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Local Surrounding of Cobalt(II) in Dithiocarbamate Complexes, Their Magnetic and Spectral Properties

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Abstract—$[Co(S_2CNRR')_2]$ complexes [R = R' = CH_3, C_2H_5, C_3H_7, C_4H_9, or $CH_2C_6H_5$; RR' = $(CH_2)_5$, $(CH_2)_6$, or $(CH_2)_2O(CH_2)_2$] were prepared via interaction of $CoCl_2$ with sodium dithiocarbamates in aqueous medium (pH 6–7). $[Co(S_2CNRR')_2]$ are low-spin compounds (μ_{eff} 2.19–2.45 μ_B) with distorted square-planar geometry of the CoS_4 coordination node. The Co–S bonds length is 2.22–2.26 Å, and the distance between cobalt and carbon atoms is 2.73–2.74 Å.

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Scientific interest to complexes of cobalt with dithiocarbamate anions $RR'NC(S)S^-$ is due to the presence of thioketone and thiol sulfur atoms in those ligands, capable of acting as σ-, π-, or (σ,π)-donor as well as π-acceptor. That enables preparation of widely applicable compounds varying in composition, structure, and oxidation state of the central ion.

In its dithiocarbamate complexes cobalt can be present in +1, +2, +3, and +4 states [1]. Structure, electrochemical, thermal, and other properties of cobalt(III) dithiocarbamates have been discussed in detail in the literature [1–2]; however, similar compounds of cobalt(II) have been less studied. That is due to spontaneous oxidation of cobalt(II) dithiocarbamates into the corresponding cobalt(III) compounds, regardless of the presence of either reducing agent (hydrazine hydrate) or oxidizer (hydrogen peroxide) [2]. In the course of complex formation with diethyl- or pyrrolidinedithiocarbamates in diluted methanol solution cobalt(II) is oxidized to cobalt(III) even in hydrogen atmosphere [3]. Rate of the complexes oxidation in aqueous solution with air oxygen depends on the ligand structure and decreases in the series diethyl- > pyrrolidine- > morpholine- > piperazine-carbodithionate [2]. With bulky substituent(s) present in the ligand, stability of cobalt(II) dithiocarbamates is improved.

So far no one $[Co(S_2CNRR')_2]$ complex has been prepared in the form of a single crystal and studied by means of X-ray diffraction (XRD) analysis. Electronic and spatial structure of such compounds is generally elucidated from IR and electron absorption spectroscopy as well as from magnetochemistry data. It has been suggested that dithiocarbamate ligands are coordinated by cobalt(II) via both sulfur atoms, and the binding is generally symmetric. For most of the $[Co(S_2CNRR')_2]$ complexes the coordination node is considered to be square-planar, whereas to some of them tetrahedral geometry is ascribed [4–5].

Detailed review and analysis of data on dithiocarbamates of transition metals published in 1978–2003 have been given in [1]. Spectral and other properties of cobalt(II) dithiocarbamates reported in the literature are often inconclusive. Even if the $[Co(S_2CNRR')_2]$ complexes do exist, they are easily oxidized; therefore, they should be prepared and processed in strictly anhydrous and deaerated medium.

In this study, we worked out conditions to prepare cobalt(II) dithiocarbamates, determined geometry of their coordination polyhedrons and structural parameters of the nearest surrounding of cobalt(II).

