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Complexation of *d*-Metal Glycinates and Glycylglycinates with 4-Phenylthiosemicarbazide

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Abstract—The complexation of cobalt(III), nickel(II), copper(II), and zinc(II) glycinates and glycylglycinates with 4-phenylthiosemicarbazide was studied.

Mixed-ligand 3*d*-metal complexes containing glycine recently attracted much researchers' attention [1–4]. The complexation of 3*d*-metal glycinates and glycylglycinates with thiosemicarbazide was studied in [5]; the complexes were isolated and characterized. Here we report on the complexation of Co(II), Ni(II), Cu(II), and Zn(II) glycinates and glycylglycinates with a substituted thiosemicarbazide, 4-phenylthiosemicarbazide.

Chemical analysis shows that cobalt(III) glycylglycinate and glycinate form with thiosemicarbazide and 4-phenylthiosemicarbazide the compounds of similar stoichiometry: cobalt : deprotonated thiosemicarbazide : amino acid residue = 1 : 2 : 1; the only difference is that the glycylglycinate complex with unsubstituted thiosemicarbazide is hydrated. Apparently, with Co(III) the deprotonation of thiosemicarbazides is the only way to avoid steric hindrance that would arise in the coordination of three neutral thiosemicarbazide molecules and binding of counterions neutralizing the charge of the complex.

Nickel(II) and copper(II) glycylglycinates and glycinates form with 4-phenylthiosemicarbazide 1 : 2 complexes; the similar complex is formed with Zn(II) glycylglycinate. In this respect, the pattern is different from that observed with unsubstituted thiosemicarbazide. As shown in [5], unsubstituted thiosemicarbazide forms with Ni(II) glycylglycinate and glycinate the same complex with deprotonated thiosemicarbazide, containing no amino acid fragments. With Cu(II) glycylglycinate, thiosemicarbazide gives a 1 : 2 complex in which one of the coordinated thiosemicarbazide molecules is deprotonated. With Cu(II) glycinate, thiosemicarbazide forms a compound containing one deprotonated semicarbazide ligand and one glycinate anion. With Zn(II), we obtained thiosemicarbazide complexes neither with glycylglycinate nor with glycinate, whereas 4-phenylthiosemicarbazide forms a complex with Zn(II) glycylglycinate but does not form a complex with Zn(II) glycinate.

Thus, we isolated the following coordination compounds with 4-phenylthiosemicarbazide: $CoL_2(HGG)$ (**I**), $Ni(HL)_2(HGG)_2$ (**II**), $Cu(HL)_2GG$ (**III**), $Zn(HL)_2 \cdot GG$ (**IV**), $CoL_2(Gly)$ (**V**), $Ni(HL)_2(Gly)_2$ (**VI**), and $Cu(HL)_2(Gly)_2$ (**VII**) (HL is 4-phenylthiosemicarbazide; H_2GG, glycylglycine; and HGly, glycine).

With Cr(III), we failed to isolate pure products of the reactions of glycylglycinate and glycinate with 4-phenylthiosemicarbazide. Apparently, the reaction products formed as mixtures with the starting compounds, and these mixtures could not be separated because of poor solubility of the components. With Fe(III) and Mn(II), the reactions were accompanied by redox transformation with decomposition of the ligands.

The X-ray diffraction patterns show that the isolated complexes are individual compounds. Below we giev as an example the calculated interplanar spacings (d, Å) and reflection intensities (I/I_0) for the starting copper(II) glycylglycinate $Cu(GG) \cdot 3H_2O$, complex **III** obtained from it, starting nickel(II) glycinate, and complex **VI** obtained from it.

$Cu(GG) \cdot 3H_2O$: 8.111 (25); 5.56 (16); 2.776 (100); 1.970 (63); 1.61 (22); 1.25 (25).

Complex **III**: 3.858 (100); 3.230 (90); 2.594 (40); 1.544 (45); 1.527 (35).

$Ni(Gly)_2 \cdot 2H_2O$: 6.566 (8); 3.133 (6); 3.126 (25); 2.832 (100); 2.200 (11); 1.992 (25); 1.624 (7); 1.409 (8); 1.259 (12).

Complex **VI**: 11.790 (100); 6.175 (16); 5.493 (21); 5.155 (34); 4.647 (11); 4.126 (44); 3.938 (25); 3.565 (51); 3.317 (15); 2.808 (12); 2.524 (11); 1.992 (7).

