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## Synthesis, Spectral, Magnetic, and Thermal Properties of Ge(IV) Tetrachlorocobaltates Complexes with 2-Hydroxyarylaldehydes Pyridinoyl(aminobenzoyl) Hydrazones

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**Abstract**—The interaction in the GeCl<sub>4</sub>–nicotinoyl(isonicotinoyl, 2-, or 4-aminobenzoyl) hydrazone of 2-hydroxybenz(2-hydroxy-1-naphth)aldehyde (H<sub>2</sub>L)–CoCl<sub>2</sub>–methanol systems has resulted in the formation of  $[Ge(L \cdot H)_2][CoCl_4] \cdot nCH_3OH$  complexes with germanium chelates  $[Ge(L \cdot H)_2]^{2+}$  protonated at the exo chelate nitrogen atom (N<sub>Py</sub> or NH<sub>2</sub>) as the cation. The type of electrolytic dissociation and character of thermolysis of the complexes have been revealed. Spectral, thermal, and magnetic properties of the complexes have been studied.

Keywords: germanium(IV) complex, nicotinoyl hydrazone, pyridinoyl hydrazone, cobalt coordination compound

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Heteronuclear complexes of metals possess a variety of structures as well as utilitarian magnetic, catalytic, and spectral properties [1]. Methods of their preparation are based on targeted molecular design (using mononuclear complexes with vacant donor atoms capable of binding with other metals and acting as bridging ligand as building blocks), or self-assembly processes.

Regardless of the synthesis method, the ligands should contain enough donor atoms to bind at least two different metals and should be able to trigger the specific ionic forms of mononuclear complexes and form stable cationic-anionic structures with different metals on their basis.

We have earlier prepared germanium(IV) complexes with  $\beta$ -,  $\gamma$ -pyridinoyl, and 2-aminobenzoyl hydrazones of 2-hydroxybenzaldehyde ( $\beta$ -H<sub>2</sub>Ns,  $\gamma$ -H<sub>2</sub>Is, and 2-NH<sub>2</sub>-H<sub>2</sub>Bs, respectively) and 2-hydroxynaphthalene-1-carbaldehyde ( $\beta$ -H<sub>2</sub>Nnf,  $\gamma$ -H<sub>2</sub>Inf, and 2-NH<sub>2</sub>-H<sub>2</sub>Bnf, respectively): [Ge(Ns·HCl)<sub>2</sub>], [Ge(Is·HCl)<sub>2</sub>] [2, 3], [Ge(2-NH<sub>2</sub>-Bs·HCl)<sub>2</sub>] [4, 5], [Ge(Nnf·HCl)<sub>2</sub>], [Ge(Inf·HCl)<sub>2</sub>] [6], [Ge(2-NH<sub>2</sub>-Bnf·HCl)<sub>2</sub>] [7]. and comprehensively characterized them by means of a set of physical and chemical methods including X-ray diffraction analysis. The mentioned ligands are bound with germanium in the hydrochloride form, revealing tridentate cyclic coordination via  $O_{C-O}$ ,  $N_{CH=N}$ , and  $O_{Ph}$  atoms. This form is obtained due to the protonation of vacant exo chelate nitrogen atoms  $N_{Py}$  and  $NH_2$  groups of hydrazide part of the hydrazones.

Hydrogen and metal atoms in a solution generally compete for the binding with the donor atoms. Therefore, we have suggested to use the above-mentioned compounds as a basis for preparation of complexes with different metals, in particular with cobalt(II).

We attempted two methods of the complexes synthesis: the interaction of previously prepared abovelisted germanium(IV) complexes with cobalt chloride in methanol and chemical self-assembly in the GeCl<sub>4</sub>– hydrazone–CoCl<sub>2</sub>–methanol system. We established the structure of the products and studied their magnetic, thermal, and spectral properties.

Using the first approach, we failed to isolate the heterometal complexes regardless of the synthesis



conditions [bubbling of gaseous hydrogen chloride, varying of the Ge(IV) complex with hydrazone–CoCl<sub>2</sub> molar ratio between 4 : 1 and 1 : 4, and altering the solvent volume, temperature, and the nature of the exo chelate atom of the ligand ( $N_{py}$ ,  $NH_2$ )]. That could be likely due to the steric hindrance impeding the formation of the heterometal (Ge, Co) complexes via the bridging by nitrogen atoms of bulky mononuclear germanium(IV) complexes.

