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Complexes $PdCl_2$ with Optically Active Hybrid Ligands Built of α-Pinene and β-Alanine Molecules

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Abstract—Complexes $Pd(LH)Cl_2$ (LH is the N-derivative of β-alanine based on (–)-α-pinene) and $PdL^{Et}Cl_2$ (L^{Et} is ethyl ester of LH) are synthesized. The X-ray diffraction analysis (CIF file CCDC no. 1471432) shows that the single crystals of the $[PdL^{Et}Cl_2]$ complex belong to the racemate. The crystal structure contains (+)- and (–)-enantiomeric molecules of the mononuclear complex. Ligand L^{Et} is bidentate chelating. The coordination $PdCl_2N_2$ core is a distorted square. The contacts Pd···Cl and hydrogen bonds N–H···Cl between molecules of the (+)- and (–)-enantiomers result in the formation of dimeric ensembles, which are joined into chains due to the C–H···Cl hydrogen bonds. According to the X-ray powder diffraction data, the products of the synthesis of complex $[PdL^{Et}Cl_2]$ contain both the racemate and (+)-enantiomer. The (+)-enantiomer is isolated by the recrystallization of the synthesis product. Complex $Pd(LH)Cl_2$ is an optically active right-handed compound. According to the NMR data, complex $PdL^{Et}Cl_2$ does not dissociate in a $CDCl_3$ solution. The results of IR and NMR spectroscopy indicate that the molecular structure of complex $Pd(LH)Cl_2$ is similar to that of $[PdL^{Et}Cl_2]$.

Keywords: Pd complexes, hybrid ligands, pinene, optical activity, structure

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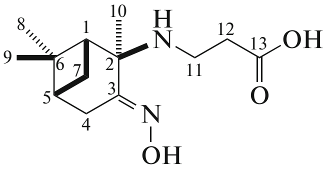
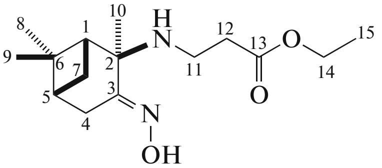
INTRODUCTION

Chiral organic reagents, viz., derivatives of natural terpenes with donor atoms O, N, and S, are actively used for the synthesis of coordination compounds [1–4]. The metal complexes with these reagents are promising for asymmetric catalysis [5, 6], chemistry of luminescent substances [7–11], and bioinorganic chemistry [12]. Heterofunctional compounds containing fragments of both terpene and amino acid (especially natural α-amino acid) are interesting as ligands among the chiral terpene derivatives. We have previously synthesized the luminescent Zn(II) and Cd(II) complexes [13] and the Cu(II) and Ag(I) compounds [14] with the chiral N-derivatives of aminoacetic acid based on natural monoterpenes (+)-3-carene and (–)-α-pinene.

In order to extend the range of complexes with reagents of this type, we carried out experiments on the synthesis and study of the properties of the $PdCl_2$ complexes with the chiral hybrid ligands: acid LH and the corresponding ethyl ester L^{Et} built of the (–)-α-pinene and β-alanine fragments.



(LH)



(L^{Et})

(atomic numeration is presented for the interpretation of the NMR spectra)

Table 1. ^{1}H NMR spectral parameters for compounds **I**, **II**, LH · HCl, and L^{Et}

i		δ_{H_i}, ppm (*J*/Hz)			
		I ($CDCl_3$)	**II** (CD_3CN)	LH · HCl (DMSO-d_6-D_2O 10 : 1 v/v)*	L^{Et} ($CDCl_3$)
1		2.46 dd (5.6, 5.6)	2.55 dd (5.9, 5.3)	2.19 dd (5.8, 5.8)	1.96 dd (6.3, 5.9)
4	*pro-R*	2.56 ddd (19.2, 2.2, 2.2)	2.62 ddd (18.5, 2.6, 2.0)	2.72 ddd (18.6, 2.7, 2.7)	2.82 ddd (18.5, 2.7, 2.1)
	pro-S	3.14 dd (19.2, 4.0)	3.00 dd (18.5, 4.0)	[2.54]	2.54 dd (18.5, 2.8)
5		2.05 dddd (5.6, 5.6, 4.0, 2.2)	1.99 dddd (5.5, 5.3, 4.0, 2.0)	1.97 dddd (5.6, 5.6, 2.7, 2.7)	1.93 dddd (5.9, 5.5, 4.0, 2.1)
7	*pro-R*	1.29 d (12.0)	1.13 d (12.0)	1.55 d (11.1)	1.52 d (10.5)
	pro-S	2.49 dddd (12.0, 5.6, 5.6, 2.2)	2.37 dddd (12.0, 5.9, 5.5, 2.6)	2.32 dddd (11.1, 5.8, 5.6, 2.7)	2.21 dddd (10.5, 6.3, 5.5, 2.7)
8		0.99 s	0.97 s	0.83 s	0.88 s
9		1.37 s	1.34 s	1.29 s	1.28 s
10		2.15 s	2.12 s	1.51 s	1.39 s
11	**a**	3.13 dddd (12.0, 8.7, 5.0, 4.5)	2.91 (12.0, 8.5, 5.0, 4.7)	3.08 ddd (12.0, 7.5, 7.5)	2.89 ddd (11.3, 6.5, 6.5)
	b	2.66 dddd (12.0, 10.5, 3.9, 1.0)	2.65 (12.0, 10.5, 3.9, 1.4)	2.83 ddd (12.0, 6.8, 6.1)	2.60 ddd (11.3, 6.5, 6.5)
12	**a**	3.40 ddd (18.4, 10.5, 5.0)	2.55 (18.3, 10.5, 4.7)	[2.55]	2.44 ddd (17.3, 6.5, 6.5)
	b	2.54 ddd (18.4, 4.5, 3.9)	2.93 (18.3, 5.0, 3.9)	[2.56]	2.42 ddd (17.3, 6.5, 6.5)
14		4.08 dq (10.8, 7.2), 4.13 dq (10.8, 7.2)			4.10 q (7.2)
15		1.24 dd (7.2, 7.2)			1.22 t (7.2)
Other signals:					
−N−H		4.83 d (8.7), ($W_{1/2}$ = 7 Hz)	4.41 d (8.4), ($W_{1/2}$ = 11 Hz)		1.6 br. ($W_{1/2}$ = 130 Hz)
=N−OH		9.79 s	9.6 br. ($W_{1/2}$ = 210 Hz)		8.1 br. ($W_{1/2}$ = 120 Hz)
−COOH			9.6 br. ($W_{1/2}$ = 210 Hz)		