For all the complexes **I**–**VII**, the thioamide II band [4-phenylthiosemicarbazide (HL), 1285 cm^{-1}; complexes, 1310–1350 cm^{-1}] is shifted toward higher frequencies without changes in the intensity. The frequency of the thioamide **IV** band (HL, 738 cm^{-1}; complexes, 692–705 cm^{-1}) decreases. The thioamide **I** band (HL, 1522 cm^{-1}; complexes, 1532–1546 cm^{-1}) is shifted toward higher frequencies and decreases in the intensity. For the thioamide III bands (HL, 972 and 914 cm^{-1}; complexes, 945–995 and 901–975 cm^{-1}), the decrease in the intensity is still more pronounced. Such trends are typical of bidentate *S*,*N*-coordination of the ligand [6].

Since the thioamide IV band is virtually exclusively due to ν(CS) vibrations, a decrease in its frequency is associated with a decrease in the multiplicity of the C–S bond and characterizes the strength of the M–S bond. Hence, apparently, the stronger the decrease in the thioamide IV frequency, the stronger the metal–sulfur bond in the complex cation. Thus, the strength of the metal–thiosemicarbazide bond can be quantitatively characterized by Δν(thioamide IV). Comparison of this parameter for complexes of 3*d*-metal glycinates and glycylglycinates with unsubstituted thiosemicarbazide and with 4-phenylthiosemicarbazide of similar compositions shows that Δν(thioamide IV) for the complexes with the unsubstituted ligand is larger than for those with the phenyl derivative. Thus, the phenyl substituent appreciably decreases the strength of the metal–thiosemicarbazide bond. This trend may be caused by the electron-withdrawing effect of the phenyl substituent on the S atom in the ligand molecule.

The thioamide IV band clearly depends on the metal cation. For both glycinate and glycylglycinate complexes of 4-phenylthiosemicarbazide, Δν(thioamide IV) decreases in the order $Cu^{2+} > Ni^{2+} \approx Co^{3+} > Zn^{2+}$. This series coincides with that observed previously with the complexes of unsibstituted thiosemicarbazide and with published data on stabilities of sulfides, Dithizonates, and thiourea complexes [7].

Analysis of a large set of data on Δν(thioamide IV) for complexes of unsubstituted thiosemicarbazide containing various anions [8] shows that the strength of the metal–thiosemicarbazide bond depends on the strength of the metal–acido ligand bond: The stronger the bond with the acido ligand, the weaker the bond with thiosemicarbazide. For the unsubstituted thiosemicarbazide, the strength of the metal–ligand bond is higher in glycylglycinates than in glycinates. The same trend is preserved with 4-phenylthiosemicarbazide. Hence, glycinate forms stronger bonds with the metals than glycylglycinate.

Like other amino acids, glycine forms chelates with metal ions, coordinating through the deprotonated carboxy group and the donor amino group. In the vibration spectra of amino acids and their salts, the most informative are the stretching vibration frequencies of the carboxy group. These frequencies are the most sensitive to the strength of the metal–oxygen interaction [9]. As the extent of the nonequivalence of the C–O bonds increases, the difference between the ν_{as}(CO) and ν_s(CO) frequencies should increase. The $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ frequencies are, respectively, 1598 and 1408 cm^{-1} for $Co(Gly)_3 \cdot 2H_2O$, 1595 and 1400 cm^{-1} for $Ni(Gly)_2 \cdot 2H_2O$, and 1608 and 1402 cm^{-1} for $Cu(Gly)_2 \cdot H_2O$; for the complexes of glycinates with 4-phenylthiosemicarbazide, these frequencies are within the ranges 1595–1605 and 1400–1450 cm^{-1}. For the complex $CoL_2(Gly)$, $\Delta\nu(COO^-)$ is somewhat larger than for the initial glycinate; for $Ni(HL)_2(Gly)_2$, it is appreciably smaller, and for $Cu(HL)_2(Gly)_2$, slightly smaller than for the initial glycinates. This fact suggests that, in the Co(III) complex, the glycinate anion remains in the inner coordination sphere of the complex and preserves its initial bidentate coordination; in the Ni(II) complex, the glycinate anion is displaced from the inner sphere; and in the Cu(II) complex, the glycinate anion remains in the inner sphere but becomes monodentate. The assumption that $\Delta\nu(COO^-)$ decreases on displacement of the anion from the inner sphere can be confirmed as follows. Previously [10, 11] we prepared coordination compounds of Ni(II) carboxylates with unsubstituted thiosemicarbazide and of Cu(II) carboxylates with 1-phenylthiosemicarbazide. For the compounds that were sufficiently soluble, we measured the molar electrolytic conductivity in DMF. We found that only the complex of nickel(II) phthalate with thiosemicarbazide was an electrolyte, and specifically for this complex $\Delta\nu(COO^-)$ decreased, whereas for the nonelectrolytes it increased by 0 to 125 cm^{-1}. For the glycylglycinate anions, we could not reveal a correlation between $\Delta\nu(COO^-)$ and coordination mode (inner or outer sphere), because of the lack of "pure" ν_{as}(CO) band; however, the similarity of the stoichiometry, diffuse reflection spectra, and thermal properties suggests that the glycylglycinate complexes obey the same relationships as the glycinate complexes.

