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Synthesis and Spectral Characteristics of Ni(II) 1-Aryl-3-Aryl(alkyl)-5-(benzothiazole-2-yl)formazanates

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Abstract—Novel mono- and binuclear metal complexes of Ni(II) based on 1-aryl-3-aryl(alkyl)-5-(benzothiazole-2-yl)formazanes were synthesized and their structures were studied by the electronic and IR spectroscopy, mass spectrometry and megnetochemical methods.

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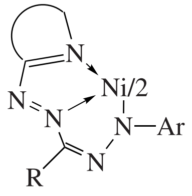
Formazanes (azohydrazones) have been known long ago as ligands for metal complexes, widely used as dyes [1, 2]. Recent years have seen the increasing interest in metal hetarylformazanates; in a number of patents, they were present as components of the optical layers of recording elements [3–6]. Thus, Ni(II) 1-aryl-3-aryl(alkyl)-5-(pyridine-2-yl)formazanates (**A**) were studied and used as the above components [3, 4].



(A)

In the patents [5–7], the heterocyclic fragment of the mono- and binuclear metal complexes of formazanes covers a wide range of azaheterocycles; the metal atom is being varied; the method and equipment for recording and replay are described.

In addition, formazane complexes containing the donating substituents in positions 1, 3, 5 of the formazane chain draw attention as the metal ligands, i.e., the building units of the coordination polymer [8].

With the aim to design different-purpose metal complexes, we synthesized Ni(II) complexes with 1-aryl-3-alkyl-5-(benzothiazole-2-yl)formazanes (**L**) (**I–XIII**) and studied their structures.

EXPERIMENTAL

Nickel(II) benzothiazolylformazanate (**I**) was synthesized by a known procedure [9].

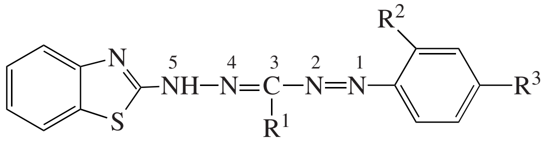
Synthesis of Ni(II) 1-phenyl-3-phenyl-5-(benzothiazole-2-yl)formazanate (III). To a solution of formazane (0.6 mmol) in 50 ml of acetone, a solution of nickel nitrate (0.3 mmol) in a minimum amount of acetone was added at 40 ± 5°C in drops with constant stirring. The mixture obtained was stirred for 30 min and concentrated to a volume of 10 ml. The precipitate formed was filtered, washed with warm distilled water, ethyl alcohol, and dried in air. Nickel(II) formazanates IV, V, VIII, XIII were synthesized similarly.

Synthesis of Ni(II) 1-(2-carboxyphenyl)-3-phenyl-5-(benzothiazole-2-yl)formazanate (II). To a solution of formazane (0.6 mmol) in 50 ml of acetone, a solution of nickel nitrate (0.6 mmol) in a minimum amount of acetone was added at 40 ± 5 in drops with const stirring. The reaction mixture was stirred for 30 min and concentrated to a volume of 10 ml. The precipitate formed was filtered, washed with warm distilled water, ethyl alcohol, and dried in air. Nickel(II) formazanates VI, VII, XI, XII were obtained similarly.

Synthesis of Ni(II) 1-(4-sulfophenyl)-3-methyl-5-(benzothiazole-2-yl)formazanate (IX). To a solution of formazane (0.6 mmol) in 50 ml of an aqueous ethanol, a solution of nickel nitrate (0.3 mmol) in 15 ml of water was added in drops at 40 ± 5°C with constant stirring. The mixture obtained was stirred for 30 min and concentrated to a 10-ml volume. The precipitate formed was filtered, washed with warm distilled water, and dried in air.

