C, 62.97; H, 5.97; N, 12.77. Found: C, 62.69; H, 5.81; N, 12.67 %.

2.3.3.2. Methyl 2-(2-((E)-5-((E)-(4-ethylphenyl)diazenyl)-2-hydroxybenzylideneamino)ethylamino)cyclopent-1-enecarbodithioate (6c)

Yield: 74%. m.p: 150 ˚C. IR (KBr, cm^{-1}): 1633 ν(C=N), 1582 ν(N=N), 1485 (Phenol ring), 1285 ν(C-O), 1106, 845, 602. ^{1}H NMR δ (500 MHz; CDCl$_3$): 13.46 (s, 1H, OH), 12.35 (s, 1H, NH), 8.49 (s, 1H, CH=N), 7-7.9 (Phenol ring), 3.86 (t, 2H, *J*=8.20 Hz), 3.75 (t, 2H, *J*=8.31 Hz), 2.73 (m, 6H), 2.52 (s, -SCH$_3$), 2.47 (q, -CH$_2$, *J*=7.64 Hz), 1.53 (t, -CH$_3$, *J*=7.79 Hz). *Anal*. Calc. for $C_{24}H_{28}N_4OS_2$: C, 63.67; H, 6.23; N, 12.38. Found: C, 63.70; H, 6.20; N, 12.48 %.

2.3.3.4. Methyl 2-(2-((E)-5-((E)-(4-chlorophenyl)diazenyl)-2-hydroxybenzylideneamino)ethylamino)cyclopent-1-enecarbodithioate (6d)

Yield: 68%. m.p: 187 ˚C. IR (KBr, cm^{-1}): 1633 ν(C=N), 1581 ν(N=N), 1479 (Phenol ring), 1283 ν(C-O), 1107, 842, 601. ^{1}H NMR δ (500 MHz; CDCl$_3$): 13.46 (s, 1H, OH), 12.35 (s, 1H, NH), 8.49 (s, 1H, CH=N), 7-7.9 (Phenol ring), 3.86 (t, 2H, *J*=6.82 Hz), 3.75 (t, 2H, *J*=7.50 Hz), 2.73 (m, 6H), 2.52 (s, -SCH_3). *Anal*. Calc. for $C_{22}H_{23}N_4OS_2Cl$: C, 57.43; H, 5.03; N, 12.18. Found: C, 57.30; H, 5.21; N, 12.07 %.

2.3.3.5. Methyl 2-(2-((E)-5-((E)-(4-nitrophenyl)diazenyl)-2-hydroxybenzylideneamino)ethylamino)cyclopent-1-enecarbodithioate (6e)

Yield: 75%. m.p: 219 ˚C. IR (KBr, cm^{-1}): 1633 *v*(C=N), 1584 *v*(N=N), 1484 (Phenol ring), 1336 *v*(NO_2), 1261 *v*(C-O), 1102, 852, 603. ^{1}H NMR δ (500 MHz; $CDCl_3$): 13.47 (s, 1H, OH), 12.45 (s, 1H, NH), 8.56 (s, 1H, CH=N), 7-7.9 (Phenol ring), 3.84 (t, 2H, *J*=7.19 Hz), 3.72 (t, 2H, *J*=7.83 Hz), 2.73 (m, 6H), 2.53 (s, -SCH_3). *Anal*. Calc. for $C_{22}H_{23}N_5O_3S_2$: C, 52.21; H, 4.58; N, 14.93. Found: C, 52.34; H, 4.26; N, 14.28 %.

2.3.4. General procedure for the synthesis of the complexes(7a-e)

To a solution of the appropriate (6a-e) ligand (0.1 mmol) in choloform/methanol (2:1 v/v) (15 mL), were added a solution of nickel(II) chloride hexahydrate (0.1 mmol) in methanol (.15 mL) The solutions were stirred for 15 min and then allowed to stand at room temperature for 24 h. The resulting powders were filtered and recrystallized from chloroform/methanol (1:1 v/v) solution.

2.3.4.1. (Methyl 2-(2-((E)-2-hydroxy-5-((E)-phenyldiazenyl)benzyledeneamino)ethyleamino)cyclopent-1-ene-carbodithioato)nickel(II) complex, (7a).

Yield: 84%. m.p: 280 ºC. IR (KBr, cm^{-1}): 1626 *v*(C=N), 1469 *v*(Phenol ring), 1283 *v*(C-O), 496-564 *v*(Ni-N), 415-435 *v*(Ni-O). ^{1}H NMR δ (500 MHz; $CDCl_3$): 7.71 (s, 1H, CH=N), 7-7.9 (Phenol ring), 3.72 (t, 2H, *J*=7.64 Hz), 3.63 (t, 2H, *J*=8.31 Hz), 2.83 (m, 6H), 2.63 (s, SCH_3). *Anal*. Calc. for $C_{22}H_{22}N_4OS_2Ni$: C, 54.91; H, 4.57; N, 11.65. Found: C, 55.32; H, 4.32; N, 11.25%.