The second synthetic route afforded complexes **1–6** in high yields from the GeCl<sub>4</sub>–pyridinoyl (or aminobenzoyl) hydrazone of 2-hydroxybenzaldehyde (or 2-hydroxy-1-naphthaldehyde)–CoCl<sub>2</sub>–CH<sub>3</sub>OH systems, if the conditions (see above) were properly chosen, especially when the solvent volume was sufficient to avoid intermediate crystallization of germanium(IV) complexes. The elemental analysis data showed that the Ge : Co : hydrazone : Cl molar ratio equaled 1 : 1 : 2 : 4 in the products irrespectively of composition of hydrazone.

Nicotinoyl and isonicotinoyl hydrazones of 2-hydroxybenzaldehyde ( $H_2Ns$ ,  $H_2Is$ ) and 2-hydroxynaphthalene-1-carbaldehyde ( $H_2Nnf$ ,  $H_2Inf$ ) as well as 2- and 4-aminobenzoyl hydrazones of 2-hydroxybenzaldehyde (2-NH<sub>2</sub>-, 4-NH<sub>2</sub>-H<sub>2</sub>Bs) were prepared as described elsewhere [5, 6, 8] according to Scheme 1.

Compounds 1–6 were crystalline substances, readily soluble in DMF and DMSO (decomposing within 24 h), moderately soluble in methanol (decomposing) and acetonitrile, and insoluble in acetone, nitrobenzene, and chloroform. The measurement of electroconductivity of freshly prepared solutions of complexes 1–6 in DMF revealed that they were electrolytes consisting of two ions ( $\lambda$  60–75  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>) [9]. The complexes decomposed gradually with crystallization of germanium(IV) compounds: [Ge(Ns)<sub>2</sub>], [Ge(Is)<sub>2</sub>], [Ge(Nnf)<sub>2</sub>], [Ge(Inf)<sub>2</sub>] [5], [Ge(2-NH<sub>2</sub>-Bs)<sub>2</sub>], [Ge(4-NH<sub>2</sub>-Bs)<sub>2</sub>] [4]. The same compounds (non-electrolytes) were isolated in quantitative yield after treatment of complexes 1-6 with aqueous methanol at heating.

Products of stage-by-stage thermolysis of complexes 1–6 were identified by means of thermal gravimetry (TG), differential thermal gravimetry (DTG), and differential thermal analysis (DTA). The first stage of complexes 1–6 thermolysis was marked by endothermal effect at 80–160°C and was accompanied by a mass loss corresponding to elimination of one (1– 4) or two (5, 6) moles of CH<sub>3</sub>OH (Table 1). The desolvation was further confirmed by isothermal treatment of the complexes at 120 (2, 4) or 90°C (1, 5). The residue contained 18.80 (1), 18.79 (2), 16.65 (4), and 18.20 (5) wt % of chlorine, corresponding to desolvated complexes 1 (2), 4, and 5 (calculated Cl, %: 18.82, 16.62, and 18.16%, respectively).

Analysis of the TG, DTG, and DTA data revealed that thermal decomposition of the complexes occurred in four stages (Table 1). The onset temperature of the first stage was determined by the composition of the hydrazide fragment of the ligand. For nicotinoyl hydrazone, a single endothermal effect was observed with a maximum at 290°C (1, 3), whereas for isonicotinoyl and aminobenzoyl hydrazones two endothermal effects were observed at 220–260 and  $300-330^{\circ}C$  (2, 4–6).

The Ge–Co–hydrazone–Cl molar ratio of 1 : 1 : 2 : 2 was found for the products of isothermal treatment of the complexes at 220°C. Since  $\Delta m \approx \Delta m(TG) \approx \Delta m_{theor}$ (–2HCl), that stage was assigned to elimination of two moles of HCl, as confirmed by the reactions of the evolving gas with AgNO<sub>3</sub> solution (presence of chloride) and KI solution (absence of Cl<sub>2</sub>).

At further heating, the complexes were stable up to  $480-500^{\circ}C$  (1-4) or  $390-400^{\circ}C$  (5, 6), their deeper thermolysis (up to  $740-890^{\circ}C$ ) being accompanied by exothermal effects assigned to decomposition and oxidation of organic part of the molecule (stages 2-4).

