

METAL HYDRAZIDE COMPLEXES

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Results of studies performed under the guidance of A. E. Shvelashvili and continued after his decease are analyzed. We consider the coordination compounds containing both mono- and dihydrazides of carbonic acids; in particular, monohydrazides of monobasic benzoic and *m*-hydroxy benzoic acids ($\text{BH}=\text{C}_6\text{H}_5\text{C}(\text{O})\text{NHNH}_2$, $m\text{-HBH}=\text{HOC}_6\text{H}_5\text{C}(\text{O})\text{NHNH}_2$) and dihydrazides (DHs) of dibasic acids: malonic, succinic, and glutaric ($\text{DM}=\text{H}_2\text{NHN}(\text{O})\text{C}(\text{CH}_2)\text{C}(\text{O})\text{NHNH}_2$, $\text{DS}=\text{H}_2\text{NHN}(\text{O})\text{C}(\text{CH}_2)_2\text{C}(\text{O})\text{NHNH}_2$, and $\text{DG}=\text{H}_2\text{NHNOC}(\text{CH}_2)_3\text{CONHNH}_2$). Complex compounds of metals with carbonic acid hydrazides are grouped by the ratio between main components ($\text{M:Lig} = 1:1$ and $\text{M:Lig} = 1:2$) and by the gross formulas: $\text{M}(\text{Lig})\text{XY}n\text{H}_2\text{O}$ and $\text{M}(\text{Lig})_2\text{XY}n\text{H}_2\text{O}$, where $\text{M}(\text{II}) = \text{Ca, Mn, Fe, Co, Ni, Cu, Zn, and Sr}$; $\text{Lig} = \text{BH, } m\text{-HBH, DM, DS, DG, X, Y}$ ($\text{X, Y} = \text{SO}_4^{2-}, \text{Cl}^-, \text{NCS}^-, \text{ClO}_4^-, \text{I}^-, \text{NO}_3^-, \text{Br}^-, \text{and NO}_2^-$) are identical or different acido ligands, $n = 0-4$. The compounds with carbonic acid dihydrazides are classified by the redistribution criterion of ligands in the $-\text{M}-\text{DH}-\text{M}-$ bonds depending on the M:DH ratio and the nature of the acido ligand. A division into two groups is performed by the criteria: 1) pairs of metal atoms with single bis-bidentate bridges; 2) pairs of metal atoms with double bis-bidentate bridges. Packing features of structural units are revealed in compounds containing residuals of carbonic acid hydrazides.

Keywords: complex compounds, X-ray diffraction analysis, carbonic acid hydrazides, benzoic acid monohydrazide, *m*-hydroxybenzoic acid monohydrazide, malonic acid dihydrazide, succinic acid dihydrazide, glutaric acid dihydrazide.

In 1968, G. B. Bokii's "Crystal Chemistry" was translated into Georgian (by K. Surguladze). In the introduction, G.B. Bokii expressed hope that the publication of the translation would promote the spread of knowledge of crystal chemical principles among chemists and increase the number of Georgian scientists engaged in studying the structure of matter. Indeed, the G. B. Bokii's book significantly helped the Georgian scientists and especially the entrants in this field. The "X-ray Diffraction Analysis" written by G. B. Bokii and M. A. Porai-Koshits became the reference book for professors and students of the Chemical and Physical Engineering Faculties of the Georgian Polytechnic Institute.

Carbonic acid hydrazides attract scientists' attention by peculiar coordination chemical behavior and promising applications. They have been studied by a wide range of physicochemical methods. The scientific literature has collected much material for analysis. Georgian scientists also participated in the beginning of the studies; in the middle of the last century, Prof. P. V. Gogorishvili, on the initiative and active support of Academician I. I. Chernyaev, began to synthesize and study by different physicochemical methods carbonic acid hydrazides in the laboratory of complex compounds at the Institute of Physical and Organic Chemistry, Georgian Academy of Sciences (later headed by A. E. Shvelashvili, Corresponding Member of GAS, M. A. Porai-Koshits's disciple). A. E. Shvelashvili, G. V. Tsintsadze, Academician of GAS, Prof. R. I. Machkhoshvily, and others greatly contributed to the studies of these compounds.

Carbonic acid hydrazides and complexes based on them that have bioactive and energy harvesting properties are used in different fields of technology and medicine. For instance, the preparations based on isonicotinic acid hydrazide are known to be applied in tuberculosis treatment [1, 2]. Carbonic acid hydrazides possess nootropic and antidepressant properties and improve the brain function [3]. Metal hydrazide complex compounds as ecologically safe chemical compounds are applied in agriculture as efficient plant growth regulating chemicals [4]. Many hydrazides are used to recover metal ions from industrial waste water [5] as reagents to form anti-corrosive metal coatings [6, 7], and so on. Due to a wide scope of applications there is a large number of publications devoted to their synthesis, structure, and properties. The researches are still actual at present.

