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Palladium(II) Benzazolylformazanates: Synthesis, Structure and Optical Properties

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Abstract—The Pd(II) complexes of 1-aryl-5-benzazolyl- and 1,5-dibenzimidazolylformazans are synthesized and characterized by UV and IR spectroscopy, mass spectrometry, and magnetochemical studies. The complexes exhibit the intense absorption in the near-IR spectral region (820–1020 nm). The interaction of the complexes with amines leads to the transformation into binuclear palladium formazanates, which absorb at 620–680 nm and whose structures were confirmed by X-ray diffraction analysis.

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INTRODUCTION

The palladium complexes based on the dimercapto-substituted derivatives are known [1] to absorb in the near-IR spectral region and are used as IR-light filters. However, the synthesis of ligands for these compounds is associated with considerable difficulties. Therefore, the search for new compounds absorbing in the near-IR spectral region continues to be an urgent task.

The palladium complexes with such nitrogen-containing ligands as 1,5-diaryl-3-R-formazans (R is the aryl, cyano, and nitro group) were synthesized earlier [2]. The structures of these complexes were studied, the spectral data were obtained, and a dependence of the position of the absorption bands in the electronic spectra on the character of the R substituent was established. For example, when R = aryl, the long-wavelength band shifts to 790–810 nm.

It could be expected that the introduction of a heterocyclic fragment into the formazan structure would elongate the conjugated ligand chain and, as a consequence, the band of the complex would further shift to the near-IR region.

The purpose of this work is to synthesize the palladium(II) complexes with 1-aryl-5-benzazolyl- and 1,5-dibenzimidazolylformazans and to study their structures and spectral characteristics.

EXPERIMENTAL

Synthesis of palladium(II) 1,3-diphenyl-5-(benzthiazol-2-yl)formazanate (I). *Method A.* A hot solution of palladium chloride (0.0024 mol) in dimethylformamide (DMF) (100 ml) was added to a solution of formazan (0.002 mol) in acetone (50 ml) at ~50°C. The resulting mixture was stirred for 30 min and evaporated to 10 ml. The precipitate that formed was filtered off, washed with acetone, and dried. Palladium formazanates **III** and **V–VII** (Table 1) were synthesized analogously.

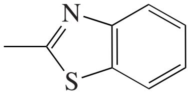
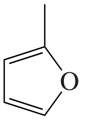
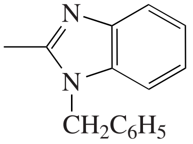
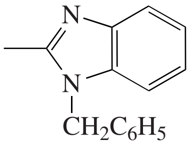
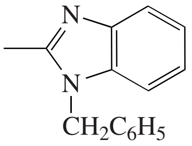
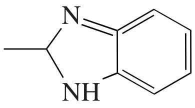
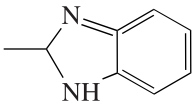
Method B. A solution of formazan (0.0011 mol) in toluene (25 ml) was added to a dilute hydrochloric acid solution (100 ml) of palladium chloride (0.0015 mol). After stirring for 2 h and keeping the solution for a day at room temperature, the toluene layer was separated and evaporated. The obtained precipitate of palladium(II) formazanate was dried. The product was identical to that synthesized by method A.

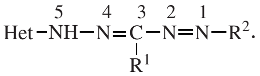
Palladium formazanates **II** and **IV** (Table 1) were synthesized analogously.

Synthesis of dichloro-bis[1,3-diphenyl-5-(benzthiazol-2-yl)formazanate]dipalladium(II) (Ia). Several drops of concentrated NH_4OH were added to a yellow-green solution of complex **I** (0.001 mol) in ethanol until the blue color was obtained. The solution was evaporated, and the regular blue crystals were used for X-ray diffraction analysis (mp > 250°C). Mass spectrum in acetonitrile (electrospray): *m*/*z* (%): 998 (1.96), 994 (1.7), 499 (16.53), 498 (9.4), 497 (12.89), 496 (8.36), 494 (6.01).