	Je i se i				
Comp. no.	Temperature range (TG)	$(t_{\max}, °C)\uparrow\downarrow (DTA)$	Δ <i>m</i> (TG), %	$\Delta m_{\text{calc}}, \%$	Assignment
1	80–120	100↓	5.0	4.07	-CH <sub>3</sub> OH
	220-320	290↓	7.5	7.28	-2HC1
	500-520	520↑	37.5		
	520–590	570↑	12.5		
	590-750	740↑	7.5		
2	100–130	120↓	5.5	4.07	-CH <sub>3</sub> OH
	160–340	250↓; 330↓	8.2	7.28	-2HC1
	480–540	520†; 540†	28.0		
	540-770	610↑	18.0		
	770-870	840↑	12.0		
3	80–130	120↓	3.5	3.6	-CH <sub>3</sub> OH
	130–320	290↓	8.3	8.23	-2HC1
	480–520	470↑; 520↑	33.3		
	520-600	560†; 580†	13.3		
	600–840	810↑	8.3		
4	80–160	150↓	4.0	3.6	-CH <sub>3</sub> OH
	220-310	260↓; 300↓	8.0	8.23	-2HC1
	480–550	520↑	42.0		
	550-640	560↑	16.0		
	640–790	770↑	8.0		
5	70–110	90↓	8.3	7.57	-2CH <sub>3</sub> OH
	140–310	220↓; 310↓	7.5	8.62	-2HC1
	390–670	650↑	31.7		
	670-860	800↑; 840↑	35.0		
	860–970	890↑	8.3		
6	70–110	90↓	6.6	7.57	-2CH <sub>3</sub> OH
	210-340	250↓; 310↓	10.0	8.62	-2HC1
	400–550	500↑	28.3		
	550-710	580↑	26.7		
	710–910	840↑	15.0		

Table 1. Study of thermal stability of complexes 1–6

In view of the elemental analysis, electroconductivity, and thermogravimetry data, the following formulas were suggested for the prepared complexes:  $[Ge(Ns\cdotH)_2][CoCl_4]\cdot CH_3OH$  (1),  $[Ge(Is\cdotH)_2][CoCl_4]\cdot CH_3OH$  (2),  $[Ge(Nnf\cdotH)_2][CoCl_4]\cdot CH_3OH$  (3),  $[Ge(Inf\cdotH)_2][CoCl_4]\cdot CH_3OH$  (4),  $[Ge(NH_2-Bs\cdotH)_2]\cdot$   $[CoCl_4]$ ·2CH<sub>3</sub>OH, where 2-NH<sub>2</sub>- (5), 4-NH<sub>2</sub>- (6). Further comprehensive studies confirmed their validity.

IR spectra of complexes 1-6 were assigned by analogy with those of the corresponding germanium(IV) complexes, [Ge(Inf·HCl)<sub>2</sub>] and [Ge(2-NH<sub>2</sub>-Bs·HCl)<sub>2</sub>];

Compound	v(>C=N- N=C<)	v(C=C) <sub>ring</sub>	δ(NCO)	v(N–N)	δ(PyH) [δ(NH <sub>3</sub> <sup>+</sup> ]	v(Ge–O)	v(Ge←N)
[Ge(Inf·HCl) <sub>2</sub> ]	1604	1583	1549	1035	418, 1020	658	616
1	1608		1548	1034	415, 998	674	616
2	1607		1547	1033	417, 1003	683	614
3	1606	1600	1549	1034	420, 1010	683	615
4	1603	1597	1548	1074	420, 1004	679	617
[Ge(2-NH <sub>2</sub> -Bs·HCl) <sub>2</sub> ]	1602	1580	1551	1035	[1623]	688	620
5	1608	1580	1550	1033	[1620]	686	619
6	1610	1581	1551	1033	[1623]	687	620

Table 2. IR spectroscopy data (cm<sup>-1</sup>) of mononuclear complexes of germanium(IV) and compounds 1-6

structures of the latter have been earlier elucidated by X-ray diffraction analysis [5, 6] (Table 2). Coordination unit of germanium typical of mononuclear Ge(IV) compounds was retained in complexes **1–6**, as indicated by the absence of the v(OH), v(NH), and v(C=O) bands (observed in the spectra of starting hydrazones at 3430–3420, 3260–3190, and 1680–1665 cm<sup>-1</sup>); the presence of the band of oxyazine (N=C–O) group stretching vibrations at 1547–1550 cm<sup>-1</sup> [10] instead of the  $\delta$ (NH) band in the spectra of hydrazones (1570–1560 cm<sup>-1</sup>); and the appearance of the v(Ge–O) and v(Ge<N) bands at ~680 and 620 cm<sup>-1</sup> evidencing the ligands coordination via nitrogen atoms of azomethine group and oxygen atoms of oxyazine and hydroxy groups [3–6].

