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Bis[4-(methylthio)phenylmethyleneaminophenyl] disulfide, 2-[4-(methylthio)phenyl]-2,3-dihydro-1,3-benzothiazole, and its nickel(II) and cobalt(II) complexes: Synthesis, adsorption on gold surface and electrochemical characterization

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2-[4-(Methylthio)phenyl]-2,3-dihydro-1,3-benzothiazole (**1**) and bis[4-(methylthio)phenylmethylene-aminophenyl] disulfide (**2**) were synthesized. Novel coordination compounds of Ni(II) and Co(II) with 2-[4-(methylthio)phenylmethyleneamino]thiophenol, M(**1**)$_2$ (M = Co (**3**); M = Ni (**4**)), were prepared by reacting **1** with M(OAc)$_2 \cdot$ 6H$_2$O or MCl$_2 \cdot$ 6H$_2$O in EtOH solution. The structure of **2** was proved by X-ray crystallography. Electrochemical behavior of **1–4** in CH$_3$CN solution and at the surface of a gold electrode was studied by cyclic voltammetry. The modification of the electrode by ligand **1** and its complexes with Ni^{2+} and Co^{2+} is described in detail. Two procedures were used to obtain a self-assembled monolayer of a metal complex on the gold surface: the adsorption of prepared coordination compound **3** or **4** on the electrode and the initial modification of the electrode with ligand **1** followed by the formation of a coordination complex between the ligand adsorbed on the electrode and a metal salt occurring in solution. On the basis of the electrochemical data, it was found that the structure of complexes formed on the surface differs from that of the complexes produced in solution.

Keywords: 2,3-Dihydro-1,3-benzothiazole; Iminothiophenols; Ni(II) complexes; Co(II) complexes; Electrochemistry; Adsorption

1. Introduction

The chemistry of monolayer films on electrode surfaces has been a focus of considerable interest for decades. Modification of gold surfaces with organosulfur compounds (thiols, disulfides, sulfides, etc.) has attracted much attention as a useful method for fabricating monolayers [1–4]. This method offers self-assembled monolayers (SAMs) of superior stability due to covalent S–Au bonding.

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Self-assembled monolayers containing redox-active functional groups and groups capable of coordinating to transition metal ions are interesting for many reasons. Redox-responsive ligands are known for their ability to electrochemically probe the binding of a given substrate and have been used in sensing applications [5]. Their molecular architecture associates an electroactive subunit to a ligating part, and the binding event is thus accompanied by a change in redox potential [6]. The development of practical sensors for the detection and quantification of metal ions in environmental samples is the subject of considerable research. The majority of this research involves the synthesis and testing of chelating ligands capable of complexing with specific metal ions. There is a growing interest in analytical applications of this method using modified electrodes [7–9]. Such electrodes have been used as sensors: for example, electrode surfaces modified with metal hexacyanoferrates show a good molecular-recognition ability for alkali metal ions [10–12].

Electroactive SAMs of metal complexes on a gold electrode can possess an electrocatalytic activity. For example, a self-assembled monolayer of the binuclear macrocyclic nickel complex dinickel(II) (2,2'-bis(1,3,5,8,12-pentaazacyclotetradec-3-yl)-diethyl disulfide) perchlorate [13] shows an excellent electrocatalytic activity toward the oxidation of NADH in aqueous $NaNO_3$ solution [14].

The objective of this work was to prepare 2-[4-(methylthio)phenyl]-2,3-dihydro-1,3-benzothiazole (**1**) and bis[4-(methylthio)phenylmethyleneaminophenyl] disulfide (**2**), to study the complexation of **1** with Ni(II) and Co(II) salts, and to examine the electrochemical behavior of these ligands and complexes in CH_3CN solution and on a gold electrode surface.