* The chemical shifts in brackets were obtained from the 2D C−H spectrum, because the corresponding signals are overlapped in the 1D ^{1}H NMR spectrum and their positions and shapes cannot be determined.

Interest in the synthesis of the Pd(II) complexes is due to the fact that the Pd(II) compounds with the chiral organic ligands manifest anticancer activity [15, 16] and are also used in asymmetric catalysis [17].

EXPERIMENTAL

The following reagents were used: $PdCl_2$ (high-purity grade), EtOH (rectificate), β-alanine (99%, Reanal (Budapest)), (−)-α-pinene (chemical purity >97%, optical purity 92%, $[\alpha]_D^{20}$ −42 ± 3, Fluka AG (cataloque no. 80600)), and 3-{[(1*R*,2*R*,3*E*,5*R*)-3-hydroxyiminopinan-2-yl]amino}propanoic acid sodium salt (LNa) with $[\alpha]_D^{23}$ −48 (*c* 0.75, H_2O) obtained from (−)-α-pinene using a described procedure [18].

Synthesis of 3-{[(1*R*,2*R*,3*E*,5*R*)-3-hydroxyliminopinan-2-yl]aminopropanoic acid hydrochloride (LH · HCl). Sodium salt LNa (1 g) was dissolved in MeOH (20 mL), and a saturated solution (3 mL) of HCl in MeOH was added to the mixture. A precipitated suspension of NaCl was filtered off, and the filtrate was evaporated in a vacuum of a water-jet pump. The yield of hydrochloride LH · HCl in the form of a white amorphous powder was ~1 g (95%). The ^{1}H NMR spectral parameters are presented in Table 1, and those of the ^{13}C NMR spectra are given in Table 2.

Synthesis of ethyl 3-{[(1*R*,2*R*,3*E*,5*R*)-3-hydroxyliminopinan-2-yl]amino}propanoate (L^{Et}). Methyl ester of β-alanine hydrochloride (1.54 g, 10.0 mmol) was dissolved in MeOH, powdered Na_2CO_3 (1.06 g, 10.0 mmol) was added to the obtained solution, the mixture was stirred for 10 min, and dimeric crystalline (−)-α-pinene nitrosochloride (2.01 g, 5.00 mmol)

Table 2. ^{13}C NMR spectral parameters for compounds **I**, **II**, LH · HCl, and L^{Et}

i	**I** ($CDCl_3$)	**II** (CD_3CN)			LH · HCl (DMSO-d_6 D_2O 10 : 1 v/v)	L^{Et} ($CDCl_3$)
	δ_{C^i}, ppm	δ_{C^i}, ppm	$^{1}J_{C^i-H^i}$, Hz	$^{n}J_{C^i-H^j}$, Hz	δ_{C^i}, ppm	δ_{C^i}, ppm
1	47.08	47.91	147.0	...*	47.24	49.92
2	74.91	75.95		...	63.67	59.80
3	169.43	173.65		...	155.53	161.91
4	29.95	30.79	2 × 133.6	7.0, 5.0	31.15	29.51
5	37.92	39.00	146.9	...	36.73	37.66
6	40.62	41.41		...	39.09	38.88
7	28.77	29.12	2 × 138.5	10.5, ...	26.52	27.84
8	23.31	23.42	3 × 124.9	...	22.07	22.55
9	27.49	27.63	3 × 125.2	...	27.09	27.64
10	24.28	24.72	3 × 129.5	5.7	21.83	23.80
11	42.72	43.07	145.1, 139.0	5.3, 3.0, 3.0	37.54	37.30
12	31.62	32.38	2 × 129.4	3 × 3.9	29.67	35.22
13	173.26	171.40			172.97	172.88
14	60.99					60.25
15	14.01					14.11

* Sign ... corresponds to small values of the spin–spin coupling constants that are not determined because of an insufficient resolution of the spectral lines.

obtained using gaseous NOCl by a described procedure [19] was added. The reaction mixture was vigorously stirred at 18–23°C to the complete dissolution of a nitrosochloride suspension (about 3 days). The solvent was removed on a rotary evaporator in a vacuum of a water-jet pump, and the residue was triturated with 1 M HCl (25 mL) and EtOAc (50 mL). The organic phase was separated and extracted with 1 M HCl (2 × 25 mL). The combined aqueous extract was treated with a concentrated aqueous solution of ammonia to pH 10–11 and extracted with EtOAc (3 × 50 mL). The combined organic extract was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The obtained crude product was purified by column chromatography on silica gel in a petroleum ether–ethyl acetate gradient system to isolate ethyl ester L^{Et} as an amber-colored viscous oil. The yield was 78%; $[\alpha]^{27}_{589}$ –48 (*c* 0.814, EtOH).