The work considers the coordination compounds containing both mono- and dihydrazides (DHs) of carbonic acids; in particular, monohydrazides of monobasic benzoic and *m*-hydroxy benzoic acids (BH=C₆H₅C(O)NHNH₂, *m*-HBH=HOC₆H₅C(O)NHNH₂) and dihydrazides of dibasic acids: malonic, succinic, and glutaric (DM=H₂NHN(O)C(CH₂)C(O)NHNH₂, DS=H₂NHN(O)C(CH₂)₂C(O)NHNH₂, and DG=H₂NHNOC(CH₂)₃CONHNH₂).

Complex compounds of metals with carbonic acid hydrazides are grouped by the ratio of main components (M:Lig = 1:1 and M:Lig = 1:2) and by the gross formulas: M(Lig)XY n H₂O and M(Lig)₂XY n H₂O, where M(II) = Ca, Mn, Fe, Co, Ni, Cu, Zn, Sr; Lig = BH, *m*-HBH, DM, DS, DG, X, Y (X, Y = SO₄²⁻, Cl⁻, NCS⁻, ClO₄⁻, I⁻, NO₃⁻, Br⁻, and NO₂⁻) are identical and different acido ligands, $n = 0-4$.

STRUCTURAL FUNCTION OF HYDRAZIDES

The structure of metal coordination compounds containing mono- and dihydrazides was studied by X-ray diffraction analysis (Table 1). Regardless of the chemical nature of hydrazids (number of CH₂ groups) and their amount in the complex, the chemical nature of metal and anion, the molecular or ionic structure of a compound, the hydrazide molecule turned out to be always present in the inner coordination sphere. Monohydrazides perform the function of a bidentate cycle-forming ligand, while dihydrazides perform the symmetric or asymmetric bis-bidentate cycle-forming function. Metal atoms are coordinated by O atoms and N(NH₂) hydrazide carbonic group (HCG) forming a five-membered metallocycle. The O(1), C(1), N(1), and N(2) HCG atoms (Fig. 1) are almost in the same plane, whereas the cycles have *envelope* conformation. The *envelope* fold line passes through O...N(2) atoms [8-32].

TABLE 1. Some Crystallographic Parameters of the Studied Coordination Compounds

No.*	Structural formula	Unit cell parameters (Å, deg)			Space group; Z	V, Å ³	R, %
		a; α	b; β	c; γ			
1	2	3	4	5	6	7	8
I	[Zn(BH) ₂ (NO ₂) ₂]	8.861(2) 70.91(3)	9.965(1) 69.01(3)	12.105(3) 69.77(3)	<i>P</i> -1; 2	384.8(3)	8.9
II	[Zn(BH) ₃](ClO ₄)BrH ₂ O	19.454(7) 90	16.045(8) 90	9.594(6) 66.7(2)	<i>P</i> 2 ₁ / <i>n</i> ; 4	2752(3)	7.6
III	[Co(<i>m</i> -HBH) ₂ (NCS) ₂].2H ₂ O	7.713(2) 101.43(2)	8.316(2) 107.19(2)	9.581(2) 108.00(2)	<i>P</i> -1; 1	614.7(4)	2.3
IV	[Mn ₂ (<i>m</i> -HBH) ₂ (SO ₄) ₂ (OH ₂) ₄]	14.418(3) 90	14.389(3) 90	5.815(1) 101.43(1)	<i>P</i> 2 ₁ / <i>a</i> ; 2	1182.4(3)	2.3
V	[Co(<i>m</i> -HBH) ₂ (OH ₂) ₂](NO ₃) ₂ .3H ₂ O	56.150(6) 90	20.045(2) 90	7.893(2) 90	<i>Fdd</i> 2; 16	8883.8(4)	5.6
VI	[Cu(<i>m</i> -HBH) ₂ (OH ₂) ₂](NO ₃) ₂ .2H ₂ O	57.415(6) 90	19.760(2) 90	7.586(2) 90	<i>Fdd</i> 2; 16	8606.5(3)	5.3
VII	[Cu(<i>m</i> -HBH) ₂ (OH ₂) ₂]SO ₄ .H ₂ O	7.154(3) 90	8.012(2) 90.56(2)	20.061(2) 90	<i>P</i> 2 ₁ ; 2	1149.8(7)	4.6

TABLE 1. (Continued)