At the same time, the spectra of compounds 1–4 contained a strong band of skeletal vibrations of the >C=N-N=C< fragment at 1603–1608 cm<sup>-1</sup>, pointing at delocalization of the C=N bonds, similarly to [Ge(Inf·HCl)<sub>2</sub>] [6] owing to the formation of enol form of the ligand. Frequencies of the pyridine ring vibrations in those compounds were by 10–12 cm<sup>-1</sup> higher than those in the corresponding hydrazones (400 and 997–1000 cm<sup>-1</sup>) confirming the protonation of the exo chelate nitrogen atoms [3, 6, 8].

The spectra of complexes **5**, **6** additionally contained a  $\delta(NH_3^+)$  band [4, 11] at 1608–1623 cm<sup>-1</sup>, evidencing the protonation of the amino group of the hydrazide fragment. That was also confirmed by the appearance of the  $v_{as/s}(NH)$  bands of the  $NH_3^+$  group at 3054–3050 cm<sup>-1</sup> [4, 11].

The v(N–N) band at  $\approx 1035 \text{ cm}^{-1}$  in the spectra of the prepared complexes (except for compound 4) was

practically identical to that of the parent hydrazones  $(1027-1030 \text{ cm}^{-1})$  thus confirming the localization of the N–N bond found by means of X-ray diffraction analysis for [Ge(Inf·HCl)] and [Ge(2-NH<sub>2</sub>-Bs·HCl)<sub>2</sub>].

The coordination polyhedrons of cobalt(II) in complexes 1-4 were determined using diffuse reflectance spectroscopy and effective magnetic moment  $(\mu_{eff})$  data (Table 3). Visible and near-IR regions of the diffuse reflectance spectra of the complexes contained two broad bands with the multiplet structure and energy independent of the hydrazone composition (Table 3). The  ${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}(F)$  and  ${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}(P)$  electron transitions evidenced the tetrahedral structure of the [CoCl<sub>4</sub>]<sup>2-</sup> polyhedron [12, 13]. That was also confirmed by the  $\mu_{eff}$  values (4.01–4.38  $\mu_B$  at room temperature, Table 3) corresponding to the high-spin state of cobalt(II). The measured  $\mu_{eff}$  values exceeded those for the purely spin character (3.87  $\mu_B$ ). That was due to the spin-orbital interaction leading to the mixing of the ground state <sup>4</sup>A<sub>2</sub> with the excited magnetic state, the latter being relatively low in energy for tetrahedral Co(II) complexes [14].

The similar nearest surrounding of germanium and cobalt ions in complexes 1-6 was confirmed by analysis of XANES spectra of *K*-edges of Co and Ge. Indeed, as shown in Fig. 1, the shape and parameters of XANES of *K*-edges of Co and Ge as well as their first derivatives were close for the studied compounds.

The shape of the *K*-edge of Ge was determined by the dipole electron transition  $1s \rightarrow 4p$  corresponding to the main maximum C of the absorption spectrum. Maxima D and E were determined by the nearest surrounding of the absorbing germanium atom. The



Fig. 1. XANES spectra of K-edges of absorption of Ge for complexes 1, 2, 4-6 (a) and the corresponding first derivatives of the edges (b).

presence of a narrow strong peak C of the *K*-edge of Ge and a single narrow maximum of the first derivative of the edge pointed at the highly symmetrical octahedral surrounding of germanium atoms in the studied compounds. Since the 3*d* atomic orbital of Ge was fully occupied, a noticeable hybridization in those compounds was impossible, as confirmed by the absence of the pre-edge structure.

In contrast to K-edge of Ge, XANES of K-edges of Co (Fig. 2) contained strong pre-edge peaks A at 7711.5 eV, corresponding to the  $1s \rightarrow 4d$  electron transitions. These transitions were restricted by the selection rules; therefore, the transition probability was mainly determined by the *p*-*d*-hybridization of the metal atomic orbitals. The latter was most efficient for the complexes containing no inversion center with respect to the metal. The presence of strong pre-edge structure A in XANES of *K*-edges of the Co complexes and additional maxima B at the edge as well as splitting of the first derivative was typical of tetrahedral surrounding of cobalt ions.