2.3.4.2. (Methyl 2-(2-((E)-2-hydroxy-5-((E)-para-tolyldiazenyl)benzyledenamino)ethyleamino)cyclopent-1-ene-carbodithioato)nickel(II) complex, (7b).

Yield: 49%. m.p: 274 ºC. IR (KBr, cm^{-1}): 1616 ν(C=N), 1467 ν(Phenol ring), 1283 ν(C-O), 496-564 ν(Ni-N), 415-435 ν(Ni-O). ^{1}H NMR δ (500 MHz; CDCl$_3$): 7.76 (s, 1H, CH=N), 7-7.9 (Phenol ring), 3.72 (t, 2H, *J*=8.92 Hz), 3.66 (t, 2H, *J*=8.58 Hz), 2.51 (m, 6H), 2.56 (s, -SCH$_3$), 2.43 (s, -CH$_3$. *Anal.* Calc. for $C_{23}H_{24}N_4OS_2Ni$: C, 55.79; H, 4.85; N, 11.31. Found: C, 55.89; H, 4.51; N, 11.75%.

2.3.4.3. (Methyl 2-(2-((E)-5-((E)-(4-ethylphenyl)diazenyl)-2-hydroxybenzylideneamino)ethylamino)cyclopent-1-enecarbodithioato)nickel(II) complex, (7c).

Yield: 76%. m.p: 285 ºC. IR (KBr, cm^{-1}): 1630 ν(C=N), 1460 ν(Phenol ring), 1285 ν(C-O), 496-564 ν(Ni-N), 415-435 ν(Ni-O). ^{1}H NMR δ (500 MHz; CDCl$_3$): 7.87 (s, 1H, CH=N), 7-7.9 (Phenol ring), 3.81 (t, 2H, *J*=7.99 Hz), 3.72 (t, 2H, *J*=8.09 Hz), 2.69 (m, 6H), 2.62 (s, -SCH$_3$), 2.47 (q, -CH$_2$, *J*=8.66 Hz), 1.55 (t, -CH$_3$, *J*=8.51 Hz). *Anal.* Calc. for $C_{24}H_{26}N_4OS_2Ni$: C, 56.61; H, 5.11; N, 11.00. Found: C, 56.82; H, 5.24; N, 11.25%.

2.3.4.4 (Methyl 2-(2-((E)-5-((E)-4-chlorophenyl)diazenyl)-2-hydroxybenzylidenamino)ethylamino)ethyleamino)cyclopent-1-ene-carbodithioato)nickel(II) *complex. (7d).*

Yield: 75%. m.p: 293 ºC. IR (KBr, cm^{-1}): 1628 ν(C=N), 1466 ν(Phenol ring), 1284 ν(C-O), 496-564 ν(Ni-N), 438 ν(Ni-O). ^{1}H NMR δ (500 MHz; CDCl$_3$): 7.59 (s, 1H, CH=N), 7-7.9 (Phenol ring), 3.92 (t, 2H, *J*=7.31 Hz), 3.81 (t, 2H, *J*=7.94 Hz), 2.64 (m, 6H), 2.64 (s, -SCH$_3$). *Anal.* Calc. for $C_{22}H_{21}N_4OS_2ClNi$: C, 57.83; H, 4.60; N, 12.27. Found: C, 58.11; H, 4.35; N, 12.43%.

2.3.4.5. (Methyl 2-(2-((E)-5-((E)-(4-nitrophenyl)diazenyl)-2-hydroxybenzylideneamino)ethylamino)cyclopent-1-enecarbodithioat)nickel(II) complex, (7e).

Yield: 88%. m.p: 291 ºC. IR (KBr, cm^{-1}): 1626 ν(C=N), 1469 ν(Phenol ring), 1333 $\nu(NO_2)$, 1283 ν(C-O), 496-564 ν(Ni-N), 437 ν(Ni-O). ^1H NMR δ (500 MHz; $CDCl_3$): 7.54 (s, 1H, CH=N), 7-7.9 (Phenol ring), 3.87 (t, 2H, *J*=7.69 Hz), 3.70 (t, 2H, *J*=8.09 Hz), 2.65 (m, 6H), 2.61 (s, -SCH_3). *Anal.* Calc. for $C_{22}H_{21}N_5O_3S_2Ni$: C, 50.22; H, 3.99; N, 13.31. Found: C, 50.47; H, 4.21; N, 13.11%.