Table 1. Elemental analysis and X-ray diffraction data of cobalt(II) dithiocarbamates **I**–**VIII**

Comp. no.	Found, %			Formula	Calculated, %			Interplanar distance, Å (relative intensity I/I_0, %)
	Co	N	S		Co	N	S	
I	19.76	9.45	43.05	$C_6H_{12}N_2S_4Co$	19.69	99.36	42.84	7.35 (100), 6.79 (49), 5.39 (35), 4.91 (23), 4.66 (25), 4.10 (23), 3.96 (24), 3.70 (15), 3.20 (19), 2.84 (11), 2.67 (13), 2.56 (14), 2.35 (15), 2.23 (15)
II	16.52	7.81	35.91	$C_{10}H_{20}N_2S_4Co$	16.58	77.88	36.08	8.10 (100), 6.70 (42), 6.40 (72), 5.23 (14), 4.97 (11), 4.47 (22), 4.14 (34), 3.92 (10), 3.34 (10), 3.25 (13), 2.95 (10), 2.79 (22), 2.69 (13), 2.36 (8), 2.16 (15), 2.10 (7), 2.04 (10), 1.89 (9)
III	14.39	6.87	31.31	$C_{14}H_{28}N_2S_4Co$	14.32	66.81	31.16	8.65 (100), 7.35 (19), 5.26 (13), 4.91 (22), 4.38 (33), 3.82 (14), 3.32 (11), 2.43 (8)
IV	12.66	6.05	27.28	$C_{18}H_{36}N_2S_4Co$	12.60	55.99	27.42	13.0 (15), 10.5 (100), 8.65 (35), 7.74 (27), 5.89 (17), 5.14 (20), 4.38 (24), 4.26 (17), 4.12 (17), 3.32 (13)
V[a]	9.81	4.68	21.14	$C_{30}H_{28}N_2S_4Co$	99.76	44.64	21.24	
VI	15.46	7.45	33.96	$C_{12}H_{20}N_2S_4Co$	15.53	77.38	33.80	8.02 (100), 5.46 (36), 4.38 (22), 4.03 (11), 2.95 (14)
VII	14.53	6.93	31.31	$C_{14}H_{24}N_2S_4Co$	14.46	66.87	31.47	9.80 (78), 8.32 (67), 7.61 (45), 6.13 (50), 5.20 (100), 4.81 (72), 4.47 (67)
VIII[a]	15.31	7.38	33.60	$C_{10}H_{16}N_2O_2S_4Co$	15.37	77.31	33.45	

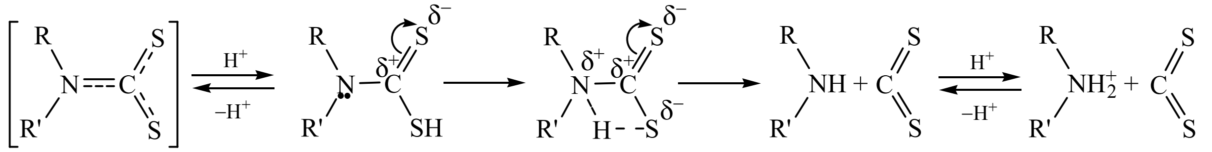
[a] X-ray amorphous.

In order to elucidate the reaction medium effect on the formation of dithiocarbamates of cobalt in different oxidation states, we studied interaction of $CoCl_2$ with sodium dithiocarbamates in water, methanol, ethanol, acetonitrile, and acetone. The solvents were chosen to comply with requirement of high solubility of starting compounds. From elemental analysis data (Table 1), interaction (1) of aqueous solutions of $CoCl_2$ and sodium dithiocarbamates (pH 6–7) in air led to cobalt(II) dithiocarbamates.

$$CoCl_2 + 2RR'NC(S)SNa \rightarrow \underset{\textbf{I–VIII}}{[Co(S_2CNRR')_2]} + 2NaCl, \quad (1)$$

R = R' = CH_3 (**I**), C_2H_5 (**II**), C_3H_7 (**III**), C_4H_9 (**IV**), $CH_2C_6H_5$ (**V**); RR' = $(CH_2)_5$ (**VI**), $(CH_2)_6$ (**VII**), and $(CH_2)_2O(CH_2)_2$ (**VIII**).

The pH conditions was chosen taking into account the formation of $Co(OH)_2$ in alkaline medium and the decomposition of carbamodithioacids into CS_2 and amine in acidic medium [2] [Scheme (2)].