1	2	3	4	5	6	7	8
VIII	[Fe ₂ (DM) ₂ (NCS) ₄].2H ₂ O	10.709(3) 76.25(2)	8.478(2) 101.62(2)	7.670(2) 73.08(2)	<i>P</i> -1; 2	619.1(3)	2.6
IX	[Fe(DM)(OH ₂) ₂](SO ₄)H ₂ O	11.529(1) 90	9.779(1) 90	11.792(1) 116.96(1)	<i>P</i> _{21/a} ; 4	1184.9(2)	2.0
X	[Co ₂ (DM) ₂ (OH ₂) ₄](NO ₃) ₄ .2H ₂ O	10.709(3) 76.25(2)	8.478(2) 101.62(2)	7.670(2) 73.08(2)	<i>P</i> -1; 2	666.7(4)	2.4
XI	[Co(DM)(OH ₂) ₂](SO ₄)H ₂ O	11.357(4) 90	9.649(3) 90	11.729(3) 116.72(2)	<i>P</i> _{21/a} ; 4	1166.3(6)	1.9
XII	[Zn(DM)(OH ₂) ₂](SO ₄)H ₂ O	11.63(2) 90	11.78(2) 90	11.99(2) 130.5(5)	<i>P</i> _{21/b} ; 4	1248(6)	11.2
XIII	[Co ₂ (DM) ₂ (OH ₂) ₄](NO ₃) ₃ (ClO ₄).2H ₂ O	10.519(2) 102.04(2)	9.786(2) 100.17(2)	7.803(2) 114.63(3)	<i>P</i> -1; 2	682.0(2)	4.5
XIV	[Co ₂ (DM) ₂ (OH ₂) ₄]I ₃ (NO ₃).4H ₂ O	17.831(3) 90	23.851(2) 90	7.453(1) 110.90(1)	<i>B</i> _{2/b} ; 8	2961.4(8)	3.4
XV	[Mn ₂ (DS) ₂ (NCS) ₄].2H ₂ O	7.585(1) 104.78(1)	8.724(1) 99.72(1)	10.903(1) 100.52(1)	<i>P</i> -1; 2	668.0(3)	3.2
XVI	[Sr(DS)(NO ₃) ₂ H ₂ O]	8.61(1) 77.9(3)	7.22(1) 102.0(3)	5.24(1) 90.1(3)	<i>P</i> ₁ ; 1	312(1)	8.0
XVII	[Ca(DG)(OH ₂) ₂]Cl ₂	15.385(2) 90	8.821(2) 90	5.595(3) 76.97(3)	<i>B</i> ₂ ; 2	739.5(5)	6.1
XVIII	[Mn(DM) ₂](SO ₄).4H ₂ O	11.582(2) 90	19.306(2) 90	8.142(1) 90	<i>F</i> ₂₂₂ ; 4	1820(6)	3.4
XIX	β-[Mn(DM) ₂]Cl ₂ .2H ₂ O	7.322(3) 90	14.563(3) 90	15.07(3) 90	<i>F</i> ₂₂₂ ; 4	1606.9(2)	3.9
XX	α-[Mn(DM) ₂]Cl ₂ .2H ₂ O	7.865(2) 90	13.130(2) 90	16.104(2) 90	<i>Pbam</i> ; 4	1663.0(3)	2.4
XXI	[Mn(DM) ₂](NCS) ₂	14.706(3) 90	7.186(2) 90	16.031(4) 90	<i>Iba</i> ₂ ; 4	1694.5(5)	5.4
XXII	[Mn(DM) ₂](ClO ₄) ₂	17.258(5) 90	6.953(1) 90	14.870(5) 90	<i>I</i> ₂₂₂ ; 4	1784.3(6)	4.2
XXIII	[Mn(DM) ₂]I ₂	19.995(6) 90	6.885(1) 134.34(1)	16.946(6) 90	<i>C</i> _{2/c} ; 4	1668.4(5)	3.8
XXIV	[Mn(DM) ₂](ClO ₄)(NO ₃)H ₂ O	6.992(3) 90	15.207(7) 90	17.175(8) 90	<i>I</i> _{2am} ; 4	1826.0(1)	3.0
XXV	[Mn(DS) ₂](ClO ₄) ₂	10.336(2) 90	17.924(2) 111.9(3)	11.543(2) 90	<i>P</i> _{21/n} ; 4	1984.1(6)	7.1

*Numbers from the table are used further to denote the compounds.

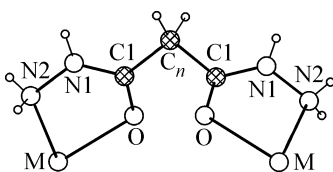
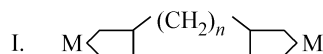


Fig. 1. Distribution and numeration of atoms in the complex containing dihydrazide.