IR (film; ν, cm^{-1}): 1732 (C=O); 1201, 1165 (C–O–C). High-resolution mass spectrum (*m/z*): found 282.1934 $[M]^+$. $C_{15}H_{26}N_2O_3$. Calculated *M* = 282.1938. Mass spectrum (EI, 70 eV, *m/z* (I_{rel} (%)): 268 $[M]^+$ (5), 266 (16), 224 (13), 170 (86), 167 (26), 166 (33), 150 (21), 142 (31), 124 (26), 110 (22), 106 (16), 82 (42), 73 (20). The ^1H NMR spectral parameters are presented in Table 1, and the parameters of the ^{13}C NMR spectrum are given in Table 2.

Synthesis of complex $[PdL^{Et}Cl_2]$ (I). Method 1. A warm (50–60°C) solution of $PdCl_2$ (0.036 g, 0.2 mmol) in a mixture of EtOH (4 mL) and concentrated HCl (0.5 mL) was added with stirring to a solution of LH · HCl (0.058 g, 0.2 mmol) in EtOH (4 mL). The resulting solution was magnetically stirred with heating, then the solution was evaporated to 1/2 of the initial volume, and water (10 mL) was added to form a light yellow precipitate. The precipitate was filtered off, washed with water, and dried in a vacuum drying box. The yield was 0.010 g (11%). $[\alpha]^{31}_{589}$ +17 (*c* 0.180, EtOH).

For $C_{15}H_{26}N_2O_3Cl_2Pd$			
anal. calcd., %:	C, 39.3;	H, 5.5;	N, 6.1.
Found, %:	C, 39.1;	H, 5.1;	N, 5.6.

Single crystals of complex **I** (racemate) were obtained by the mixing of a heated to ~50°C solution of $PdCl_2$ (0.036 g, 0.2 mmol) in a mixture of EtOH (3 mL) and concentrated HCl (0.5 mL) with a solution of LH · HCl (0.058 g, 0.2 mmol) in EtOH (5 mL). The formed yellow-brown solution was kept at ~20°C in a not tightly closed beaker from which several crystals suitable for X-ray diffraction analysis precipitated in 4 days. The crystals were taken out of the solution and poured with Nujol.

Method 2. A warm (~60°C) solution of $PdCl_2$ (0.089 g, 0.5 mmol) in a mixture of EtOH (4 mL) and concentrated HCl (0.5 mL) was added with stirring to a solution of L^{Et} (0.141 g, 0.5 mmol) in EtOH (5 mL). The resulting solution was kept in an ice-cold bath, and the solvent was evaporated to a solution volume of ~2 mL. The formed orange precipitate was filtered off, washed with cooled EtOH, and dried in a vacuum drying box. The yield was 0.138 g (60%).

For $C_{15}H_{26}N_2O_3Cl_2Pd$			
anal. calcd., %:	C, 39.3;	H, 5.5;	N, 6.1.
Found, %:	C, 39.0;	H, 5.7;	N, 5.9.

$[\alpha]_{589}^{30}$ +34.5 (c 0.243, $CHCl_3$). The ^1H NMR spectral parameters are presented in Table 1, and the parameters of the ^{13}C NMR spectrum are given in Table 2.

The (+)-enantiomer of complex **I** was isolated by the recrystallization from EtOH of the product synthesized using method 2. For the recrystallized substance, $[\alpha]_{589}^{31}$ +52 (c 0.169, $CHCl_3$).

Synthesis of complex Pd(LH)Cl$_2$ (II). A warm (50–60°C) solution of $PdCl_2$ (0.036 g, 0.2 mmol) in a mixture of water (4 mL) and concentrated HCl (0.5 mL) was added with stirring to a solution of LH · HCl (0.058 g, 0.2 mmol) in water (5 mL). The resulting dark brown solution was evaporated in a water bath to 1/2 of the initial volume, and the solution was rapidly cooled to 0°C to form an orange precipitate. The solution with the precipitate was kept for ~3 h. The precipitate was filtered off, washed with cold water, and dried in a vacuum drying box. The yield was 0.045 g (52%).

For $C_{13}H_{22}N_2O_3Cl_2Pd$			
anal. calcd., %:	C, 36.3;	H, 4.9;	N, 6.5.
Found, %:	C, 36.3;	H, 5.2;	N, 6.4.

$[\alpha]_{589}^{30}$ +16.3 (c 0.492, EtOH). The ^1H NMR spectral parameters are presented in Table 1, and the parameters of the ^{13}C NMR spectrum are given in Table 2.