Elemental analysis was carried out on a PE2400SII automated CHN analyzer (PerkinElmer, United States). The metal in the complexes was determined by express

Table 1. Yields, melting points, and elemental analysis data for the palladium(II) complexes*

Complex	L^{1-7}			Yield, %	T_m, °C	Content (found/calculated), %		
	Het	R^1	R^2			C	H	N (Cl)
I		C_6H_5	C_6H_5	72	>250	48.9/48.3	3.0/2.8	14.4/14.1
II		C_6H_5	2-$COOHC_6H_4$	56	>250	50.3/49.9	2.8/2.6	14.1/13.9
III		2-$OCH_3C_6H_4$	C_6H_5	40	>250	48.0/47.7	3.2/3.2	(6.2/6.7)
IV			4-$CH_3C_6H_4$	58	>250	45.9/45.4	3.1/2.8	14.3/14.0
V		2-$OCH_3C_6H_4$	4-$N(CH_3)_2C_6H_4$	80	>250	51.6/51.9	4.4/4.1	(8.0/7.8)
VI		CH_3		65	>250	54.8/54.7	4.3/4.2	17.7/17.1
VII		CH_3		60	>250	42.4/41.8	4.0/3.0	24.1/24.8

* L = 
$\text{Het}-\overset{5}{\text{N}}\text{H}-\overset{4}{\text{N}}=\underset{\mathrm{R}^1}{\overset{3}{\text{C}}}-\overset{2}{\text{N}}=\overset{1}{\text{N}}-\text{R}^2$.

gravimetry using an equipment of the OAO Khimlaborpribor (Klin, Moscow oblast, Russia).

The electronic absorption spectra of the samples were measured with Specord UV-Vis and Model 26 detecting two-beam spectrophotometers (Beckman) and using an SF-256UVI instrument at a concentration in the solutions of (1–5) × 10^{-5} mol/l.

The IR spectra of compounds **I**–**VII** were recorded on a Specord 75IR spectrophotometer (KBr pellets and suspensions in Nujol) at 400–4000 cm^{-1}.

The magnetic characteristics of the compounds were measured by the relative Faraday method at 293 K [3].

The studies of the palladium formazanates (compounds **I**, **Ia**, **II**, and **IV**) by mass spectrometry were carried out on an LCMS-2010 liquid chromatograph coupled with a mass spectrometer (Shimadzu) using chemical ionization under atmospheric pressure and electrospray with positive and negative ion detection. Samples were injected into the mass spectrometer through the chromatograph with an SPD-M10Avp diode matrix using direct injection into the ion source. The field desorption mass spectra for complexes **I**, **III**, and **V**–**VII** were obtained on a MAT 311A instrument (Varian) under the earlier described conditions [4].

X-Ray diffraction analysis. The crystals of complex **Ia** ($C_{40}H_{28}N_{10}Cl_2S_2Pd_2$) as dark blue needles are monoclinic: a = 23.119(5) Å, b = 16.3993(3) Å, c = 15.4966(9) Å, β = 125.767(13)°, V = 4767.3(11) $Å^3$, ρ_{calcd} = 1.567 g/cm^3, Z = 4, space group $C2/c$.

The unit cell parameters and the set of experimental data were measured in an Xcalibur 3 autodiffractometric system equipped with a CCD detector at 295(2) K. The completeness of the experiment ($\theta \leq 28.30°$) was 98.3% (ω scan mode with an increment of 1° and an exposure of 20 s per frame, crystal–detector distance 50 mm). The experimental data were collected and edited and the unit cell parameters were refined using the CrysAlis CCD program [5].

Structure **Ia** was solved by a direct method using the SHELXS-97 [6] program package and refined using the SHELXL-97 program package [6] by the least-squares method in the anisotropic (isotropic approximation for hydrogen atoms) approximation to $R_1 = 0.0446$, $wR_2 = 0.0892$ for 2566 reflections with $F^2 \geq 2\sigma(F^2)$. An absorption correction was applied analytically according to the polyhedral crystal model [7].

The bond lengths and bond angles in structure **Ia** are given in Table 2.

The coordinates of atoms and other parameters for structure **Ia** were deposited with the Cambridge Structural Database (no. 695 480).

