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Synthesis of Binuclear Complexes of $PdCl_2$ with Chiral Ethylenediamine Dioxime (H_2L^1), Piperazine Dioxime (H_2L^2), and Propylenediamine Dioxime (H_2L^3), the Derivatives of the Natural Monoterpenoid (R)-(+)-Limonene. The Crystal Structures of $[Pd_2(H_2L^1)Cl_4]$ and $[Pd_2(H_2L^2)Cl_4]$

Z. A. Savel'eva[a], A. V. Tkachev[b], L. A. Glinskaya[a], S. N. Bizyaev[b], R. F. Klevtsova[a], and S. V. Larionov[a]*

[a] *Nikolaev Institute of Inorganic Chemistry, Siberian Division, Russian Academy of Sciences, pr. akademika Lavrent'eva 3, Novosibirsk, 630090 Russia*

[b] *Vorozhtsov Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences, Novosibirsk, Russia*

**E-mail: lar@che.nsk.su*

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Abstract—The diamagnetic complexes $[Pd_2(H_2L^1)Cl_4]$ (I), $[Pd_2(H_2L^2)Cl_4]$ (**II**), and $Pd_2(H_2L^3)Cl_4$ (**III**) with chiral ligands derived from the natural monoterpenoid (R)-(+)-limonene are obtained (H_2L^1 is ethylenediamine dioxime, H_2L^2 is piperazine dioxime, and H_2L^3 is propylenediamine dioxime). According to X-ray diffraction data, the crystal structures of complexes **I** and **II** are composed of binuclear acentric molecules. The coordination polyhedra PdN_2Cl_2 are trapeziums (squares distorted in a tetrahedral manner) made up of two N atoms of the tetradentate bridging cyclic ligands H_2L^1 and H_2L^2 and two Cl atoms. The fragments $PdCl_2$ are *trans* in the complexes. The ^{13}C and ^1H NMR spectra of complexes **I** and **II** in $CDCl_3$ also suggest their binuclear structures.

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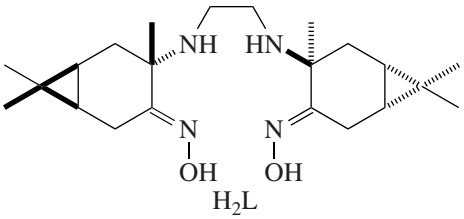
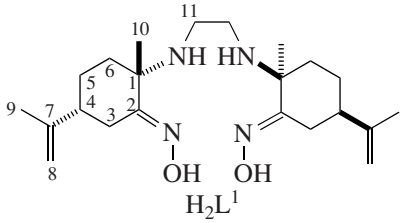
Chemically modified natural substances are promising ligands for the synthesis of novel coordination compounds. Derivatives of chiral natural compounds (including terpenoids) obtained by processing renewable wood-chemical raw materials are of particular interest [1–4]. (+)-3-Carene, α-pinene, and limonene are natural monoterpenoids; their ethylenediamine and propylenediamine dioximes [3, 4] form mononuclear complexes with 3*d* metals (e.g., Ni(II)) [4–7]. Recently, a reaction of $PdCl_2$ (4*d* metal salt) with ethylenediamine dioxime of (+)-3-carene (**H_2L**) has been studied [8].



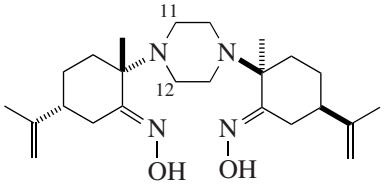
H_2L

The reaction product is the molecular binuclear complex $[Pd_2(H_2L)Cl_4]$ with H_2L as a tetradentate bridging cyclic ligand. According to X-ray diffraction data, the complex contains two coordination entities $PdCl_2N_2$; the fragments $PdCl_2$ are *trans*. It was interesting to obtain complexes of $PdCl_2$ with other chiral monoterpenoid dioximes.

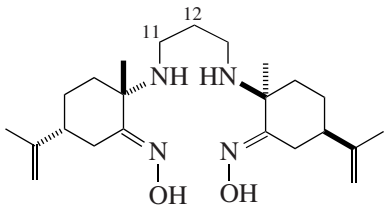
The goal of this study was to synthesize and examine complexes of $PdCl_2$ with chiral ligands based on the monoterpenoid (R)-(+)-limonene: ethylenediamine dioxime (**H_2L^1**), piperazine dioxime (**H_2L^2**), and propylenediamine dioxime (**H_2L^3**). Unlike H_2L and H_2L^1, the dioxime H_2L^2 contains two chains $-(CH_2)_2-$ in the bridge connecting the carbocyclic fragments.



H_2L^1



H_2L^2



H_2L^3

EXPERIMENTAL

Compound H_2L^1 was prepared as described in [7]: $[\alpha]_{578}^{20}$ +86 (*c* 1.5, MeOH). Compound H_2L^3 was prepared as described in [7, 9]: $[\alpha]_{578}^{20}$ +71 (*c* 0.3, MeOH). (R)-(+)-Limonene (Fluka AG, $[\alpha]_D^{20}$ +123), $PdCl_2$ (high-purity grade), fractionally distilled ethanol, and CH_3CN (analytical grade) were used.