Parameters of local atomic surrounding of germanium and cobalt ions in the complexes were elucidated by analysis of EXAFS of Co and Ge *K*-edges of X-ray absorption spectra. Figures 3 and 4 display the Fourier transform magnitudes (FTM) of

EXAFS of both edges in the studied complexes, and parameters of the nearest surrounding of the metal ions are collected in Tables 4 and 5.

From the data in Fig. 3 it is seen that FTM of EXAFS of *K*-edges of Ge for the studied samples contained a major peak, r 1.45-1.48 Å, and the peaks with lower magnitude at larger r. The major peak for the studied samples corresponded to the scattering of photoelectron wave at the six nearest atoms of nitrogen and oxygen of the ligands, constituting the first coordination sphere. The first coordination sphere was fitted by two spheres; since the difference in the scattering amplitudes of nitrogen and oxygen was similar, it was impossible to separate their contributions. The thus obtained parameters of the first

Table 3. Electron transitions energy and effective magneticmoments of complexes 1–4

Comp. no.	Electron trar			
	$v_2 - {}^4A_{2g} \rightarrow {}^4T_{1g}(F)$	$_2 \xrightarrow{4} A_{2g} \xrightarrow{4} T_{1g}(F) $ $\nu_3 \xrightarrow{4} A_{2g} \xrightarrow{4} T_{1g}(P)$		
1	6095–4937	15954–14384	4.38	
2	6096–4889	15895–14289	4.24	
3	6098–4902	15896-14400	4.14	
4	6096–4866	15890–14471	4.01	



Fig. 2. XANES spectra of *K*-edges of absorption of Co for complexes 1, 2, 4-6 (a) and the corresponding first derivatives of the edges (b).

coordination sphere for the studied samples were close. The second peak in FTM was assigned to the distance to the second coordination sphere constituted by carbon atoms of the ligand.

The FTM of EXAFS of *K*-edges of Co contained a single main peak, r 1.79–1.83 Å, its magnitude being close for the studied samples (Fig. 4). The local atomic surrounding coincided well with the model assuming surrounding of cobalt by four chlorine atoms. The Co…Cl distance was identical for the studied samples (within the determination accuracy 0.02 Å).

The results of EXAFS analysis were in good correspondence with XANES data for those compounds and confirmed the stated identical local sur-



Fig. 3. FTM of EXAFS of *K*-edges of absorption of Ge for complexes 1, 2, 4–6 [(circles) for theory, (solid line) for experiment].

rounding of the metal atoms in compounds 1-6 (Scheme 2).

In summary, the conditions of self-assembly of the reactants in the presence of sufficient amount of hydrogen chloride formed in the reaction favored the

RUSSIAN JOURNAL OF GENERAL CHEMISTRY Vol. 87 No. 1 2017

FTM. a. u.

Cl

formation of tetrachlorocobaltates(II) containing the corresponding mononuclear germanium complexes with the ligand protonated at the exo chelate nitrogen atom ( $N_{Py}$ . or  $NH_2$ ) as the cation.

## **EXPERIMENTAL**

Diffuse reflectance spectra were registered using a Lambda-9 spectrophotometer (Perkin-Elmer), using MgO ( $\beta$ MgO 100%) as the reference. IR absorption spectra (4000–400 cm<sup>-1</sup>, KBr pellets) of the ligands and the complexes were recorded using a Shimadzu FTIR-8400S spectrometer.

Cobalt content was determined by complexometric titration [15]; germanium content was determined by potentiometric titration [16] and atomic emission spectroscopy with inductively coupled plasma (a Perkin Elmer Optima 2000 DV instrument). Carbon, hydrogen, and nitrogen content was determined using a Flash EA 1112 CHN-analyzer; chlorine content was determined using Schöniger method [17].

Thermogravimetric studies were performed using a Q-derivatograph of the Paulik–Paulik–Erdey system (heating in air, 20–1000°C at 10 deg/min rate, specimen mass 100 mg, open platinum crucible, annealed alumina as a reference). The solvate composition of the complexes was determined by isothermal treatment of the specimens at temperature corresponding to onset of the respective stage found by means of DTA (TG) analysis, followed by elemental analysis of the thermolysis products.

Specific resistance of  $10^{-3}$  mol/L solutions of compounds in DMF was determined using an Ekonomiks– ekspert digital device, the electrolyte type was determined from the reference tables [9].

