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Synthesis and Structure of the Cobalt(II) Coordination Compounds with *N,N*-Dimethyl-*N*',*N*'-dimethylthiocarbamoylsulfenamide

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Abstract—The $CoLX_2$ complexes were obtained by the reaction of *N*,*N*-dimethyl-*N*',*N*'- dimethylthio-carbamoylsulfenamide (L) with CoX_2 (X = Cl, Br, I, NCS). The complexes were investigated by elemental and X-ray analysis, IR, ^{1}H NMR, and electron spectroscopy, conductometry, magnetochemistry, thermogravimetry. It is found that these compounds are high-spin complexes of pseudotetraedral structure with bidentate coordination of L through the thione sulfur atom and sulfenamide nitrogen atom.

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Interest in thiocarbamoylsulfenamides as polydentate ligand systems is due to the presence of several donor atoms (N, S) in their molecules, capable of binding with the central atom in many ways, with the formation of coordination compounds of various composition and structure. The choice of cobalt(II) as a complexing agent is due to its ability to exist in the compounds with dithiocarbamic acid derivatives in the degree of oxidation II, III, and IV [1]. The need for a comprehensive study of thiocarbamoylsulfenamides and their complexes complexes is connected not only with scientific, but also with practical purposes. It is known [2, 3] that thiocarbamoylsulfenamides are effective accelerators of vulcanization of the compounds based on natural and synthetic rubbers, however they did not find industrial applications because of their low stability. Therefore, it is urgent to study the effect of complexation with transition metal ions on the stability of the resulting compounds and the prospects of their application in industrial processes.

This situation defined the purpose of this work: synthesis, establishment of structure, and investigation of physical and chemical properties of the new coordinaton cobalt(II) compounds with *N*,*N*-dimethyl-*N*',*N*'-dimethylthiocarbamoylsulfenamide (L).

By the reaction of cobalt(II) salts with L complexes **I–IV** were obtained with molar ratio metal: ligand = 1: 1 (Table 1). The compounds are well soluble in acetonitrile, DMF, DMSO, acetone, ethanol, and poorly soluble in chloroform and benzene, almost insoluble in water. It should be noted that complex **III** is unstable: Over time it changes color from green to brown, which is probably due to its oxidation by atmospheric oxygen and the formation of free iodine.

X-ray phase analysis of L and the complexes showed that each compound was characterized by its own set of interplanar distances (*d*, Å) and relative intensities (I/I_0). L: 2.16 (16), 2.49 (22), 2.59 (10), 2.76 (35), 2.8 (33), 2.83 (19), 2.98 (13), 3.12 (33), 3.33 (80), 3.73 (71), 4.59 (53), 4.608 (17), 4.82 (11), 5.23 (99), 5.313 (73), 7.4 (100). [$CoLCl_2$] (**I**): 2.60 (20), 2.84 (26), 2.90 (29), 3.22 (27), 3.39 (22), 3.52 (26), 3.64 (33), 3.70 (21), 3.99 (26), 4.22 (24), 4.56 (31), 4.91 (100), 5.66 (31), 5.97 (39), 7.12 (53), 8.5 (26). [$CoLBr_2$] (**II**): 1.832 (13), 1.888 (14), 1.97 (16), 2.085 (10), 2.205 (11), 2.319 (21), 2.442 (15), 2.58 (12), 2.63 (23), 2.75 (13), 2.866 (44), 2.936 (30), 2.985 (34), 3.133 (34), 3.24 (71), 3.43 (33). [$CoL(NCS)_2$] (**IV**): 1.82 (17), 1.97 (27), 2.03 (21), 2.14 (25), 2.22 (25), 2.36 (21), 2.43 (40), 2.56 (25), 2.75 (30), 2.84 (40), 2.95 (27), 3.01 (27), 3.25 (23), 3.39 (45), 3.58 (21), 3.88 (47).

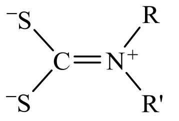
These data point to the chemical idividuality and crystalline nature of the compounds under study.