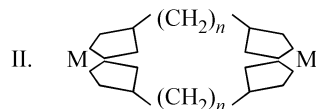
The works [14-32] show that in the coordination compounds containing carbonic acid DHs, their packing is characterized by complexity and specificity, which is likely to be due to the ligand geometry. DM, DS, and DG are different from each other only in the number of CH₂ groups. In coordinated carbonic acid mono- and dihydrazides, the identical (corresponding) fragments mainly repeat the conformation of the uncoordinated molecule. This refers, first and foremost, to HCG (in this fragment the geometry of the –C(O)–NH– group is very close to the geometry of the peptide link [33]). In dihydrazides, a change in the angles between planar HCGs in a wide range (78-120°) is explained by the possibility to turn around C1–C_n bonds, which determines the flexibility of the structural metal–ligand–metal fragment. A wide range change in the dihedral fold angle (0-23°) causes an increase in flexibility. The particular values of angles between the planes are determined by packing facility conditions for all components of the compound in crystal structures, which are, of course, different depending on the composition. It is quite possible to state that the geometries of the coordinated and free DH ligand do not differ significantly. This indicates that no substantial electron density redistribution occurs between π- and σ-bonds in the DH amide tautomeric form [9]. The permanence of DM geometric characteristics relates to one half of the ligand in compound XXIII, in which the Mn–N bond is drastically weakened (2.744(5) Å). This is the only case when DM performs the tridentate function.

PACKING FEATURES OF STRUCTURAL UNITS

Carbonic acid dihydrazides as bridging type ligands are divided into two groups. The first group is compounds with the structures in which carbonic acid dihydrazides act as single bis-bidentate-cyclic bridges.



The second group is the structures in which carbonic acid dihydrazides act as double bis-bidentate-cyclic bridges.



The second type of bridges between metal atoms is unique. The presence of double bridges is caused not only by the existence of $\leftarrow\text{NH}_2\text{--NH--C=O}\rightarrow$ fragments, but also the angular configuration at the C_n atom, C1–C_n–C1 fragment (Fig. 1). In this fragment, because of the single C1–C_n bond in HCG, it is the possibility to turn around this bond as the axis that determines the flexibility of the M((DH)₂)M structural fragment. In turn, this is the essential condition for the optimal distribution to occur in the space of carbonic acid dihydrazides between the solvent molecules and anions of different nature. The considered compounds are distributed over these two groups as follows: as type I bridges (β-[Mn(DM)₂]Cl₂·2H₂O; [Mn(DM)₂](SO₄)₄·4H₂O; [Fe(DM)(OH₂)₂](SO₄)₂·H₂O; [Co(DM)(OH₂)₂](SO₄)₂·H₂O; [Zn(DM)(OH₂)₂](SO₄)₂·H₂O; [Co₂(DM)₂·(OH₂)₄]I₃(NO₃)₄·4H₂O; [Sr(DS)(NO₃)₂·2H₂O]; [Ca(DG)(OH₂)₂]Cl₂) and type II bridges (α-[Mn(DM)₂]Cl₂·2H₂O; [Mn(DM)₂](NCS)₂; [Mn(DM)₂](ClO₄)₂; [Mn(DM)₂]I₂; [Mn(DM)₂](ClO₄)(NO₃)₂·H₂O; [Mn(DS)₂](ClO₄)₂; [Fe₂(DM)₂(NCS)₄]·2H₂O; [Co₂(DM)₂(OH₂)₄](NO₃)₄·2H₂O; [Co₂(DM)₂(OH₂)₄](NO₃)₃(ClO₄)₂·2H₂O; [Mn₂(DS)₂(NCS)₄]·2H₂O).

As seen, the bridge type depends on the anion nature. Sulfates form type I bridges regardless of the metal nature, its coordination number, and the M:DH ratio. Rhodanides, perchlorates, and iodides form type II bridges, while chlorides and nitrates can form bridges of both types. For instance, α- and β-modifications of the Mn(DM)₂Cl₂·2H₂O compound exist, which indicates a small difference between the crystal lattice energies. When mixed acido ligands are present, also the two types of bridges occur.

At a ratio of M:DH = 1:2, type I bridges form networks (Fig. 2a) with four-membered nodes in the structure, i.e. organize two intersecting lines of beads. With a ratio of M:DH = 1:1, the networks break, and beads form in one direction (Fig. 2b). Finally, a structure of the polymer bead type is produced instead of the polymer layer (network) structure.