(2)

With organic solvents (methanol, ethanol, acetonitrile, and acetone) instead of water, cobalt(III) dithiocarbamates were isolated.

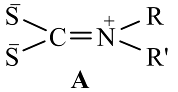
XRD analysis of the prepared cobalt(II) dithiocarbamates (Table 1) showed that compounds **V** and **VIII** were X-ray amorphous, whereas compounds **I**–**IV**, **VI**, and **VII** showed up sets of interplanar spacings (d, Å) and respective relative intensities (I/I_0, %). The compounds did not contain admixtures of cobalt(III) dithiocarbamates as seen from comparison of X-ray diffraction patterns of analogous complexes of cobalt(II) and cobalt(III) [see for example, data of **I** and tris(dimethyldithiocarbamato)cobalt(III) in Fig. 1].

Solid cobalt(II) dithiocarbamates were stable; however, they were easily oxidized with air oxygen to give cobalt(III) dithiocarbamates when dissolved in organic solvents (chloroform, acetone, and others).

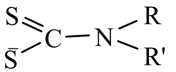
$$3[Co(S_2CNRR')_2] \xrightarrow{O_2,\ H_2O} 2[Co(S_2CNRR')_3] + Co(OH)_2{\cdot}2H_2O.$$

Gravimetric study confirmed that the process was quantitative.

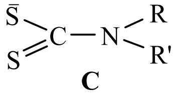
In IR spectra of cobalt(II,III) dithiocarbamates, bands assigned to individual vibrations of C–N, C=S, C–C, and other bonds could be hardly distinguished due to their significant shift (with respect to pure ligands), typical of thioamide-containing compounds. Therefore, the IR spectra were assigned using the "thioamide bands I–V" approach [6]. Bands I (1480–1540 cm^{-1}), IV (960–980 cm^{-1}), and V (530–585 cm^{-1}) are mainly due to ν(C–N), ν(C=S, and δ(NCS), respectively, whereas bands II (1230–1280 cm^{-1}) and III (1120–1160, 1010–1050 cm^{-1}) are assigned to skeletal vibrations with significant contribution of all bonds of thioamide system and its nearest surrounding [6]. Theoretically, dithiocarbamate ion structure can be represented as combination of three equally probable structures **A–C** differing in length and order of C–N bond.



A



B



C

In IR spectra of compounds **I–VIII** and the corresponding cobalt(III) complexes, thioamide band I was observed at 1486–1525 cm^{-1} (Table 2), intermediate between typical bands of ν(C=N) (1640–1690 cm^{-1}) and ν(C–N) (1250–1360 cm^{-1}) vibrations. Increase in the C=N bond order due to mesomeric shift of electron cloud of the NCS_2 towards metal ion suggested high contribution of resonance form **A** into the real dithiocarbamate structure. That symmetric form was realized under condition of bidentate coordination of dithiocarbamate ligands. Stretching of Co–S bond was observed at 359–372 cm^{-1}. The comparison of IR spectra of cobalt(II) and cobalt(III) dithiocarbamates with the same substituents at nitrogen atom in Spectrum 10 software showed that the spectra were identical (correlation coefficient of 0.98–0.99). Hence, geometry parameters of dithiocarbamate ligands estimated for $[Co(S_2CNRR')_3]$ with X-ray diffraction method should be close if not identical. In cobalt(III) dithiocarbamates, average bond lengths were 2.270 Å (Co–S), 1.322 Å (C–N), 1.715 Å (C–S), and 1.475 Å (N–R), seven atoms of the CoS_2CNC_2 group being located almost in the same plane [1]. Dithiocarbamate ligands are considered stereochemically rigid [7] and should not change the conformation upon transformation of cobalt(II) complexes into cobalt(III) ones; only the nearest surrounding of cobalt atom should be changed.