Synthesis of N,N'-bis{(1*S*,4*R*)-2-[(*E*)-hydroxyimino]-1-methyl-4-(1-methylethenyl)cyclohexyl}piperazine (H_2L^2). A suspension of Na_2CO_3 (0.88 g, 8.3 mmol) and the limonene *trans*-nitrosochloride dimer (3.35 g, 8.33 mmol) prepared from (R)-(+)-limonene and alkyl nitrite according to a routine procedure [3] was stirred in a mixture of piperazine (0.78 g, 9.0 mmol) and methanol (15 ml) at 50°C to complete homogenization. The solvent was removed *in vacuo* and the residue was stirred with 3M HCl (20 ml). Organic material was extracted with *tert*-butyl methyl ether (3 × 10 ml). The organic extracts were discarded. The aqueous phase was treated with concentrated aqueous ammonia (7 ml). The white crystals that formed were filtered off, washed with *tert*-butyl methyl ether (3 × 10 ml), and dried in air. The yield of H_2L^2 was 40%; T_m = 185–189°C (from CH_3CN), $[\alpha]_{578}^{20}$ +48 (*c* 0.84, CH_3OH : THF = 7 : 1).

For $C_{24}H_{40}N_4O_2$			
anal. calcd. (%):	C, 69.2;	H, 9.7;	N, 13.4.
Found (%):	C, 68.7;	H, 9.5;	N, 13.2.

IR (KBr, ν_{max}, cm^{-1}): 3279 (O–H); 1646 (C=CH_2); 938 (N–O).

MS (*m*/*z*, %): 416.31441 (6, $[M]^+$, for $C_{24}H_{40}N_4O_2$ anal. calcd.: $[M]^+$ = 416.31511), 399 (6), 250 (10), 248 (10), 234 (25), 233 (12), 210 (113), 209 (100), 205 (23), 195 (17), 191 (44), 167 (14), 166 (71), 152 (9), 151 (10), 150 (9), 139 (12), 123 (5), 110 (14), 107 (15), 96 (13), 93 (17), 87 (11), 85 (86), 83 (30), 79 (14), 77 (8), 58 (28), 56 (41), 55 (35), 43 (51), 41 (32).

^{1}H NMR (δ, ppm): 0.92 s (6H, H(10)), 1.17 ddd (2H, *J* = 14.4 Hz, *J* = 13.6 Hz, *J* = 3.1 Hz, $H(6_{ax})$), 1.33 d (2H, *J* = 13.1, $W_{1/2}$ = 8, $H(5_{eq})$), 1.66 s (6H, H(9)), 1.68 m (2H, $H(5_{ax})$), 1.89 dd (2H, *J* = 12.9 Hz, *J* = 11.2 Hz, $H(3_{ax})$), 1.95 ddd (2H, *J* = 12.7 Hz, *J* = 12.7 Hz, *J* = 3.0 Hz, *J* = 3.0 Hz, H(4)), 2.02 ddd (2H, *J* = 13.8 Hz, *J* = 3.0 Hz, *J* = 3.0 Hz, $H(6_{eq})$), 2.18 d (4H, *J* = 7.5 Hz, H(11a)), 2.39 s (4H, $W_{1/2}$ = 35 Hz, H(11b)), 3.08 d (2H, *J* = 10.5 Hz, $H(3_{eq})$), 4.62 m (2H, H(8a)), 4.66 m (2H, H(8b)), 9.89 br.s (2H, O–H).

^{13}C NMR ((δ, ppm): 13.63 (C(10)), 19.87 (C(9)), 24.42 (C(3)), 24.56 (C(5)), 36.56 (C(6)), 44.67 (C(4)), 44.87 (C(11)), 59.69 (C(1)), 108.35 (C(8)), 148.47 (C(7)), 162.19 (C(2)).

Synthesis of $[Pd_2(H_2L^1)Cl_4]$ (I). Palladium dichloride (0.035 g, 0.2 mmol) was dissolved in concentrated HCl (~ 0.2 ml) under heating. Ethanol (2 ml) was added and so was a solution of H_2L^1 (0.039 g, 0.1 mmol) in a mixture of EtOH (2 ml) and CH_3CN (1 ml). The resulting solution was filtered through a filter paper and left at room temperature overnight. The yellow precipitate that formed was filtered off under suction, washed with cooled ethanol, and dried in air. The yield was 0.043 g (60%), $[\alpha]_{578}^{20}$ –90 (*c* 0.3, CH_2Cl_2).

For $C_{22}H_{38}N_4Cl_4O_2Pd_2$				
anal. calcd. (%):	C, 35.5;	H, 5.2;	N, 7.5;	Cl, 19.0.
Found (%):	C, 36.2;	H, 5.2;	N, 7.9;	Cl, 18.9.