Microanalyses to C, H, and N were carried out on an Euro EA 3000 analyzer. IR spectra were recorded in a range of 4000–100 cm^{-1} on a Scimitar FTS 2000 and a Vertex 80 FT-IR spectrometers. X-ray phase analysis of polycrystals was carried out on a Shimadzu XRD-7000 diffractometer (CuK_α radiation, Ni filter, 2θ range 5°–60°, increment 0.03° 2θ, scan 1 s per point). Samples for the study were prepared as follows. Polycrystals were triturated in an agatic mortar in the presence of heptane. The obtained suspension was deposited on the polished side of a standard quartz cell. After heptane was dried, the sample represented a thin smooth layer (thickness ~100 μm). Diffraction pattern indexing and quantitative X-ray powder diffraction analysis were performed using the single crystal data. NMR spectra were recorded on a Bruker DRX-500 spectrometer (^1H 500.13 MHz, ^{13}C 125.77 MHz) at 30°C for solutions with a concentration of 15–40 mg/mL in $CDCl_3$, DMSO-d_6, or CD_3CN (OAO Izotop, St. Petersburg) with the atomic fraction of deuterium not lower than 99.8%. A signal of the solvents was used as an internal standard: $CDCl_3$ (δ_C = 76.90 ppm, δ_H = 7.24 ppm), DMSO-d_6 (δ_C = 39.50 ppm, δ_H = 2.50 ppm), and CD_3CN (δ_C = 1.30 ppm, δ_H = 1.93 ppm). The sign of spin–spin coupling constants was not determined. Signal assignment was performed using the ^{13}C NMR spectra recorded in the J-modulation mode (noise proton decoupling, opposite phase for signals of atoms with odd and even numbers of added protons with tuning to the constant J = 135 Hz) and using the 2D spectra of homonuclear ^1H–^1H, heteronuclear ^{13}C–^1H on short-range spin–spin coupling constants (tuning to the constant J = 135 Hz), and heteronuclear ^{13}C–^1H correlation on far-range spin–spin coupling constants (tuning to the constant J = 10 Hz). The values of spin–spin coupling constants of the ^{13}C–^1H spectra were obtained from the ^{13}C NMR spectra recorded in the monoresonance mode. The strong-coupled spin systems were analyzed using the SpinWorks 4.2.0 program package [20]. The ^1H NMR spectral parameters for ligand L^{Et} and the complexes are presented in Table 1, and the parameters of the ^{13}C NMR spectra are given in Table 2.

X-ray diffraction analysis. An experimental array of X-ray reflections for a single crystal of complex **I** was obtained on an X8 APEX automated diffractometer using a standard procedure. The structure of the complex was solved by a direct method and refined by full-matrix least squares in the anisotropic (for non-hydrogen atoms) approximation using the SHELXL-97 program package [21]. The positions of the hydrogen atoms at the carbon atoms were localized geometrically and included into the refinement in the riding model. The main crystallographic characteristics for complex **I** are listed in Table 3. Selected interatomic distances and bond angles are given in Table 4.

The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 1471432; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk) and are available from the authors.

RESULTS AND DISCUSSION

Complex **I** was synthesized by the reaction of $PdCl_2$ in a mixture of EtOH and concentrated HCl with L^{Et} or LH · HCl. Therefore, as a result of the esterification of acid LH due to its interaction with EtOH in the presence of HCl, L^{Et} rather than LH molecule enters as a ligand into the composition of the complex synthesized using method 1. Complex **I** is poorly soluble in water and soluble in $CHCl_3$ and CH_2Cl_2.

According to the X-ray diffraction data, the single crystals of complex **I** belong to the racemate. The crystal structure contains equal amounts of right- and left-handed enantiomeric molecules of the mononuclear complex (Fig. 1). The C(16) atom has an *S* configuration, and the C(26) atom exists in the *R* configuration. The N(11)C(11)C(16)C(18) and N(21)C(21)C(26)C(28) torsion angles in two molecules are −77.4° and +79.1°, respectively. The formation of the racemic compound is due to the optical purity of the starting reagents. The declared optical purity of (−)-α-pinene used in the work was 92%, i.e., the (−)-α-pinene contained (−)- and (+)-enantiomers in a ratio of 96 : 4. Therefore, ligand LH synthesized from this pinene had the ratio of enantiomers at least 96 : 4. Thus, a solid phase of complex **I** (racemate) can be formed in the theoretical yield up to 8%, which is related to a lower solubility and better crystallization of the racemic compound. This situation is not unique for the α-pinene derivatives. There are examples of a better crystallization of the racemic compound in the synthesis of α-substituted oximes of the pinane series [22].

In complex **I**, the Pd^{2+} ion coordinates the N atoms of the oxime group and NH fragment of the bidentate chelating ligand L^{Et} and two Cl^- ions. The coordination PdN_2Cl_2 cores are distorted squares (trapeziums): N···N 2.601 and 2.632, N···Cl 3.080–3.318, and Cl···Cl 3.268 and 3.271 Å. The Pd–N distances vary in a range of 2.003(4)–2.088(5) Å, whereas the bond lengths of the Pd atoms with the N atoms of the oxime groups are shorter. The Pd–Cl distances differ slightly (Table 3). The five-membered chelate PdN_2C_2 ring has an envelope conformation. In two molecules of the complex, the N(12) and N(22) atoms deviate from the planes of four other atoms of the cycle by 0.594(8) and −0.614(7) Å, respectively. In addition, the five-membered hydrogen cycle PdNOHCl is formed in the molecules of the complex due to the strong intramolecular hydrogen bond O–H···Cl (O···Cl 3.071(7) and 3.078(9) Å). In two enantiomeric molecules of complex **I**, the six-membered carbocycles have an Y-like conformation with an insignificant deviation from the planes of the atoms C(11)C(12)C(13)C(15)C(16) and C(21)C(22)C(23)C(25)C(26). The C(14), C(17), and C(24), C(27) atoms deviate from these planes by 0.96(1) and 1.16(1), 1.024(9) and −1.136(8) Å, respectively. The inflection angles in the carbocycles along the C(13)C(15) and C(23)C(25) lines are 143.4(5)° and 141.2(4)°, respectively.