RESULTS AND DISCUSSION

The Pd(II) complexes based on 1-aryl-benzazolyl- and 1,5-dibenzimidazolylformazans ($\mathbf{L}^{1-7}$) were synthesized by the reactions of benzazolylformazans with palladium(II) chloride in a DMF solution (complexes **I**, **III**, and **V**–**VII**) or in a toluene–water two-phase system (complexes **I**, **II**, and **IV**).

According to the elemental analysis data, compounds **I** and **III**–**VII** have the composition Pd(L)Cl, and complex **II** has the composition PdL', where L and L' are the mono- and dianionic forms of the ligand, respectively (Table 1). The studies by mass spectrometry show that the synthesized complexes correspond to the above compositions and are detected in the mass spectrum as a group of ions with the corresponding isotope distributions for the Pd and Cl atoms (polyisotopic peaks M^+ and $(M + H)^+$ with the 60–100% intensity) (Table 3).

The participation of the NH group of the initial formazan molecule in complex formation is confirmed by the absence of the absorption band corresponding to the ν(NH) stretching vibrations at 3200–3500 cm^{-1} in the IR spectra of compounds **I** and **III**–**VII**. The carboxy group in compound **II** is also involved in the design of formazanate **II**, which is indicated by the shift of the ν(CO) band to the low-frequency region (1630 cm^{-1}) compared to the free ligand (1690 cm^{-1}).

Crystalline complexes **I**, **III**, and **V**–**VII** are diamagnetic ($\mu_{\text{eff}} = 0$ μB), which can be due to the square structure of the metallochelate unit.

The electronic absorption spectra of complexes **I**–**VII** exhibit low-intense absorption bands in the visible region (450–550 nm, 30–40% absorption) and more intense bands in the near-IR region (820–1020 nm, absorption >80%) (Table 3).

The solvent exerts almost no effect on the position of absorption bands. However, the character of the substituents of the formazan group influences on the position of