^{1}H NMR (δ, ppm): 1.73 dddd (2H, *J* = 14 Hz, *J* = 13 Hz, *J* = 4 Hz, *J* = 3 Hz, $H(5_{ax})$), 1.77 br.s (6H, H(9)), 1.90 (2H, *J* = 13 Hz, *J* = 3 Hz, *J* = 3 Hz, $H(6_{eq})$), 2.02 (2H, *J* = 14 Hz, *J* = 3 Hz, *J* = 3 Hz, *J* = 3 Hz, *J* = 2 Hz, $H(5_{eq})$), 2.10 s (6H, H(10)), 2.16 ddd (2H, *J* = 13 Hz, *J* = 13 Hz, *J* = 3 Hz, $H(6_{ax})$), 2.21 dd (2H, *J* = 18 Hz, *J* = 6 Hz, $H(3_{ax})$), 2.54 m ($W_{1/2}$ = 13 Hz, 2H, H(4)), 2.83 XX' as part of the spin system AA'MM'XX' (2H, H(11a)), 3.39 ddd (2H, *J* = 18 Hz, *J* = 2 Hz, *J* = 2 Hz, $H(3_{eq})$), 4.30 MM' as part of the spin system AA'MM'XX' (2H, H(11b)), 4.54 br.s (2H, H(8a)), 5.00 br.s (2H, H(8b)), 6.02 AA' as part of the spin system AA'MM'XX' (2H, –NH), 9.66 s (2H, –OH). The parameters of the spin system: $\delta_A = \delta_{A'} = 6.02$ ppm, $\delta_M = \delta_{M'} = 4.30$ ppm, $\delta_X = \delta_{X'} = 2.83$ ppm, $J_{AM} = J_{A'M'} = 1$ Hz, $J_{AX} = J_{A'X'} = 11$ Hz, $J_{MX} = J_{M'X'} = -12$ Hz, $J_{MX'} = J_{M'X} = 1.5$ Hz, $J_{MM'} = 12$ Hz, $J_{XX'} = 2$ Hz.

^{13}C NMR (δ, ppm): 169.21 (C(2)), 146.07 (C(7)), 111.98 (C(8)), 71.36 (C(1)), 50.12 (C(11)), 37.83 (C(4)), 29.07 (C(6)), 28.66 (C(10)), 27.86 (C(3)), 24.12 (C(5)), 21.77 (C(9)).

Synthesis of $[Pd_2(H_2L^2)Cl_4]$ (II). Palladium dichloride (0.035 g, 0.2 mmol) was dissolved in concentrated HCl (~ 0.2 ml) under heating. Ethanol (3 ml) was added and so was a solution of H_2L^2 (0.042 g, 0.1 mmol) in a mixture of EtOH (3 ml) and CH_3CN (1 ml). Then the reaction mixture was treated as described for complex **I**. The yield of the red-orange product was 0.050 g (65%), $[\alpha]_{578}^{20}$ –40 (*c* 0.5, CH_2Cl_2).

Table 1. Crystallographic parameters and a summary of data collection and refinement for complexes **I** and **II**

Parameter	Value	
Compound	I	II
M	745.16	771.20
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1$
a, Å	7.4464(2)	8.3766(2)
b, Å	12.9063(3)	12.8615(3)
c, Å	29.9218(8)	14.3601(4)
β, deg		104.396(1)
V, Å^3	2875.65(13)	1498.52(7)
Z; ρ_{calcd}, g/cm^3	4; 1.721	2; 1.709
μ, mm^{-1}	1.649	1.585
Crystal size, mm	0.32 × 0.25 × 0.08	0.32 × 0.08 × 0.06
θ scan range, deg	2.08–25.49	2.16–25.67
Number of measured reflections	18550	10335
Number of independent reflections	5338	5512
R_{int}	0.0308	0.01381
Number of reflections with $I > 2\sigma(I)$	4883	5409
Number of parameters refined	351	337
GOOF for F^2	1.020	0.995
R factor, $I > 2\sigma(I)$		
R_1	0.0218	0.0149
wR_2	0.0459	0.0380
R factor (for all I_{hkl})		
R_1	0.0275	0.0156
wR_2	0.0478	0.0384
Absolute structural parameter	0.00(2)	–0.014(14)
Residual electron density (max/min) e Å^{-3}	0.342/–0.214	0.537/–0.209

For $C_{24}H_{40}N_4Cl_4O_2Pd_2$

anal. calcd. (%):	C, 37.4;	H, 5.2;	N, 7.3;	Cl, 18.4.
Found (%):	C, 37.5;	H, 5.2;	N, 7.5;	Cl, 17.4.

^{1}H NMR (δ, ppm): 1.75 dddd (2H, J = 14 Hz, J = 12 Hz, J = 4 Hz, J = 3 Hz, H(5_{ax})), 1.80 br.s (6H, H(9)), 1.95 ddd (2H, J = 13 Hz, J = 4 Hz, J = 3 Hz, H(6_{eq})), 2.00 ddddd (2H, J = 14 Hz, J = 4 Hz, J = 4 Hz, J = 3 Hz, J = 2 Hz, H(5_{eq})), 2.22 s (6H, H(10)), 2.32 ddd (2H, J = 13 Hz, J = 12 Hz, J = 3 Hz, H(6_{ax})), 2.42 dd (2H, J = 18 Hz, J = 6 Hz, H(3_{ax})), 2.52 m ($W_{1/2}$ = 13 Hz, 2H, H(4)), 3.08 m (2H, H(11a)), 3.33 ddd (2H, J = 18 Hz, J = 2 Hz, J = 2 Hz, H(3_{eq})), 3.34 m (2H, H(11b)), 4.21 m (2H, H(11c)), 4.26 m (2H, H(11d)), 4.56 br.s (2H, H(8a)), 5.05 br.s (2H, H(8b)), 9.85 s (2H, –OH).