In the crystal structure of compound **I**, there are contacts Pd···Cl between two nearest molecules of the (+)- and (−)-enantiomers (Pd(1)···Cl(21) 3.822(2), Pd(2)···Cl(11) 3.807(2) Å) and weak hydrogen bonds Cl···H–N (Cl(11)···N(22) 3.377(5), Cl(21)···N(12) 3.438(5) Å). This results in the formation of a dimeric ensemble (Fig. 1). The structure of complex **I** contains short intermolecular contacts O=C···Cl–Pd (C···Cl 3.208 and 3.234 Å) between two molecules of the dimeric ensemble. In this ensemble, the Pd···Pd distance equal to 3.627(2) Å is substantially shorter than the doubled van der Waals radius of palladium (4.2 Å). The N(11)N(12)Pd(1)Cl(11)Cl(12) and N(21)N(22)Pd(2)Cl(21)Cl(22) fragments are nearly parallel. The arrangement of the dimeric ensembles in the crystal structure of complex **I** is presented in Fig. 2 as a projection onto the (100) plane. The dimeric ensembles form chains (Cl(21)···C(22) 3.404(6), Cl(11)···C(12) 3.467(5) Å) due to the system of hydrogen bonds C···H–C.

Table 3. Crystallographic characteristics and experimental and structure refinement details for complex **I** (racemate)

Parameter	Value
FW	459.68
Crystal system	Monoclinic
Temperature	150(2)
Space group	$P2_1$
a, Å	10.0050(4)
b, Å	12.8413(5)
c, Å	14.3790(6)
β, deg	91.647(1)
V, $Å^3$	1846.6(1)
Z; ρ_{calcd}, g/cm^3	4, 1.653
μ, mm^{-1}	1.309
Crystal size, mm	0.35 × 0.24 × 0.21
Scan range, θ, deg	1.42–26.02
Number of measured reflections	11458
Number of independent reflections (R_{int})	6736 (0.0210)
Number of reflections with $I > 2\sigma(I)$	5928
Number of refined parameters	429
GOOF on F^2	1.028
R factor, $I > 2\sigma(I)$	$R_1 = 0.0379$ $wR_2 = 0.0952$
R factor (for all I_{hkl})	$R_1 = 0.0420$ $wR_2 = 0.0975$
Parameter of absolute structure	0.07(3)
Residual electron density (max/min) *e*/Å^3	1.482/−0.327

Table 4. Selected interatomic distances (d, Å) and bond angles (ω, deg) in the structure of complex **I** (racemate)

Bond	d, Å	Bond	d, Å
Pd(1)–N(11)	2.003(4)	Pd(2)–N(21)	2.003(5)
Pd(1)–N(12)	2.078(5)	Pd(2)–N(22)	2.088(5)
Pd(1)–Cl(12)	2.278(1)	Pd(2)–Cl(22)	2.280(2)
Pd(1)–Cl(11)	2.305(2)	Pd(2)–Cl(21)	2.304(2)
O(11)–N(11)	1.377(7)	O(21)–N(21)	1.399(7)
O(11)–H(11)	0.8400	O(21)–H(21)	0.8400
O(12)–C(123)	1.203(7)	O(22)–C(223)	1.193(7)
O(13)–C(123)	1.319(7)	O(23)–C(223)	1.342(7)
O(13)–C(124)	1.440(8)	O(23)–C(224)	1.454(8)
N(11)–C(11)	1.280(9)	N(21)–C(21)	1.248(9)
N(12)–C(121)	1.486(6)	N(22)–C(221)	1.503(6)
N(12)–C(16)	1.530(7)	N(22)–C(26)	1.515(7)
Angle	**ω, deg**	**Angle**	**ω, deg**
N(11)Pd(1)N(12)	80.3(2)	N(21)Pd(2)N(22)	78.9(2)
N(11)Pd(1)Cl(12)	176.4(1)	N(21)Pd(2)Cl(22)	176.0(1)
N(12)Pd(1)Cl(12)	98.0(1)	N(22)Pd(2)Cl(22)	98.8(1)
N(11)Pd(1)Cl(11)	91.0(2)	N(21)Pd(2)Cl(21)	91.5(2)
N(12)Pd(1)Cl(11)	169.8(1)	N(22)Pd(2)Cl(21)	168.9(1)
Cl(12)Pd(1)Cl(11)	90.98(7)	Cl(22)Pd(2)Cl(21)	91.04(8)

A comparison of the diffraction pattern of the powdered sample of non-crystallized complex **I** synthesized by method 2 with the theoretical diffraction pattern of complex **I** (racemate) indicates that the sample is not single-phase and contains both the phase of racemic compound **I** and an unknown phase (phases) (Fig. 3). The value of specific rotation [α] +34 for non-crystallized complex **I** indicates that the (+)-enantiomer predominates in the synthesis product. The difference in positions of the lines between the theoretical and experimental diffraction patterns of racemic compound **I** is due to the fact that the powder and single-crystal experiments were carried out at different temperatures and to different predominant orientations of the crystallites. The diffraction pattern of the powdered sample of recrystallized complex **I** already contains no lines of the racemic compound. It is most likely that the recrystallized substance is the (+)-enantiomer with [α] +52.