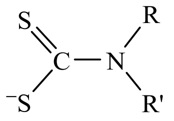
To establish the centers of coordination bond localization, we carried out a comparative analysis of

Table 1. Analytical data of the synthesized complexes

Comp. no.	Found, %				Formula	Calculated, %			
	N	S	Hlg	Co		N	S	Hlg	Co
I	9.66	21.86	24.18	20.11	$C_5H_{12}N_2S_2Cl_2Co$	9.52	21.80	24.11	20.04
II	7.45	16.81	41.79	15.43	$C_5H_{12}N_2S_2Br_2Co$	7.31	16.74	41.72	15.39
III	5.99	14.01	53.29	12.38	$C_5H_{12}N_2S_2I_2Co$	5.87	13.44	53.21	12.35
IV	16.64	37.85	–	17.39	$C_7H_{12}N_4S_4Co$	16.51	37.79	–	17.36

infrared spectra of L and the complexes (Table 2) using the concept of thioamide bands [10–12]. As is known, the structure of the dithiocarbamate ion as a fragment of the L molecule can be represented by three equally probable canonical structures differing by the length and the multiplicity of the C–N bond:


A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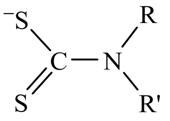

C

Table 2 shows that the thioamide **I** band containing the main contribution of ν(C–N) undergoes the greatest changes. A significant shift of this band to higher frequencies indicates an increase in the multiplicity of the C–N bond and the increasing contribution of polar resonance structure **A**, which clearly indicates the participation of the thione sulfur atom in the coordination with cobalt(II).

Note that the ambident NCS group can be bonded with the complex forming agent through the nitrogen or sulfur atom or through both at once. According to the criterion [13], the presence in the IR spectra of complex **IV** of the absorption bands at 2065, 875 and 475 cm^{-1} assigned to ν(CN), ν(CS), and δ(NCS), respectively, indicates the N-binding of NCS. Basing on the composition of the complexes, as well as considering as the most probable the coordination number of cobalt(II) equal to four, one can assume that the second center of localization of the coordination bond is the sulfenamide nitrogen atom. To test this hypothesis we used the ^{1}H NMR spectroscopy.

In the ^{1}H NMR spectrum of L a singlet (3.10 ppm) is observed corresponding to six protons of two methyl groups at the sulfenamide nitrogen atom. At the same time, the protons of methyl groups at the thiocarbamoyl nitrogen atom give rise to two broad singlets (3.38, 3.14 ppm), due to the restricted rotation with respect to the magnetic anisotropy cone of the C=S bond. Because of deshielding influence of the latter, one methyl group gives a signal at weaker field than another. The presence of magnetically nonequivalent methyl groups confirms the polar nature of C–N bond and equal probability of structures **A**, **B,** and **C**.

In the ^{1}H NMR spectrum of **II** the methyl groups protons at thiocarbamoyl nitrogen atom remain nonequivalent (46.6, 44.4 ppm). By comparison with them the signals of methyl groups at the sulfenamide nitrogen atom are noticeably broader and even more displaced downfield (70 ppm), which clearly indicates its involvement in coordination. Thus, we can conclude that the bidentate ligand is coordinated to cobalt(II) cations through the sulfur atom and sulfenamide nitrogen atom to form five-membered metalocycle. This complex is paramagnetic and its central atom is in the oxidation state +2.

The values of molar conductivity (λ) of the complexes in acetonitrile (Table 3) are lower than those of two-ion electrolytes (120–160 Ω^{-1} cm^2 mol^{-1} [14]), hence they are non-electrolytes. The exception is complex **III** whose solution in acetonitrile is of brown color, while the solutions of other cobalt(II) complexes

Table 2. Main vibrational frequencies (cm^{-1}) in the infrared spectra of compounds

Compound	Tioamide band, ν				
	I	**II**	**III**	**IV**	**V**
L	1500	1250	1155, 1045	980	560
I	1535	1250	1155, 1055	980	575
II	1535	1250	1160, 1055	985	575
III	1535	1250	1155, 1055	990	580
IV	1540	1245	1155, 1055	975	565

Table 3. Parameters of the EAS, the values of molar conductivity in CH_3CN, and effective magnetic moments of compounds at room temperature