2.4. X-ray Crystallography

The X-ray diffraction studies were obtained on a STOE IPDS IIT diffractometer with graphite monochromated Mo-Kα radiation. A dark red plate crystal (complex 7b) with a dimension of 0.27 × 0.11 × 0.05 mm and A dark red plate crystal (complex 7d) with a dimension of 0.42 × 0.08 × 0.03 mm were mounted on a glass fiber and used for data collection. Structures determination were obtained by least-squares refinement of diffraction data from 3047 unique reflections for complex 7b and 4073 unique reflections for complex 7d. Data were collected at a temperature of 291(2) K to a maximum 2θ value of 51.00° and in a series of ω scans in 1° oscillations and integrated using the Stoe X-AREA [21] software package. The numerical absorption coefficient, μ, for Mo-Kα radiation are 1.076 mm^{-1} (complex 7b) and 1.204 mm^{-1} (complex 7d). A numerical absorption correction was applied using X-RED [22] and X-SHAPE [23] software's. The data were corrected for Lorentz and Polarizing effects. The structure was solved by direct methods [24] and subsequent difference Fourier map and then refined on F^2 by a full-matrix procedure using anisotropic displacement parameters. All of hydrogen atoms were positioned geometrically in ideal positions and then after refined isotropically. Atomic factors are taken from International Tables for X-ray Crystallography [25]. All refinements were performed using the X-STEP32 crystallographic software package [26]. A summary of the crystal data, experimental details and refinement results for complexes 7b and 7d are given in Table 1.

3. Results and discussion

Methyl-2-{*N*-(2'-aminoethane)}-amino-1-cyclopentenedithiocarbooxylate is a convenient starting material for the synthesis of asymmetric ligands containing NNOS coordination spheres. Schiff base condensation of the methyl-dithiocarboxylate ester with azo-substituted aldehydes yields the desired ligand in a facile manner and with high yields.

The complexes have a sulfur donor atom that can act as a π acceptor, an oxygen donor atom as a π donor and the coordination around the nickel ion allows for π electronic delocalization, as depicted in Scheme 2. The compounds were characterized by elemental analysis, IR, UV-Vis and NMR. The 7b and 7d complexes were characterized further by X-ray crystallography in order to determine their molecular and crystal structures to evaluate the degree of tetrahedral distortion in square planar geometry. The structures and the electrochemical results are compared with those obtained for the corresponding symmetric N_2O_2 and N_2S_2 formulations in order to correct possible dietary deficiencies. Also, it has been implicated as a Ni(II) complexes.

3.1. Crystal structures of 7b and 7d complexes

Selected bond distances and bond angles for 7b and 7d complexes are collected in Table 2. The ORTEP representation of the structures of 7b and 7d complexes with atomic numbering Scheme and their unit cell diagrams are presented in Figs. 1-4, respectively. The bond distances and bond angles are within the expected range for nickel(II) complexes with Schiff base ligands. 7b and 7d complexes are crystalliz in the space group P_{bca} with eight molecules per unit cell. The nickel(II) ions are coordinate to a sulfur atom the methyl dithiocarboxylate moiety, phenolic oxygen atom and two nitrogen atoms from the imine moiety of the ligands,. In these complexes, the Ni center and its four neighbors (O(1), N(1), N(2) and S(1)) are nearly coplanar. The deviations from the mean coordination plane are at the best 0.002 Å for the donors and equal to 0.005(4) Å for the metal ion. Tetrahedral distortion relative to the square-planar geometry are 4.05(9)˚ in 7b complex and 3.94(3)˚ in 7d complex. In these complexes, the geometry around the coordination centre are more planar than that in the homologous N_2OS complex with the dihedral angle of 5.28˚ and 11.52˚ (for the two crystallographically independent molecules) [14], homologous N_2S_2 complex with the dihedral angle of about 20˚[27-28], and analogous N_2O_2 complex with dihedral angle of about 7˚ [29].

3.2. IR Spectra

In the IR spectrum of Ni(II) complexes a strong band around 1600-1630 cm^{-1} is assigned to the ν(C=N) band [30], and the bands in the range 1230-1296 cm^{-1} can be related to the phenolic (C-O) group vibrations [31-32]. The ring skeletal vibrations (C=S) were in the region of 1440-1496 cm^{-1} [33]. The bands in the range 700-800 cm^{-1} belong to (C-S) and the bands between 1103 and 1190 cm^{-1} are due to the coupling of ν(C-S)+ν(C-N) [34-35]. These data compared with those of the ligands, indicate that the ν(C=N), ν(C-O), ν(C=C), ν(C-S), and ν(C-S)+ν(C-N) bands are shifted to lower energy. These results show that Ni(II) ions are coordinated through the nitrogen atoms of the amine group, oxygen atom of the phenolic group and sulfur of the (C-S) group for Ni(II) complexes[30-35]. These data are in accord to the proposed structures.

3.3. ^{1}H NMR Spectra

The ^{1}H NMR resonance of azomethine proton (CH=N) in ligands (8.49-8.56 ppm), are shifted to higher field in the Ni(II) complexes, confirming the coordination of the metal ion to that group.

In the ^{1}H NMR spectra of the free ligands, OH, NH, or SH exhibit single resonance at δ= 13.39-13.46 ppm, and δ= 12.35-12.45 ppm, respectively, which disappear in the nickel(II) complexes, indicating that the OH and NH or SH groups have been deprotonated and bonded to the Ni(II) ions[36].