The reaction of $PdCl_2$ with LH · HCl in an aqueous medium in the presence of HCl affords right-handed complex **II** containing the LH molecule and soluble in water, EtOH, and MeOH. The pH of an aqueous solution of complex **II** is acidic.

The IR spectrum of hydrochloride LH · HCl exhibits a strong band $\delta(NH_2^+)$ at 1589 cm^{-1} indicating the protonation of the NH fragment. There is only one absorption band at 3239 cm^{-1} in a range of 3500–3000 cm^{-1} assigned to ν(OH) of the oxime group. This is consistent with the position of the ν(OH) band at 3200 cm^{-1} in the IR spectrum of 3-*N*,*N*-dimethylaminocaran-4-one oxime [23] and those at 3215 and 3285 cm^{-1} in the spectra of *cis*-verbenone and *cis*-caran-4-one oximes, respectively [24]. It should be mentioned that these oximes contain no NH group. The positions of maxima of the bands corresponding to vibrations of the main functional groups in the IR spectra of free ligand L^{Et} and complexes **I** and **II** are presented in Table 5. The spectrum of L^{Et} exhibits two bands in a range of 3500–3050 cm^{-1}. The band at 3182 cm^{-1} was assigned to ν(OH) on the basis of a comparison with the position of a similar band in the spectrum of LH · HCl, whereas the band at 3330 cm^{-1} was assigned to ν(NH). The data of IR spectroscopy for complex **I** agree with the X-ray diffraction results. In the spectrum of complex **I**, the ν(NH) and ν(OH) bands of the coordinated molecule L^{Et} are shifted to the high-frequency range compared to the positions of the absorption bands of the NH and OH groups in the spectrum of the free ligand L^{Et}. This is consistent with the coordination of the N atoms of these groups to the Pd^{2+} ions. The ν(C=N) and ν(N–O) bands are shifted to the low-frequency range compared to the positions of similar bands in the spectrum of L^{Et}, which is also due to the coordination to the Pd^{2+} ion of the N atom of the oxime group. The frequencies ν(OH), ν(NH), ν(C=N), and ν(NO) for L^{Et} and complex **I** are similar to those found in the IR

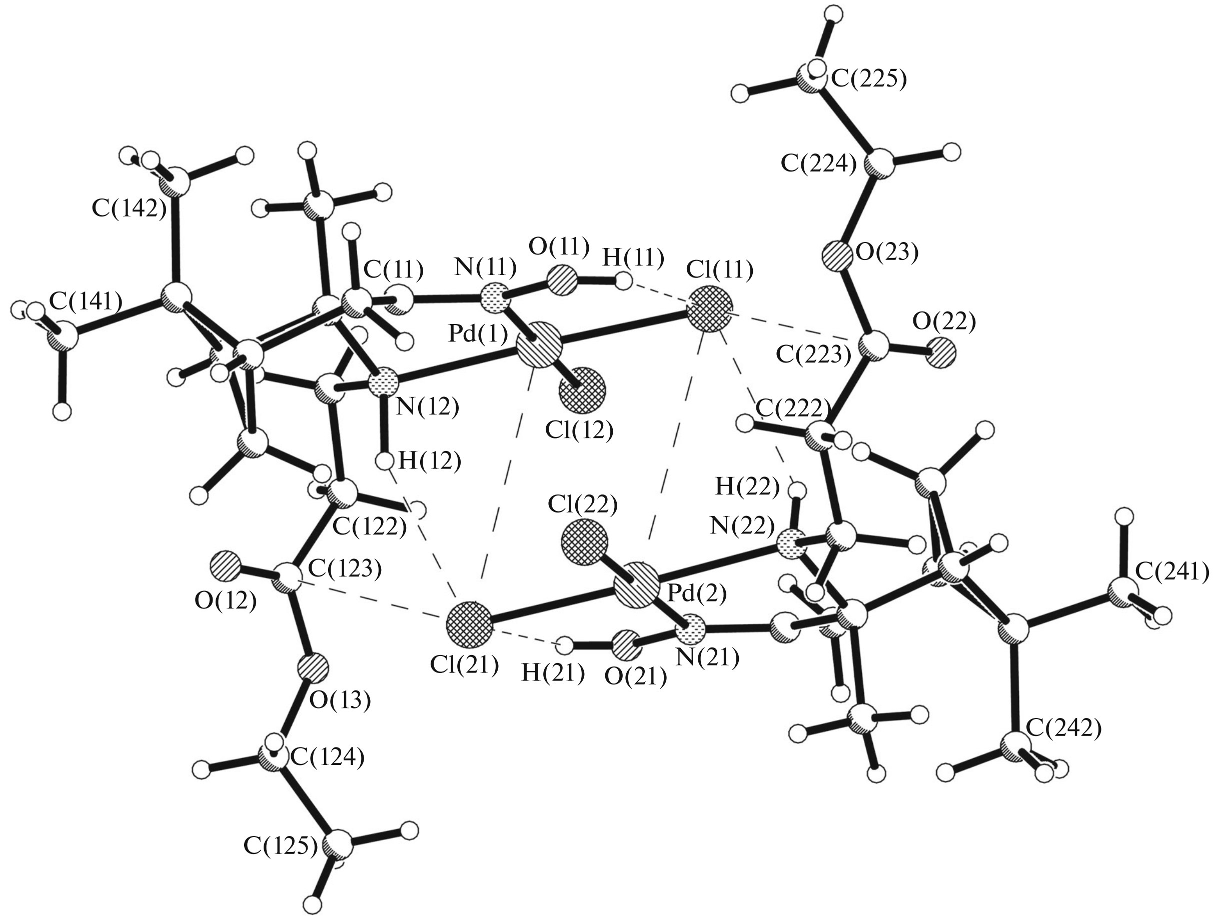


Fig. 1. Dimeric ensembles of the enantiomeric molecules in the crystal structure of complex **I** (racemate).

spectra of α-(*o*-anisidino)pinanone and its complex with $PdCl_2$, whose structures were established by X-ray diffraction analysis [25].