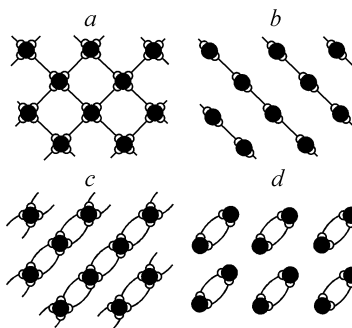


Fig. 2. Scheme of M–Lig–M bond distribution in the compounds.

At a ratio of M:DH = 1:2, type II bridges form polymer chains (two ligands in the ring, Fig. 2c). At a ratio of M:DH = 1:1, the chains terminate, and centrosymmetric dimeric complexes appear (two ligands in the ring, Fig. 2d).

COORDINATION POLYHEDRA OF METALS

In all compounds with a ratio of M:Lig = 1:1, the metal coordination number is six (in structures II–XV, the polyhedra are more or less distorted octahedra, in none of the cases a trigonal prism is found). In compounds with a ratio of M:Lig = 1:2, metal has c.n. of 8, unusual for 3*d*-elements of VII and VIII groups of the Periodic system. Uncommon polyhedra also occur in compounds I, XVI, and XVII with metal c.n. of 8, 9, and 8 respectively. An increase in c.n. of compounds of the second type (M:Lig = 1:2) is mainly determined by the tendency of the ligand to ultimately exhaust the coordination possibilities. For non-transition metals Ca(II) and Sr(II), an increase in c.n. to 8 and 9 can be due to both the tendency of the ligand to occupy four coordination sites and an increase in the ionic radius. In compounds I and XVII–XXV, the eight-vertex polyhedron has the form of the Chord dodecahedron that can be distorted either to the tetragonal antiprism or the two-cap trigonal prism. Other forms, including the cube, are excluded.

Stereoisomers in eight-vertex polyhedra are denoted by those polyhedron edges that are included in metalocycles. It would be natural to expect the symmetric isomers to form when four identical metalocycles are present. Since in the DH complexes the ligand is coordinated by atoms of different nature, then chelation must proceed along the edge *m* that links the nodes of different *A* and *B* types (Fig. 3) [34]. Indeed, in all structures considered in this work, the most symmetric variant $m_O m_O / m_O m_O$ is implemented, while in XVIII structure it is $m_N m_N / m_N m_N$ (index denotes the nature of the atom in the *B* node).

Angular distortions of the metal polyhedra are well explained by the presence of five-membered metalocycles. The intracyclic angles at the metal atom are less than 90° in all cases. In the octahedra, these angles lie within 73.1–78.4°; in the eight-vertex complexes they are in a range of 63° to 70.2° (Table 2), whereas in the dodecahedron, not distorted by chelation, the bond angles opposite to *m* edges should have a value of 73.5°. It is possible to assume that a decrease in the intracyclic angles at the metal in eight-vertex polyhedra (63–70.2°) is caused by steric hindrances in the contacts between the neighboring ligands (tightness produced by the metal coordination by all atoms simultaneously) rather than the constrictive effect of chelating ligands. While in the octahedral complexes, a decrease in the same angles (73.1–78.4°) must be due to only the constrictive effect of metalocycles.

CONCLUSIONS

The performed study provides the opportunity to set forth the following reasons.

1. In complex compounds based on carbonic acid hydrazides, regardless of the chemical nature and the number of hydrazides, the chemical nature of metal and anion, the molecular or ionic structure of the compound, the hydrazide molecule

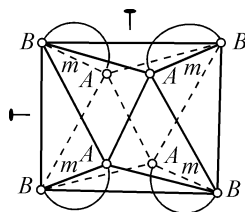


Fig. 3. Dodecahedron.

TABLE 2. Some Linear and Angular Parameters of $(\text{NH}_2\text{NHC}(\text{O}))_2(\text{CH}_2)_n$, $n = 1, 2, 3$ (Å, deg)