The absorption bands of the glycylglycinate anion in the IR spectra were assigned according to [12]. The IR spectra of complexes of glycylglycinates with 4-phenylthiosemicarbazide contain no ν(C=O) absorption bands at 1700–1710 cm^{-1}, characteristic of the nondissociated carboxy groups. The bands at 1660–1590 cm^{-1} are due to amide I + $\delta(NH_2)$ + $\nu_{as}(COO^-)$ vibrations; at 1440–1405 cm^{-1}, to amide II vibrations; and at 1407–1378 cm^{-1}, to $\nu_s(COO^-)$ vibrations. For the starting glycylglycinates, they are observed, respectively, at 1614, 1440, and 1392 cm^{-1} for $NaCo(GG)_2 \cdot 2H_2O$; at 1606, 1440, and 1394 cm^{-1} for $Ni(HGG)_2 \cdot 2H_2O$; at 1641, 1629, 1405, and 1378 cm^{-1}

for $Cu(GG)\cdot 3H_2O$; and at 1660, 1610, 1440, and 1395 cm^{-1} for $Zn(HGG)_2\cdot 2H_2O$. The complexity of the structures of even the initial glycylglycinates containing no thiosemicarbazide prevents accurate empirical assignment of the bands, especially of those below 1400 cm^{-1}. Strong hydrogen bonds in peptides complicate interpretation of the band shifts upon metal coordination, because of the concomitant changes in the extent and nature of hydrogen bonding. The potential donor atoms of the coordinated dipeptides are the terminal NH_2 group, one or both oxygen atoms of the carboxy group, or oxygen or nitrogen atom of the peptide group. The stretching and bending vibration bands of the N–H bonds are poorly informative for interpretation of the bonding, as such bonds are present both in 4-phenylthiosemicarbazide and in glycylglycine.

The diffuse reflection spectra (Table 1) suggest the octahedral structure for the Co(III) compounds, the *cis*-distorted octahedral structure for the Cu(II) compounds, and the tetrahedral structure for the Ni(II) compounds [13]. For each metal, the diffuse reflection spectra of the glycylglycinate and glycinate complexes are similar in the shape and position of bands. The temperatures at which the 4-phenylthiosemicarbazide complexes start to decompose are also close for the complexes of a given metal with both anions (Table 2). Apparently, this may be due to the fact that the first step of the thermolysis involves dissociation of the metal–4-phenylthiosemicarbazide bonds. The DTA curves of the majority of complexes exhibit exoeffects only, except the first effect for **IV** and the second effect for **VII**, which are endothermic. This fact distinguishes the 4-phenylthiosemicarbazide complexes of 3*d* metal with the examined anions from the related compounds with unsubstituted thiosemicarbazide, which always showed one or several endoeffects in the DTA curves. This distinction is apparently associated with the high heat of combustion of the benzene ring present in the ligand molecule.

Table 1. Diffuse reflection spectra of complexes of 3*d*-metal glycinates and glycylglycinates with 4-phenylthiosemicarbazide

Comp. no.	λ_{max}, nm	Comp. no.	λ_{max}, nm	Assignment
I	330	**V**	300	$^1A_{1g} > {}^1T_2$
	410		410	$^1A_{1g} > {}^1T_1$
II	580	**VI**	584	$^3T_1 > {}^3T_1(P)$
	2116		2116	$^3T_1 > {}^3A_2$
III	1100	**VII**	700, 1136	

Table 2. Thermogravimetric data for complexes of 3*d*-metal glycinates and glycylglycinates with 4-phenylthiosemicarbazide

Comp. no.	Exoeffects		Total weight loss, %
	T, °C	Δ*m*, %	
I	110–260 (170)	31.0	63.3
	260–435 (370)	16.6	
II	200–280 (250)	33.5	46.8
III	100–200 (150)	13.5	42.0
	200–290 (225)	22.3	
IV[a]	175–205	7.4	50.3
	350–410 (390)	4.1	
V	105–210 (175)	20.1	60.9
	210–380 (250)	24.7	
	380–450 (430)	5.2	
VI	235–285 (270)	30.4	75.6
	285–440 (400)	20.9	
	450–520 (500)	8.4	
VII[b]	95–200 (135)	18.0	48.4
	255–350 (300)	12.0	

[a] Endoeffect: 75–175 (105)°C, Δ*m* 19.9%.
[b] Endoeffect: 200–255 (230)°C, Δ*m* 16.3%.