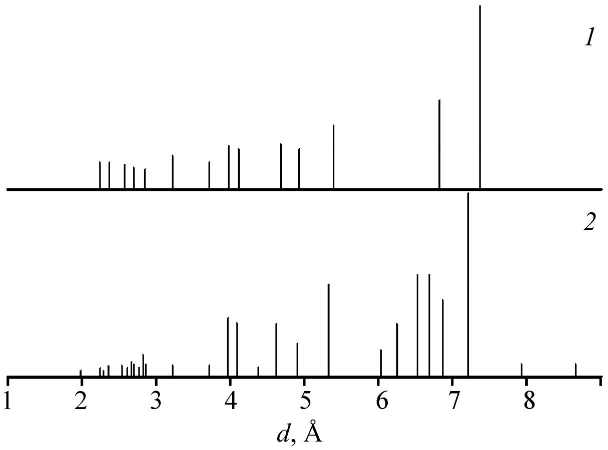


Fig. 1. X-ray diffraction patterns of (*1*) cobalt(II) and (*2*) cobalt(III) dimethyldithiocarbamates.

Effective magnetic moment of compounds **I–VIII** at room temperature was 2.19–2.45 μ_B (Table 2), corresponding to one unpaired electron of low-spin cobalt(II) complexes (*s* of 1/2) with distorted square-planar ligand surrounding. The higher μ_{eff} than the purely spin value (1.73 μ_B) was due to the orbital contribution, the latter being a function of ligand field and the complexes symmetry.

The analysis of diffuse reflection spectra of complexes **I–VIII** revealed that nature of substituents in dithiocarbamate ligand did not much affect the position and shape of the absorption bands; they were similar and close to those of cobalt(II) bis(dibutyldithiocarbamate) (Fig. 2). Three absorption bands in the visible spectral range indicated the D_{2h} symmetry of square-planar cobalt(II) complexes, coinciding with the data of magnetochemical studies. A well defined band with a maximum at 640–653 nm (Table 2) was assigned to *d–d*-transitions $^2B_{1g}\leftarrow{}^2A_g$ ($d_{x^2-y^2}\rightarrow d_{xy}$) and $^2B_{3g}\leftarrow{}^2A_g$ ($d_{xz}\rightarrow d_{xy}$), whereas shoulders at ~490 and ~400 nm corresponded to transitions accompanied with charge transfer from metal to ligand: $^2B_{2u}\leftarrow{}^2A_g$ [$d_{xz}\rightarrow L(\pi^*)$] and $^2B_{3u}\leftarrow{}^2A_g$ [$d_{yz}\rightarrow L(\pi^*)$], respectively [8–9].

The square-planar geometry of cobalt(II) dithiocarbamates **I–VIII** was confirmed by the analysis of the normalized XANES spectra of Co*K* edge of X-ray absorption spectra and their first derivatives. As seen from Fig. 3, the shape and parameters of XANES were close in the cases of all studied compounds, pointing at the similar geometry of cobalt(II) nearest surrounding in these complexes. The only exception was XANES

Table 2. Principal vibration frequencies in IR spectra, *d–d* transitions in diffuse reflectance spectra, and effective magnetic moments at 292.5 K of cobalt(II) dithiocarbamates **I–VIII**

Comp. no.	Thioamide bands, cm^{-1}					ν(Co–S), cm^{-1}	λ_{max}, nm	μ_{eff}, μ_B
	I	II	III	IV	V			
I	1525	1253	1143, 1050	985	580	362	640	2.19
II	1493	1271	1148, 1077	1002	582	362	645	2.30
III	1491	1241	1155, 1101	984	618	362	642	2.31
IV	1494	1290	1149, 1109	983	615	362	645	2.45
V	1495, 1479	1218	1155, 1080	992	560	372	641	2.36
VI	1489	1236	1129, 1020	1004, 995	545	360	651	2.27
VII	1489	1267	1168, 1055	986	560	359	653	2.21
VIII	1486	1232	1111, 1066	1005	550	360	649	2.22

