N,S,O-Containing organic ligands based on salicylaldehyde and 2-thiosubstituted ethylamines and their complexes with Co^{II}, Ni^{II}, and Cu^{II}

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The reaction of 2,2'-di(2-hydroxybenzaliminoethyl) disulfide (H_2L^1) and 2-[(2-thioethyl)iminomethyl]phenol (H_2L^2) with MCl₂·xH₂O (M = Co, Ni, Cu) afforded the $[M_2(L^1)Cl_2]$ and $[M(L^2)]_2$ complexes, respectively. Their structures were determined by the data of electronic and IR spectroscopy and PM3 quantum chemical calculations. The H_2L^1 ligand and the complexes were studied by electrochemistry (CV and using a rotating disk electrode). The primary electronic changes are localized on the ligand fragment upon the electrochemical oxidation and reduction of the complexes.

Key words: 2,2'-di(2-hydroxybenzaliminoethyl) disulfide, 2-[(2-thioethyl)imino-methyl]phenol, nickel(II), cobalt(II), copper(II), transition metal complexes, electrochemistry.

Transition metal complexes, particularly, of nickel(II), cobalt(II), and copper(II), with organic N,S,O-containing ligands attract attention as models for metal enzymes and electroactive catalysts.¹⁻³ A series of enzymes of various structural types containing in the active center one or two transition metal atoms are presently known.^{4,5} Most of them react according to the electron transfer mechanism (redox enzymes). In these redox enzymes, the metal center usually has a square-planar or tetrahedral ligand environment and is coordinated to the N, S, and O atoms of the protein fragment of the molecule.

The purpose of this work is to synthesize complexes of nickel(II), cobalt(II), and copper(II) with organic ligands 1 and 2 of the NSO type derived from salicylaldehyde and 2-thiosubstituted alkylamines, which are potentially capable of forming binuclear metal complexes.



Results and Discussion

Ligand **1** was synthesized from salicylaldehyde and cystamine (2,2'-diaminodiethyl disulfide) hydrochloride (Scheme 1).

Compound 1 is formed as the single geometric isomer, in which the *anti*-configuration of the C=N bond

Scheme 1



was proved by the NMR experiment using NOE. The irradiation of the proton of HC=N (δ 8.40) results in the NOE on the protons of the CH₂N group at δ 3.94.

Ligand **2** formed from salicylaldehyde and cystamine (2-aminoethanethiol) *via* similar reaction (Scheme 2) cannot be isolated in the pure state: according to the NMR spectroscopy data, a mixture of the target product, *viz.*, benzothiazoline formed due to the interaction of the aldehyde group of salicylaldehyde and the amino and mercapto group of the starting amine,⁶ and, probably, the product of oxidation of the target mercaptoimine **2** to the corresponding disulfide. However, according to the data of TLC and NMR spectroscopy, ligand **2** is stable in solution.

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Therefore, further, when synthesizing the complexes of ligand **2**, the latter were not isolated from its ethanolic solution and the formation of the product was monitored by TLC (by the disappearance of the starting compounds).

Scheme 2



The reactions of ligand **1** with nickel(II), cobalt(II), and copper(II) chlorides (Scheme 3) afforded complexes corresponding, according to the elemental analysis data, to the simplest molecular formula $M_2(L^1)Cl_2$ (M = Ni, Co, Cu).

Scheme 3

$$H_{2}L^{1} + MCl_{2} \cdot nH_{2}O \xrightarrow{MeOH} H_{2}[L^{1}]Cl_{2}$$

$$1 \qquad \qquad 3-5$$

M = Ni (3), Co (4), Cu (5)

The complexes were characterized by UV—Vis and IR spectroscopy. According to the IR spectroscopy data, the formation of the nickel and copper complexes is accompanied by the low-frequency shift of vibrations of the C=N group by 10-15 cm⁻¹ compared to the starting ligand, indicating that the nitrogen atom of the imino group is involved in coordination.

