N,N′-Bis(2-mercaptophenyl)propane-1,3-diamine as a new organic ligand of the N_2S_2 type and its coordination compound with nickel(II)

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A method for the synthesis of new tetradentate organic ligand of the N_2S_2 type, *viz.*, *N,N′*-bis-(2-mercaptophenyl)propane-1,3-diamine has been developed, starting from 2-(*tert*-butylthio)aniline and malonyl dichloride. Coordination compound of this ligand with Ni^{II} according to the X-ray diffraction data has a square-planar geometry of the metal ion coordination sphere.

Key words: nickel(II), transition metal complexes, N_2S_2 ligands.

Active centers of many redox enzymes contain transition metal ions (Cu ions in hydrogenases and oxygenases, Co and Ni ions in synthases, transferases, and isomerases) coordinated with the nitrogen and sulfur atoms of the amino acid fragments.[1—3] The synthesis of low-molecular-weight N,S-containing ligands and their complex compounds, simulating geometric specificities of natural metalloenzymes and being their functional analogs, is of significant interest from the point of view of possible catalytic activity. Nowadays, low-molecular-weight complexes of nickel, cobalt, and copper are used for catalysis of a wide range of organic reactions including reactions of asymmetric synthesis, epoxidation of alkenes,[4—6] cyclopropanation,[7] aziridination,[8] oxidation of sulfides,[9,10] the Diels—Alder reactions,[11] activation of the CH bonds,[12,13] epoxide ring opening.[14—18]

In the most naturally occurring metalloenzymes, the metal atom is in the square-planar (or distorted tetrahedron) ligand environment; the apical positions in the coordination sphere are spatially available for the coordination with one or two additional ligands and can be occupied by molecules of substrate and reagent in the process of catalytic cycle. Therefore, square-planar complexes are of the highest interest as the models of metal-containing enzymes. In addition to spatial criteria, electronic factors should be considered as well. From this point of view, it is desirable the presence in the ligand molecule of soft donors capable of effective stabilization of the low-valent state of metal ions, the intermediates of catalytic cycles in the oxidation reactions, for example, of sulfur atoms.

One of promising classes of N,S-containing ligands for the synthesis of metalloenzyme analogs are thio-substituted amines. Earlier, we have synthesized a series of acyclic and macrocyclic amino and imino sulfides of the N_2S_2 type, the *ortho*-aminobenzenethiol derivatives,[19,20] some of which proved capable of reversible electrochemical reduction and, therefore, are promising as catalysts of oxidation-reduction reactions.

By now, several Ni^{II} coordination compounds with tetradentate N,S-containing ligands of the series of *N,N′*-bis-*ortho*-mercaptophenyl-substituted alkanediamines have been described in the literature.[21—25] 1,2-Diaminoethane derivatives serve as the ligands in all these complexes. Probably, this is due to the simple synthesis of such organic compounds, which are easy to obtain by reduction of the corresponding diimines or thiazolidines, the condensation products of glyoxal and *ortho*-mercapto-substituted anilines.[26] However, all the known by now nickel(II) coordination compounds with neutral *N,N′*-bis-(2-mercaptophenyl)ethane-1,2-diamines (see Refs above) have octahedron geometry of the coordination environment. *N,N′*-Bis(2-mercaptophenyl)propane-1,3-diamines contain longer polymethylene bridge between the nitrogen atoms, which increases its conformational lability and can lead to the formation of complexes with other geometry. Nevertheless, there is no literature data on ligands of the N_2S_2 type, *i.e.*, 1,3-diaminopropane derivatives. In the present work, we suggest a convenient method for the preparation of *N,N′*-bis(2-mercaptophenyl)propane-1,3-diamine (in the dihydrochloride form) and its coordination compound with Ni^{II} starting from *ortho*-aminobenzenethiol and malonyl dichloride.

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Results and Discussion

It is known from the literature[27] that the reaction of 1,3-dicarbonyl compounds and *ortho*-aminobenzenethiol usually stops at the stage of monoimine and, therefore, the method successfully used in the synthesis of *N,N′*-bis-(2-mercaptophenyl)ethane-1,2-diamines, reduction of diimines, is not suitable for the preparation of 1,3-diaminopropane derivatives. An alternative is alkylation or acylation of *ortho*-aminobenzenethiol at the nitrogen atom with 1,3-dihaloalkane or 1,3-dicarboxylic acyl dichloride. However, undesirable competing alkylation at the sulfur atom is possible in this case, hence it is necessary to preliminary protect the SH group in the starting compound.