Our results suggest that the interaction in the examined systems follows Eqs. (1)–(7):

$$\mathrm{NaCo(GG)_2 + 2HL \longrightarrow \underset{\textbf{I}}{CoL_2(HGG)} + NaHGG} \quad (1)$$

$$\mathrm{Ni(HGG)_2 + 2HL \longrightarrow \underset{\textbf{II}}{Ni(HL)_2(HGG)_2}}, \quad (2)$$

$$\mathrm{Cu(GG) + 2HL \longrightarrow \underset{\textbf{III}}{Cu(HL)_2GG}}, \quad (3)$$

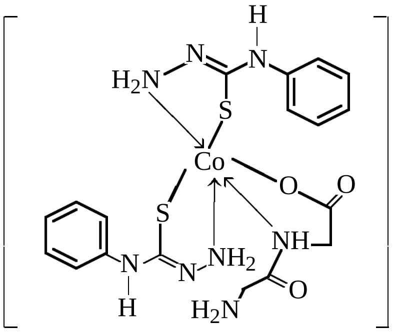
$$\mathrm{Zn(HGG)_2 + 2\ HL \longrightarrow \underset{\textbf{IV}}{Zn(HL)_2GG} + H_2GG}, \quad (4)$$

$$\mathrm{Co(Gly)_3 + 2HL \longrightarrow \underset{\textbf{V}}{CoL_2(Gly)} + 2HGly}, \quad (5)$$

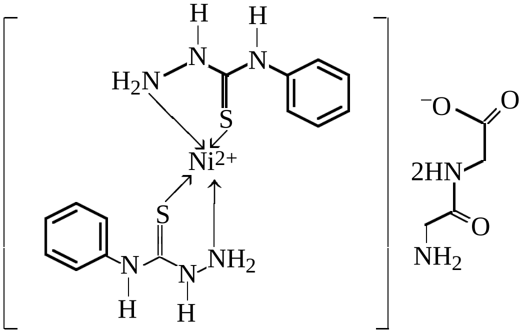
$$\mathrm{Ni(Gly)_2 + 2HL \longrightarrow \underset{\textbf{VI}}{Ni(HL)_2(Gly)_2}}, \quad (6)$$

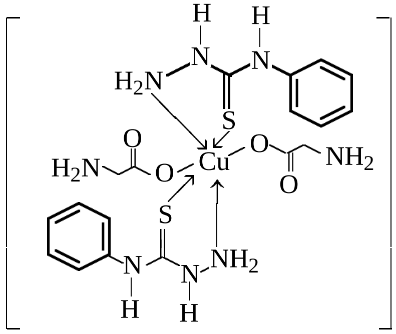
$$\mathrm{Cu(Gly)_2 + 2HL \longrightarrow \underset{\textbf{VII}}{Cu(HL)_2(Gly)_2}}, \quad (7)$$

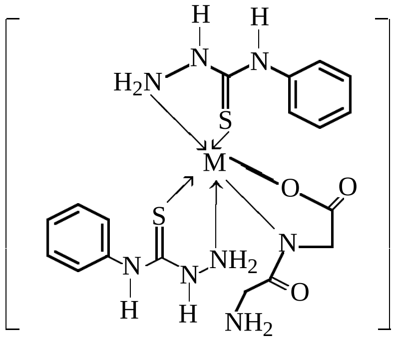
The structures of the complexes synthesized are, apparently, as follows:



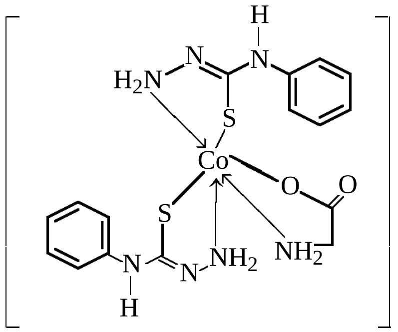
I

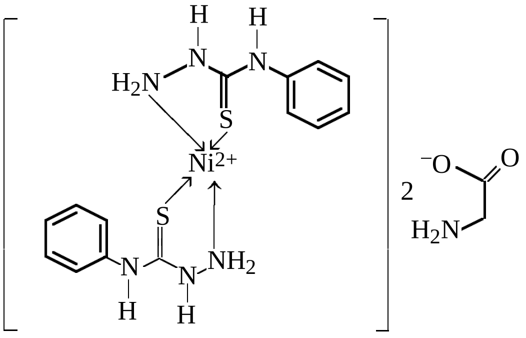

II


VII


III, IV

M = Cu^{2+} (**III**), Zn^{2+} (**IV**).