^{13}C NMR (δ, ppm): 167.72 (C(2)), 146.00 (C(7)), 112.00 (C(8)), 76.97 (C(1)), 53.38 (C(11a)), 49.23 (C(11b)), 37.47 (C(4)), 29.46 (C(6)), 28.00 (C(10)), 25.29 (C(3)), 24.68 (C(5)), 21.67 (C(9)).

Synthesis of $Pd_2(H_2L^3)Cl_4$ (III). Palladium dichloride (0.035 g, 0.2 mmol) was dissolved in concentrated HCl (~ 0.2 ml) under heating. Ethanol (2 ml) was added and so was a solution of H_2L^3 (0.040 g, 0.1 mmol) in EtOH (2 ml). The yellow precipitate formed upon the mixing of the solutions was treated as described for complex **I**. The yield was 0.035 g (45%), $[\alpha]_{578}^{20}$ –90 (c 0.7, CH_2Cl_2).

For $C_{23}H_{40}N_4Cl_4O_2Pd_2$ (M_{exp} = 761; M_{calcd} = 759)

anal. calcd. (%):	C, 36.4;	H, 5.3;	N, 7.4;	Cl, 18.7.
Found (%):	C, 36.6;	H, 5.3;	N, 7.0;	Cl, 19.4.

Microanalyses of the complexes obtained were performed on Hewlett Packard 185 and Carlo Erba 1106 analyzers. Their molecular masses were determined by vapor-phase osmometry in acetone on a Knauer instrument. Static magnetic susceptibility was measured by the Faraday method at room temperature.

^{1}H and ^{13}C NMR spectra (500 and 125 MHz, respectively) were recorded on a Bruker DRX 500 instrument at 30°C in $CDCl_3$–DMSO-d_6 (4 : 1 v/v, 30 mg/ml) for H_2L^2 and in $CDCl_3$ (5–10 mg/ml) for the complexes. The signals of the solvent at δ_H 7.24 and δ_C 76.90 ppm (for solutions in $CDCl_3$) and at δ_H 2.50 and δ_C 39.50 ppm (for solutions containing DMSO-d_6) were used as the internal standards.

Specific rotation was measured on a Palamat A polarimeter. IR spectra were recorded on a Bruker Vector-22 instrument. Mass spectra (EI, 70 eV) were recorded on a Finnigan MAT-8200 spectrometer.

X-ray diffraction analysis. A single crystal of complex **I** was grown by slow evaporation of its solution in EtOH–CH_3CN–$CHCl_3$ (1 : 1 : 2). A single crystal of complex **II** was selected from the precipitate obtained

in its synthesis. No single crystals of complex **III** suitable for X-ray diffraction analysis were obtained. Experimental material was collected on an X8 APEX automated diffractometer at room temperature according to a standard procedure (MoK_α radiation, graphite monochromator, φ scan mode, small scan steps). Crystallographic parameters and a summary of data collection and refinement for complexes **I** and **II** are given in Table 1. Structures **I** and **II** were solved by the direct method and refined by the full-matrix least-squares method in the anisotropic approximation for non-hydrogen atoms with the SHELXL-97 program package [10]. All H atoms were located geometrically and refined isotropically together with the non-hydrogen atoms. Comprehensive tables of the atomic coordinates and the bond lengths and angles have been deposited with the Cambridge Crystallographic Data Collection (CCDC Nos. 681 982 and 681 983) and can be made available from the authors upon request. Selected bond lengths and angles in structures **I** and **II** are given in Table 2.

RESULTS AND DISCUSSION

Reactions of $PdCl_2$ with H_2L^1–H_2L^3 gave complexes **I**–**III** similar in composition to the complex $[Pd_2(H_2L)Cl_4]$ (**IV**) [8]. The complexes obtained are diamagnetic, which suggests the low-spin configuration d^8. Unlike the dextrorotatory ligands H_2L^1–H_2L^3, complexes **I**–**III** are levorotatory.

X-ray diffraction analysis showed that the crystal structures of complexes **I** and **II** are made up of binuclear acentric molecules (Fig. 1). In structures **I** and **II**, each Pd atom coordinates two N atoms of the tetradentate bridging cyclic ligand H_2L^1 or H_2L^2 and two Cl atoms in the *cis*-positions. The coordination of Pd with H_2L^n (n = 1 and 2) closes the five-membered chelate rings PdN_2C_2. The Pd–N distances differ in both complexes: 1.978(3), 1.984(3) and 2.059(2), 2.066(2) Å in **I** and 1.983(2), 1.984(2) and 2.120(2), 2.136(2) Å in **II**. The shorter distances relate to the bonds between the Pd atoms and the oxime N atoms. The Pd–Cl distances are 2.279–2.300 Å in **I** and 2.288–2.315 Å in **II**. The coordination entities PdN_2Cl_2 can be regarded as distorted squares (trapeziums) (N···N 2.596–2.616, N···Cl 3.041–3.412, Cl···Cl 3.303–3.332 Å). This geometry correlates with the diamagnetism of complexes **I** and **II**. The largest deviations of the N and Cl atoms from the four planes N_2Cl_2 are 0.090 Å; the Pd atom deviates from these planes by ≤0.0024 Å (in **II**). The shortest Pd···Pd distances are 5.367(1) and 5.662(1) Å in **I** and 5.952(2) and 5.786(2) Å in **II**. The planes N_2Cl_2 in the coordination entities are *trans* and make, on average, an angle of ~110.4° in **I** and 97.4° in **II**. The Pd–N and Pd–Cl bond lengths and angles in complexes **I** and **II** are close to the corresponding parameters for **IV** [8]. The five-membered H rings PdNOHCl are made by the intramolecular hydrogen bonds O–H···Cl (Cl(2)···O(1) and Cl(4)···O(2) are 3.072(3) and 3.033(4) Å in **I** and