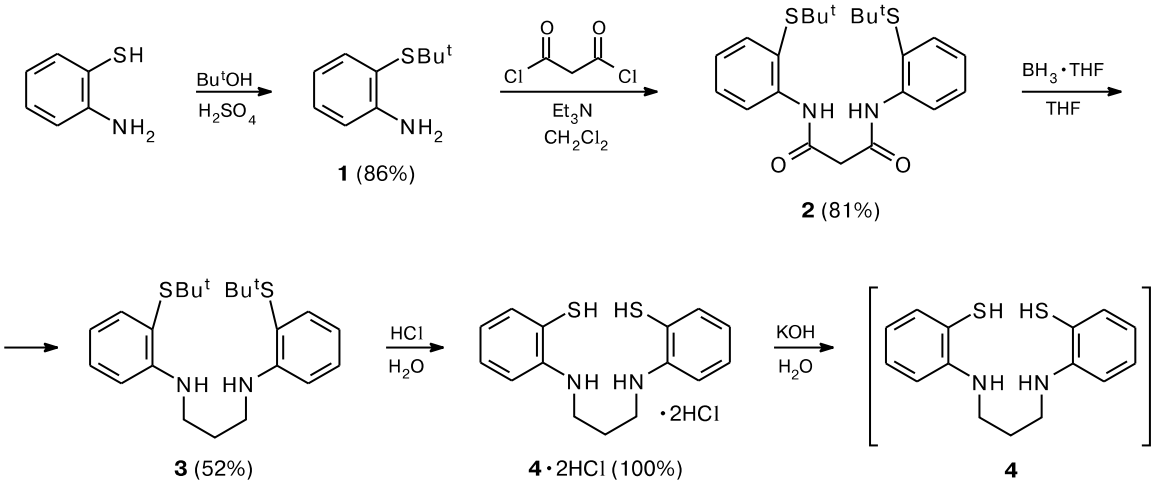
We synthesized *N,N′*-bis(2-mercaptophenyl)propane-1,3-diamine hydrochloride (**4**) in four steps (Scheme 1).

In the first step, *ortho*-aminobenzenethiol was alkylated with *tert*-butyl alcohol in aqueous sulfuric acid for the protection of the SH group; protonation of the amino group under these conditions interferes alkylation of the nitrogen atom. Several protecting groups for the benzenethiol SH groups are described in the literature. We tried the most simple from them, acetyl protection. It is stable under conditions of further reactions, however, the reaction of *ortho*-aminobenzenethiol with acetyl chloride or acetic anhydride is unselective and proceeds at both the nitrogen and the sulfur atoms. The benzylation with benzyl chloride in the presence of sodium ethoxide[28] proceeded selectively due to the higher nucleophilicity of the sulfur atom as compared to the amino group, moreover, the benzyl protection is stable in the presence of most acids and bases; however, the both methods described for the removal of this protection, *viz.*, reduction of benzyl sulfide with sodium in liquid ammonia[29] and cleavage with aluminum tribromide[28] or trichloride,[30] gave no satisfactory results. The first method requires relatively time-consuming and complicated isolation of the thiol including purification by column chromatography, which is accompanied by significant oxidation of the thiol to disulfide. Obviously, this method can be applied only to the final products stable in air. Aluminum tribromide is a strong Lewis acid and in the case of compounds studied causes cleavage of the molecule at both the C—S and the C—N bonds. In contrast to this, trityl and *tert*-butyl protecting groups are stable in basic and weakly acidic media, as well as in the most reducing processes. Removal of such a protection is performed by reflux in concentrated hydrochloric[31] or trifluoroacetic acids;[32] the yields are quantitative, whereas the excess of acid can be then removed by heating the solution under argon at reduced pressure to prevent oxidation of the thiol. We have chosen more available *tert*-butyl protecting group, this allowed us to obtain the target product in preparative yield.

Aminosulfide **1** obtained in the first step of the synthesis was further involved into the reaction with malonyl dichloride to yield diamide **2**. Initially, we planned to conduct direct alkylation of the amino group in protected *ortho*-aminobenzenethiol with dibromoethane, however, this reaction gave no satisfactory results. As an alternative, alkylation of the amino group was carried out in two synthetic steps: with initial acylation of the amino group and subsequent reduction of the amide obtained.