spectrum of cobalt(II) bis(dimethyldithiocarbamate) showing some difference in the range of principal absorption maximum **D**. Fine structure of XANES spectra of compounds **I**–**VIII** around the very absorption edge and above, up to about 50 eV, was primarily due to 1*s* → 4*s* and 1*s* → 4*p* electron transitions along with multielectron (shake-down) ligand–metal transitions (see the features of **B**–**E** edge at Fig. 3). XANES spectra of cobalt(II) dithiocarbamates were rather complex, containing several maxima. Shoulder **C** (assigned to $1s \rightarrow 4p_z$ electron transition, *z* axis being orthogonal to S_4 plane) was especially nicely developed, typical of square-planar complexes. Appearance of pre-edge peak **A** at about 7110 eV was connected with weak quadrupole electron transitions $1s \rightarrow 3d$ as well as with dipole transitions to vacant orbitals formed via *p*–*d* hybridization of metal atomic orbitals. However, such hybridization is strictly forbidden in the cases of centrosymmetric coordination polyhedrons [10], for example, in the cases of octahedral and square-planar coordination of the absorbing atom. In the cases of cobalt(II) dithiocarbamates, the energy, fine structure, and noticeable intensity of the pre-edge peak **A** around 7110 eV indicated the distorted structure of square-planar coordination node CoS_4.

Quantitative parameters of local atomic surrounding of cobalt(II) dithiocarbamates **I–VIII** were elucidated from the analysis of Co*K* edge of their EXAFS spectra. From Fig. 4 it is seen that all Fourier transform modules of EXAFS spectra consisted of the principal peak at *r* of 1.80 Å that was definitely assigned to scattering at the nearest coordination spheres consisting of sulfur atoms of dithiocarbamate ligands, and peak at *r* of 2.34 Å that could be assigned to the carbon atoms nearest to cobalt (taking into account the structure of the S_2CNRR' fragment). Peaks at lower *r* of 1.40 Å did not correspond to any structural feature and appeared due to Fourier transform of the signal and the features of the amplitude function of scattering at sulfur atoms.

Computation of parameters of local atomic surrounding of cobalt(II) in compounds **I–VIII** with suitable choice of models of atomic structure of the coordination node (Table 3) revealed closeness of the corresponding structural parameters in the cases of all the complexes. Four sulfur atoms were located around cobalt(II) at a distance of 2.22–2.26 Å, and two carbon atoms of the S_2CNRR' fragments were found at 2.73–2.74 Å from the metal. The Co–S bonds were

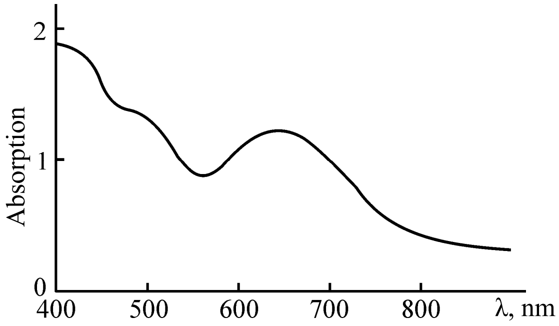


Fig. 2. Diffuse reflectance spectrum of bis(dibutyldithiocarbamato)cobalt(II).