Synthesis of Ni(II) 1-(2-hydroxy-5-sulfophenyl)-3-methyl-5-(benzothiazole-2-yl)formazanate (X). A solution of nickel nitrate (0.5 mmol) in 15 ml of water was added in drops to a solution of formazane (0.5 mmol) in 50 ml of an aqueous ethanol at 40 ± 5°C with constant stirring. The reaction mixture was con-

Table 1. The elemental analysis of Ni(II) complexes I–XIII, their yields and melting point



Ligand	R^1	R^2	R^3	Complex	Yield, %	T_m, °C	Content (found/calcd.) %			
							C	H	N	Ni
L^1	C_6H_5	H	H	I	53	285	61.68/62.20	3.87/3.65		7.30/7.48
L^2	C_6H_5	COOH	H	II	56	265	54.89/55.05	3.62/2.87	16.09/15.29	12.46/12.81
L^3	C_6H_5	H	4-COOH	III	54	260	58.74/58.68	3.35/3.29	16.16/16.30	6.99/6.83
L^4	C_6H_5	H	4-$N(CH_3)_2$	IV	61	245	61.49/61.61	4.25/4.43	19.54/19.60	7.07/6.88
L^5	$CH(CH_3)_2$	H	H	V	55	240	57.93/58.04	4.21/4.59	19.40/19.91	8.72/8.34
L^6	$CH(CH_3)_2$	COOH	H	VI	54	265	48.68/48.87	2.97/3.39	15.36/15.14	13.14/13.35
L^7	$CH(CH_3)_2$	OH	5-NO_2	VII	49	280	46.36/46.28	3.23/3.21	19.54/19.06	13.00/13.30
L^8	CH_3	H	4-$N(CH_3)_2$	VIII	52	250	55.80/55.66	4.93/4.68	22.53/22.92	8.33/8.00
L^9	CH_3	H	4-SO_3H	IX	62	>250	44.28/44.61	3.07/3.00	16.90/17.35	6.78/7.27
L^{10}	CH_3	OH	5-SO_3H	X	53	>250	40.30/40.20	2.40/2.48		13.05/13.10
L^{11}	CH_3	OH	4-NO_2	XI	48	>250	44.46/44.47	3.25/3.52	18.40/18.31	13.25/12.78
L^{12}	C_4H_9	OH	4-NO_2	XII	56	145	48.57/47.92	4.25/4.43	17.07/16.77	11.82/11.71
L^{13}	C_4H_9	H	4-$N(CH_3)_2$	XIII	55	270	59.23/58.74	5.65/5.68	20.25/20.56	7.61/7.18

centrated to a volume of 10 ml. The precipitate obtained was washed with warm distilled water and dried in air.

The analysis for C, H, and N was performed on a PE2400SII analyzer (Perkin Elmer); nickel was determined by the gravimetry method.

IR spectra of ligands L^2, L^3, L^6, L^7, L^{11}, L^{12}, and their complexes with Ni(II) were recorded on a Specord 75IR spectrophotometer at 400–4000 cm^{-1} (with KBr pellets and Nujol suspension). The electronic absorption spectra were measured on a UV-5200 spectrophotometer (Beckman) at 350–800 nm.

The magnetic characteristics of compounds V, VII, VIII, XIII were measured on a Quantum Du-sign 5-XL magnetometer at 0–300 K and 30 and 50 kOe magnetic field strength.

Mass spectra of nickel formazanates were recorded on a Shimadzu LCMS-2010 liquid chromatomass spectrometer using the atmospheric-pressure chemical ionization (APCI) method with recording of the positive and negative ions. The samples were introduced to the mass spectrometer through the chromatograph with the SPD-M10Avp diode matrix using the method of direct injection to the ionic source.

RESULTS AND DISCUSSION.

Two series of benzothiazolylformazanes (L) were used in the synthesis of Ni(II) coordination compounds. The first series contains at the N^1 atom of the aryl fragment the 4-COOH, 4-$N(CH_3)_2$, 4-SO_3H groups capable of forming the additional coordination bonds, whereas the second series contains the groups 2-COOH, 2-OH participating in the formation of the metal chelate unit (Table 1).

Thus, benzothiazolylformazanes of the first series (L^1, $L^{3–5}$, L^8, L^9, and L^{13}) were used to obtain Ni(II) complexes with the participation of only the chelate group of the initial ligand. As follows from the elemental analysis data, benzothiazolylformazanates I, III–V, VIII, IX, XIII synthesized on the basis of the above benzothiazolylformazanates have the composition NiL_2. The electronic spectra of these complexes contain one absorption maximum at 620–675 nm (Table 2).