Specific magnetic susceptibility of complexes 1–4 in the solid state at room temperature was determined by relative Faraday method in 9 kOe magnetic field with Hg[Co(CNS)<sub>4</sub>] as the reference. The molar magnetic susceptibility ( $\chi_M$ ) was determined correcting for the atoms diamagnetism via the additive Pascal scheme [18]. Effective magnetic moment was calculated using the following equation:

$$\mu_{\rm eff} = \sqrt{\left(\frac{3k}{N}\mu_{\rm B}\right)\chi T} \approx \sqrt{8\chi T,} \qquad (1)$$

with k, the Boltzmann constant; N, the Avogadro number;  $\mu_B$ , Bohr's magneton.

Fig. 4. FTM of EXAFS of *K*-edges of Co absorption for complexes 1, 2, 4–6 [(circles) for theory, (solid line) for experiment].

X-ray *K*-edges of absorption of solid Ge and Co complexes were obtained in the transmission mode of EXAFS spectrometer ("Structural Material Science" station, Kurchatov Synchrotron Center, Moscow). Energy of the electron beam (source of X-ray synchrotron radiation) was 2.5 GeV at a current of 80–

**Table 4.** Parameters of local atomic surrounding of germanium atoms in complexes 1, 2, 4–6 determined by multisphere fitting of EXAFS data of *K*-edges of Ge absorption<sup>a</sup>

Comp. no.	Ν	r, Å	$\sigma^2$ , Å <sup>2</sup>	Atom	$Q^{\mathrm{b}}, \%$
1	4 2 2	1.88 1.94 2.70	0.0033 0.0033 0.0033	O/N O/N C	0.5
2	4 2 2	1.88 1.96 2.70	0.0028 0.0028 0.0028	O/N O/N C	0.4
4	4 2 2	1.87 1.93 2.69	0.0028 0.0028 0.0028	O/N O/N C	1.6
5	4 2 2	1.88 1.94 2.70	0.0033 0.0033 0.0033	O/N O/N C	0.5
6	4 2 2	1.86 2.01 2.68	0.0028 0.0028 0.0028	O/N O/N C	2.2

<sup>a</sup> r, interatomic distance; N, coordination number;  $σ^2$ , Debye–Waller factor, Q, goodness of fit function. <sup>b</sup>  $\Delta r = 1.032-1.874$  Å.

100 mA. The X-ray radiation was monochromatized using a double-crystal Si(111) monochromator. A solid specimen of the complex was placed between thin Lavsan films. X-ray absorption spectra were processed via conventional procedures [19] including background correction, normalization by the K-edge jump, separation of atomic absorption  $\mu_0$ , and Fourier transformation of the obtained EXAFS ( $\chi$ )-spectra in the photoelectrons wave vector range of k 3.0 to 13.0 Å<sup>-1</sup> with cubic weight function  $k^3$ . The so determined Fourier transform magnitudes (FTM) were pseudo radial functions of atoms distribution around the absorbing atoms (cobalt and germanium) accounting to the phase corrections. The threshold ionization energy  $E_0$  was chosen from the maximum of the first derivative of the *K*-edge and then varied during fitting.

Precise structural parameters of nearest surrounding of cobalt and germanium atoms in compounds 1, 2, 4– 6 were determined by means of nonlinear fitting of the respective coordination spheres parameters until coincidence of the calculated EXAFS signal and that extracted from the full EXAFS spectrum by Fourier filtration, as implemented in IFFEFIT-1.2.11 software package [20]. Phases and amplitudes of the photoelectron wave required for calculation of the model spectrum were determined using FEFF7 software [21]

**Table 5.** Parameters of local atomic surrounding of cobalt ions in complexes 1, 2, 4–6 determined by multisphere fitting of EXAFS data of *K*-edges of Co absorption<sup>a</sup>

Comp. no.	Ν	<i>r</i> , Å	$\sigma^2$ , Å <sup>2</sup>	Atom	$Q^{\mathrm{b}}$ , %
1	4	2.27	0.0042	Cl	0.07
2	4	2.26	0.0040	Cl	0.04
4	4	2.26	0.0042	Cl	0.2
5	4	2.25	0.0055	Cl	0.04
6	3.2	2.23	0.0055	Cl	2.2

*r*, interatomic distance; *N*, coordination number;  $\sigma$ , Debye–Waller factor; *Q*, goodness of fit function. <sup>b</sup>  $\Delta r = 1.194-2.1384$  Å.

and atomic coordinates for the structurally similar compounds elucidated by X-ray diffraction [5, 6].