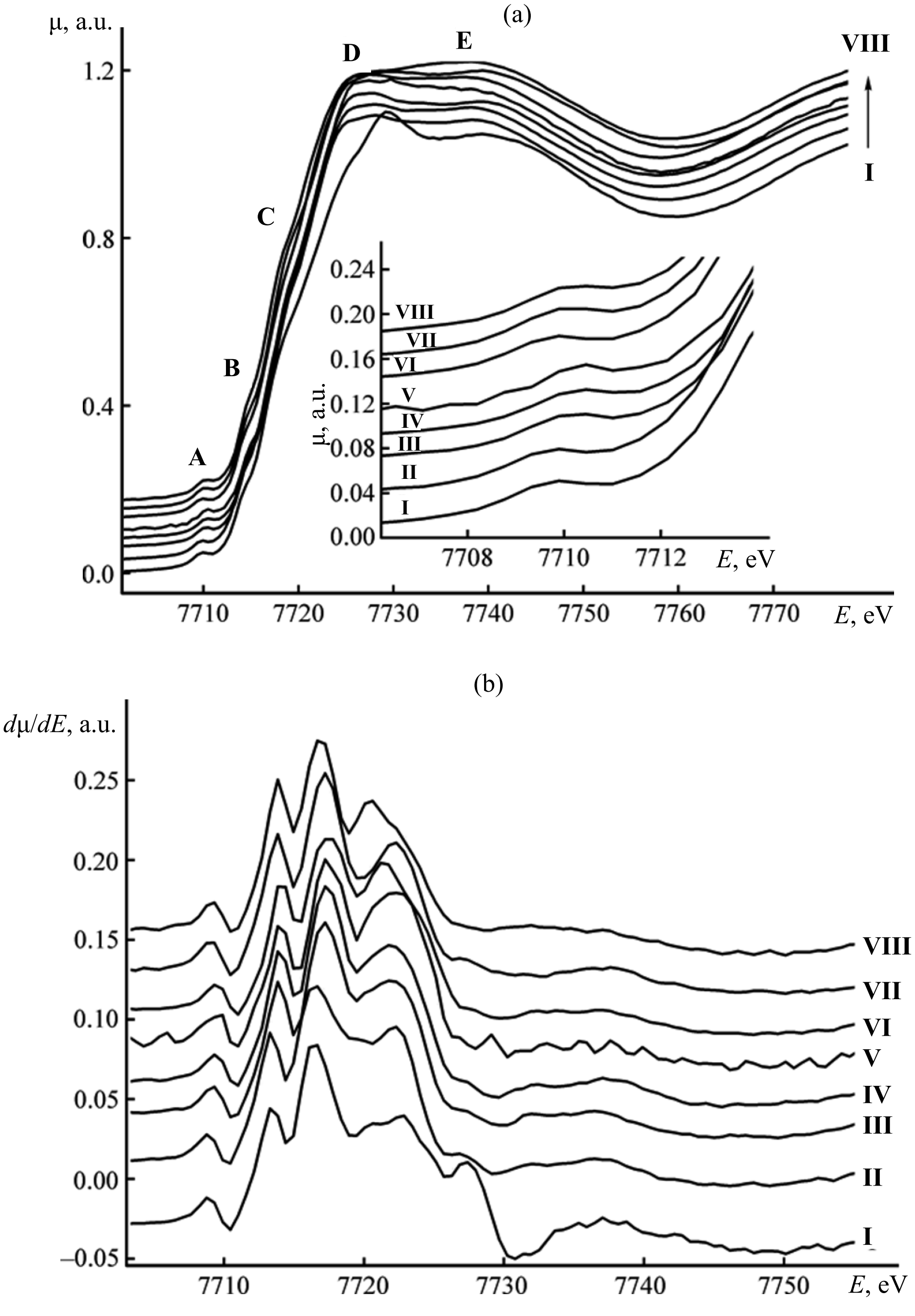


Fig. 3. XANES spectra of Co*K* absorption edges of (a) cobalt(II) dithiocarbamates **I–VIII** and (b) the first derivatives of the corresponding edges. The insert displays pre-edge region.

somewhat shorter than those in cobalt(III) dithiocarbamates (~2.270 Å) [1], even though in general the decrease in the oxidation level of the complex forming ion leads to the elongation of metal–ligand bonds. However, these bonds are shorter in the case of square-planar complexes as compared to octahedral ones. As the decrease of cobalt oxidation level from +3 to +2 was accompanied by geometry change from octahedral into distorted square-planar, these two factors compensated one another.