The results of studying compounds 1, 3, and 5 by UV-Vis spectroscopy are presented in Table 1. Only UV absorption bands corresponding to the $\pi - \pi^*$ and $n-\pi^*$ transitions in an organic molecule are observed for ligand 1. Additional bands of the resolved medium-intensity d-d transitions in the visible region (500-830 nm) are observed for the complexes. Based on the obtained results on absorption in the visible region and literature data on the position and intensity of bands of the d-d transitions for the tetrahedral, planar-square, and octahedral nickel(II) and copper(II) complexes,⁷ we can assert that the reactions with the copper and nickel salts gave the complexes containing metal ions in the tetrahedral and flattened tetrahedral ligand environments. In the case of cobalt complex 4, no unambiguous conclusion about the geometry of the coordination environment of the metal ion can be made on the basis of the

Table 1. UV–Vis spectra of compounds 1, 3, and 5–8 $(10^{-3} \text{ mol } L^{-1}, \text{DMF})$

Com- pound	λ/nm ($\epsilon/L mol^{-1} cm^{-1}$)	Coordination mode of metal ion	
1	318 (6947), 375 (108)	_	
3	283 (29508), 321 (14207),	Flattened	
	377 (20546), 527 (1464)	tetrahedron	
5	271 (122358), 301 (50056),	Tetrahedron	
	370 (48943), 675 (845)		
6	290 (38760), 318 (19574),	Flattened	
	370 (14729), 527 (2345)	tetrahedron	
7	360 (24419), 647 (1938)	Tetrahedron	
8	318 (5614), 370 (4840),	Tetrahedron	
	555 (1016)		

electronic spectroscopy data: no pronounced absorption bands are observed in the visible region of the spectrum. However, the absorption intensity decreases gradually in the region from 260 to 830 nm, *i.e.*, the visible region contain several absorption bands and the observed curve is their envelope.

We failed to prepare crystals of complexes 3-5 suitable for X-ray experiment. Two structures that satisfy the elemental analysis and spectral data can be proposed for the chloro-containing complexes: binuclear complex **A**, in which two disulfide sulfur atoms are involved in coordination of two different metal ions, or structure **B** with the bridging chloride anions in which the sulfur atom is not involved in coordination. 2,2'-Dipyridyl disulfide is described as a bidentate ligand coordinating the metal atoms only through the nitrogen atoms.



We optimized the geometric parameters of the nickel, cobalt, and copper complexes of types **A** and **B** by the PM3 semiempirical method⁸ in the HyperChem program package (HyperCube Inc., FL, USA). The convergence gradient is ≤ 10 cal Å⁻¹ mol⁻¹. The geometric parameters of the cobalt and copper complexes were optimized for the triplet and singlet states of the binuclear complex. According to the calculation results, complexes **4** and **5**



Fig. 1. Optimized structures of complexes **5** (*a*), **6** (*b*), and **7** (*c*) (PM3, convergence gradient ≤ 10 cal Å⁻¹ mol⁻¹).

should exist in singlet form A. The optimized structure of complex 5 is shown in Fig. 1, a.

For complex **3**, according to the calculation data, the species with the bridging and nonbridging chlorine atoms should possess approximately equal thermodynamic stabilities. Nevertheless, the complex is nonbridged in this case as well. This assumption is confirmed by a resembling behavior of all three complexes **3**–**5** during electrochemical investigation (see further).

In the case of ligand 2 (H_2L^2) capable of being deprotonated to both the oxygen and sulfur atoms, powdery precipitates of the complexes are formed immediately in the reactions with nickel chloride and nickel, cobalt, and copper acetates (Scheme 4). According to the elemental analysis data, the isolated complexes have the molecular formula $M(L^2)$. However, for tridentate ligand 2, according to earlier published data,⁹ the binuclear structure with the bridging sulfur atoms (C) seems to be most probable.

The reactions of cobalt and copper chlorides also afford powdery complexes, whose IR spectra are analogous to the spectrum of nickel complex **6**; however, no satisfactory elemental analysis data were obtained for them.