3.4. The electronic spectra

The UV-Vis absorption spectra of the ligands (6a-e) and related nickel complexes (7a-e) in DMF solution at 298 K are shown in Fig. 5 and Fig. 6, respectively. The electronic spectra of the ligands are similar to each other. The UV-Vis absorption spectra of the ligands show three bands. The first band appearing at *ca* 260 nm is attributed to the π-π* transition of the benzene rings, the second band appearing around 300-424 nm arose from a transition involving electron migration along the entire conjugate system of the ligands. The entire conjugate system includes both the aryl rings and azo groups. The broadness of the intramolecular CT band is quite common for azo or azomethine dyes having a hydroxyl group in opposition to the N=N or C=N bond on the aromatic ring [37]. The third band observed in the range 430–500 nm can be assigned to an n-π* electronic transition of azo-aromatic chromophore [37,38].

The UV-Vis absorption spectra of the complexes were compared to the spectra of the ligands. In all spectra of the metal complexes, the n-π* absorption bands of the free ligand has shifted to lower frequencies upon the coordination of ligand with metal ions.

3.5. Cyclic voltammetry studies

Because the Ni-complexes(7a-e) are insoluble in water, the bulk-modified carbon paste electrode (Ni-CPE) becomes the optimal choice to investigate their redox properties of it. Cyclic voltammograms of the 7b complex carbon paste electrode (1-CPE) and 7d complex carbon paste electrode (2-CPE) were carried out at room temperature.

The modified 1-CPE and 2- CPE were fabricated as following: 10 mg of each 7b and 7d complex, 50 mg graphite powder and proper amount of anhydrous ethanol were mixed to form a uniform mixture, which was left to evaporate the solvent at room temperature in the air. Then 20 ml paraffin oil was added into the graphite-Ni complex mixture.

The 1-CPE and 2-CPE were packed into a piston glass tube electrode (3 mm in diameter). Prior to the measurements the 1-CPE and 2-CPE were smoothed out on a piece of transparent paper to get a fresh surface. All the potentials reported in this work were versus Ag|AgCl electrode. Unmodified carbon paste electrode was prepared by adding 20 ml paraffin oil to 50 mg graphite powder. A cyclic voltammograms of modified 1-CPE, 2-CPE were similar, therefore just cyclic voltammogram of 1- CPE was shown.

A cyclic voltammograms of modified 1-CPE and unmodified carbon paste electrodes at scan rate of 50mVs^{-1} are shown in Fig.7.

As can be seen, there is no redox peak at the surface of bare CPE in the potential range of -0.5 to 0.9V. A pair of well-defined redox peaks with formal potential of 0.18 V versus Ag|AgCl electrode was observed when Ni-CPE was used. This anodic and cathodic peaks are due to redox reaction of the Ni(III)/Ni(II) couple at the electrode surface. The cyclic voltammograms of Ni-CPE electrode in 0.1 M NaOH solution at different scan rates are shown in Fig.8. The potential was cycled between -0.4 and 0.6 mV in 0.1 M NaOH aqueous solution. The peaks current of the voltammograms are linearly proportional to the scan rate (ν) up to 300 mV s^{-1} for the redox couples (Fig. 8B). According to the following equation this results confirms a surface type reactions [39]:

$$I_p = n^2F^2\nu AC/4R\Gamma \qquad (1)$$

4. Conclusions

In the present work five novel, azo-containing Schiff bases were obtained by condensation reaction of methyl-2-{*N*-(2'-aminoethane)}-amino-1-cyclopentenedithiocarboxylate (Hcden) with azo-containing aldehydes that are favorable to formation of the complexes with Ni(II) ion. IR, ^{1}H NMR and UV-Vis spectra and cyclic voltammogram of the nickel(II) complexes were recorded and compared with together. The crystal structure analysis of nickel(II) complexes by using X-ray crystallography confirmed the complexes are slightly distorted square-planar structures based on experimental studies.

5. Supplementary data

CCDC 836471 and 836470 are contain the supplementary crystallographic data for 7b and 7d complexes respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Table 1
Crystal and structure data for the nickel complexes