Table 2. Bond lengths and bond angles in structure **Ia***

Bond	*d*, Å	Angle	ω, deg
Pd(1)–Pd(1*A*)	3.1298(11)	Pd(1A)Pd(1)Cl(1)	100.96(4)
Pd(1)–N(1)	1.988(4)	N(1)Pd(1)N(4)	80.80(16)
Pd(1)–N(4)	2.024(4)	N(1)Pd(1)N(5*A*)	90.65(14)
Pd(1*A*)–N(5)	2.075(4)	N(1)Pd(1)Cl(1)	174.98(12)
Pd(1)–Cl(1)	2.3072(12)	N(1)Pd(1)Pd(1*A*)	82.87(12)
S(1)–C(2)	1.737(5)	N(1)C(2)S(1)	119.4(4)
S(1)–C(3)	1.747(5)	N(1)N(2)C(1)	118.3(4)
N(1)–N(2)	1.324(5)	N(2)N(1)C(2)	114.8(4)
N(1)–C(2)	1.369(5)	N(2)N(1)-Pd(1)	120.5(3)
N(2)–C(1)	1.327(6)	N(2)C(1)N(3)	123.7(5)
N(3)–C(1)	1.369(6)	N(2)C(1)C(9)	118.5(5)
N(3)–N(4)	1.275(5)	N(3)N(4)C(15)	114.0(4)
N(4)–C(15)	1.428(6)	N(3)N(4)Pd(1)	118.2(3)
N(5)–C(2)	1.296(5)	N(3)C(1)C(9)	116.8(5)
N(5)–C(8)	1.416(5)	N(4)Pd(1)N(5*A*)	162.21(16)
C(1)–C(9)	1.453(7)	N(4)Pd(1)Cl(1)	94.41(12)
C(3)–C(4)	1.384(6)	N(4)Pd(1)Pd(1*A*)	120.39(11)
C(3)–C(8)	1.391(6)	N(4)N(3)C(1)	123.7(4)
C(4)–C(5)	1.359(7)	N(5*A*)Pd(1)Pd(1*A*)	73.44(10)
C(5)–C(6)	1.376(7)	N(5*A*)Pd(1)Cl(1)	93.55(9)
C(6)–C(7)	1.367(7)	N(5)C(2)N(1)	123.1(4)
C(7)–C(8)	1.382(6)	N(5)C(2)S(1)	117.5(4)
C(9)–C(10)	1.336(8)	C(2)S(1)C(3)	88.3(2)
C(9)–C(14)	1.383(8)	C(2)N(1)Pd(1)	122.4(3)
C(11)–C(12)	1.382(11)	C(2)N(5)C(8)	109.5(4)
C(10)–C(11)	1.390(10)	C(2)N(5)Pd(1*A*)	133.5(3)
C(12)–C(13)	1.380(10)	C(3)C(8)N(5)	114.5(4)
C(13)–C(14)	1.378(9)	C(4)C(3)C(8)	121.3(5)
C(15)–C(16)	1.371(7)	C(4)C(3)S(1)	128.5(4)
C(15)–C(20)	1.382(7)	C(4)C(5)C(6)	121.8(5)
C(16)–C(17)	1.367(8)	C(5)C(4)C(3)	117.9(5)
C(17)–C(18)	1.333(11)	C(6)C(7)C(8)	119.5(5)
C(18)–C(19)	1.381(11)	C(7)C(6)C(5)	120.4(5)
C(19)–C(20)	1.375(9)	C(7)C(8)C(3)	119.1(4)
		C(7)C(8)N(5)	126.4(4)
		C(8)C(3)S(1)	110.1(3)
		C(8)N(5)Pd(1*A*)	116.9(3)
		C(9)C(10)C(11)	121.4(7)
		C(10)C(9)C(1)	121.0(6)
		C(10)C(9)C(14)	119.4(6)
		C(12)C(11)C10	118.9(9)
		C(13)C(14)C(9)	121.1(8)
		C(13)C(12)C(11)	120.4(9)
		C(14)C(9)C(1)	119.5(6)
		C(14)C(13)C(12)	118.7(8)
		C(15)N(4)Pd(1)	127.5(4)
		C(16)C(15)C(20)	120.7(6)
		C(16)C(15)N(4)	118.2(5)
		C(17)C(16)C(15)	119.2(7)
		C(17)C(18)C(19)	119.2(9)
		C(18)C(17)C(16)	121.7(9)
		C(19)C(20)C(15)	117.9(7)
		C(20)C(15)N(4)	120.9(6)
		C(20)C(19)C(18)	121.2(8)

* Coordinates of the A atom: $-x$; y; $1/2 - z$.

Table 3. Data of electronic spectroscopy and mass spectrometry for the palladium(II) complexes

Complex	Empirical formula	$\lambda_{\text{Ï‡1}}$, nm	M^+	
			found (*m*/*z*)	calculated (*m*/*z*)
I	$C_{20}H_{14}N_5SClPd$	480, 820, 900 sh	495, 496, 497, 498, 499, 501, 503	498.3
II	$C_{21}H_{13}N_5SO_2Pd$	450, 900, 1000 sh	504, 505, 506, 507, 508, 509, 510	505.87
III	$C_{21}H_{17}N_5SOClPd$	450, 830	525, 526, 527, 528, 529, 531, 533	529.4
IV	$C_{19}H_{14}N_5SOClPd$	840, 900 sh	499, 500, 501, 502, 503, 504, 505	502.3
V	$C_{30}H_{28}N_7OClPd \cdot 2H_2O$	550, 840, 900 sh	641, 642, 643, 644, 645, 647, 649	644.5
VI	$C_{30}H_{26}N_8ClPd \cdot H_2O$	505, 810, 1020	636, 637, 638, 639, 640, 643, 645	640.5
VII	$C_{16}H_{14}N_8ClPd$	460, 540, 820, 960	456, 457, 458, 459, 460, 462, 464	460.3

the long-wavelength band. The 1-(2-carboxyphenyl)-3-phenyl-5-(benzthiazol-2-yl)formazan complex (**II**) and the complexes of symmetric 1,5-dibenzylbenzimidazolyl- and 1,5-dibenzimidazolylformazans (**VI** and **VII**) are characterized by the shift of this band to the long-wavelength region compared to the complexes of nonsymmetric formazans **I** and **III**–**V** (Table 3, Fig. 1).