M = Ni (**6**), Co (**7**), Cu (**8**)



M = Ni, Co, Cu

The results of IR spectral studies of complexes 6-8 indicate the presence of the C=N group. The electronic spectroscopy data for compounds 6-8 are presented in Table 1.

Complexes 6-8 contain the ligands with the sulfur atoms, which is confirmed by the experiment on alkylation of complex 6: no new compounds were formed upon the addition of MeI excess to a solution of 6 in DMF. According to Refs 10 and 11, the test for the bridging sulfur atom is the ability to alkylate the complex at the sulfur atom: the complexes with the nonbridging thiolate ligands form complexes of the corresponding sulfides upon the addition of alkyl halides, whereas the complexes containing the ligands with the bridging thiolate atoms do not enter into these reactions.

The PM3 optimization of the geometry of the nickel, cobalt, and copper complexes of ligand **2** showed that the singlet species with the tetrahedral environment of the metal ion is most stable for complexes **7** and **8** (Fig. 1, *c*). At the same time, in the case of complex **6**, the geometry of the coordination environment of Ni^{II} represents a strongly flattened tetrahedron (Fig. 1, *b*), which agrees with the electronic spectroscopy data (see Table 1).

To reveal applicability of the synthesized complexes as electroactive catalysts, we studied ligand 1 and complexes 3-8 by the electrochemical methods (CV and rotating disk electrode (RDE)) at a platinum electrode in a DMF solution.

The Ni^{II}-containing metal centers in natural synthases and reductases in the catalytic cycle undergo reduction to Ni^I and subsequent methylation at nickel to form the Ni^{III}-Me organometallic compound, which is transformed, in the case of synthase, into the acetyl compound Ni^{III}-COMe. These organic compounds of nickel(III) are mediators of the Me groups from the sulfur atom of the MeS-CoM or MeCO group to various substrates. To

Com- po- und	Oxidation		Reduction	
	$\overline{E_{1/2}^{\mathrm{ox}}}$	$E_{\rm p}^{\rm ox}$ (reverse cathodic peaks)	$-E_{1/2}^{\text{red}}$	$-E_{\rm p}^{\rm red}$ (reverse anodic peaks)
1	1.28	1.41 (-0.26, 0.40)	0.86	0.88, 1.52 (0.82)
3	_	1.03(-0.30, 0.30)	_	0.84 (0.64)
4	_	0.96 (-0.22, 0.34)	_	0.94 (0.55)
5	1.21	1.30	0.58	0.90 (0.76)
		(-0.40, 0.29)		
6	1.01	1.01	0.83	1.12 (1.05)
7	0.87,	0.91, 1.29	0.78,	0.76
	1.36		1.20	(0.30, 0.61)
8	0.70	0.74 (0.34)	0.78	0.78 (0.64)
9	1.31	1.29	0.80	0.83, 1.25
		(-0.34, 0.40)		(1.08)

Table 2. Electrochemical redox potentials (V) for compounds 1and 3-9 (DMF, Bu_4NBF_4 , Ag/AgCl/KCl (sat.), 20 °C)

use a complex as an electroactive catalyst mediating alkyl groups, it is necessary that the transfer of at least the first electron during reduction would be reversible.

The electrochemical redox potentials of compounds 1 and 3-8 are given in Table 2.

Compounds 1 and 3-5 are oxidized in one irreversible electrochemical step. Two reduction peaks of the decomposition products of the oxidized compounds are observed in the reverse cathodic scan (see Table 2, Figs 2 and 3, peaks *A* and *B*).

The compounds under study can be oxidized and reduced either at the S–S bond or O–X bond (X = H or M). To answer the question at which fragment the oxidation occurs, we carried out an additional electrochemical study of 4,4'-di(benzalimino)ethyl disulfide **9** containing no hydroxyl group. Compound **9** is oxidized in one two-electron irreversible step, and the reverse cathodic scan also exhibits two reduction peaks of the oxidized products, and the peak potentials for compounds **1**, **3–5**, and **9** are very close (see Table 2). Our data indicate



Fig. 2. CV curves for compounds 1 (1) and 9 (2) (DMF, Bu_4NBF_4 , Pt electrode, 10^{-3} mol L⁻¹, 20 °C, *vs*. Ag/AgCl/KCl).