2. Results and discussion

2.1 *Synthesis of ligands and complexes*

Compounds **1** and **2** were prepared from 4-methylthiobenzaldehyde and *ortho-* aminothiophenol or 2,2'-diaminodiphenyl disulfide, scheme 1.
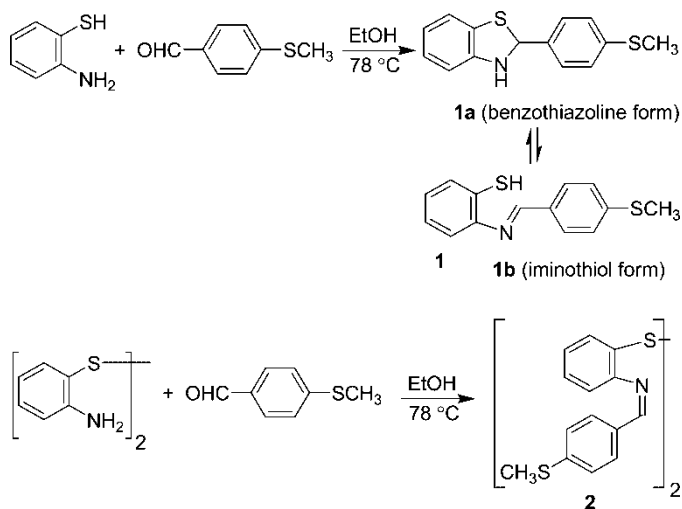
SCHEME 1

According to ^{1}H NMR data, ligand **1** in CHCl$_3$ exists in the cyclic benzothiazoline form (**1a**). However, a solution of benzothiazoline **1a** contains a certain amount of tautomeric iminothiol **1b**, as shown [15, 16].
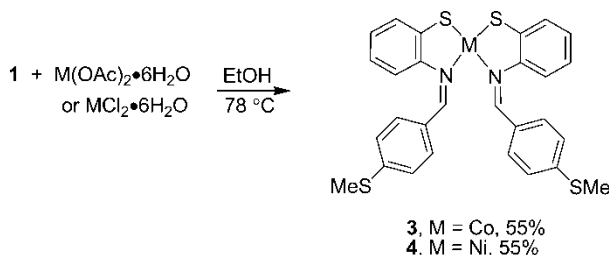
To prepare coordination compounds **3** and **4**, a mixture of **1** with M(OAc)$_2$ · 6H$_2$O or MCl$_2$ · 6H$_2$O (M = Co, Ni) taken in the 1:2 ratio was heated in ethanol; under these conditions, Lewis acids (metal salts) mediate the quantitative cycle opening of the benzothiazoline form of **1** [15,17] to yield iminothiolate complexes **3** and **4**, scheme 2.

3, M = Co, 55%
4, M = Ni, 55%

SCHEME 2

Compounds **1**–**4** were characterized by IR and electronic absorption spectra. The IR spectra of the complexes **3**, **4** exhibit a shift of the C=N-absorption band to greater wavenumbers (1620 cm^{-1}) relative to parent compound **1** (1585 cm^{-1}) and disulfide **2** (1595 cm^{-1}). The electronic absorption spectrum of nickel complex **4** displays two bands in the visible region at 452 nm and 823 nm with $\varepsilon = 2300$ mol l^{-1}cm^{-1} and 570 mol l^{-1}cm^{-1}, respectively. Such a pattern of the spectrum and values of the molar absorption coefficient are typical of coordination compounds with the square planar ligand environment of the central ion Ni^{2+} [18, 19]. It is likely that the central atom in complexes **3** and **4** is coordinated to the nitrogen and sulfur atoms of both ligand molecules.

2.2   *Molecular structure of 2*

The structure of disulfide **2** was established with the use of X-ray analysis.[†] Crystals suitable for X-ray crystallographic study were prepared by slow evaporation of an EtOH solution. The crystallographic data, experimental details, and structure refinements are presented in table 1, while bond lengths and bond angles are given in table 2. The molecular structure of **2** is shown in figure 1. The X-ray data confirm the (*E*)-arrangement of substituents at both C=N bonds of the imine moiety. As in the case of most organic disulfides, the C−S−S−C dihedral angle is $\sim 90°$(88.2(2)°) in the given case). Two benzene rings of the disulfide moiety are at an angle of 90° to one another. Each −C$_6$H$_4$ −N=CH−C$_6$H$_4$ fragment is nonplanar; the benzene rings are not coplanar is these fragments, being at an angle of about 30°.

2.3   *Adsorption of 1–4 on gold surface and their electrochemical behavior in solution and self-assembled monolayers*

We studied the feasibility of adsorption of ligand **1** and complexes **3** and **4** on the surface of a gold electrode. To modify the gold surface with the coordination compounds, two methods,


[†]"CCDC 601364" contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: 44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Table 1. Crystallographic data, experimental details and structure refinement of compound **2**.