Number of the parameters varied during the multisphere fitting never exceeded the number of independent parameters  $N_{ind}$  that could be reliably determined from the experimental EXAFS spectrum within the given  $\Delta k$  and  $\Delta r$  ranges:

$$N_{\rm ind} = (2\Delta r \Delta k/\pi) + 1, \qquad (2)$$

with  $\Delta k$ , analyzed range of EXAFS spectrum in the photoelectron wave vector space;  $\Delta r$ , region of the *R*-space taken for Fourier filtration.

The fitting procedure presumed minimization of the goodness of fit function *Q*:

$$Q(\%) = \frac{\sum [k\chi_{\exp}(k) - k\chi_{th}(k)]^2}{\sum [k\chi_{\exp}(k)]^2} \times 100\%.$$
 (3)

Germanium(IV) chloride (specially pure grade, d 1.89 g/cm<sup>3</sup>) and organic solvents of (specially pure grade) were used. Cobalt(II) chloride was obtained via dehydration of the crystal hydrate  $CoCl_2 \cdot 6H_2O$  (specially pure grade) at 140°C.

Purity of nicotinoyl and isonicotinoyl hydrazones of 2-hydroxybenzaldehyde (H<sub>2</sub>Ns, H<sub>2</sub>Is) and 2-hydroxynaphthalene-1-carbaldehyde (H<sub>2</sub>Nnf, H<sub>2</sub>Inf) as well as 2- and 4-aminobenzoyl hydrazones of 2-hydroxybenzaldehyde (2-NH<sub>2</sub>-, 4-NH<sub>2</sub>-H<sub>2</sub>Bs) was monitored by TLC on Silufol UV-254 plates using 1 : 10 chloroform–acetone (H<sub>2</sub>Ns, H<sub>2</sub>Is, 2-NH<sub>2</sub>-H<sub>2</sub>Bs) and 20 : 1 chloroform–methanol (H<sub>2</sub>Nnf, H<sub>2</sub>Inf, 4-NH<sub>2</sub>-H<sub>2</sub>Bs) mixtures as eluents. The prepared compounds were identified by their melting points.



 $\beta$ -NH<sup>+</sup> (1),  $\gamma$ -NH<sup>+</sup> (2),  $\beta$ -NH<sup>+</sup> (3),  $\gamma$ -NH<sup>+</sup> (4), 2-NH<sup>+</sup><sub>3</sub> (5), 4-NH<sup>+</sup><sub>3</sub> (6).

**Preparation of complexes 1–6** (general procedure). To a hot solution of  $2 \times 10^{-3}$  mol of a ligand in 15 (2-NH<sub>2</sub>-H<sub>2</sub>Bs, 4-NH<sub>2</sub>-H<sub>2</sub>Bs, H<sub>2</sub>Ns), 75 (H<sub>2</sub>Nnf, H<sub>2</sub>Inf), or 20 mL (H<sub>2</sub>Is) of methanol was added at stirring 0.24 mL of GeCl<sub>4</sub>. The obtained solution was kept during 10 min at 50°C, and then a solution of  $2 \times 10^{-3}$  mol of cobalt(II) chloride in methanol was added. In the case of complexes **3** and **4**, the formed precipitate was separated after cooling the mixture to ambient temperature. For isolation of other complexes, the solution was additionally kept at about 50°C during 10 min and left for crystallization. The precipitate was separated, washed with anhydrous methanol (2×5 mL), and dried at 80°C to a constant mass. Yield 73–85%.

**Complexes 1, 2.** Found, %: C 41.14, 41.17; H 3.06, 3.08; Co 7.54, 7.49; Cl 18.10, 18.07; Ge 9.20, 9.21; N 10.71, 10.74. C<sub>27</sub>H<sub>24</sub>Cl<sub>4</sub>CoGeN<sub>6</sub>O<sub>5</sub>. Calculated, %: C

41.11; H 3.04; Co 7.62; Cl 18.08; Ge 9.24; N 10.69. *M* 788.

**Complexes 3, 4.** Found, %: C 47.45, 47.35; H 3.18, 3.19; Co 6.61, 6.70; CI 16.05, 16.04; Ge 8.20, 8.19; N 9.44, 9.52.  $C_{35}H_{28}Cl_4CoGeN_6O_5$ . Calculated, %: C 47.40; H 3.16; Co 6.65; CI 16.04; Ge 8.20; N 9.49. *M* 886.