To conclude, $[Co(S_2CNRR')_2]$ should be prepared by interaction of cobalt(II) with sodium dithiocarbamates in water, whereas $[Co(S_2CNRR')_3]$ should

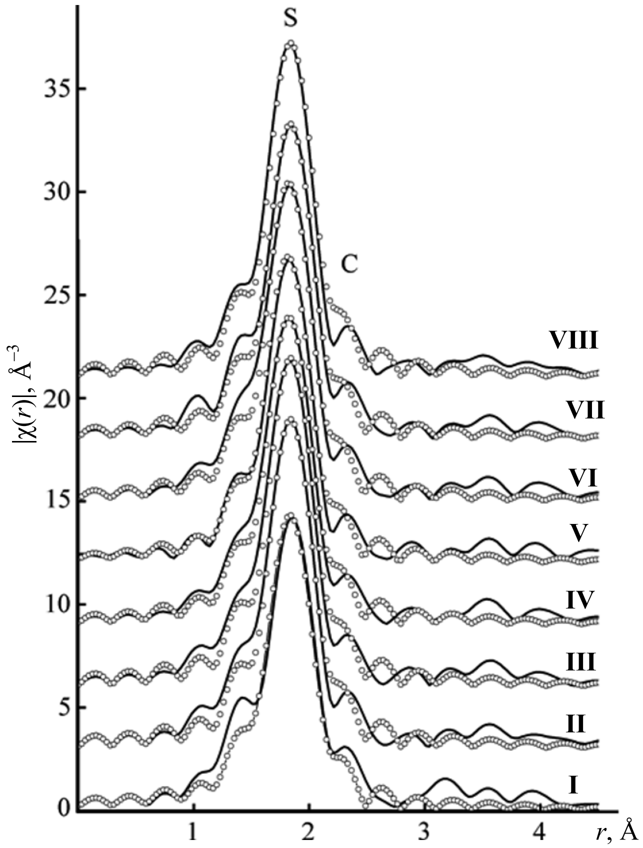


Fig. 4. Modules of Fourier transform of EXAFS spectra of Co*K* absorption edges of cobalt(II) dithiocarbamates **I**–**VIII** (experimental data in solid lines, calculated data in circles).

be synthesized in methanol, ethanol, acetonitrile, or acetone. Solid cobalt(II) dithiocarbamates were stable in air, being oxidized upon dissolution in organic solvents. [Co(S$_2$CNRR')$_2$] were low-spin compounds (μ_{eff} of 2.19–2.45 μ_B) with distorted square-planar geometry of the CoS$_4$ coordination node. Length of Co–S and Co–C bonds were 2.22–2.26 and 2.73–2.74 Å, respectively.

EXPERIMENTAL

IR spectra (KBr, 350–4000 cm^{-1}) were registered using the Frontier FT-IR (Perkin Elmer) spectrometer. X-ray diffraction patterns were recorded with Dron-3 diffractometer (CoK_α radiation, Fe filter). Diffusion reflectance spectra (solid sample, 400–900 nm) were obtained using the Specord M 42/M 400 spectrophotometer equipped with the 45/0 diffuse reflectance attachment.

Magnetic susceptibility of the complexes was measured by the Faraday method at 292.5 K. Diamagnetic correction was made according to the increments [11].

The following chemicals were used: sodium *N,N*-dimethyl- and *N,N*-diethyldithiocarbamates, CoCl$_2$·6H$_2$O (pure for analysis grade), CS$_2$, NaOH (pure grade), dipropyl-, dibutyl-, and dibenzylamines, piperidine, hexamethylenimine, and morpholine (Merck, synthesis grade). Carbon disulfide, amines, and organic solvents were purified using standard procedures. Sodium dithiocarbamates were obtained via reaction of equimolar amounts of the corresponding amine, CS$_2$, and NaOH in cooled (–5 to 0°C) aqueous solution [2].