Empirical formula	$C_{28}H_{24}N_2S_2$
Molecular mass	516.73
Color/habit	Brown prisms
Crystal dimensions, mm	$0.31 \times 0.23 \times 0.15$
Crystal system	Monoclinic
Space group	P 21/n
Unit cell parameters	$a = 10.163(2)$Å $\alpha = 90°$
	$b = 22.768(5)$Å $\beta = 90.67(3)°$
	$c = 11.365(2)$Å $\gamma = 90°$
V, Å^3	2629.6(9)
Z	4
Calculated density, g cm^{-3}	1.305
Linear absorption coefficient, mm^{-1}	0.381
F(000)	1080
θ range, deg	1.79–27.00°
Intervals of reflection indexes	$0 \leq h \leq 12, -3 \leq k \leq 29, -14 \leq l \leq 14$
No. of reflections observed	6102
No. of independent reflections	5721 [$R_{int} = 0.0489$]
No. of reflections with $I > 2\sigma(I)$	1706
No. of refined parameters	259
Goodness of fit on F^2	1.087
R factors on $I > 2\sigma(I)$	$R1 = 0.0721, wR2 = 0.1230$
R factors (all data)	$R1 = 0.2757, wR2 = 0.1615$
Residual electron density(min/max)/e · E^{-3}	$-0.220/0.334$

Table 2. Some interatomic distances (d) and bond and torsion angles (ω) for compound **2** (atom numbering is the same as that in figure 1).

Bond	d/Å	Angle	ω/deg
C(5)–C(8)	1.445(7)	C(8)–N(1)–C(9)	124.4(6)
N(1)–C(8)	1.246(7)	C(10)–S(2)–S(3)	105.44(18)
N(1)–C(9)	1.380(5)	C(15)–S(2)–S(3)	104.45(16)
S(2)–C(10)	1.759(3)	N(1)–C(8)–C(5)	125.9(6)
S(2)–S(3)	2.029(2)	C(6)–C(5)–C(8)	120.6(4)
S(1)–C(2)	1.744(4)	C(10)–C(9)–N(1)	116.0(4)
S(1)–C(1)	1.745(7)	C(10)–S(2)–S(3)–C(15)	88.2(2)
		C(9)–N(1)–C(8)–C(5)	176.5(5)
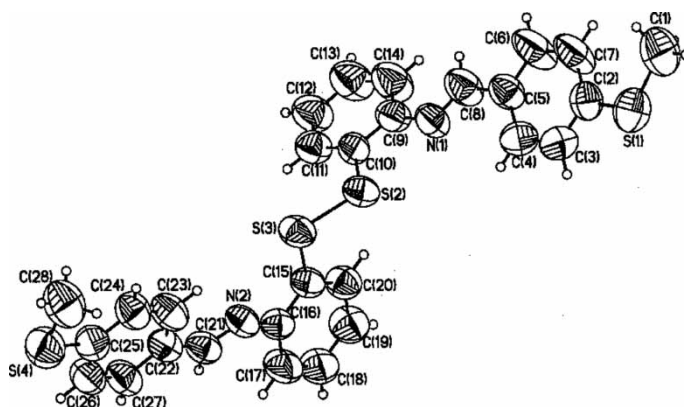
Figure 1. Molecular structure of compound 2. The atomic-displacement ellipsoids correspond to a 50% probability.

which differ in the sequence of adsorption and complexation steps, were employed (scheme 3).
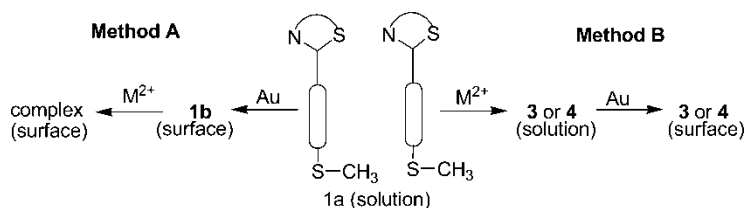
SCHEME 3

In one case (method **A**), the self-assembled layer of **1** was first formed on the Au surface that was further treated with a corresponding metal salt. According to method **B**, preliminarily prepared complex **3** or **4** was adsorbed onto the Au surface. As shown by the results of electrochemical study (see below), these methods afford layers of the different structure (with not identical electrochemical characteristics).