The third step of the synthesis included reduction of diamide **2** to the corresponding diamine using complex of boron hydride with tetrahydrofuran. Lithium aluminum hydride[33,34] and boron hydrides[35,36] are the most known reducing agents for amides. Attempted reduction of diamide **2** upon the action of $LiAlH_4$ in tetrahydrofuran gave a complex mixture of products, from which we failed to isolate the target diamine in the pure form even after

Scheme 1

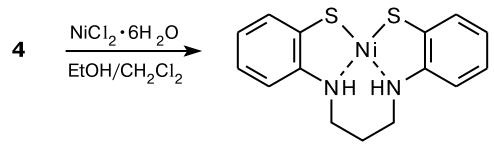


purification by column chromatography. After the reaction of **2** with $NaBH_4$ in the presence of $BF_3 \cdot OEt_2$, the starting amide was isolated from the reaction mixture in quantitative yield. Reduction with the complex borane—tetrahydrofuran[36] proved the optimum method for the synthesis of the target diamine **3**, which was isolated from the reaction mixture by column chromatography in 52% yield.

The protecting *tert*-butyl group was removed from the synthesized diamino-bis-sulfide **3** by reflux in aqueous hydrochloric acid. The ligand **4** obtained is stable in aqueous solution as a hydrochloride; however, it is rapidly oxidized to disulfide on the transformation to the free base by treatment with equivalent amount of 1 *M* aqueous KOH. Therefore, for further preparation of coordination compound **5** it is convenient to use aqueous solution of dihydrochloride **4** without isolation and additional purification of the ligand.

Method of slow diffusion of the compound **4** solution in CH_2Cl_2 into the solution of nickel chloride hexahydrate in ethanol was used for obtaining Ni^{II} complex compound. This results in the isolation of coordination compound **5** (Scheme 2), the structure of which was confirmed by the X-ray diffraction data.

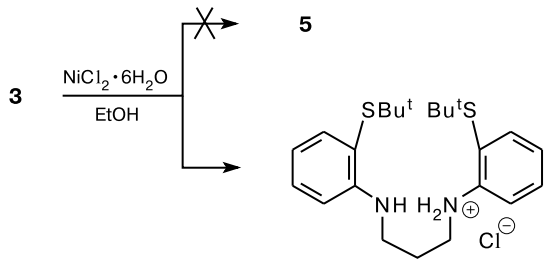
Scheme 2



5 (71%)

In the literature, there are known examples of removal of *tert*-butyl protection from mercapto groups in the complexation reactions; however, our effort to synthesize complex **5** by reflux of bis-sulfide **3** with ethanolic solution of nickel chloride resulted in only diamine **3** monohydrochloride (compound **3a**), which was also characterized by the X-ray diffraction data (Scheme 3).

Scheme 3



3a (92%)

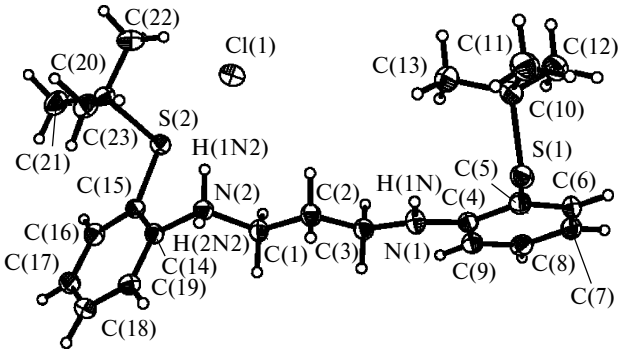


Fig. 1. Molecular structure of compound **3a**.

The most important bond distances and bond angles for compounds **3a** and **5** are given in Tables 1 and 2. Molecular structures of compounds **3a** and **5** are shown in Figs 1 and 2; the molecule packing in the crystal structure of **5** is shown in Fig. 3.

In the molecule **3a**, the donor nitrogen and sulfur atoms of each of two aminobenzenethiol groups are arranged in the same plane with the carbon atoms of the benzene rings bound to them. However, all four donor atoms of the N_2S_2 system are not placed in one plane; the angle between the planes of two N—C—C—S fragments is ~70°. The C—S—C angles are 106.25 and 101.50° that is typical for aryl alkyl sulfides.