The absorption band ν(NH) at 3500–3200 cm^{-1} is lacking from the IR spectra of the above compounds, which indicates the involvement of the NH group in the complex formation process. Besides, in the IR spectrum of formazanate III, the band ν(CO) is retained in the same region as in the initial ligand

Table 2. The electronic spectroscopy and mass spectrometry data for Ni(II) complexes I–XIII

Complex	Empirical formula	λ_{max}, nm	*m*/*z* (*I*, %)	
			found	calculated
I	$C_{40}H_{28}N_{10}S_2Ni$	620	771(100)	771.59
II	$C_{42}H_{26}N_{10}S_2O_4Ni_2$	550, 1080, 1200	917(5)	916.28
III	$C_{42}H_{28}N_{10}S_2O_4Ni$	645	859(29)	859.61
IV	$C_{44}H_{38}N_{12}S_2Ni$	670		
V	$C_{34}H_{32}N_{10}S_2Ni$	600		
VI	$C_{36}H_{30}N_{10}S_2O_4Ni_2 \cdot 2H_2O$	540, 1080, 1200	847(28)	848.26
VII	$C_{34}H_{28}N_{12}S_2O_6Ni_2$	540; 675	881(1)	882.24
VIII	$C_{34}H_{34}N_{12}S_2Ni$	670		
IX	$C_{30}H_{24}N_{10}S_4O_6Ni \cdot H_2O$	630		
X	$C_{15}H_{11}N_5S_2O_4Ni$	545; 660	445(100)	448.12
XI	$C_{30}H_{20}N_{12}S_2O_6Ni_2 \cdot 2C_2H_5OH$	565; 720	825(10)	826.12
XII	$C_{36}H_{32}N_{12}S_2O_6Ni_2 \cdot 2C_2H_5OH$	570; 710	909(9)	910.3
XIII	$C_{40}H_{45}N_{12}S_2Ni$	675		

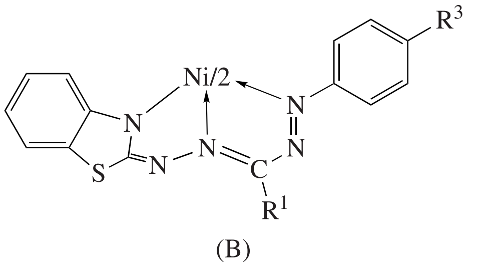
(1700–1690 cm^{-1}) (Table 3), i.e., the COOH group does not participate in the complex formation.

The magnetic moments (**μ_{eff}**) of complexes V, VIII, XIII measured at T = 295 K lie in the interval 2.68–2.85 μ_B (for V, VIII, and XIII, μ_{eff} = 2.68, 2.72, and 2.85 μ_B, respectively), which agrees with the literature data [9] and suggests the octahedral structure of the above metal complexes.

The composition NiL_2 was confirmed also by mass spectra using compounds I, III as examples (Table 2).

Previously [10], the structure of the analogous complexes was studied by X-ray diffraction, for example, Ni(II) 1-butylphenyl-3-butyl-5-(benzothiazole-2-yl)formazanate. The metal was found to be coordinated through the N^1 and N^4 atoms of the formazane chain and the N atom of the benzothiazole fragment with the formation of pseudo-octahedron with the NiN_6 coordination core.

Benzothiazolylformazanes L^1, L^{3-5}, L^8, L^9, and L^{13} are supposed to be coordinated to the Ni^{2+} ions to give the analogous structure (**B**):



(B)

The compounds L^2, L^6, L^7, L^{11}, and L^{12} containing in the aryl fragment of the formazane chain the 2-OH, 2-COOH groups are the tetradentate ligands and can give complexes of two types with different structures: ML_2 with the MN_6 coordination core or ML with the MN_3O coordination core.