Note that ligand **1** principally possess to adsorb on gold surface in two manners: either by sulfur atom of methylthio group, or by thiolate sulfur atom. Note, that in the last case the more firm layer must form because of covalent S-Au producing. We suppose that cyclic form **1a**, which prevalently exists in solution, presumably takes acyclic iminothiol form **1b** during the adsorption of ligand **1** on the gold surface, as shown in scheme 3. This conclusion was drawn on the basis of electrochemical data presented below.

Compounds **1–4** were studied by cyclic voltammetry (CV) and rotating disk electrode (RDE) techniques on gold electrode in anhydrous CH_3CN with 0.05 M Bu_4NBF_4 as the supporting electrolyte. The electrochemical oxidation and reduction potentials are given in table 3. For the estimation of redox-processes localization areas we executed quantum chemical calculations of frontier molecular orbitals (MO) by means of semi-empirical PM3 method [20].

Table 3. Electrochemical reduction (E^{Red}) and oxidation (E^{Ox}) potentials for compounds **1–4**, as measured by CV (E_p is the peak potential) and RDE ($E_{1/2}$ is the half-wave potential) techniques on an Au electrode. The values given in parenthesis are the numbers of transferred electrons determined on an RDE with reference to the one-electron oxidation wave of ferrocene. The values after slash marks refer to peak potentials relevant to reverse scans of CV curves.

Compound	E^{Ox}, V		E^{Red}, V	
	$E_{1|2}$(number of electrons)	$E_p(E_p^{Red})$	$-E_{1|2}$ (number of electrons)	$-E_p(E_p^{Ox})$
1 (solution)		0.83/0.71; 1.46		1.69/1.64
1 (ads.)		1.53/0.88		0.83/0.66; 1.75
2 (solution)	0.93(0.2);	1.26; 1.89	1.02(0.8);	0.99/0.16;
			1.72(1.4)	1.86/1.66
3 (solution)	0.97(0.15);	1.18;	1.10(0.7);	1.20; 1.49(1.26);
	1.10; 1.50	1.52	1.70(0.4)	1.74
3 (ads., method **A**)		1.42/1.06		0.93/0.63; 1.73
3 (ads., method **B**)		1.66/1.02		1.20; 1.41; 1.74
4 (solution)		0.78/0.66;		0.96/0.68;
		1.45/1.12	0.90(2.3)	1.45; 1.72
4 (ads., method **A**)		1.47/1.04		0.94/0.55; 1.75
4 (ads., method **B**)		1.56/0.86		0.87/0.70;
				1.27; 1.70

HOMO LUMO

1a

1b

2
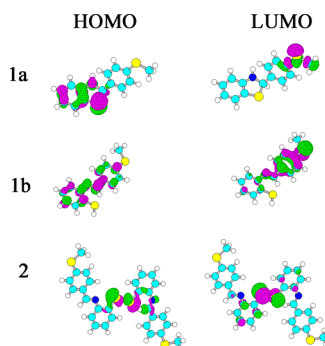
Figure 2. The frontier MO of compounds 1 (in cyclic and acyclic forms) and 2; PM3 calculations results.

The reduction of **1** takes place at considerable cathode potentials ($-1.69\,\text{V}$) and presumably involves the methyl sulfide sulfur atom, yielding the electrochemically stable radical anion, a result that is consistent with published data on electrochemical reduction of sulfides [22] and performed quantum-chemical calculations of frontier (MO) localization for the compounds **1** and **2**. According to these calculations, HOMOs of **1** and **2** are localized in general on C=N (C−N) or S−S bond, respectively, while LUMOs – in general on SMe fragment (figure 2).

The oxidation of **1** is a two-stage and its reduction is a single-stage one-electron process. It is likely that the oxidation involves the benzothiazoline nitrogen atom, since the potential of the first oxidation peak lies in the region characteristic of amines (0.8–$1.2\,\text{V}$) [21] The potential of the second oxidation peak lies in the region of oxidation potentials of organic sulfides [23].