The nickel atom in compound **5** is coordinated by two sulfur and two nitrogen atoms of the organic ligand and has square-planar ligand environment. The Ni atom is placed almost strictly in the plane of N_2S_2 atoms of the macrocyclic ligand. The S—Ni—N angles are close to 90°, the angle S(1)—Ni—S(2) is somewhat less than 90°, whereas the angle N(1)—Ni—N(2), *vice versa*, is somewhat larger than 90°, that, most likely, is due to the different number of carbon atoms in the chelating cycles. The benzene ring planes are virtually coplanar to the basic plane of the ligand (determined by the N, S, and Ni atoms) and to each other. All three carbon atoms of the

Table 1. Selected bond distances (*d*), bond (ω) and dihedral (θ) angles in compound **3a**

Value	Value
Bond	*d*/Å
C(1)—N(2)	1.509(2)
C(15)—S(2)	1.7716(17)
Bond angle	ω/deg
C(15)—S(2)—C(20)	101.50(8)
S(2)—C(15)—C(14)	120.67(14)
C(14)—N(2)—C(1)	112.27(13)
Dihedral angle	θ/deg
S(1)—C(5)—C(4)—N(1)	1.7(2)

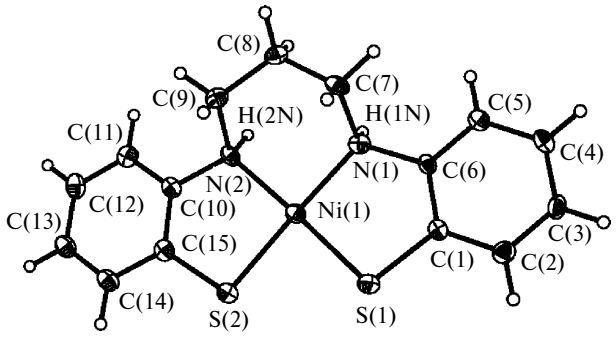


Fig. 2. Molecular structure of compound **5**. The Figure shows one of two crystallographically independent molecules.

methylene groups between nitrogen atoms are on the same side of the basic plane. Such a configuration, probably, is due to the chair conformation of the six-membered NiN_2C_3 ring.

In conclusion, a method for the preparation of new tetradentate organic ligand of the N_2S_2 type, *viz.*, *N,N′*-bis-(2-mercaptophenyl)propane-1,3-diamine, has been developed starting from available 2-(*tert*-butylthio)-aniline and malonyl dichloride. A coordination compound of this ligand with Ni^{II} has been synthesized, which according to the X-ray diffraction data has the square-planar geometry of the metal ion coordination environment, which makes it promising for further study on catalytic activity in oxidation and electroinduced reduction reactions.

Table 2. Selected bond distances (*d*), bond (ω) and dihedral (θ) angles in compound **5**

Parameter	Value
Bond	*d*/Å
Ni(1)—N(1)	1.952(3)
Ni(1)—N(2)	1.958(3)
Ni(1)—S(1)	2.1517(11)
Ni(1)—S(2)	2.1622(11)
Bond angle	ω/deg
S(1)—Ni(1)—N(1)	90.13(10)
N(1)—Ni(1)—N(2)	92.22(13)
S(2)—Ni(1)—N(2)	90.46(10)
C(1)—S(1)—Ni(1)	98.78(13)
C(15)—S(2)—Ni(1)	98.34(13)
C(6)—N(1)—C(7)	111.3(3)
C(6)—N(1)—Ni(1)	115.0(2)
Dihedral angle	θ/deg
S(1)—C(1)—C(6)—N(1)	0.2(4)
Ni(1)—N(1)—C(6)—C(1)	2.1(4)

Experimental

The reaction courses were monitored by TLC on a fixed layer of silica gel (Silufol plates). Preparative chromatographic separation of reaction mixtures was carried out on columns with silica gel (70/230) and hexane—dichloromethane (1 : 1) solvent mixture as the eluent.