It was earlier shown [8] that the addition of amines to solutions of nickel(II) formazanates absorbing in the near-IR region resulted in changes in the electronic absorption spectra: the absorption band at ~1000 nm disappeared and the absorption intensity in the visible spectral region increased.

We studied the interaction of the synthesized palladium formazanates (complexes **I**, **II**, and **IV**) with amines. The addition of ammonia, pyridine, or ethylenediamine to alcoholic solutions of these complexes resulted in the color change from yellow-green to blue, the appearance of a new absorption band at 620–680 nm, and the disappearance of the absorption band at 820–1000 nm. The reaction of palladium 1,3-diphenyl-5-(benzthiazol-2-yl)formazanate (**I**) with pyridine leads to a gradual decrease in the absorption band intensity in the near-IR region and the appearance of absorption bands in the visible region with a maximum at 630 nm (Fig. 2). In this case, the titration pattern is characterized by one isosbestic point, indicating that two types of the complexes are equilibrated in the solution. A similar change in the color occurs immediately upon the addition of a stronger base (ammonia) to a solution of complex **I**. Palladium formazanate **Ia** with λ_{max} = 630 nm was isolated in the crystalline state. According to the X-ray diffraction data, compound **Ia** is the dichlorobis[1,3-diphenyl-5-(benzthiazol-2-yl)formazanate]dipal-

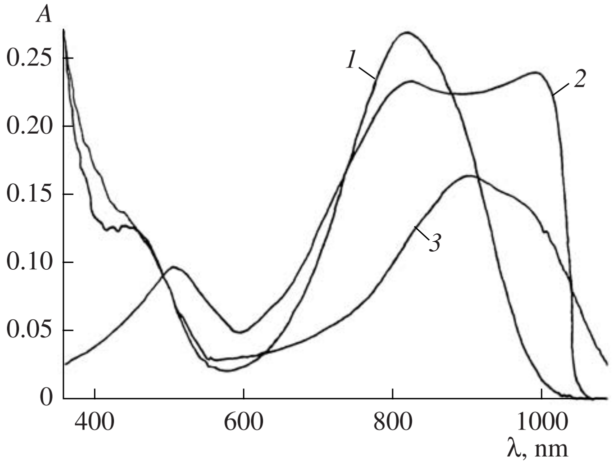


Fig. 1. Electronic absorption spectra of complexes (*1*) **I**, (*2*) **VI**, and (*3*) **II**.

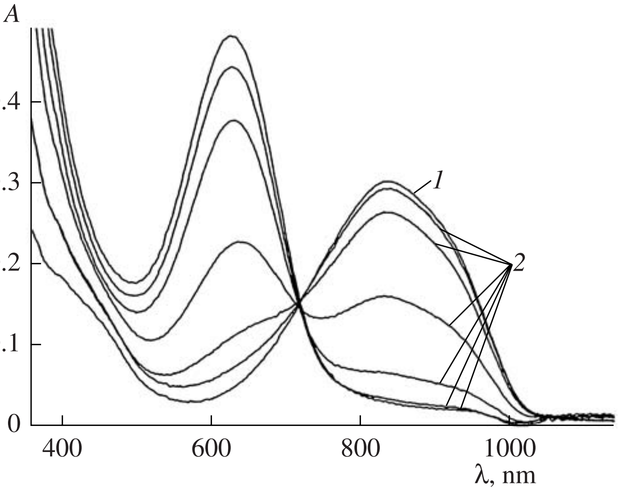


Fig. 2. Electronic absorption spectra of compound **I** in (*1*) ethanol and (*2*) with the addition of pyridine.