No.	Distances				Intracyclic angles					Angles
	N1–N2	N2–C1	C1–O	C1–C _n	M	N2	N1	C1	O	C _n
DM	1.426(6)	1.310(6)	1.230(5)	1.512(8)	—	—	122.8(4)	123.2(6)	—	112.0(4)
	1.423(6)	1.319(7)	1.256(6)	1.518(7)			120.9(4)	122.8(6)		
VIII	1.416(5)	1.320(4)	1.238(4)	1.517(6)	73.15(6)	110.0(4)	117.7(3)	121.6(4)	117.3(1)	107.9(3)
	1.412(4)	1.315(4)	1.243(5)	1.508(5)	74.20(7)	108.7(1)	117.7(3)	123.4(3)	115.2(1)	
IX	1.427(4)	1.318(3)	1.237(3)	1.513(5)	75.6(1)	108.1(1)	117.8(2)	122.5(3)	115.7(2)	108.9(3)
	1.423(3)	1.316(4)	1.248(2)	1.507(4)	76.2(1)	106.5(1)	118.4(2)	122.7(2)	114.8(1)	
X	1.411(6)	1.315(6)	1.245(4)	1.509(2)	76.9(1)	107.2(3)	118.2(3)	121.8(5)	115.0(3)	109.2(2)
	1.422(7)	1.320(5)	1.239(5)	1.515(9)	77.6(2)	108.2(2)	118.3(4)	123.5(7)	112.3(6)	
XI	1.418(3)	1.317(3)	1.235(2)	1.498(3)	78.45(7)	105.6(1)	118.9(2)	122.8(2)	112.6(1)	108.8(2)
	1.406(4)	1.318(4)	1.241(4)	1.496(5)	77.88(7)	107.6(2)	117.8(2)	122.6(3)	113.7(2)	
XII	1.40(1)	1.34(1)	1.32(1)	1.46(1)	75.9(2)	110.5(1)	116.9(2)	120.5(2)	115.1(2)	111.5(2)
	1.46(1)	1.41(2)	1.27(1)	1.52(1)	76.9(2)	107.1(2)	117.4(2)	121.0(2)	115.6(2)	
XIII	1.414(6)	1.321(8)	1.228(7)	1.523(5)	77.5(2)	108.1(5)	118.1(6)	123.9(4)	118.2(2)	109.2(3)
	1.413(7)	1.322(8)	1.244(7)	1.495(7)	76.8(2)	107.2(3)	118.3(5)	121.3(5)	115.5(4)	
XIV	1.431(8)	1.316(9)	1.236(9)	1.513(9)	77.7(2)	108.4(4)	117.9(6)	122.8(6)	113.4(4)	110.4(2)
	1.413(7)	1.350(1)	1.210(1)	1.508(8)	78.2(2)	107.9(4)	116.8(6)	123.2(5)	113.3(4)	
XV	1.412(4)	1.329(3)	1.241(3)	1.502(3)	72.98(8)	109.4(1)	118.6(2)	121.6(2)	117.2(1)	113.0(2)
	1.419(3)	1.324(4)	1.240(4)	1.505(4)	71.98(8)	106.9(1)	118.1(2)	122.7(2)	118.1(1)	113.6(2)
XVI	1.45(2)	1.26(2)	1.24(2)	1.51(2)	56(1)	107(2)	119(3)	121(3)	118(2)	120(2)
	1.38(2)	1.31(2)	1.26(2)	1.54(2)	63(1)	109(2)	124(3)	125(3)	117(2)	108(7)
XVII	1.427(4)	1.342(6)	1.259(3)	1.484(4)	63.73(2)	108.8(2)	119.0(1)	121.1(1)	122.3(2)	112.1(1)
XVIII	1.428(2)	1.310(3)	1.243(3)	1.513(3)	67.6(1)	113.2(2)	117.7(1)	122.2(1)	118.0(2)	109.4(8)
XIX	1.417(3)	1.322(3)	1.237(3)	1.504(4)	68.31(7)	111.4(2)	117.6(2)	122.7(2)	118.3(2)	110.7(2)
	1.418(3)	1.320(3)	1.237(3)	1.520(3)	67.87(7)	109.3(1)	117.7(1)	123.4(7)	114.8(6)	
XX	1.420(3)	1.318(3)	1.238(3)	1.523(3)	68.44(7)	113.6(1)	118.4(4)	123.3(3)	115.9(1)	110.2(2)
XXI	1.377(9)	1.34(1)	1.263(9)	1.51(1)	65.5(2)	124.5(4)	107.6(5)	123.3(6)	118.1(4)	110.9(5)
	1.417(6)	1.325(1)	1.214(7)	1.52(1)	69.5(8)	106.8(3)	121.3(4)	124.1(5)	117.2(4)	
XXII	1.49(2)	1.35(5)	1.28(4)	1.46(1)	69(1)	108(2)	114(2)	125(2)	119(2)	113(2)
	1.32(2)	1.30(7)	1.21(5)	1.21(5)	66(1)	106(3)	121(3)	122(3)	123(3)	108(3)
XXIII	1.437(5)	1.340(4)	1.235(5)	1.501(5)	64.5(8)	105.4(2)	115.2(5)	124.4(1)	128.9(4)	108.7(5)
	1.415(6)	1.326(5)	1.248(5)	1.508(6)	70.2(3)	109.5(4)	118.3(5)	123.8(6)	117.9(4)	
XXIV	1.411(4)	1.320(4)	1.230(4)	1.505(5)	68.20(8)	108.2(3)	118.2(3)	123.7(3)	121.2(1)	108.7(2)
	1.417(5)	1.327(4)	1.236(4)	1.514(5)	69.04(9)	119.9(3)	117.9(3)	123.1(3)	119.7(2)	
XXV	1.42(2)	1.34(2)	1.22(2)	1.52(2)	68.3(6)	110(1)	115(1)	122(1)	118(1)	111(1)
	1.41(3)	1.37(2)	1.23(2)	1.51(3)	68.1(5)	109(1)	114(1)	122(1)	122(1)	109(1)
	1.42(3)	1.41(2)	1.17(2)	1.54(4)	68.2(6)	109(1)	112(1)	123(2)	123(1)	109(1)
	1.32(2)	1.35(3)	1.26(2)	1.46(2)	66.2(6)	111(1)	118(1)	118(1)	122(1)	109(1)