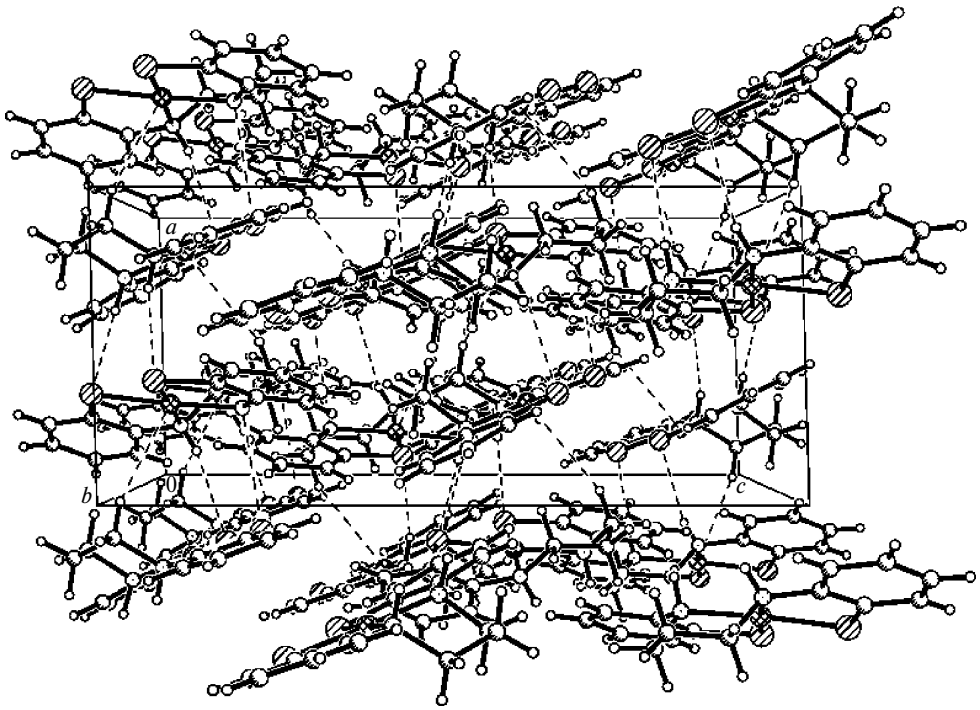


Fig. 3. Molecular packing in the crystal structure of complex **5**.

^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury-400 or Bruker Avance-400 spectrometers (400 MHz (^{1}H) or 100 MHz (^{13}C)) in $CDCl_3$. Electronic spectra were recorded on a Perkin-Elmer λ-25 spectrometer, IR spectra, on a UR-20 spectrometer in Nujol, mass spectra, on a Finnigan MAT SSQ 7000 GC-MS instrument (70 eV, an OV-I (25 m) quartz capillary column with temperature regime: 70 °C (2 min) — 20 deg min^{-1} — 280 °C (10 min or 30 min).

The X-ray study was performed on a Bruker Smart 1000 CCD frea detector single-crystal automatic diffractometer (graphite monochromator, λ(MoKα) = 0.71073 Å, ω-scanning). The structure was solved by the direct method[37] and refined by the full-matrix anisotropic least square method from F^2 for all the nonhydrogen atoms.[38] All the hydrogen atoms were localized objectively and refined in the isotropic approximation. The crystallographic data, experimental and structure refinement details for compounds **3a** and **5** are given in Table 3.

2-(*tert*-Butylthio)aniline (1).[39] Water (25 mL) and concentrated sulfuric acid (34 mL) were placed into a 100-mL round-bottom flask equipped with a dropping funnel, thermometer, and magnetic stirring bar, then *tert*-butanol (11 mL, $1.2 \cdot 10^{-1}$ mol) was added at 0 °C, followed by a slow addition of 2-aminobenzenethiol (10 g, $8.0 \cdot 10^{-2}$ mol) over 40 min at the same temperature. The reaction mixture was stirred for 1 h at 0 °C and poured into a saturated aq. $KHSO_4$ (60 mL), followed by addition of 30% aq. NaOH at 10—15 °C to pH 9. The mixture was extracted with diethyl ether (2×20 mL), the ethereal solution was dried with Na_2SO_4. The solvent was evaporated at reduced pressure to yield 2-(*tert*-butylthio)aniline (12.50 g, 86%) as a yellowish oil. ^{1}H NMR, δ: 7.40 (d, 1 H, arom., J = 8.3 Hz); 7.18 (t, 1 H, arom., J = 8.4 Hz); 6.77 (d, 1 H, arom., J = 8.3 Hz); 6.71 (t, 1 H, arom., J = 8.4 Hz); 4.46 (br.s, 1 H, NH); 1.35 (s, 9 H, CH_3).