The positions of the ν(OH) bands of the oxime groups and ν(N–O) bands in the IR spectra of complexes **I** and **II** differ insignificantly. The ν(NH) band in the spectrum of complex **II** is shifted to the low-frequency range compared to that of complex **I**, while the ν(C=N) band did not appear. It is most likely that in complex **II** ligand LH is coordinated to the Pd^{2+} ion similarly to L^{Et} (coordination $PdCl_2N_2$ core). A very intense band in the IR spectrum at 1707 cm^{-1} belongs to ν(C=O) of the COOH group. This value of ν(C=O) indicates a possible association of two molecules of complex **II** due to the interaction of the COOH groups. A range of 2700–2500 cm^{-1} also contains a group of weak bands that can be assigned to ν(OH) of the carboxyl group.

NMR spectroscopy was used to obtain information about the structures of ligand L^{Et} and the complexes dissolved in organic media. The pinane fragment of molecules of compounds similar to LH and L^{Et} was found to exist in the Y-like conformation distorted toward a "bridging boat" [26]. In this form, the N–C(2)–C(3)–N dihedral angle has a value of ~80° (according to the quantum-chemical calculation data) and, hence, the pair of hydrogen atoms of the methylene group C-4 is arranged nonsymmetrically relative to the adjacent oxime group, and the *pro*-*R*-H^4 atom is closer to the plane of the oxime group. As a result of this arrangement, the *pro*-*R*-H^4 atom in the ^1H NMR spectrum is more strongly deshielded due to

Table 5. Main vibrational frequencies (cm^{-1}) in the IR spectra of compounds L^{Et}, **I**, and **II**

L^{Et}	I	II	Assignment
3330	3453	3320	ν(NH)
3182	3202	3214	ν(OH)
1733	1720	1707	ν(C=O)
1645	1619		ν(C=N)
1201, 1165	1195, 1156		ν(C–O–C)
950, 934	947, 919	946, 918	ν(N–O)

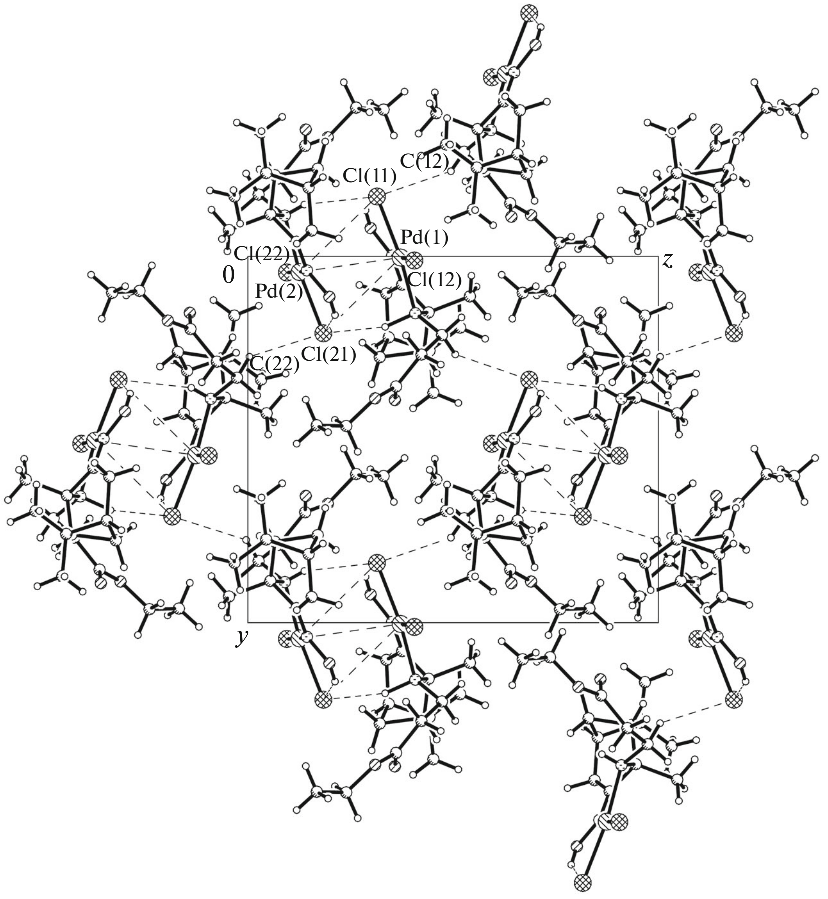


Fig. 2. Projection of the crystal structure of compound **I** onto the (100) plane.