	7b	7d
Formula	$C_{23} H_{24} N_4 Ni O S_2$	$C_{22} H_{21} Cl N_4 Ni O S_2$
Formula weight	495.29	515.71
Temperature /K	291(2)	291(2)
Wavelength λ /Å	0.71073	0.71073
Crystal system	*orthorhombic*	*orthorhombic*
Space Group	*Pbca*	*Pbca*
Crystal size /mm^3	0.27 x 0.11 x 0.05	0.42 x 0.08 x 0.03
a /Å	22.380(5)	22.674(3)
b /Å	7.8917(16)	7.7860(7)
c /Å	25.366(5)	25.170(2)
Volume / Å^3	4480.0(16)	4443.5(8)
Z	8	8
Density (calc.) /g cm^{-1}	1.469	1.542
θ ranges for data collection	1.82-25.25°.	1.80-25.50°..
F(000)	2064	2128
Absorption coefficient	1.076	1.204
Index ranges	$-26 \leq h \leq 24$	$-27 \leq h \leq 26$
	$-8 \leq k \leq 8$	$-9 \leq k \leq 8$
	$-30 \leq l \leq 26$	$-26 \leq l \leq 30$
Data collected	7091	11925
Unique data (R_{int})	3047, (0.0863)	4073, (0.0878)
Parameters, restrains	282	281
Final R_1, wR_2^a (Obs. data)	0.0429, 0.0453	0.0509, 0.0887
Final R_1, wR_2^a (All data)	0.1531, 0.0590	0.1099, 0.1033
Goodness of fit on F^2 (S)	0.717	0.878
Largest diff peak and hole /e.Å^{-3}	0.182, -0.177	0.311, -0.526

Table 2
Selected bond distance (Å) and bond angles (˚) for 7b and 7d complexes

	7b	7d
Ni1-N1	1.858(4)	1.870(3)
Ni1-N2	1.867(4)	1.868(4)
Ni1-O1	1.879(3)	1.882(3)
Ni1-S1	2.1524(17)	2.1505(12)
N1-Ni1-S1	173.12(17)	173.64(13)
N2-Ni1-O1	176.3(2)	176.94(15)
N1-Ni1-O1	93.16(19)	93.26(14)
O1-Ni1-S1	82.22(14)	82.30(9)
S1-Ni1-N2	97.9(2)	97.82(13)
N2-Ni1-N1	87.0(2)	86.86(17)

Figure Captions:

Fig. 1. Graphical representations of 7b complex with the adopted numbering scheme.

Fig. 2. Graphical representations of 7d complex with the adopted numbering scheme

Fig. 3. Stereoview of the unit cell of 7b complex.

Fig. 4. Stereoview of the unit cell of 7d complex.

Fig. 5. UV-Vis absorption spectra of the ligands (6a-e)

Fig. 6. UV-Vis absorption spectra of the complexes (7a-e)

Fig.7. Cyclic voltammetric responses of unmodified carbon paste elctrode (a) and 1-CPE (b) at scan rate $50 mVs^{-1}$.

Fig.8. Cyclic voltammograms of Ni-CPE at various scan rates: 10, 25,50,75,100,150, 200,300,400,500,600 and 700 mVs^{-1} , respectively. (B) the variation of anodic and cathodic peak currents vs. potential scan rate.