***N*,*N*′-Bis[2-(*tert*-butylthio)phenyl]malonamide (2).** A solution of compound **1** (5 g, $2.76 \cdot 10^{-2}$ mol) in CH_2Cl_2 (30 mL) and Et_3N (2.78 g, $2.76 \cdot 10^{-2}$ mol) were placed under Ar into a 100-mL round-bottom flask equipped with a dropping funnel, thermometer, and magnetic stirring bar, then malonyl dichloride (2.11 g, $1.38 \cdot 10^{-2}$ mol) was added dropwise at 0 °C. The mixture was stirred for 16 h, followed by addition of 1 *M* hydrochloric acid to pH 1. The product was extracted with CH_2Cl_2 (2×20 mL), washed with saturated aq. $NaHCO_3$ (2×20 mL) and water (10 mL), dried with Na_2SO_4. The solvent was evaporated at reduced pressure to yield compound **2** (4.96 g, 81%) as a yellow powder, m.p. 100—102 °C. ^{1}H NMR, δ: 9.83 (br.s, 2 H, NH); 8.56 (d, 2 H, arom., J = 7.5 Hz); 7.55 (d, 2 H, arom., J = 7.7 Hz); 7.42 (t, 2 H, arom., J = 7.7 Hz); 7.09 (t, 2 H, arom., J = 7.5 Hz); 5.31 (s, 2 H, CH_2); 1.30 (s, 18 H, CH_3). ^{13}C NMR, δ: 164.4, 141.2, 138.8, 130.6, 123.9, 120.9, 120.0, 48.5, 48.7, 30.7. IR, ν/cm^{-1}: 3290 (NH), 1760 (CO). MS, m/z: 431 $[MH]^+$. Found (%): C, 64.37; H, 7.18; N, 6.43. $C_{23}H_{30}N_2O_2S_2$. Calculated (%): C, 64.14; H, 6.98; N, 6.51.

***N*,*N*′-Bis[2-(*tert*-butylthio)phenyl]propane-1,3-diamine (3).** Amide **2** (4 g, $9.30 \cdot 10^{-3}$ mol) in THF (40 mL) was placed under inert gas into a 150-mL round-bottom flask equipped with a dropping funnel, thermometer, and magnetic stirring bar, followed by a dropwise addition of a solution of $BH_3 \cdot THF$ (1 *M*, 93 mL, $9.30 \cdot 10^{-2}$ mol) in the same solvent at 0 °C. The mixture was stirred for 3 h at 0 °C, then for 16 h at room temperature and, after a dropwise addition of CH_3OH (75 mL), for another 16 h. The solvent was evaporated at reduced pressure, CH_3OH (3×30 mL) was added to the residue, followed by evaporation of the solvent at reduced pressure. The product was purified by column chromatography on silica gel (hexane—CH_2Cl_2, 1 : 1) to yield compound **3** (1.94 g, 52%) as a white powder, R_f = 0.64 (hexane—CH_2Cl_2, 1 : 1), m.p. 60—62 °C. ^{1}H NMR, δ: 7.42 (d, 2 H, arom., J = 7.9 Hz); 7.27 (m, 4 H, arom.); 6.65 (d, 4 H, arom., J = 7.9 Hz); 3.32 (t, 4 H, CH_2CO, J_1 = 6.8 Hz); 2.00 (quint, 2 H, $C\underline{H}_2CH_2CO$, J = 6.8 Hz); 1.31 (s, 18 H, CH_3). ^{13}C NMR, δ: 151.0, 139.6, 131.0, 156.7, 116.1, 115.6, 110.3, 47.7, 41.4, 37.1, 29.3. IR, ν/cm^{-1}: 3300 (NH). Found (%): C, 68.67; H, 8.70; N, 6.84. $C_{23}H_{34}N_2S_2$. Calculated (%): C, 68.66; H, 8.46; N, 6.97.