Fig. 3. CV curves for compound 5 (DMF, Bu_4NBF_4 , Pt electrode, 10^{-3} mol L⁻¹, 20 °C, *vs.* Ag/AgCl/KCl).

that these compounds are oxidized *via* the same mechanism, presumably the mechanism presented in Scheme 5.

The first reduction peak of the oxidation products of compounds 1, 3-5, and 9 corresponds, most likely, to the reduction of the radical formed upon the S–S bond cleavage, whereas the second cathodic peak corresponds to the reduction of the R⁺ species.



P are products $R^+ = H^+$, CoCl⁺, NiCl⁺

Scheme 5



Fig. 4. PM3-calculated HOMO (a-c) and LUMO (d-f) for ligand 1 (a, b) and nickel complexes 3 (b, e) and 6 (c, f).

For complex 5, the oxidation, possibly, involves both the disulfide fragment and coordinated chloride anions (this can be indicated by the presence of peak C in Fig. 3).

The compounds are reduced in one quasi-reversible one-electron step forming radical anions that underwent slow cleavage at the sulfur—sulfur bond. This is indicated by the observed reduction peaks of the corresponding S anions (0.46, 0.24, and 0.40 V for the reduction of compounds **1**, **2**, and **4**, respectively).

To confirm the assignment of the electrochemical oxidation and reduction peaks, we calculated the frontier orbitals of ligand 1 and its complexes 3-5 by the PM3 method. The data obtained confirm the conclusions: the lowest unoccupied MO (LUMO) of all the studied compounds are localized at the S–S bond, whereas the highest occupied MO (HOMO) are localized at the S–S bond (for the ligand) or at the S–S bond and coordinated chloride anion (for the complexes). Therefore, it is most probable that the primary electronic changes are localized on the disulfide fragment. The HOMO and LUMO of ligand 1 and complex 3 are shown in Fig. 4.

In the case of complexes 6-8, the oxidation is directed, most likely, to the thiolate fragment, because the potential of the first oxidation peak lies in the region characteristic of organic disulfides¹² (see Table 2). This is also indicated by the results of quantum chemical calculations, according to which the HOMO of all the three complexes are localized mainly on the thiolate fragment of the ligand (see Fig. 4).

The reduction of complexes 6-8, according to the electrochemical data and results of calculations (see

Table 2 and Fig. 4), is directed, most likely, to the imine C=N bond (potential of the first reduction peak lies in the region characteristic of imines¹³).

Thus, the results of the electrochemical study of the complexes ligands 1 and 2 show that their redox processes are localized on the ligand fragments rather than on the metal atoms.

Experimental

¹H NMR spectra were recorded at 25 °C on a Bruker–Evance-400 instrument (400 MHz) in CDCl₃. IR spectra were obtained on a UR-20 instrument in Nujol. Electronic spectra were recorded on a Perkin–Elmer λ -25 instrument.

Electrochemical oxidation and reduction potentials were measured with a PI-50-1.1 potentiostat coupled with a PR-8 programmer. Cyclic voltammograms and waves at the RDE were recorded on a two-coordinate recorder. Tetrabutylammonium perchlorate Bu_4NBF_4 (highest purification grade, 99.8%, Fluka) served as a supporting electrolyte. The electrolyte concentration was 0.05 mol L⁻¹.

2,2⁻**Di(2-hydroxybenzaliminoethyl) disulfide (1).** A solution of potassium hydroxide (0.5 g, 8 mmol) in a minimum amount of boiling ethanol was added to a solution of cystamine (2 g, 8 mmol) in ethanol (10 mL). The reaction mixture was stirred under reflux for 0.5 h. After cooling to ~20 °C, a flaky white precipitate that formed was filtered off. Salicylaldehyde (2.17 g, 1.87 mL, 16 mmol) was added with stirring to the resulting solution. The reaction mixture was stirred for 5 h and cooled to -10 °C. Needle-like yellow crystals that formed were filtered off and washed with a minor amount of ethanol. After drying in air, compound **1** (1.55 g, 49%) was obtained as light yellow crystals, m.p. 76–77 °C. Found (%): C, 59.97; H, 5.44; N, 7.72. C₁₈H₂₀O₂N₂S₂. Calculated (%): C, 60.00; H, 5.56; N, 7.78.