is always in the inner coordination sphere. Monohydrazides perform the function of a bidentate, cycle-forming ligand, while dihydrazides perform the symmetric or asymmetric bis-bidentate cycle-forming function. Metal atoms are coordinated by O atoms and the hydrazide carbonic group N(NH₂) with the formation of a five-membered metallocycle.

2. Coordination compounds with carbonic acid dihydrazides can be classified by the criterion of redistribution of the ligands in–M–DH–M– bonds depending on the M:DH ratio and the nature of the acido ligand. They can be divided into two groups:

I contains the pairs of metal atoms with single bis-bidentate bridges,

II contains the pairs of metal atoms with double bis-bidentate bridges.

The type of the bridge in the compound depends on the nature of the acido ligand.

At a ratio of M:DH = 1:2, bridges of the first type form networks with eight-vertex nodes, i.e. two intersecting bead rows, while at a ratio of M:DH = 1:1 the networks break, and only bead rows with six-vertex nodes are formed in one direction. Accordingly, the structure can be described as a polymer-network or polymer-bead structure. At a ratio of M:DH = 1:2, bridges of the second type form polymeric chains with eight-vertex nodes, and at a ratio of M:DH = 1:1 the chains terminate, and centrosymmetric dimers with six-vertex nodes appear.

In both cases, the dodecahedron node is substituted by the octahedron.

3. The structural type of hydrazide-containing coordination compounds depends on the M:DH ratio. At a ratio of M:DH = 1:2, the structural type is ionic polymer-layered or polymer-bead in all cases, and at a ratio of M:DH = 1:1, it is polymer-bead or dimeric one. Polymer-bead compounds belong to only polymer-bead ionic structural type, whereas dimeric compounds can belong to both ionic and molecular island structural types.

REFERENCES

1. *Antiphthisic Preparations* (<http://www.antibiotic.ru/ab/065-75.shtml>).
2. M. D. Mashkovskii, *Pharmaceuticals* [in Russian], Vol. 2., Izd. Novaya Volna (2002).
3. I. I. Semina, E. V. Shilovskaya, R. I. Tarasova, et al., *Khim. Farm. Zh.*, **36**, No. 4, 3-6 (2002).
4. S. A. Kravtsov, *Am. Veget. Grow.*, **15**, No. 6, 17-21 (1987).
5. G. I. Zubareva, *Khim. Prom.*, No. 10 (2001)
6. A. V. Radushev, A. B. Shein, R. G. Aitov, et al., *Zashchita Metallov*, **28**, No. 5, 845 (1992).
7. R. G. Aitov, A. B. Shein, A. E. Lesnov, and A. V. Radushev, *ibid.*, **308**, No. 5, 548 (1994).
8. A. E. Shvelashvili, È. B. Miminoshvili, T. O. Vardosanidze, and M. G. Tavberidze, *Georg. Engineering News*, No 1, 100-104 (2001).
9. È. B. Miminoshvili, *X-Ray Diffraction Study of Coordination Compounds of Biometals(II) with Carbonic Acid Hydrazides, Guanidine and Aminoguanidine Obtained by Chemical Synthesis* [in Russian], Diss. ... Doct. Chem. Sciences, Izd. State Technical University, Tbilisi (2003).
10. È. B. Miminoshvili, K. È. Miminoshvili, L. A. Beridze, et al., *Georg. Engineering News*, No. 1, 90-93 (2006).
11. È. B. Miminoshvili, K. È. Miminoshvili, S. R. Zazashvili, and L. A. Beridze, *ibid.*, No. 2, 245/246.
12. È. B. Miminoshvili, K. È. Miminoshvili, S. R. Zazashvili, and L. A. Beridze, *J. Struct. Chem.*, **47**, No. 6, 1188-1192 (2006).
13. È. B. Miminoshvili, K. È. Miminoshvili, S. R. Zazashvili, and L. A. Beridze, *ibid.*, **49**, No. 2, 335-340 (2008).
14. A. E. Shvelashvili, T. O. Vardosanidze, and È. B. Miminoshvili, *Stereochemistry of Some Coordination Compounds of Metals with Carbonic Acid Dihydrazides* [in Russian], Metsniereba, Tbilisi (1987).
15. R. I. Machkhoshvili, *Chemistry of Carbonic Metal Dihydrazide Complexes* [in Russian], Nauka, Moscow (1996).
16. A. E. Shvelashvili, È. B. Miminoshvili, P. V. Gogorishvili, et al., *Zh. Neorg. Khim.*, **21**, No. 1, 292/293 (1976).
17. A. E. Shvelashvili, R. I. Machkhoshvili, È. B. Miminoshvili, et al., *ibid.*, **25**, No. 7, 1779-1783 (1980).
18. A. E. Shvelashvili, T. O. Vardosanidze, A. N. Sobolev, et al., *Soobshch. Akad. Nauk Gruzii*, **110**, No. 2, 49-52 (1983).