Both oxidation and reduction of disulfide **2** proceed in two consecutive one-electron steps, in which the anodic processes are accompanied by surface passivation of the gold electrode, thus making it impossible to measure the number of electrons transferred at this stage owing to a dramatic fall in current even during the recording of the first current–voltage curve. The first stages of both oxidation and reduction of **2** seem to include S−S bond dissociation. The conclusion that electronic changes upon oxidation are localized on the sulfur–sulfur bond are based on the fact that the CV oxidation curve displays a new pair of peaks after the first anodic stage ($E_p^{\text{Red}} = 0.63\,\text{V}/E_p^{\text{Ox}} = 0.81\text{V}$) (peaks A and B in figure 3). Since the potential of the newly formed anodic peak is practically the same as that of the first oxidation peak of **1**, we assume that the oxidation of **2** in solution involves a reaction that generates amine **1**, as shown in scheme 4.

The reduction curve of **2**, which is reverse to the anodic curve, displays the corresponding oxidation peak of the anion RS$^-$ at a potential of $E_p^{\text{Red}} = -0.15\,\text{V}$ (figure 3, peak C) [24].
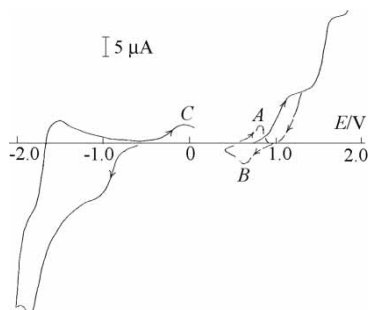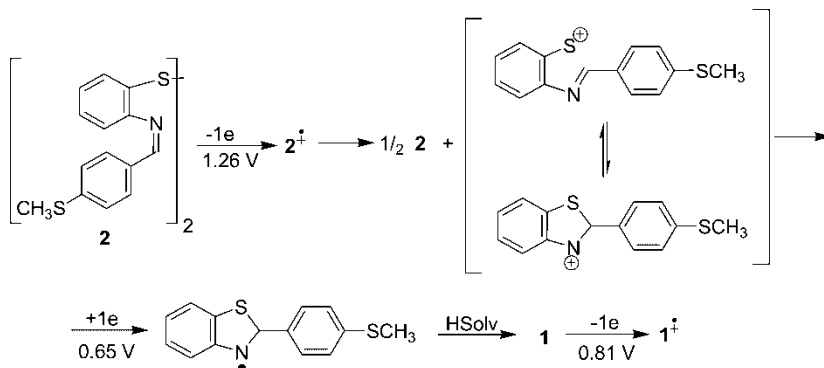
Figure 3. Cyclic voltammograms (Au electrode, $0.05\,\text{M Bu}_4\text{NBF}_4$, $20\,°\text{C}$) of compound 1 (10^{-3} mol/l in CH_3CN).

SCHEME 4

As we can see from the data presented in table 3, the oxidation of **1** adsorbed on the gold electrode surface is retarded by approximately 700 mV and the reduction is facilitated approximately to the same extent. This finding indicates that compound **1** adsorbed on the electrode surface may have a structure other than that in solution. Note that the oxidation and reduction potentials of **1** adsorbed on the gold electrode are very close to those observed for disulfide **2** (see table 3), thus suggesting their structures to resemble each other. Hence, it is evident that the sulfur atom, not the imine moiety, is oxidized on the surface of the gold electrode modified with **1**, whereas the reduction involves the imine fragment. Based on the electrochemical data obtained for **1**, we may propose the following scheme (scheme 5) of processes occurring at the surface of the gold electrode, assuming that compound **1** is adsorbed in the open iminothiol form, rather than the cyclic benzothiazole form. The driving force of this process is probably the formation of a thiol self-assembled monolayer during the adsorption of **1** in its open form **1b**, scheme 5.
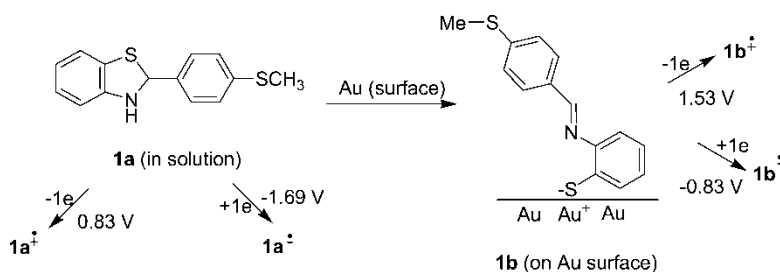
SCHEME 5