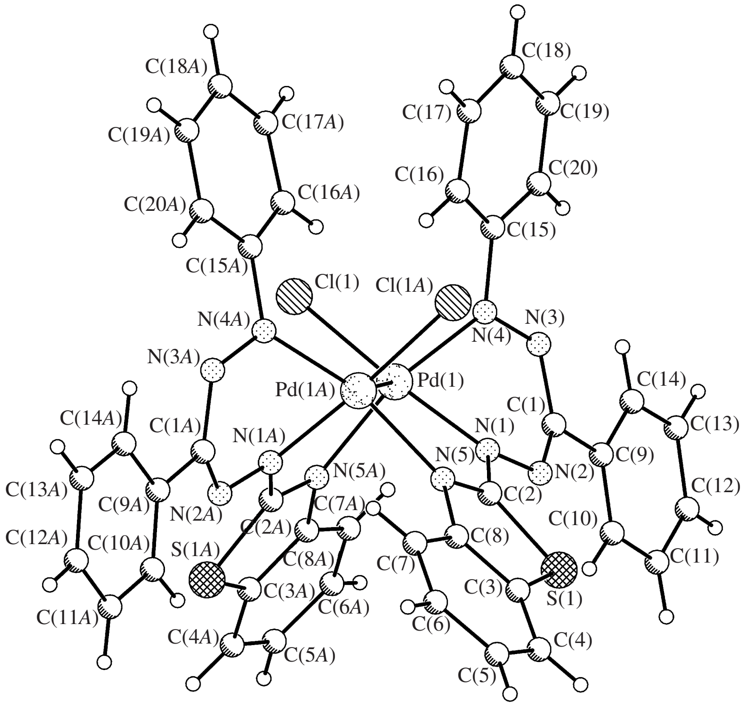
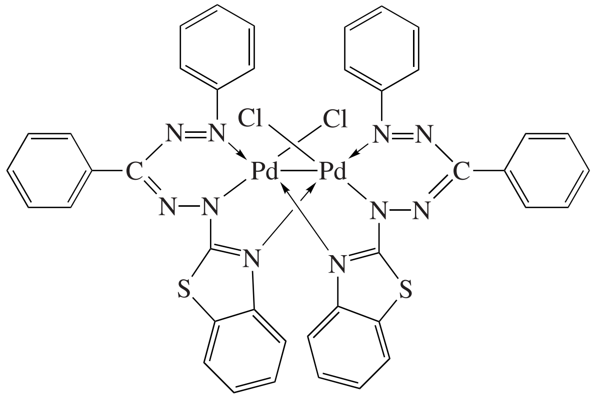


Fig. 3. General view of molecule **Ia**.

ladium(II) binuclear complex $Pd_2Cl_2L_2$, where L is the anionic formazan ligand (Fig. 3)



(**Ia**)

Binuclear molecule **Ia** occupies the partial position in the *2* axis. The Pd atom is coordinated to the vertices of a distorted square pyramid with the second palladium atom in the axial position. The base of the pyramid is formed by the N(1) and N(4) atoms of the formazan fragment of the first ligand L, the N(5A) atom of the benzthiazole fragment of the second ligand L, and the chlorine atom forming the five- and six-membered metallocycles. This coordination mode results in the strong distortion of the angles of the square pyramid: in the deviation of the axial vertex of the pyramid from the normal to the equatorial plane and the strong distortion of the formazan ligand planarity. The metalloformazan cycle exists in an envelope conformation, which is not typical of conjugated chelate systems, and the dihedral angle between the root-mean-square planes of the phenyl substituent at the C(1) atom and the thiazole cycle of formazan is 35°.

The crystal packing of the binuclear molecules forms tunnels (Fig. 4) occupied by the solvate ethanol molecules. However, the orientation of the molecule of the latter was not established because of the strong thermal disordering of the atoms, and the solvate is included into the refined model as a group of the oxygen atoms disordered over several positions with site occupancies of 0.25–0.5. This, very rough assumption results in violations of a series of the calculated experimental parameters and introduces an additional inaccuracy to the determination of the atomic coordinates. However, these violations are insignificant and do not basically change the observed molecular structure. This is indicated, in particular, by the satisfactory R factor value: $R_1 = 0.0446$. Since we did not aimed at achieving high accuracy of structural data as the main task of the study, the obtained result can be accepted satisfactory.