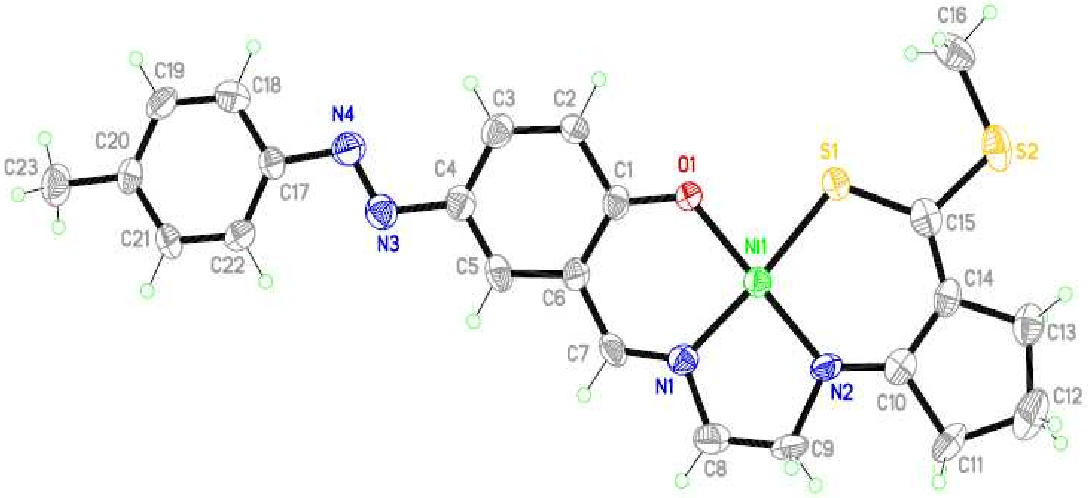


Figure 1

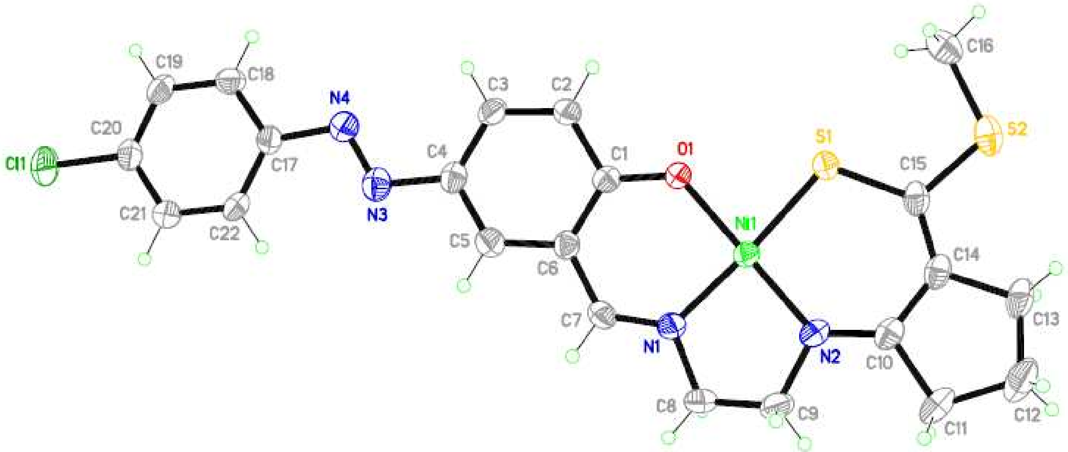


Figure 2

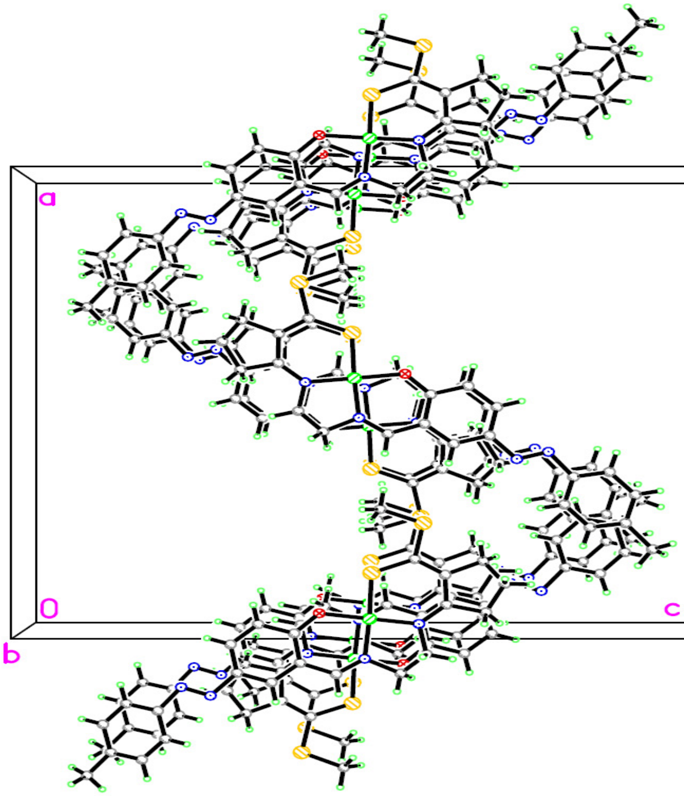
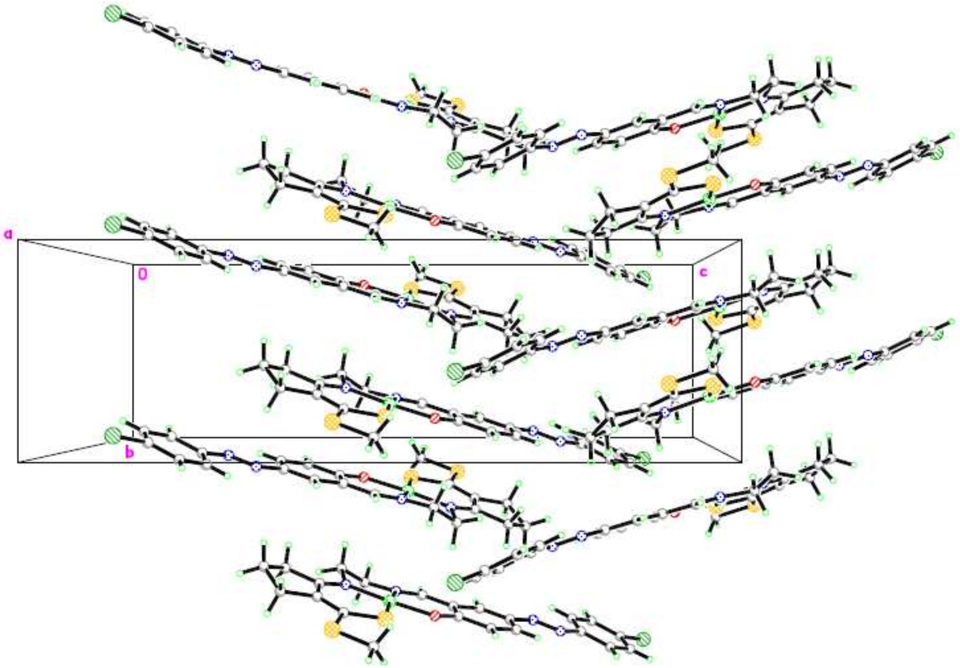