The assumption that **1** exists in form **1b** on the electrode surface is supported by the results of our experiments with the monolayers of complexes **3** and **4** prepared according to two alternative procedures shown in scheme 3. As is seen from the data presented in table 3 and figure 4, the complexes in solution, metal complex layers prepared by holding the gold electrode in a solution of a preliminarily synthesized complex (method B), and layers obtained by treating the monolayer of **1** with a corresponding metal salt (method A) exhibit not identical electrochemical characteristics.
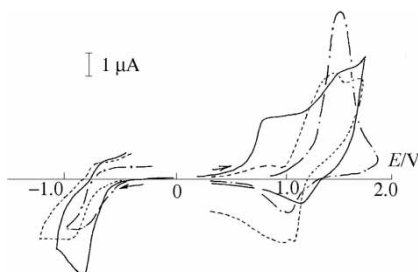
Figure 4. Cyclic voltammograms (Au electrode, 0.05 M Bu$_4$NBF$_4$, 20 °C) of compound 4 in CH$_3$CN solution (10^{-3} mol/l) (solid line) and compound 4 adsorbed according to methods A (dotted line) and B (dash-dotted line).

3. Experimental

^{1}H NMR spectra were recorded with a Varian-VXR-400 instrument operating at 400 MHz. IR spectra were measured in nujol with an UR-20 spectrometer. Electronic absorption spectra were recorded on Specord-M40 (200–900 nm) and Nicolet Gelios-α (200–1100 nm) instruments at 20–22°C using a quartz cell with an optical path length of 0.1 cm. Electron-ionization mass spectra were recorded on Jeol JMS-D300 mass spectrometer interfaced to a JMA-2000 computer and an HP-5890 gas chromatograph.

Experimental intensities of diffraction reflections were measured at room temperature using a CAD-4 fully automated single-crystal diffractometer (CuKα-radiation, graphite monochromator, ω-scanning).

Electrochemical studies were performed using a PI-50-1.1 potentiostat. Polycrystalline Au electrodes of 1 mm diameter were polished with a diamond slurry and were sonicated for 10 min in water. The supporting electrolyte was an 0.05 M Bu$_4$NBF$_4$ solution, and the reference electrode was an Ag | AgCl | KCl(sat.) electrode. A potential scan rate was 200 mV s^{-1} (CV) or 20 mV s^{-1} (RDE), 2800 rpm. All measurements were made under argon; samples were dissolved in a preliminarily deaerated solvent. The SAMs of **1**, **3**, and **4** were fabricated by immersing the Au electrode in a 10^{-3} M acetonitrile solution of a test compound for a least 24 h (method **A**). Then, the electrode was rinsed several times with CH$_3$CN, dried in air, and transferred into the pure supporting electrolyte; after that, CV curves were recorded. To obtain complexes **3** and **4** adsorbed on the electrode, an alternative procedure (method **B**) was also used. The electrode modified with compound **1** according to method **A** was immersed in a 10^{-3} M solution of a corresponding metal salt in CH$_3$CN to be held for $15 - 30$ min and was dried again; then, cyclic voltammograms were recorded.

3.1 *2-[4-(Methylthio)phenyl]-2,3-dihydro-1,3-benzothiazole (1)*

4-Methylthiobenzaldehyde (1.29 g, 5 mmol) was added to an alcohol solution (10 ml) of 2-aminothiophenol (0.625 g, 5 mmol). The reaction mixture was refluxed with stirring for an hour, cooled, and filtered to give product **1**. Yield: 81%. Mp 135°C. δ_H (400 MHz, CDCl$_3$): 8.08(d, 1H, $J = 8.0$ Hz, 1H), 8.04 (d, $J = 8.3$ Hz, 2H), 7.91 (d, $J = 8.1$, 1H), 7.42 (t, $J = 6.8$ Hz, 1H), 7.35 (d, $J = 8.6$ Hz, 2H), 7.24 (t, $J = 8.3$ Hz, 1H), 6.38 (s, 1H, CH), 5.08 (bs, 1H , NH), 2.57 (s, 3H , S−CH$_3$). IR (cm^{-1}): 3312 (NH), 1685 (C=N), 1470, 1440, 1405, 1380, 1318, 1100, 970. Found: C, 64.86; H, 4.70; N, 5.42. Calc. for C$_{14}$H$_{12}$NS$_2$: C, 65.12; H, 4.65; N, 5.43.