**Complexes 5, 6.** Found, %: C 42.58, 42.57; H 3.80, 3.78; Co 6.72, 6.99; Cl 16.80, 16.79; Ge 8.60, 8.56; N 9.95, 9.97.  $C_{30}H_{32}Cl_4CoGeN_6O_6$ . Calculated, %: C 42.55; H 3.78; Co 7.09; Cl 16.79; Ge 8.59; N 9.93. *M* 846.

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## REFERENCES

- Garnovskii, A.D., Vasil'chenko, I.S., and Garnovskii, D.A., Sovremennye aspekty sinteza metallokompleksov. Osnovnye ligandy i metody (Modern Aspects of the Synthesis of Metal Complexes. Basic Ligands and Methods), Rostov-on-Don: LaPO, 2000, p. 354.
- 2. Seifullina, I.I., Shmatkova, N.V., and Starikova, Z.A., *Russ. J. Inorg. Chem.*, 2005, vol. 50, no. 11, p. 1676.
- Seifullina, I.I., Shmatkova, N.V., and Starikova, Z.A., *Russ. J. Inorg. Chem.*, 2004, vol. 49, no. 3, p. 352.
- 4. Shmatkova, N.V., Seifullina, I.I., and Tkachenko, V.N., *Vopr. Khim. Khim. Tekhnol.*, 2004, no. 6, p. 33.
- 5. Seifullina, I.I., Shmatkova, N.V., and Starikova, Z.A., *Russ. J. Inorg. Chem.*, 2005, vol. 50, no. 7, p. 992.
- Seifullina, I.I., Shmatkova, N.V., Shishkin, O.V., and Zubatyuk, R.I., *Russ. J. Inorg. Chem.*, 2007, vol. 52, no. 4, p. 486. doi 10.1134/S0036023607040055
- 7. Shmatkova, N.V., Seifullina, I.I., and Verbetskaya, T.G., *Vest. ONU, Ser. Khim.*, 2004, vol. 9, no. 4, p. 5.
- Seifullina, I.I., Shmatkova, N.V., and Starikova, Z.A., J. Coord. Chem., 2015, vol. 41, no. 5, p. 259. doi 10.7868/S0132344X15050072
- 9. Geary, W.J., Coord. Chem. Rev., 1971, no. 7, p. 81.
- 10. Aggarwal, R.C., Singh, N.K., and Singh, R.P., Inorg.

Chem., 1981, vol. 20, p. 2794. doi 10.1021/ic50223a012

- Nakamoto, K., *Infra-Red Spectra of Inorganic and Coordination Compounds*, New York: John Willey and Sons, 1970.
- 12. Liver, A.B.P., *Inorganic Electronic Spectroscopy*, Amsterdam: Elsevier, 1984.
- 13. Zelentsov, V.V. and Bogdanov, A.P., *Zh. Neorg. Khim.*, 1976, vol. 21, no. 8, p. 2003.
- 14. Drago, R., *Fizicheskie metody v khimii* (Methods in Physical Chemistry), Moscow: Mir, 1981, p. 452.
- Shvarcenbakh, G. and Flashka, G., Kompleksonometricheskoe titrovanie (Complexometric Titration), Moscow: Khimiya, 1970, p. 360.
- Nazarenko, V.V., Analiticheskaya khimiya germaniya (Analytical Chemistry of Germanium), Moscow: Nauka, 1973, p. 116.
- 17. Cheng, F.W., *Microchem. J.*, 1959, vol. 24, no. 6, p. 989. doi 10.1016/0026-265X(59)90085-2
- Rakitin, Yu.V. and Kalinnikov, V.T., *Sovremennaya* magnetokhimiya (Modern Magnetochemistry), St. Petersburg: Nauka, 1994, p. 276.
- Kochubei, D.I., Babanov, Yu.A., and Zamaraev, K.I., *Rentgenospektral'nyi metod izucheniya struktury amorfnykh tel: EXAFS-spektroskopiya* (X-Ray Spectral Method for Studying the Structure of Amorphous Solids: EXAFS-Spectroscopy), Novosibirsk: Nauka, Sib. Otd., 1988, p. 306.
- Newville, M., J. Synchrotron Rad., 2001, no. 8, p. 96. doi 10.1107/S0909049500016290
- Zabinski, S.I., Rehr, J.J., Ankudinov, A., and Alber, R.C., *Phys. Rev.*, 1995, vol. 52, p. 2995. doi 10.1103/ PhysRevB.52.2995