the anisotropy of magnetic susceptibility of the C=N bond and oxime oxygen than the *pro-S*-H^4 atom (Table 2). A similar difference in chemical shifts of the signals of the *pro-R*-H^4 and *pro-S*-H^4 atoms is characteristic of various 2-substituted aminooximes, viz., isopinocamphone derivatives [27] and structurally related compounds [22, 28]. According to the X-ray diffraction data for complex **I**, the N–C(2)–C(3)–N dihedral angle decreases to 36° upon complex formation due to the formation of a five-membered chelate ring. The pinane fragment of the molecule of the complex takes the Y-like conformation distorted toward a bridging chair. In this form, the *pro-S*-H^4 atom is closer to the plane of the oxime fragment and has a high chemical shift in the ^1H NMR spectrum (Table 2). Thus, the relative position of the signals of the geminal hydrogen atoms *pro-S*-H^4 and *pro-R*-H^4 in the ^1H NMR spectrum is a diagnosis characteristic of the coordination of L^{Et} to the Pd^{2+} ion with the formation of the chelate PdN_2C_2 ring due to the participation in coordination of the N atoms of the vicinal pair of the nitrous functional groups NH and NOH.

The signal of the hydrogen atom of the amino group in the ^1H NMR spectrum of the free molecule L^{Et} appears as a broad line at ~1.6 ppm, which is typical of free amines. In the spectra of complexes **I** and **II**, the signal of the hydrogen atom of the amino group undergoes a downfield shift due to complex formation and appears at 4.4–4.8 ppm as a doublet with the broadened components. It is impossible to establish an exact multiplicity of these signals because of the strong line broadening due to the quadrupole moment of the ^{14}N nucleus. However, it was shown by the double homonuclear resonance method that the hydrogen atom of the amino group in the complexes had two different values of vicinal spin–spin coupling constants with the hydrogen atoms of the adjacent methylene group (~8 and ~1 Hz). The different values of these spin–spin coupling constants and the character of splitting of the signals of the hydrogen atoms in the $-CH_2-CH_2-$ group of the β-alanine fragment indicate the absence of free rotation around the N–C(11), C(11)–C(12), and C(12)–C(13) bonds. The anomalous chemical shifts of the hydrogen atoms of the $-CH_2-CH_2-$ group assume that in solutions of complexes **I** and **II** the fragment of β-alanine (or of the

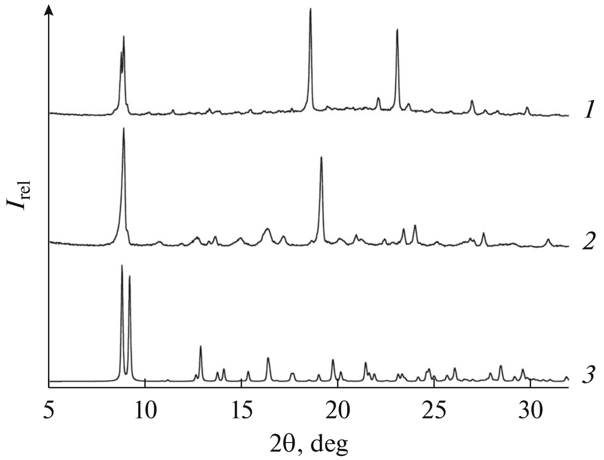


Fig. 3. Experimental diffraction patterns for the powdered samples of complex **I**: (*1*) after recrystallization, (*2*), for non-recrystallized complex **I** obtained by method 2, and (*3*) theoretical diffraction pattern of racemic compound **I**.

corresponding ethyl ester of β-alanine) was fixed in the conformation stabilized by additional interactions between the O atoms of the ester group of L^{Et} and the Pd atoms. The NMR spectra of the complexes show the chemical purity of the synthesized compounds at the level ≥96%. The estimate is given by the signal intensity of impurities compared to the intensity of the satellites C-13 of the major substance in the ^{1}H NMR spectra.

Compounds $PdL^{Et}Cl_2$ (**I**) and $Pd(LH)Cl_2$ (**II**) were synthesized as a result of the study performed. The X-ray diffraction method showed that the single crystals of mononuclear complex **I** belonged to the racemic compound. The Pd^{2+} ion coordinates the N atoms of the oxime group and the NH fragment of the bidentate chelating ligand L^{Et} and two Cl^- ions. The (+)-enantiomer was isolated by the recrystallization of the synthesis product of complex **I** using L^{Et}. Complex **II** is an optically active right-handed compound. According to the data of IR spectroscopy, the molecular structure of complex **II** is similar to that of complex **I**. The composition and structure of compound **II** differ from those of the Cu(II) and Zn(II) complexes with the chiral derivatives of aminoacetic acid based on (+)-3-carene and (–)-α-pinene [13, 14]. Unlike complex **II**, the anions of the derivatives of this acid are coordinated in the Cu(II) and Zn(II) complexes. The anions perform the bidentate bridging function due to the coordination to the metal ions of both the N atoms of the NH and NOH groups and the O atoms of the deprotonated carboxyl group (coordination number 5). This results in the formation of coordination polymers. Unlike the Cu(II) and Zn(II) complexes, the COOH group of compound **II** is not involved in coordination because, most likely, Pd(II) has a higher affinity to the N atom than the affinity to the O atom. In addition, a coordination number of 4 is characteristic of Pd(II). According to the NMR data, in a $CDCl_3$ solution complex **I** retains the mononuclear structure. The Pd atom coordinates two N atoms of the molecule of ligand L^{Et}. Complex **II** is similar to complex **I** by the character of the signals of both the pinane fragment and β-alanine fragment. This indicates the same character of the coordination modes of L^{Et} and LH and the same configuration of the N atom, which became asymmetric due to Pd–N bond formation.

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