Table 2. Selected bond lengths and angles in structures **I** and **II**

Bond	*d*, Å	Bond	*d*, Å
	I		
Pd(1)–N(2)	1.984(3)	Pd(2)–N(4)	1.978(3)
Pd(1)–N(1)	2.059(2)	Pd(2)–N(3)	2.066(2)
Pd(1)–Cl(1)	2.2783(10)	Pd(2)–Cl(3)	2.2867(9)
Pd(1)–Cl(2)	2.2957(9)	Pd(2)–Cl(4)	2.3011(9)
N(1)–C(21)	1.490(4)	N(3)–C(22)	1.496(4)
N(1)–C(1)	1.533(4)	N(3)–C(11)	1.546(4)
N(2)–C(2)	1.287(4)	N(4)–C(12)	1.282(4)
N(2)–O(1)	1.389(3)	N(4)–O(2)	1.389(3)
C(4)–C(7)	1.504(5)	C(14)–C(17)	1.514(5)
C(7)–C(8)	1.321(5)	C(17)–C(18)	1.306(6)
C(7)–C(9)	1.500(5)	C(17)–C(19)	1.500(5)
C(21)–C(22)	1.513(4)		
	II		
Pd(1)–N(2)	1.983(2)	Pd(2)–N(4)	1.984(2)
Pd(1)–N(1)	2.136(2)	Pd(2)–N(3)	2.120(2)
Pd(1)–Cl(1)	2.2888(7)	Pd(2)–Cl(3)	2.2926(7)
Pd(1)–Cl(2)	2.3148(7)	Pd(2)–Cl(4)	2.2952(6)
N(1)–C(21)	1.499(3)	N(3)–C(24)	1.496(3)
N(1)–C(22)	1.501(3)	N(3)–C(23)	1.504(3)
N(1)–C(1)	1.552(3)	N(3)–C(11)	1.553(3)
N(2)–C(2)	1.262(3)	N(4)–C(12)	1.275(3)
N(2)–O(1)	1.387(3)	O(2)–N(4)	1.390(3)
C(4)–C(7)	1.517(3)	C(14)–C(17)	1.514(3)
C(4)–C(5)	1.552(3)	C(14)–C(15)	1.525(4)
C(5)–C(6)	1.532(3)	C(15)–C(16)	1.510(4)
C(7)–C(8)	1.311(4)	C(17)–C(18)	1.307(4)
C(7)–C(9)	1.490(4)	C(17)–C(19)	1.502(4)
C(21)–C(24)	1.524(3)	C(22)–C(23)	1.508(3)
Angle	**ω, deg**	**Angle**	**ω, deg**
	I		
N(2)Pd(1)N(1)	79.88(10)	N(4)Pd(2)N(3)	80.23(10)
N(2)Pd(1)Cl(1)	170.13(8)	N(4)Pd(2)Cl(3)	173.12(8)
N(1)Pd(1)Cl(1)	95.38(8)	N(3)Pd(2)Cl(3)	96.13(7)
N(2)Pd(1)Cl(2)	91.40(8)	N(4)Pd(2)Cl(4)	91.54(9)
N(1)Pd(1)Cl(2)	171.10(8)	N(3)Pd(2)Cl(4)	171.75(7)
Cl(1)Pd(1)Cl(2)	93.51(4)	Cl(3)Pd(2)Cl(4)	92.12(4)
C(2)N(2)Pd(1)	117.9(2)	C(12)N(4)Pd(2)	119.6(2)
O(1)N(2)Pd(1)	124.6(2)	O(2)N(4)Pd(2)	123.1(2)
C(2)N(2)O(1)	116.7(3)	C(12)N(4)O(2)	116.9(3)
C(1)N(1)Pd(1)	105.1(2)	C(11)N(3)Pd(2)	106.3(2)
	II		
N(2)Pd(1)N(1)	78.75(7)	N(4)Pd(2)N(3)	78.91(7)
N(2)Pd(1)Cl(1)	174.91(6)	N(4)Pd(2)Cl(3)	174.77(6)
N(1)Pd(1)Cl(1)	100.88(5)	N(3)Pd(2)Cl(3)	100.49(5)
N(2)Pd(1)Cl(2)	89.71(6)	N(4)Pd(2)Cl(4)	89.10(6)
N(1)Pd(1)Cl(2)	167.34(5)	N(3)Pd(2)Cl(4)	167.59(5)
Cl(1)Pd(1)Cl(2)	91.08(3)	Cl(3)Pd(2)Cl(4)	91.74(3)
C(2)N(2)Pd(1)	119.8(2)	C(11)N(3)Pd(2)	101.2(1)
O(1)N(2)Pd(1)	123.1(2)	O(2)N(4)Pd(2)	124.3(1)
C(2)N(2)O(1)	117.1(2)	C(12)N(4)O(2)	117.4(2)
C(1)N(1)Pd(1)	102.6(1)	C(11)N(3)Pd(2)	101.2(1)