Compound	λ_{max}, nm (log ε)	Transition	λ, Ω^{-1} cm^2 mol^{-1}	μ_{eff}, BM
L	345 (1.78)	$n\to\pi^*$	–	–
	277 (3.98)	$n\to\sigma^*$		
	231 (4.07)	$\pi\to\pi^*$		
I	690 (2.46), 595(2.58)	$^4A_2\to{}^4T_1(P)$	92	4.41
	278 (3.89)	$n\to\sigma^*$		
	230 (4.07)	$\pi\to\pi^*$		
II	700 (2.72), 641 (2.52), 625(2.54)	$^4A_2\to{}^4T_1(P)$	99	4.51
	275 (3.94)	$n\to\sigma^*$		
	233 (4.07)	$\pi\to\pi^*$		
III	360 (4.12)	$\sigma_g\to\sigma_u^*$	173	3.87
	292 (4.25)	$\sigma_g\to\sigma_u^*$		
IV	625 (2.26), 570 (2.74)	$^4A_2\to{}^4T_1(P)$	70	4.39
	338 (3.64)	$n\to\pi^*$		
	278 (3.99)	$n\to\sigma^*$		
	230 (4.27)	$\pi\to\pi^*$		

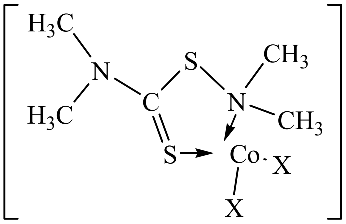
are of blue-green color. Apparently, in the case of **III** iodide ion is oxidized by atmospheric oxygen to free iodine, which is capable to form charge transfer complexes with thiocarbonyl compounds [15]. The presence of the absorption bands with maxima at ~ 360 and ~ 290 nm in the EAS of acetonitrile solution of **III** (Table 3) characteristic of diiodoiodate(I) ion ($\pi_g \to \sigma_u^*$ and $\sigma_g \to \sigma u_g^*$ transitions in the $[I_3]^-$ ion) confirms this assumption.

The electron spectrum of the L contains a band of low intensity at ~345 nm associated with the transition in the excited state on antibonding π-orbital of one of two unshared electrons localized on the thione sulfur atom. The absence of this band in the UV spectra of the complexes clearly indicates the participation of the thione sulfur atom in the coordination. Bands of high intensity at ~277 and ~231 nm in the spectra of the compounds are induced by $n \to \sigma^*$ transitions in the N–C=S group and $\pi \to \pi^*$ transitions from the bonding orbital of the ground state to the orbital with a higher energy in S–C=S group typical for derivatives of dithiocarbamic acid, respectively [1].

In the diffuse reflectance spectra (DRS) of the compounds $CoLX_2$ (see the figure) in the near infrared and visible regions two bands appear, at 5500–7700 and 14200–16900 cm^{-1}, corresponding to $^4A_2 \to {}^4T_1(F)$ and $^4A_2 \to {}^4T_1(P)$ transitions in the tetrahedral cobalt(II) complexes [16]. The width and multiplicity of the DRS bands point to the spin–orbital interaction, vibratonic structure, and distortion of symmetry of the complexes.

Measurement of molar magnetic susceptibility of $CoLX_2$ compounds (Table 3) showed that they are paramagnetic high-spin cobalt(II) complexes ($S = 3/2$). Higher values of μ_{eff} than the pure spin value (3.87 BM) are due to orbital contribution, which is a function of the ligand field and the symmetry of the complexes.

Based on the analysis of the set of experimental data the complexes $CoLX_2$ structure can be represented by **V**:



V

The thermogravimetry (Table 4) revealed that thermal decomposition of the complexes occurs in steps. A feature of their thermal decomposition is the presence of a distinct irreversible exothermic effect at 130–150°C that is not accompanied by changes in the sample weight. At these temperatures the bright-blue complexes are converted to the dark-green insoluble modifications. The explanation of the nature of these processes requires further research. The occurring thermal transformations obviously are accompanied by an energy gain. The final product of thermolysis of the $CoLX_2$ complexes is Co_3O_4 that at heating above 900°C is decomposed to CoO, showing a reversible endothermic effect in the DTA curve, with an insignificant weight loss in the TG curve.

Thus, we first obtained pseudotetrahedric molecular cobalt(II) complexes with *N*,*N*-dimethyl-*N*',*N*'- dimethylthiocarbamoylsulfenamide and characterized them by a set of physicochemical methods. The bidentate ligand in these complexes is coordinated through the thione sulfur atom and sulfenamde nitrogen atom to form five-membered metallocycle.

EXPERIMENTAL

The starting reagents $CoCl_2$, $CoBr_2$, and CoI_2 were obtained by dehydration of $CoCl_2{\cdot}6H_2O$, $CoBr_2{\cdot}6H_2O$, and $CoI_2{\cdot}6H_2O$ along the procedure in [4]. $Co(NCS)_2$ and KI were of analytical grade, I_2, sodium *N*,*N*-dimethyldithiocarbamate and dimethylamine were of pure grade. Organic solvents were purified by standard methods [5].

