ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2009, Vol. 35, No. 4, pp. 286–295. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © S.V. Larionov, A.V. Tkachev, L.I. Myachina, Z.A. Savel'eva, L.A. Glinskaya, R.F. Klevtsova, A.M. Agafontsev, S.N. Bizyaev, 2009, published in Koordinatsionnaya Khimiya, 2009, Vol. 35, No. 4, pp. 291–300.

Synthesis of Binuclear Complexes of $PdCl_2$ with Chiral α,α'-Diamino-*meta*-Xylene Dioximes H_2L^1, H_2L^2, and H_2L^3, the Derivatives of the Terpenes (+)-3-Carene, (*R*)-(+)-Limonene, and (*S*)-(–)-α-Pinene. Crystal Structure of $[Pd_2(H_2L^1)Cl_4]$

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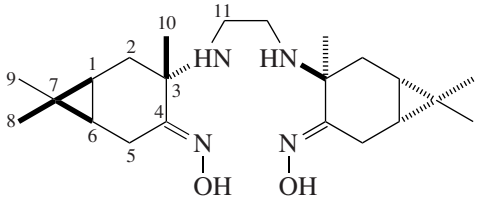
Received July 7, 2008

Abstract—Chiral α,α'-diamino-*meta*-xylene dioximes H_2L^1, H_2L^2, and H_2L^3 were obtained from the naturally occurring terpenoids (+)-3-carene, (*R*)-(+)-limonene, and (*S*)-(–)-α-pinene, respectively. Reactions of these ligands with $PdCl_2$ gave 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**). According to X-ray diffraction data, the crystal structure of complex **I** consists of acentric binuclear molecules $[Pd_2(H_2L^1)Cl_4]$. The coordination polyhedron PdN_2Cl_2 is a square distorted in a tetrahedral manner (trapezium) made up of two N atoms of the tetradentate bridging cyclic ligand H_2L^1 and two Cl atoms. The fragments $PdCl_2$ in the complex are *cis* to each other. According to the ^1H NMR spectra of complexes **I**–**III** in $CDCl_3$, the organic ligands are coordinated through the N atoms; in solution, the complexes exist in several forms.

DOI: 10.1134/S1070328409040095

Chemically modified natural substances are promising ligands, along with naturally occurring and synthetic organic ligands, for the synthesis of novel coordination compounds. Chiral ligands (including natural terpenoid derivatives) are of particular interest [1–4]. Among them are chiral ethylenediamine and propylenediamine dioximes of (+)-3-carene, α-pinene, and limonene [3, 4]. Various mononuclear complexes of Co(II), Co(III), Ni(II), and Cu(II) with these reagents have been obtained [4–11]. Recently, a reaction of $PdCl_2$ with ethylenediamine dioxime of (+)-3-carene (H_2L) has been studied [12].