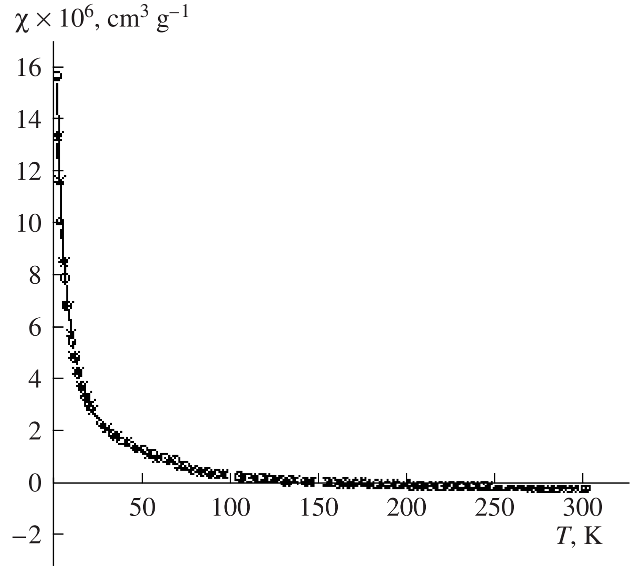
The elemental analysis data indicate that Ni(II) benzothiazolylformazanates II, VI, VII, XI, XII synthesized from the above ligands have the composition Ni_2L_2. The electronic absorption spectra of the 1-(2-carboxyphenyl)-containing complexes II, VI contain absorption maxima at 540–550 nm and in the near-IR region (at 1080 and 1200 nm). According to the literature data, the latter bands indicate the planar structure of these complexes [11]. At the same time, the absorption spectra of metal complexes VII, XI, XII based on 1-(2-hydroxyphenyl)-containing formazanes exhibit, in addition to the absorption at 540–570 nm, the second band at 675–720 nm (Table 2).

The disappearance of a high-frequency band ν(CO) at 1700–1690 cm^{-1} and its shift toward low frequencies (1640 cm^{-1}) in IR spectra of complexes II, VI (Table 3) points to the involvement of the carboxyl group to the complexation process.

Note that the absorption band appears at 1680 cm^{-1} in the IR spectrum of the 1-(2-hydroxy-5-nitrophenyl)-containing formazane L^7 that is shifted toward low-fre-

Table 3. IR spectra of Ni(II) complexes

Complex	ν(CO)	ν(Ni–N) [ν(Ni–O)]
II	1640	460
III	1690	460
VI	1640	470
VII	1650	480
XI	1660	500
XII		480 [640]



The temperature dependence of the magnetic susceptibility of nickel formazanate VII.

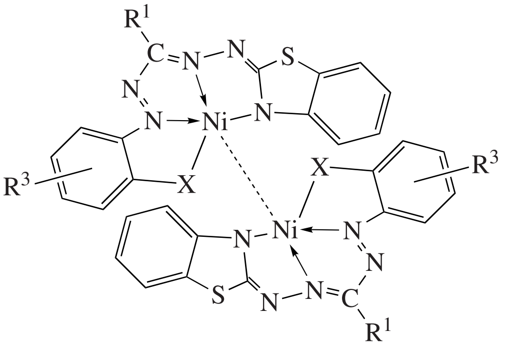
quency region in its nickel complex VII and can be assigned to ν(CO) of the ligand quinoid fragment. In the case of 1-(2-hydroxy-4-nitrophenyl)-substituted analogs, the band at 1660 cm^{-1} appears only in the IR spectrum of complex XI. The analogous situation was observed for the previously described 1-(2-hydroxy-4,5-nitrophenyl)-substituted formazanes and their complexes [12]. Thus, in all the above cases, the shift of the band ν(CO) in the IR spectra indicates the participation of this group in the coordination with a central metal atom (Table 3).

In accordance with the data [13], we assigned the absorption bands at 460–500 cm^{-1} in the IR spectra of metal complexes II, VI, VII, XI, and XII to the stretching vibrations of the Ni-N bonds. The absorption band at 640 cm^{-1}, which appears in the IR spectrum of compound XII but is absent from the spectrum of the corresponding ligand, was assigned to the stretching vibration of the Ni-O bond [13], which suggests the involvement of the O atom in binding of the metal ion (Table 3).

Metal chelate VII was studied by the static magnetic susceptibility method, and its effective magnetic moment was found to be 0.63 μ_B (T = 295 K), which suggests the coordination core structure close to the square. The study of the temperature dependence of the magnetic susceptibility showed that starting from T = 150 K, the magnetic susceptibility increases (see in the figure). The analogous behavior was observed previously for Ni(II) 1-(*o*-carboxyphenyl-5-benzozaylformazanates [14].

The peaks due to the molecular ions corresponding to the composition Ni_2L_2 (Table 2) are observed in mass spectra of compounds II, VI, VII, XI, XII.