¹H NMR, δ : 13.02 (s, 2 H, OH); 8.40 (s, 2 H, CHN); 7.32 (dt, 2 H, Ar, J = 7.2 Hz); 7.25 (dd, 2 H, Ar, J = 7.6 Hz); 6.96 (d, 2 H, Ar, J = 8.2 Hz); 6.88 (dt, 2 H, Ar, J = 7.4 Hz); 3.94, 3.04 (both t, 4 H each, CH₂, J = 6.65 Hz). IR, v/cm⁻¹: 1635 (C=N); 1580, 1500, 1470, 1380, 1340.

Synthesis of complexes with ligand 1 (general procedure). Compound 1 (1 equiv.) was dissolved in a minimum amount of methanol on heating, and a solution of a metal salt (2 equiv.) in methanol and triethylamine (2 equiv.) were added. The reaction mixture was refluxed for 3-5 h. The crystals that precipitated were filtered off, washed with MeOH and diethyl ether, and dried in air.

[2,2'-Di(2-hydroxybenzaliminoethyl) disulfide]dinuckel(II) dichloride (3). Complex 3 (0.05 g, 42%) was synthesized from compound 1 (0.08 g, 0.2 mmol), NiCl₂·6H₂O (0.11 g, 0.4 mmol), and triethylamine (0.06 mL, 0.05 g, 0.4 mmol). Green powder, m.p. 170 °C (with decomp.). Found (%): C, 39.75; H, 3.33; N, 5.23. $C_{18}H_{18}Cl_2N_2Ni_2O_2S_2$. Calculated (%): C, 39.54; H, 3.32; N, 5.12. IR, v/cm⁻¹: 1620 (C=N); 1545, 1475, 1460, 1380, 1335.

[2,2'-Di(2-hydroxybenzaliminoethyl) disulfide]dicobalt(II) dichloride (4). Complex 4 (0.24 g, 80%) was synthesized from compound 1 (0.2 g, 0.55 mmol), $CoCl_2 \cdot 6H_2O$ (0.26 g, 1.1 mmol), and triethylamine (0.15 mL, 0.11 g, 1.1 mmol). Dark brown powder, m.p. 180 °C (with decomp.). Found (%): C, 39.41; H, 3.57; N, 5.16. $C_{18}H_{18}Cl_2Co_2N_2O_2S_2$. Calculated (%): C, 39.51; H, 3.32; N, 5.12. IR, v/cm⁻¹: 1620 (C=N); 1600, 1545, 1455, 1380, 1350, 1320.

[2,2´-Di(2-hydroxybenzaliminoethyl) disulfide]dicopper(II) dichloride (5). Complex 5 (0.33 g, 96%) was synthesized from compound 1 (0.2 g, 0.55 mmol), $CuCl_2 \cdot 2H_2O$ (0.27 g, 1.1 mmol), and triethylamine (0.15 mL, 0.11 g, 1.1 mmol). Green powder, m.p. 142 °C (with decomp.). Found (%): C, 38.06; H, 3.86; N, 5.46. $C_{18}H_{18}Cl_2Cu_2N_2O_2S_2$. Calculated (%): C, 38.85; H, 3.26; N, 5.03. IR, v/cm⁻¹: 1620 (C=N); 1600, 1545, 1475, 1460, 1400, 1380, 1355, 1340.