Based on the obtained spectral data and results of studying the behavior of complexes **I** and **III–VII** with amines, we can assume structure A for these complexes. In structure A, formazan acts as a triden-

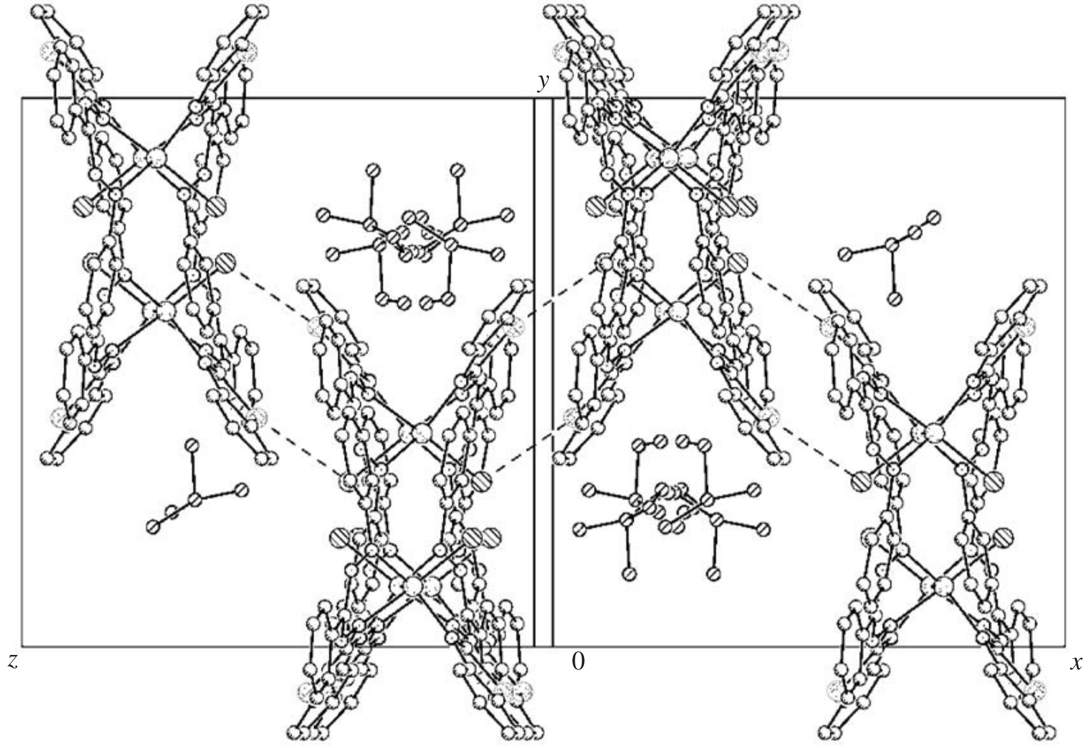
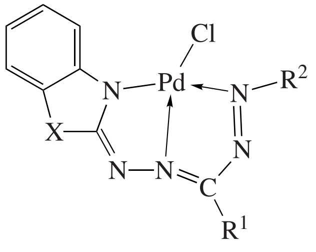
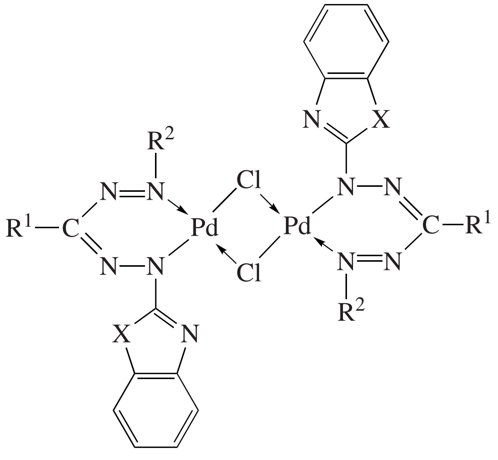


Fig. 4. Fragment of the crystal packing of molecules **Ia**.

tate ligand and the palladium atom enters into the composition of the five-membered metallocycles to form three Pd–N bonds (the chlorine atom occupies the fourth coordination site).