Figure 3



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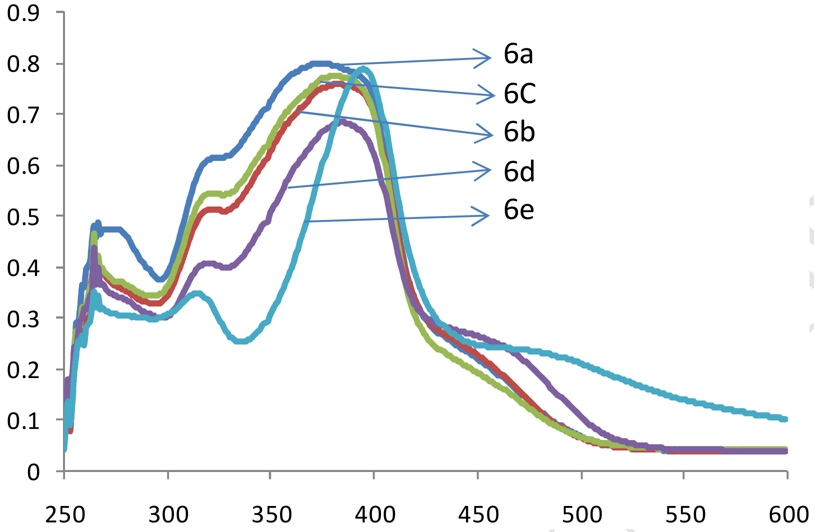

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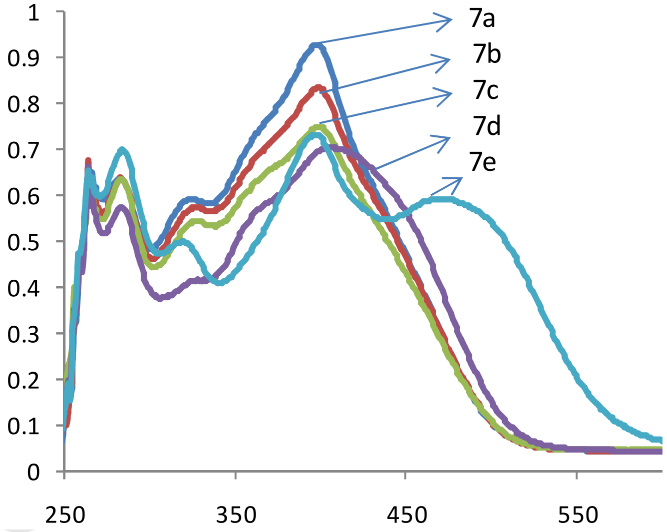

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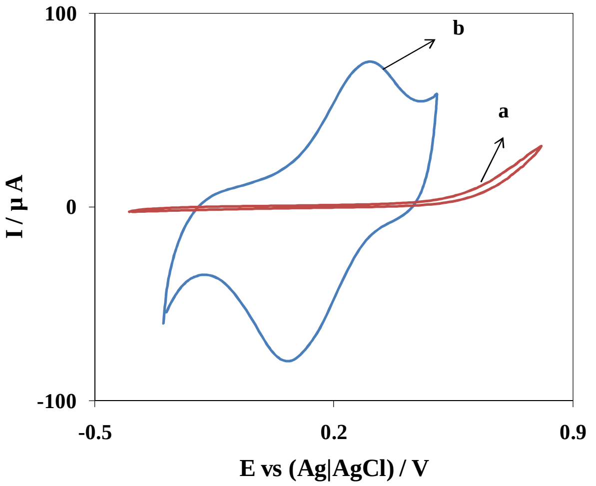