3.2 *Bis[4-(methylthio)phenylmethyleneaminophenyl] disulfide (2)*

4-Methylthiobenzaldehyde (1.29 g, 5 mmol) was added to an alcohol suspension (30 ml) of bis[2-aminophenyl]disulfide (1.25 g, 10 mmol). The reaction mixture was refluxed with stirring for an hour, cooled, and filtered to give product **2**. Yield: 89%. Found: C, 64.15; H, 4.00; N, 5.24. Calc. for $C_{28}H_{22}N_2S_4$: C, 65.12; H, 4.34; N, 5.43. δ_H (400 MHz, CDCl$_3$): 8.57 (s, 2H, HC=N), 8.08 (d, 2H, $J = 8.0$ Hz, 2H), 8.02 (d, $J = 8.3$ Hz, 4H), 7.92 (d, $J = 8.0$, 2H), 7.51 (t, $J = 7.4$ Hz, 2H), 7.40 (d, $J = 7.4$ Hz, 2H), 7.35 (d, $J = 8.3$ Hz, 4H), 7.24 (t, $J = 8.3$ Hz, 1H), 6.38 (s, 1H, NH), 2.57 (s, 6H, S−CH$_3$). IR (cm^{-1}): 1695 (C=N), 1470, 1445, 1405, 1385, 1320, 1130, 1100, 970.

3.3 *Nickel(II) and cobalt(II) complexes (3,4)*

2-Aminothiophenol and 4-methylthiobenzaldehyde taken in equivalent amounts were dissolved in ethanol with heating. After refluxing the solution for 30 min, 0.5 equivalent of metal acetate was added and the reaction mixture was further refluxed for 1 h with stirring. The precipitated solid was filtered off and washed with ethanol.

3.3.1   Co^{II}(1-H)$_2$ (3).
Yield: 48%. Mp = 192°C. IR (cm^{-1}): 1620, 1595, 1570, 1555, 1467, 1385, 1180, 1100. Found: C, 58.40; H, 4.05; N, 4.82. Calculated for $C_{28}H_{24}N_2S_4Co$: C, 58.42; H, 4.20; N, 4.87.

3.3.2   Ni^{II}(1-H)$_2$ (4).
Yield: 52%. Mp = 195°C . IR (cm^{-1}): 1620, 1595, 1570, 1555, 1467, 1385, 1180, 1100. Found: C, 57.82; H, 3.94; N, 5.08. Calculated for $C_{28}H_{24}N_2S_4Ni$: C, 58.44; H, 4.20; N, 4.87.

4. Conclusions

In this investigation, we have shown that 2-[4-(methylthio)phenyl]-2,3-dihydro-1,3-benzothiazole (**1**) readily forms coordination compounds with Ni(II) and Co(II) under reflux in alcoholic solution. The complex formation involves thiazoline cycle opening in **1** yielding 2-[4-(methylthio)phenylmethyleneamino]thiophenol coordination complexes. The electrochemical study of **1**, its complexes with Co^{2+} and Ni^{2+}, and bis[4-(methylthio)phenylmethyleneaminophenyl] disulfide **2** in solution and in a self-assembled monolayer on the Au electrode showed that ligand **1** is adsorbed in the form of 2-[4-(methylthio)phenylmethyleneamino]thiophenol on the gold surface. The adsorbed cobalt and nickel complexes of **1** on an Au surface can be obtained by two methods, namely, by the adsorption of preliminarily prepared coordination compound **3** or **4** on the electrode or by the initial modification of the electrode with ligand **1** followed by the complexation reaction between a metal salt occurring in solution and **1** adsorbed on the electrode. On the basis of electrochemical data, it was found that the structure of complexes formed on the surface differs from the structure of the complexes produced in solution.

Acknowledgements

and Experimental Investigation into the Nature of Chemical Bonding and Mechanisms of Chemical Reactions and Processes."

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