Complexes 6–8 (general procedure). Potassium hydroxide (0.098 g, 1.76 mmol) was dissolved in a minimum amount of ethanol on heating and added to a solution of 2-aminoethanethiol hydrochloride (0.2 g, 1.76 mmol) in ethanol (2 mL). The reaction mixture was stirred on heating for 1 h until white flakes of potassium chloride stopped precipitating. The KCl precipitate was separated by filtration. Salicylaldehyde (0.185 mL, 0.22 g, 1.76 mmol) was added to the resulting solution, and in the reactions with metal chlorides triethylamine (0.18 g, 0.24 mL, 1.76 mmol) was additionally added. The reaction mixture was refluxed for 3.5 h. The precipitate that formed was filtered off, washed with diethyl ether, and dried in air.

Bis{2-[(2-thioethyl)iminomethyl]phenoxy}dinickel(II) (6). In the reaction with NiCl₂·6H₂O (0.42 g, 1.76 mmol) the yield of complex **6** was 0.27 g (64%), whereas in the reaction with Ni(OAc)₂·4H₂O (0.44 g, 1.76 mmol) the yield was 0.25 g (52%). Brown powder, m.p. >300 °C. Found (%): C, 44.24; H, 4.06; N, 6.00. C₁₈H₁₈N₂Ni₂O₂S₂. Calculated (%): C, 45.43, H, 3.79; N, 5.89. IR, v/cm⁻¹: 1620 (C=N); 1590, 1520, 1465, 1445, 1400, 1380, 1350, 1310.

Bis{2-[(2-thioethyl)iminomethyl]phenoxy}dicobalt(II) (7). Complex 7 (0.28 g, 64%) was synthesized in the reaction with $Co(OAc)_2 \cdot 4H_2O$ salt (0.44 g, 1.76 mmol). Dark brown powder, m.p. >300 °C. Found (%): C, 44.90; H, 3.92; N, 5.98. $C_{18}H_{18}Co_2N_2O_2S_2$. Calculated (%): C, 45.43; H, 3.79; N, 5.89. IR, v/cm⁻¹: 1635, 1620 (C=N); 1600, 1540, 1470, 1455, 1380, 1350, 1325.

Bis{2-[(2-thioethyl)iminomethyl]phenoxy}dicopper(11) (8). Complex **8** (0.18 g, 42%) was synthesized in the reaction with $Cu(OAc)_2 \cdot H_2O$ (0.35 g, 1.76 mmol). Black powder, m.p. >300 °C. Found (%): C, 44.50; H, 3.75; N, 5.87. $C_{18}H_{18}Cu_2N_2O_2S_2$. Calculated (%): C, 44.52; H, 3.74; N, 5.77. IR, v/cm⁻¹: 1630, 1620 (C=N); 1600, 1540, 1500, 1470, 1455, 1400, 1380, 1355, 1330.

Di(2-benzalimino)diethyl disulfide (9). A solution of potassium hydroxide (0.26 g, 4.6 mmol) in a minimum amount of boiling ethanol was added to a solution of cystamine (2 g, 2.3 mmol) in ethanol (10 mL). The reaction mixture was stirred on heating for 1 h. After the reaction mixture was cooled to ~ 20 °C, the flakes were separated by filtration, benzaldehyde (0.5 g, 0.48 mL, 4.6 mmol) was added with stirring to the resulting solution, and the mixture was stirred for 12 h. The solvent was removed on a rotary evaporator. An oil was formed and added with CHCl₃ (10 mL), and an orange powder that formed was filtered off and dried in air. The yield was 0.3 g (40%). Found (%): C, 65.50; H, 6.05; N, 8.87. C₁₈H₂₀N₂S₂. Calculated (%): C, 65.81; H, 6.14; N, 8.52. ¹H NMR, δ: 8.33 (s, 2 H, HC=N); 8.13 (d, 1 H, Ar, J = 7.4 Hz); 7.91 (d, 1 H, Ar, J = 7.0 Hz); 7.75 (d+t, 4 H, Ar); 7.65 (t, 1 H, Ar, J = 7.4 Hz); 7.56 (t, 1 H, Ar, J = 7.6 Hz); 7.45 (d, 2 H, Ar); 3.97, 3.10 (both t, 4 H each, CH_2 , J = 6.65 Hz).

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