Table 3. Crystallographic data, experimental and structure refinement details for compounds **3a** and **5**

Parameter	**3a**	**5**
Molecular formula	$C_{23}H_{35}ClN_2S_2$	$C_{15}H_{16}N_2NiS_2$
Molecular weight	439.10	347.13
T/K	120(2)	120(2)
Crystal size/mm	0.45×0.35×0.20 *	0.55×0.35×0.30 **
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P21/n$
Parameters of the unit cell		
a/Å	7.7895(4)	8.1844(7)
b/Å	12.3728(7)	19.4128(16)
c/Å	13.2039(7)	18.2774(15)
α/deg	99.8880(10)	90
β/deg	94.1430(10)	91.563(2)
γ/deg	104.6260(10)	90
V/Å^3	1204.08(11)	2902.9(4)
Z	2	8
d_{calc}/g cm^{-3}	1.211	1.589
Absorption coefficient/mm^{-1}	1.343	1.614
F(000)	472	1440
Range of θ/deg	1.58—28.00	1.53—30.00
Ranges of reflection indices		
h	$-10 \le h \le 10$	$-11 \le h \le 11$
k	$-16 \le k \le 16$	$-27 \le k \le 27$
l	$-17 \le l \le 17$	$-25 \le l \le 25$
Number of reflections measured/independent (R_{int})	12416/5765 (0.0228)	31659/8390 (0.0805)
Number of variables of refinement	271	377
Q-factor on F^2	1.015	1.015
Number of reflections with $I > 2\sigma(I)$	2371	2371
R-factors		
R_1	0.0493	0.0521
wR_2	0.1237	0.0811
R-factors (on all the data)		
R_1	0.0613	0.1200
wR_2	0.1334	0.0891

* Orange plates.
** Light yellow needles.

***N,N′*-Bis[2-(*tert*-butylthio)phenyl]propane-1,3-diamine monohydrochloride (3a).** Diamine **3** (0.2 g, $4.98 \cdot 10^{-4}$ mol) in ethanol (25 mL) was placed into a 50-mL round-bottom flask equipped with a reflux condenser and magnetic stirring bar, then $NiCl_2 \cdot 6H_2O$ (0.12 g, $4.98 \cdot 10^{-4}$ mol) in ethanol (10 mL) was added. The mixture was refluxed for 12 h with stirring. The solvent was half evaporated at reduced pressure. The solution was kept at 0—5 °C until crystals formed. The crystals were filtered off, washed with cold ethanol (5 mL), then with diethyl ether (5 mL) to yield hydrochloride **3a** (0.2 g, 92%) as light brown crystals. Found (%): C, 62.67; H, 8.29; N, 6.57. $C_{23}H_{35}N_2S_2Cl$. Calculated (%): C, 62.94; H, 7.98; N, 6.39.

***N,N′*-Bis(2-mercaptophenyl)propane-1,3-diamine dihydrochloride (4).** Diamine **3** (0.3 g, $7.45 \cdot 10^{-4}$ mol) was placed under Ar into a 50-mL round-bottom flask equipped with a reflux condenser and magnetic stirring bar, to which conc. hydrochloric acid (25 mL) was added. The mixture was refluxed for 8 h with stirring. The solvent was evaporated at reduced pressure to yield compound **4**·2HCl (0.27 g, 100%) as white powder. ^{1}H NMR, δ: 7.92 (d, 2 H, arom., J = 7.7 Hz); 7.50 (d, 2 H, arom., J = 8.0 Hz); 7.28 (m, 4 H, arom.); 3.66 (t, C$\underline{H}_2$CO, 1 H, J = 7.1 Hz); 3.23 (q, C$\underline{H}_2$CH$_2$CO, 2 H, J = 7.1 Hz). MS, m/z: 289 $[MH]^+$.

[*N,N′*-Bis(2-mercaptophenyl)propane-1,3-diamine]nickel(II) (5). Ethanol (200 μL) was added to a solution of dihydrochloride **4** (0.01 g, $3.45 \cdot 10^{-5}$ mol) in dichloromethane (1 mL) until two layers were formed. Then a solution of $NiCl_2 \cdot 6H_2O$ (8 mg, $3.45 \cdot 10^{-5}$ mol) in ethanol (1 mL) was slowly added. The reaction mixture was tightly capped and stored until crystals formed to yield compound **5** (9 mg, 75%) as brown crystals, m.p. 264—266 °C. IR, ν/cm^{-1}: 3025 (NH). UV: λ_1 = 280 nm, ε_1 = 12847 L (mol cm)$^{-1}$, λ_2 = 310 nm, ε_1 = 20139 L (mol cm)$^{-1}$. Found (%): C, 51.94; H, 4.71; N, 8.14. $C_{15}H_{16}N_2S_2Ni$. Calculated (%): C, 51.87; H, 4.61; N, 8.07.

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