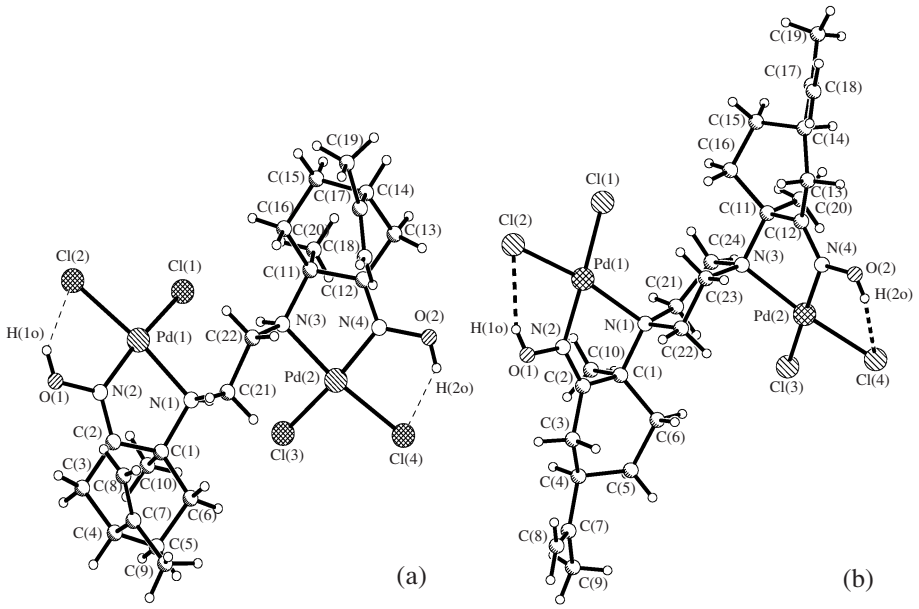


Fig. 1. Structures of binuclear complexes (a) **I** and (b) **II** with numbering of the non-hydrogen atoms.

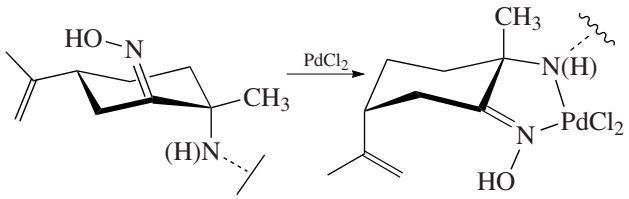
2.991(3) and 3.011(3) Å in **II**; the angle O(1)H(1o)Cl(2) is 136° and 149° and the angle O(2)H(2o)Cl(4) is 137° and 150° in **I** and **II**, respectively).

The chelate rings PdN_2C_2 in both complexes exist in an envelope conformation: the N(1) and N(3) atoms deviate from the planes of the other four atoms by 0.662 and 0.583 Å in **I** and by 0.745 and 0.807 Å in **II**. The conformations of the six-membered carbocycles C(1)–C(6) and C(11)–C(16) in the menthane fragments are different for complexes **I** and **II**. In **I**, the conformation of the carbocycles is a slightly distorted chair with methyl and isopropenyl groups in axial positions. The C(2), C(5), C(12), and C(15) atoms deviate from the planes of the other four C atoms of the rings by 0.482, –0.718, –0.457, and 0.687 Å, respectively. In complex **II**, analogous six-membered carbocycles exist in a twist form with the following endocyclic torsion angles: –30.3°, 53.4°, –19.6°, –38.0°, 60.2°, and –25.7°. The H-rings PdNOHCl exist in an envelope conformation.

The relative positions of binuclear molecules in crystal structures **I** and **II** are shown in Fig. 2 as a projection onto the plane (100). The weak hydrogen bonds C–H···Cl (Cl(3)–C(5) 3.706(4) Å, Cl(2)–C(20) 3.733(4) Å, and Cl(2)–C(15) 3.799(4) Å) in structure **I** are indicated with dashed lines (Fig. 2a).

In complex **I**, each binuclear molecule is linked by H bonds with the Cl and O atoms of the adjacent molecule (O(2)···C(20) 3.380(4) Å, Cl(1)···N(4) 3.563(3) Å). Crystal structure **II** shows a Pd(1)···Cl(4) contact (3.653(2) Å), which is shorter than the sum of the van der Waals radii of the Pd and Cl atoms (3.90 Å) (Fig. 2b).

When dissolved in $CDCl_3$, complexes **I** and **II** retain the topology of their molecular structures found for the crystalline state: two fragments $PdCl_2$ coordinate two pairs of the vicinal N atoms of bis(α-amino oximes). This is evident from the ^1H and ^{13}C NMR spectra of complexes **I** and **II** in $CDCl_3$: almost identical sets of the $^3J_{^1H-^1H}$ coupling constants suggest similarly shaped six-membered carbocycles in the complexes. The coupling constants correspond to the six-membered carbocycle in a distorted chair conformation (as in crystal structure **I**). The NMR spectra of both complexes show characteristic differences from the spectra of H_2L^1 and H_2L^2; this indicates a changed conformation of the six-membered carbocycle of the *para*-menthane fragments upon the complexation involving two vicinal N atoms. As the result, the conformation "chair 1" of the six-membered carbocycle with an equatorial isopropenyl group and an equatorial methyl C(10) atom, which is characteristic of free ligands, changes into the conformation "chair 2" with an axial isopropenyl group and an axial C(10) atom:



"chair 1" "chair 2"

It follows from X-ray diffraction data that the conformation of the six-membered carbocycle (distorted

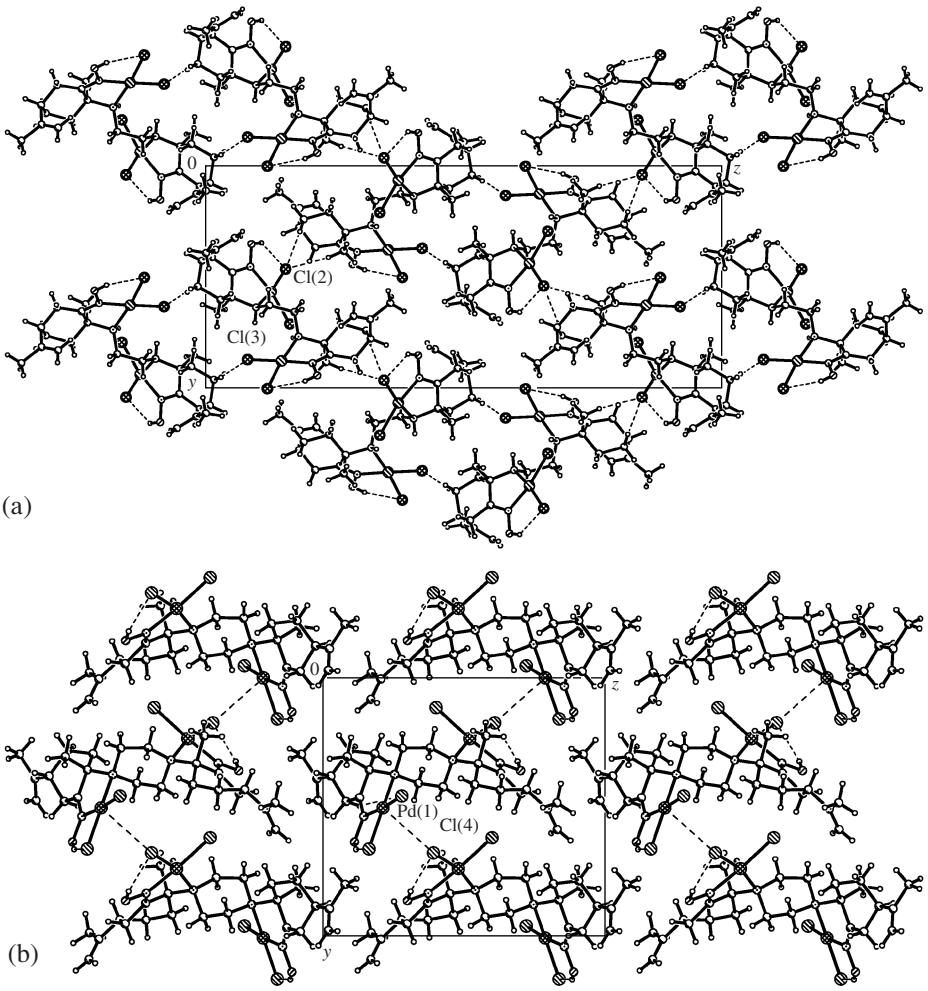


Fig. 2. Molecular packing in crystal structures **I** and **II** (projection onto the plane (100)). Weak hydrogen bonds in complex **I** (a) and the Pd(1)···Cl(4) contact in complex **II** (b) are indicated with dashed lines.

chair) is retained upon the crystallization of complex **I**. In contrast, the less strained chair conformation of this ring in complex **II** changes, upon crystallization, into a *twist* form; this is probably due to more compact packing in the solid state.

As for the conformations of structures **I** and **II** in solution, NMR spectra provide a definite pattern only for complex **I**. The signals for the H atoms of the linker ethylene group and for the amino H atoms in its ^{1}H NMR spectrum give a characteristic spin system AA'MM'XX'; its parameters are identical with those of an analogous system for complex **IV** [8]. One can state that in $CDCl_3$, the conformation of the bridging ethylenediamine fragment in complex **I** is the same as in complex **IV**.

Like complexes **I** and **II**, complex **III** is soluble at room temperature in low-polarity chlorine-containing organic solvents and in acetone (in the latter, complex **III** exists as a monomer). However, an analysis of the ^{1}H NMR spectra of complex III revealed substantial differences between its structure and structures **I** and **II** in solution. The ^{1}H NMR spectra of complexes **I** and **II** show close chemical shifts of the diagnostic signals, except for the signal of the amino H atom absent from structure **II** (Fig. 3). First, in contrast to complexes **I** and **II**, the spectrum of complex **III** (Fig. 3a) contains signals for at least four structurally different species (four narrow signals for the oxime proton with the intensity ratio 1 : 3 : 3 : 15). This can be due to either the formation of four isomers during the synthesis of the complex or the formation of a single structural isomer that, when dissolved, behaves like a set of conformers which are in dynamic equilibrium and undergo slow interconversions (on the time scale of the NMR experiment). Second, the spectrum of complex **III** does not contain the signal for the amino H atom at δ 5.7–6.3 ppm characteristic of complexes **I** and **IV** with an analogous structural type [8]. Third, the spectrum of complex **III** does not contain the signal for