Cobalt(II) dithiocarbamates. Solution of HCl was added to 0.2 mol of the corresponding sodium

Table 3. Structural parameters of cobalt(II) dithiocarbamates elucidated from multi-sphere fitting of EXAFS data (*R* is an interatomic distance, *N* is a coordination number, σ^2 is rhe Debye–Waller factor, Q is a fitting quality function, approximation range is shown in the footnote)

Comp. no.	*N*	*R*, Å	σ^2, Å^2	Atom	Q, %[a]
I	2	2.24	0.0039	S	1.6
	2	2.25	0.0039	S	
	2	2.74	0.0039	C	
II	2	2.24	0.0030	S	1.5
	2	2.25	0.0030	S	
	2	2.74	0.0030	C	
III	2	2.24	0.0031	S	1.7
	2	2.26	0.0031	S	
	2	2.74	0.0031	C	
IV	2	2.23	0.0035	S	1.4
	2	2.25	0.0035	S	
	2	2.74	0.0035	C	
V	2	2.22	0.0036	S	1.5
	2	2.24	0.0036	S	
	2	2.73	0.0036	C	
VI	2	2.23	0.0033	S	1.7
	2	2.24	0.0033	S	
	1	2.73	0.0033	C	
VII	2	2.24	0.0034	S	1.4
	2	2.25	0.0034	S	
	2	2.74	0.0034	C	
VIII	2	2.24	0.0030	S	1.6
	2	2.25	0.0030	S	
	2	2.74	0.0030	C	

[a] *r*-Space, Δr of 1.0–2.1 Å.

dithiocarbamate in 100 mL of water till pH 6–7 at stirring; then, 0.1 mol of $CoCl_2{\cdot}6H_2O$ in 100 mL of water was added. The so formed green precipitate was filtered off, washed with water till no chloride ions was detected, and dried over freshly calcined $CaCl_2$ in vacuum dessicator.

The content of cobalt in the prepared compounds was determined by chelatometric titration, sulfur contend was determined by the Shoeniger method, nitrogen content was determined by the Dumas method.

X-ray Co*K* absorption edge of solid cobalt(II) dithiocarbamates was determined in the absorption mode using EXAFS spectrometer (station of Structural Material Science, Kurchatov Synchrotron Center, Moscow). X-ray source was electron beam with energy of 2.5 GeV at a current of 80–100 mA. The double-crystal Si(111) monochromator was applied to X-ray beam. The registered spectra were processed by standard procedures of background subtraction, normalization to the *K*-edge jump, and subtraction of the atomic absorption μ_0 [12] followed by Fourier transform of the processed EXAFS (χ)-spectra at photoelectrons wave vector k of 3.0 to 13.0 $Å^{-1}$ with the k^3 weight function. The so obtained modules of Fourier transform represented the pseudo-radial distribution of atoms in the nearest coordination spheres around the absorbing cobalt atom, radii of coordination spheres estimated accurate within phase corrections. Ionization energy threshold E_0 was chosen according to the maximum of the first derivative of *K*-edge and was further adjusted. Accurate structural parameters of the nearest surrounding of cobalt(II) ions were determined via nonlinear fitting of the calculated EXAFS signal to the experimental signal extracted from the full EXAFS spectrum via Fourier filtration of Fourier transform modulus. The nonlinear fitting was performed using IFFEFIT-1.2.11 software package [13]. The phases and amplitudes of the photoelectron wave diffusion required to construct the model spectrum were calculated using FEFF7 software [14] and atomic coordinates of the compounds of similar structure. The minimized fitting quality function Q was calculated according to Eq. (3).

$$Q\,(\%) = \{\Sigma[k\chi_{\mathrm{exp}}(k) - k\chi_{\mathrm{th}}(k)]^2/\Sigma[k\chi_{\mathrm{exp}}(k)]^2\}\times 100, \qquad (3)$$

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