V


VI

Comparison of the results of this study with the data on the related complexes of unsubstituted thiosemicarbazide [5] shows that introduction of the phenyl substituent into the thiosemicarbazide molecule weakens the tendency of the ligand to deprotonate in the course of the complexation.

EXPERIMENTAL

The IR spectra were recorded on a Perkin–Elmer Spectrum BX-II-FT-IR spectrometer; samples were pelletized with KBr. The diffuse reflection spectra were taken on a Perkin–Elmer Lambda-9 UV-Vis-NIR spectrophotometer.

The thermogravigrams were measured with a Paulik–Paulik–Erdey derivatograph in air at a heating rate of 10 deg min^{-1}.

Cobalt(II), nickel(II), copper(II), and zinc(II) chlorides, glycine, glycylglycine, and 4-phenylthiosemicarbazide were of analytically pure grade.

Analysis for metals was performed by complexometric titration [14]; for S, by the Schoeniger method (gravimetrically, in the form of $BaSO_4$) [15]; and for N, by the Dumas method [15]. The X-ray diffraction patterns were taken on a URS-50-IM diffractometer with an iron anode (voltage 35 kV, slits 0.5 × 0.5 × 0.5 mm, scanning rate 1 deg min^{-1}).

Complexes I and V. 4-Phenylthiosemicarbazide (0.835 g) was dissolved with heating in 25 ml of ethanol, and 0.0017 mol of anhydrous cobalt(III) glycylglycinate or glycinate was added. The solution immediately turned brown-red. In the case of glycylglycinate, the mixture was stirred on a magnetic stirrer until the precipitate became uniformly brown. In the case of glycinate, the solution was transferred into a porcelain cup and kept at room temperature until the solvent was evaporated. Then the precipitates were filtered on a glass frit, washed with a small amount of ethanol, and dried in a desiccator over $CaCl_2$ to constant weight.

Complexes II–IV, VI, and VII. 4-Phenylthiosemicarbazide (0.835 g) was dissolved on heating in 25 ml of ethanol, and 0.0025 mol of anhydrous copper(II), nickel(II), or zinc(II) glycylglycinate or glycinate was added. A precipitate formed immediately; it was filtered off on a glass frit, washed with a small amount of ethanol, and dried in a desiccator over $CaCl_2$ to constant weight.

Compound I. IR spectrum, cm^{-1}: 3435, 1601, 1405, 1391, 1350, 995, 975, 694. Found, %: Co 10.9; N 21.1; S 12.0. $CoL_2(HGG)$. Calculated, %: Co 11.3; N 21.5; S 12.3. **Compound II.** IR spectrum, cm^{-1}: 3437, 3295, 3216, 1591, 1540, 1436, 1404, 1322, 986, 901, 694. Found, %: Ni 9.4; N 21.8; S 10.1. $Ni(HL)_2(HGG)_2$. Calculated, %: Ni 9.0; N 21.4; S 9.8. **Compound III.** IR spectrum, cm^{-1}: 3436, 3288, 3055, 1601, 1532, 1435, 1407, 1312, 918, 692. Found, %: Cu 12.5; N 21.1; S 12.3. $Cu(HL)_2GG$. Calculated, %: Cu 12.1; N 21.2; S 12.1. **Compound IV.** IR spectrum, cm^{-1}: 3438, 1620, 1546, 1430, 1391, 1310, 934, 696. Found, %: N 21.1; S 12.2; Zn 12.7. $Zn(HL)_2GG$. Calculated, %: N 21.2; S 12.1; Zn 12.3. **Compound V.** IR spectrum, cm^{-1}: 1605, 1545, 1400, 1330, 945, 920, 705. Found, %: Co 12.3; N 21.5; S 14.1. $CoL_2(Gly)$. Calculated, %: Co 12.7; N 21.1; S 13.8. **Compound VI.** IR spectrum, cm^{-1}: 1595, 1540, 1450, 1330, 920, 705. Found, %: N 21.1; Ni 11.1; S 12.0. $Ni(HL)_2(Gly)_2$. Calculated, %: N 20.7; Ni 10.9; S 11.8. **Compound VII.** IR spectrum, cm^{-1}: 1600, 1535, 1400, 1320, 970, 935, 700. Found, %: Cu 12.1; N 20.1; S 11.3. $Cu(HL)_2(Gly)_2$. Calculated, %: Cu 11.7; N 20.5; S 11.7.

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