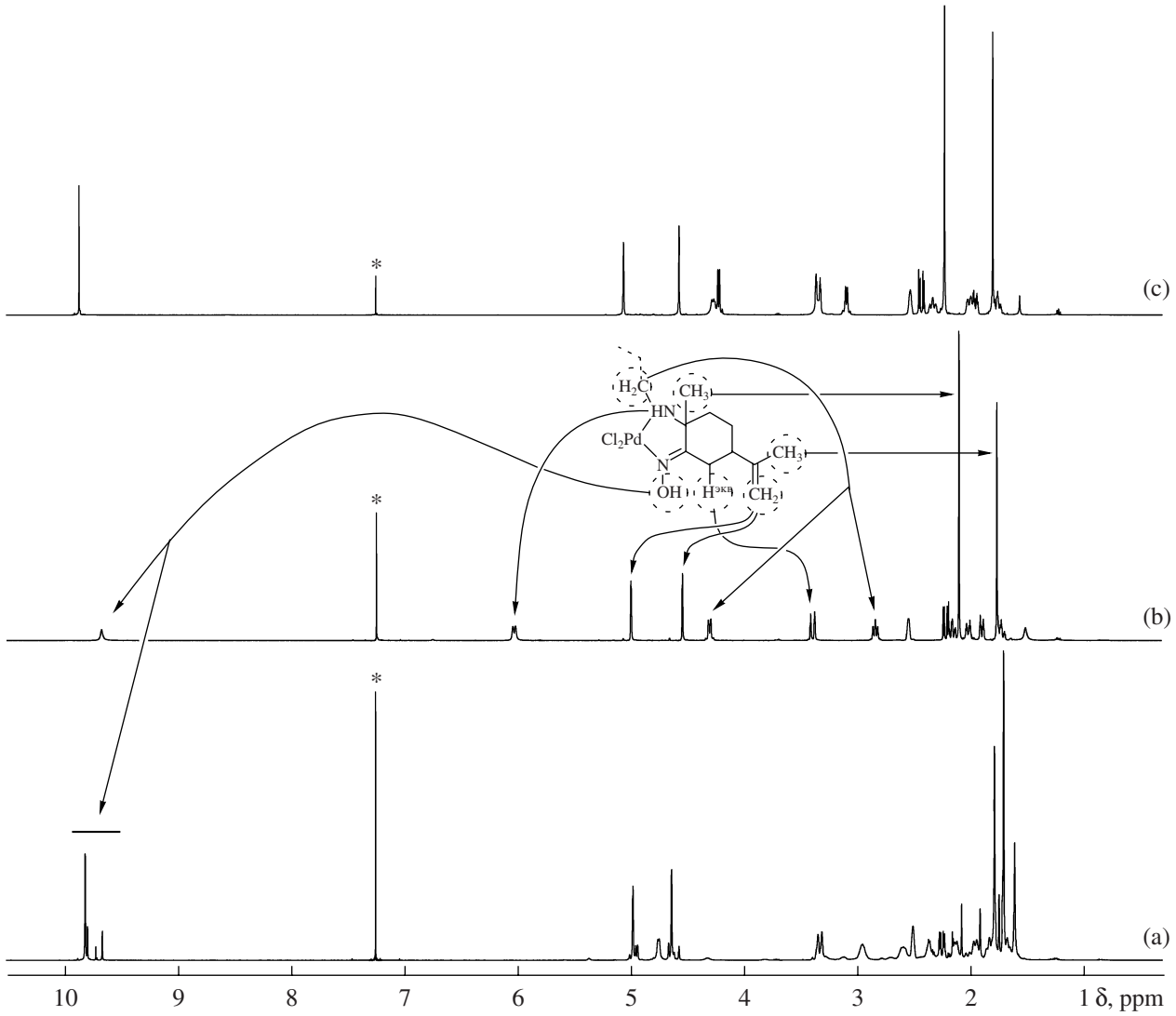


Fig. 3. ^{1}H NMR spectra of complexes (a) **III**, (b) **I**, and (c) **II** with the assignments of the diagnostic signals for complex **I**. The signals for the solvent are asterisked.

the methyl group that is geminal to the amino group at δ 2.0–2.4 ppm characteristic of structures **I**, **II**, and **IV**. Earlier, with bis(α-amino oximes) based on monoterpenes and various diamino linkers as examples, it has been shown that the structures of the complexes are sometimes determined by the character of the diamino linker rather than the structure of the terpene fragment. The examples include Co(II) and Co(III) complexes with bis(α-amino oximes) containing ethylenediamine and propylenediamine linkers [5, 11]. In structure H_2L^3, the propylenediamine linker creates much lower internal strains and makes the bis(α-amino oxime) fragment much more flexible regarding its conformation than do the linkers in H_2L^1 and H_2L^2. This allows other ways of coordination for H_2L^3 that are impossible for H_2L, H_2L^1, and H_2L^2. The character of these coordination ways is unclear.

The presented results, as well as data in [8], showed that the structures of solid-state complexes **I**, **II**, and **IV** with different terpenoid fragments but equal (in length) diamino linkers are similar (except for the conformation of the six-membered carbocycles). In $CDCl_3$, complexes **I** and **II** retain analogous binuclear structures. With an increase in the linker length (complex **III**), complex species present in solution can structurally differ from the above three complexes.

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