19. T. O. Vardosanidze, A. E. Shvelashvili, M. A. Porai-Koshits, and A. N. Sobolev, *Zh. Neorg. Khim.*, **30**, No. 1, 364-367 (1985).
20. T. O. Vardosanidze, A. N. Sobolev, A. E. Shvelashvili, and M. A. Porai-Koshits, *ibid.*, **30**, No. 7, 1745-1751 (1985).
21. T. O. Vardosanidze, A. N. Sobolev, A. E. Shvelashvili, and L. Sh. Chareshvili, *Soobshch. Akad. Nauk Gruzii*, **119**, No. 2, 305-308 (1985).
22. A. E. Shvelashvili, L. Sh. Chareshvili, T. O. Vardosanidze, and A. N. Sobolev, *ibid.*, **119**, No. 3, 528-532 (1985).
23. N. B. Zhorzholiani, A. E. Shvelashvili, A. N. Sobolev, and T. O. Vardosanidze, *ibid.*, **123**, No. 3, 541-544 (1986).
24. A. E. Shvelashvili, N. B. Zhorzholiani, A. N. Sobolev, et al., *Izv. Akad. Nauk Gruzii, Ser. Khim.*, **13**, No. 2, 102-110 (1987).
25. A. E. Shvelashvili, M. A. Porai-Koshits, T. O. Vardosanidze, et al., in: *Studies in the Field of Chemistry and Simple Compounds of Some Transition and Rare Metals* [in Russian], Metsniereba, Tbilisi (1987), pp. 3-39.
26. A. E. Shvelashvili, L. Sh. Chareshvili, T. O. Vardosanidze, and A. N. Sobolev, *Soobshch. Akad. Nauk Gruzii*, **130**, No. 1, 89-92 (1988).
27. L. Sh. Chareshvili, A. E. Shvelashvili, T. O. Vardosanidze, and A. N. Sobolev, *ibid.*, **130**, No. 1, 93-96 (1988).
28. A. E. Shvelashvili, T. O. Vardosanidze, E. B. Miminoshvili, et al., *Twelfth Europ. Crystallographic Meeting*, Vol. 2, 314-319 (1989).
29. A. E. Shvelashvili, G. S. Turmanuli, I. A. Beshkenadze, et al., *Method to Obtain the Coordination Compound of Cobalt Bromide, Histidine, and Benzoyl Hydrazine Hexahydrate Manifesting Spasmolytic Activity* [in Russian], Inventor's Certificate No. 1575549, 04.12. 1987, 01.03.1990.
30. A. E. Shvelashvili, T. O. Vardosanidze, È. B. Miminoshvili, et al., *Koordinats. Khim.*, **16**, No. 12, 1657-1660 (1990).
31. È. B. Miminoshvili, A. E. Shvelashvili, T. O. Vardosanidze, et al., *Soobshch. Akad. Nauk Gruzii*, **142**, No. 2, 313-316 (1991).
32. A. E. Shvelashvili and R. I. Machkhoshvili, *Zh. Neorg. Khim.*, **41**, No. 4, 570-586 (1996).
33. T. L. Blundell and L. N. Johnson, *Protein Crystallography*, Academic Press, London and New York (1976).
34. M. A. Porai-Koshits and L. A. Aslanov, *Zh. Strukt. Khim.*, **13**, No. 2, 266-276 (1972).