(A)



(B)

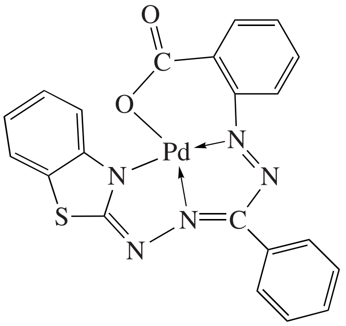
The participation of the N(1) and N(4) atoms of the formazan group and the atom of the benzthiazole cycle of 1-aryl-5-(benzthiazol-2-yl)formazans in coordination with such metals as Ni(II), Co(II), and Fe(II) was confirmed earlier by the X-ray diffraction data [9–11].

Structure B retaining the Pd_2Cl_2 fragment with the haloid bridge characteristic of the palladium(II) compounds is an alternative for complexes **I** and **III**–**VII** [12]. This structure is favored by the low-intensity peaks in the mass spectra (*m*/*z* (%): 994 (2.7) for **I** and 1005

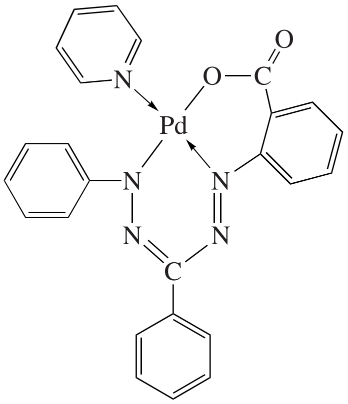
(3.6) for **III**) corresponding to the $Pd_2Cl_2L_2$ composition. In this structure, formazan coordinates the Pd atom only by the N(1) and N(5) atoms of the formazan chain.

Comparing structures A and B (using complex **I** as an example) with structure **Ia** (according to the X-ray diffraction data), we should prefer structure B from which the transformation into compound **Ia** can occur more easily than from structure A. However, the final conclusion about the structures of complexes **I** and **III–VII** can be made on the basis of the X-ray diffraction data.

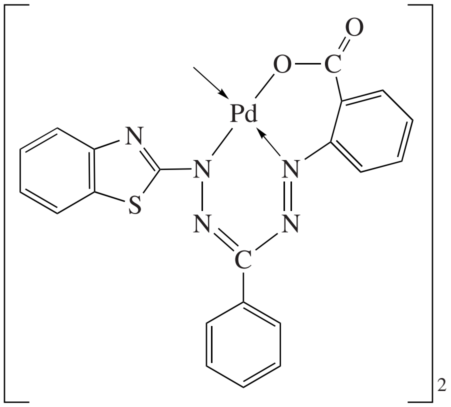
Structure B with two five-membered and one six-membered metallocycles seems probable for palladium formazanate **II**. This structure resembles that described previously for [1-(2-carboxyphenyl)-3,5-diphenylformazanate](pyridine)palladium(II) (structure D confirmed by the X-ray diffraction data [13]).



(C)



(D)



(E)

The coordination site in structures C and D is the same: (PdN_3O). The only difference is that the N(1) and N(5) atoms of the formazan group and the pyridine nitrogen atom are involved in coordination with palladium in structure D, whereas the N(1) and N(4) atoms of the formazan fragment and the benzthiazole nitrogen atom participate in coordination in structure C.

Structure E for complex **II** cannot be excluded, because the mass spectrum of this compound contains low-intensity peaks with $m/z = 1009$, 1011 (~2%) corresponding to Pd_2L_2 along with the 100% peak $m/z = 505$. The fact of the simultaneous presence in solution of two types of the palladium complexes was mentioned for 3-nitro-1,5-diarylformazans [14]. These complexes are shown to differ by the composition (mono- or binuclear) and electronic spectra and are capable of mutual transformations, being treated with amines and hydrochloric acid.

Thus, the palladium(II) complexes that intensely absorb in the near-IR spectral region were synthesized. The good solubility of these compounds in organic solvents, high stability of their solutions in time, and spectral characteristics allow us to recommend the complexes as components for IR-light filters.

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