Based on the above-indicated spectra data, the structure of Ni(II) formazanates II, VI, VII, XI, XII can be presented as a binuclear dimer (**C**), by the analogy with a nickel complex based on 1-(2-carboxyphenyl)-3-isopropyl-5-(benzimidazole-2-yl)formazane, whose structure was established by X-ray diffraction [15].



X = O, COO

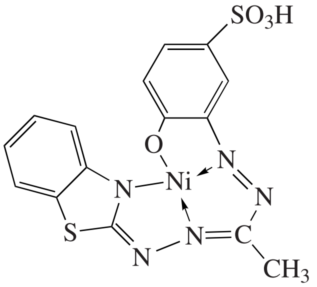
(C)

According to the elemental analysis data, nickel benzothiazolylformazanate X obtained from 1-(2-hydroxy-5-sulfophenyl)-containing formazane has the composition NiL. The electronic absorption spectrum of this compound shows two absorption bands at 545 and 660 nm, similarly to Ni(II) 1-(2-hydroxy-5-nitrophenyl)formazanate VII (Table 2).

The IR spectrum of compound X does not exhibit the bands ν(NH) and ν(OH) of the initial ligand, which suggests that both groups containing the labile hydrogen atom take part in the complex formation process.

In mass spectrum of the above compound, the most intense peak corresponds to a molecule ion of the composition NiL (Table 2).

On the basis of the above data, one can assume that complex X has the structure **D**, containing the MN_3O coordination core, as in the case of copper(II) benzothiazolylformazanate [16]:



(D)

The study of the spectral parameters of the synthesized metal complexes that differ in the chemical composition of the initial ligand showed that both mono- and binuclear complexes can be obtained, depending on the nature of substituents R^1, R^2, R^3 of the formazane molecule.

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REFERENCES

1. Buzykin, B.I., Lipunova, G.N., Sysoeva, L.P., and Rusinova, L.P., *Khimiya formazanov* (The Chemistry of Formazans), Moscow: Nauka, 1992.
2. Sigeikin, G.I., Lipunova, G.N., and Pervova, I.G., *Usp. Khim.*, 2006, vol. 75, no. 10, p. 980.
3. Chapman, D.D., Pat.Eur.Appl., 837.457; 22.04.1998.
4. Chapman, D.D., Pat.Eur.Appl., 837.462; 22.04.1998.
5. Aizawa, Y., Kawata, T., and Yasui, S., Pat.Eur.Appl., 1.347.030; 24.09.2003.
6. Noguchi, S. and Sato, T., Pat.Eur.Appl., 1.335.357; 13.08.2003.
7. Tomura, T., Sato, T., Ueno, Y., and Noguchi, S., US Patent, 2006, p. 23.
8. Frolova, N.A., Vatsadze, S.Z., Zavodnik, V.E., et al., *Izv. Akad. Nauk, Ser. Khim.*, 2006, no. 10, p. 1745.
9. Lipunova, G.N., Krylov, E.I., Bednyagina, N.P., and Sharov, V.A., *Zh. Obshch. Khim.*, 1969, vol. 39, no. 6, p. 1293.
10. Shmelev, L.V., Lipunova, G.N., Kessenikh, A.V., et al., *Koord. Khim.,* 1993, vol. 19, no. 3, p. 215.
11. Drago, R.S., *Physical Methods in Chemistry*, Philadelphia: Saunders, 1977, vol. 2.
12. Krivonogova, T.I., Lipunova, G.N., Garnovskii, A.D., et al., *Zh. Obshch. Khim.*, 1988, vol. 58, no. 1, p. 184.
13. Nakomoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, New York: Wiley, 1986.
14. Validuda, G.I., Lipunova, G.N., Garnovskii, A.D., et al., *Zh. Obshch. Khim.*, 1986, vol. 56, no. 4, p. 827.
15. Rezinskikh, Z.G., Slepukhin, P.A., Lipunova, G.N., et al., *Koord. Khim.,* 2008, vol. 34, no. 9, p. 663 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 34, no. 9, p. 653].
16. Vishnevskaya, G.P., Frolova, E.N., Pervova, I.G., et al., *Koord. Khim.*, 2005, vol. 31, no. 11, p. 828 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 31, no. 11, p. 828].