N,*N*-dimethyl-*N*',*N*'-dimethylthiocarbamoylsulfenamide was prepared by the reaction of sodium *N*,*N*-dimethyldithiocarbamate with dimethylamine by the procedure [6]. The resulting white precipitate was filtered off, washed with water, and dried in air. It was purified by a double crystallization from ethanol. The purity of recrystallized L was monitored by TLC on glass plates with a layer of neutral Al_2O_3, eluent CCl_4–hexane 1:2. Yield 76.8%, mp 51°C. The compound is well soluble in the cold in the diethyl ether, dioxane, acetone, chloroform, benzene, acetonitrile; in methanol, ethanol at heating; in water it is practically insoluble.

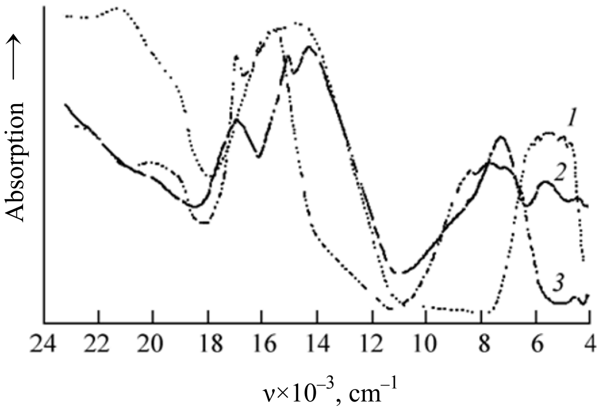
Synthesis of complexes was carried out by mixing anhydrous cobalt(II) salts in diethyl ether ($CoCl_2$ in acetone) with saturated solutions of L in diethyl ether in equimolar amounts at room temperature. The resulting blue (green in the case of CoI_2) precipitates formed were washed with a little diethyl ether and dried in air. Yields 64–83%.

Cobalt in the compounds was determined by complexonometry [7], chlorine, bromine, and sulfur, by the Schoeniger method, and nitrogen, by the Dumas method [8].

The diffractograms of the compounds were obtained on a Dron-3 diffractometer with CoK_α-radiation and Fe-filter. The IR absorption spectra of the samples with KBr tablets were recorded on a Specord 75 IR instrument in the frequency range 400–4000 cm^{-1}. The ^1H NMR spectra of solutions of compounds in $(CD_3)_2CO$ were recorded on a MSL–400 Bruker spectrometer, internal reference TMS. Molar conductivity of the complexes were calculated from the values of the resistivity of 0.001 M solution in CH_3CN measured on a digital measuring unit LCR E7-8 in a glass cell with platinum electrodes coated with platinum black at 25°C. The electron absorption spectra (EAS) of the solutions of compounds in

Table 4. The results of thermal analysis of systems

Compound	Temperature range for TG, °C	t_{max} by DTA, °C	Total weight loss on TG, %
I	75–200	150(↑)	–
	200–280	215(↑)	27
	280–390	335(↓)	37
	390–650	460(↓), 530(↑)	57
	650–870	695(↑), 855(↓)	74
	870–920	870(↑),920(↓)	76
II	50–190	130(↑)	–
	190–290	270(↓)	16
	290–390	360(↑)	32
	390–690	565(↑), 690(↓)	82
	840–940	920(↓)	85
IV	100–180	140(↑)	–
	180–310	235(↓)	25
	500–560	560(↑)	68
	760–810	800(↓)	77
	900–920	910(↓)	79



Diffuse reflectance spectra of complexes (*1*) **I**, (*2*) **II**, and (*3*) **IV**.

CH_3CN were recorded on a Specord UV VIS spectrophotometer in quartz cells with the absorbing layer thickness 1 cm. The Diffuse reflectance spectra (DRS) were recorded on a Perkin-Elmer Lambda 9 UV VIS NIR spectrophotometer in the range 4000-25000 cm^{-1}. The magnetic susceptibility was measured at room temperature by Gouy method, with calibration on $Co[Hg(CNS)_4]$. Diamagnetic corrections were introduced using the increments from [9]. Thermal stability of the compounds was studied on a Paulik-Paulik-Erdey derivatograph in platinum crucibles in the air in the temperature range 20–1000°C, heating at a rate of 10 deg min^{-1}. The DTA and DTG sensitivity was 1/5 of the maximum sensitivity. As a reference was used Al_2O_3.

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