Figure 7

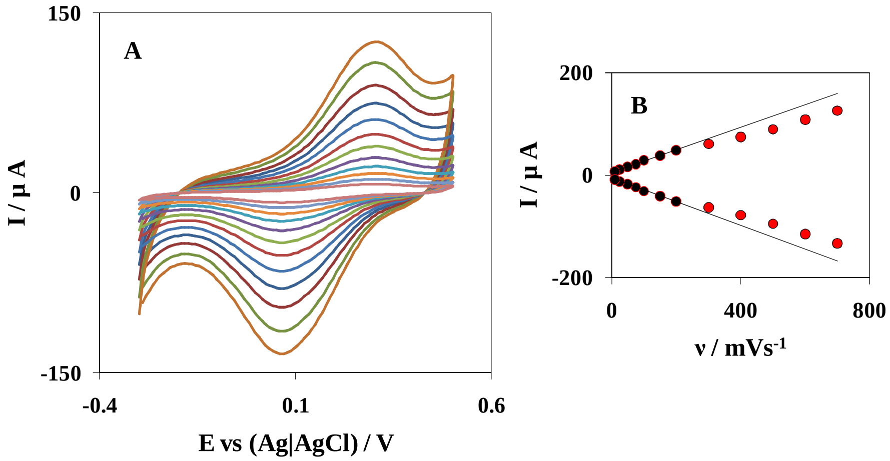
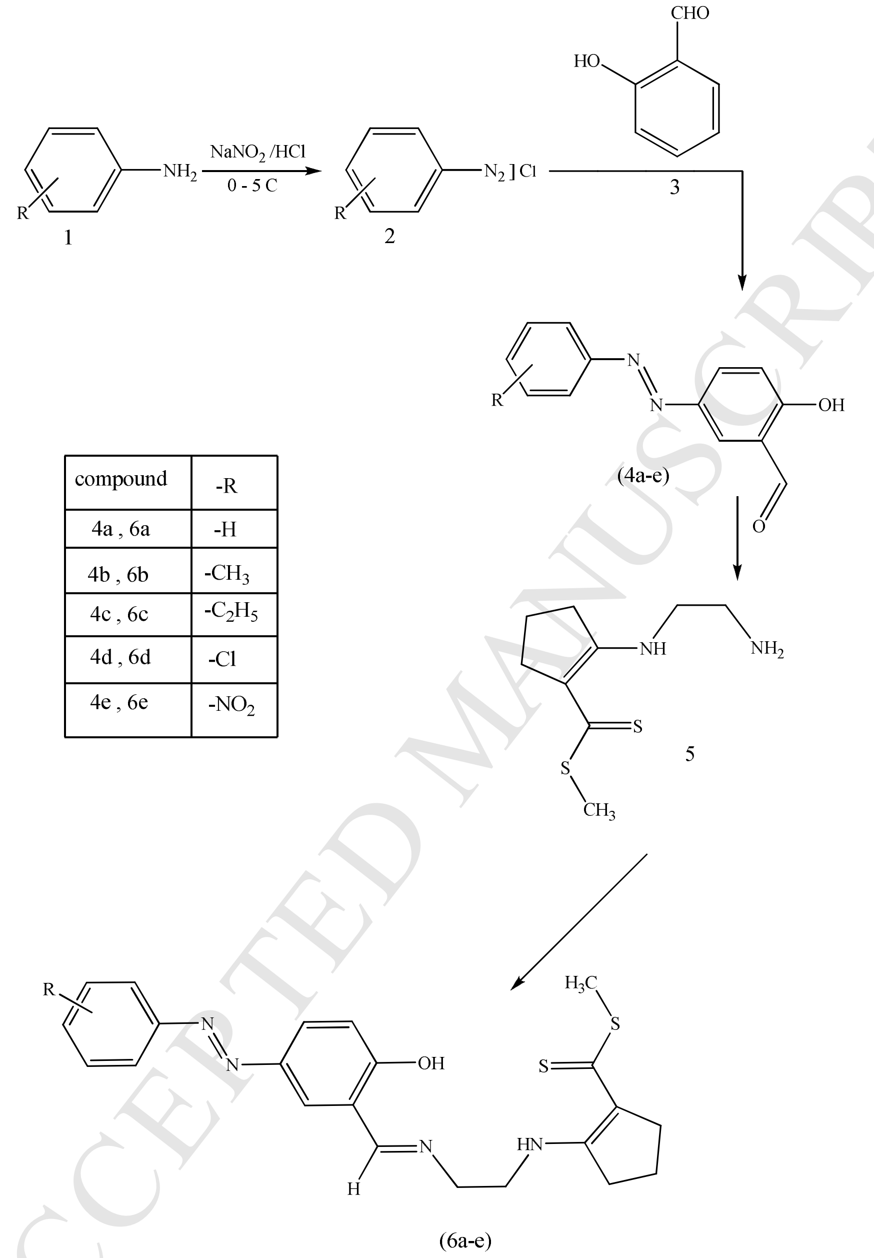
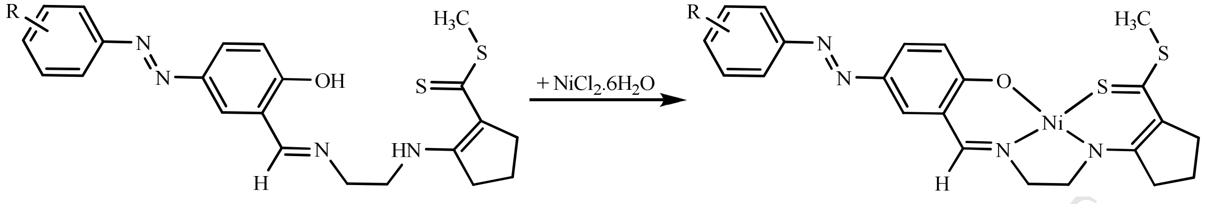


Figure 8



compound	-R
4a , 6a	-H
4b , 6b	$-CH_3$
4c , 6c	$-C_2H_5$
4d , 6d	-Cl
4e , 6e	$-NO_2$

Scheme 1. General syntheses of azo-containing Schiff bases (6a-e)



(6a-e)

(7a-e)

Scheme 2. Syntheses of (7a-e) complexes.