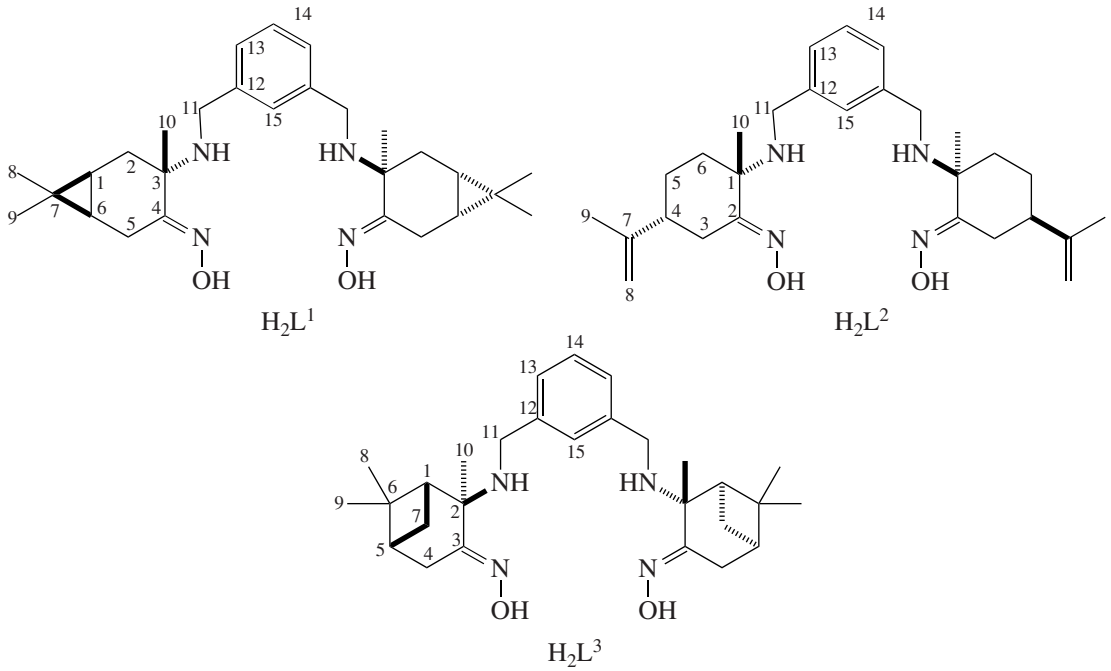
H_2L

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 in the *transoid* position. It was interesting to obtain complexes of $PdCl_2$ with other chiral terpenoid derivatives in the molecules of which the oxime fragments are linked by different (compared to H_2L) chains of atoms.

The goal of this study was to synthesize and examine complexes of $PdCl_2$ with chiral *meta*-α,α'-diaminoxylene dioximes H_2L^1, H_2L^2, and H_2L^3, the derivatives of the naturally occurring terpenoids (+)-3-carene, (*R*)-(+)-limonene, and (*S*)-(–)-α-pinene, respectively. In contrast to H_2L, these reagents contain the aromatic ring in the bridge linking the terpene fragments (Scheme).

EXPERIMENTAL

The optically active monoterpenes (1*S*,6*R*)-(+)-3-carene ($[\alpha]_{578}^{20}$ +16, isolated from pine pitch), (*R*)-(+)-



Scheme.

limonene (Fluka AG, $[\alpha]_D^{20}$ +123), and (1*S*,5*S*)-(–)-α-pinene (Aldrich, $[\alpha]_D^{20}$ –51) and α,α'-diamino-*meta*-xylene (Fluka 33 421) were used. Dimeric nitrosochlorides were prepared according to a standard procedure by passing gaseous nitrosyl chloride through solutions of the terpenes in CH_2Cl_2 [3]. Palladium dichloride was a high-purity chemical. The other reagents and solvents were of analytical or reagent grade.

Synthesis of ligands H_2L^1–H_2L^3. α,α'-Diamino-*meta*-xylene (0.85 g, 6.2 mmol) and ethyl(diisopropyl)amine (1.25 g, 12.4 mmol) were added to a suspension of a dimeric nitrosochloride of (+)-3-carene, (+)-limonene, or (–)-α-pinene (2.5 g, 6.2 mmol) in methanol (40 ml). The reaction mixture was stirred at 50°C for 1 h and concentrated *in vacuo*. The residue was treated with 3 M HCl (15 ml) under continuous stirring and cooling in an ice bath. The resulting solution was extracted with *tert*-butyl methyl ether (3 × 10 ml). The organic phase was discarded. The aqueous phase was neutralized with concentrated aqueous ammonia (6 ml), extracted with *tert*-butyl methyl ether (3 × 10 ml), saturated with NaCl, and reextracted with *tert*-butyl methyl ether (10 ml). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The product was chromatographed on Al_2O_3 in methanol–*tert*-butyl methyl ether (checking by TLC). Bis(α-amino oximes) H_2L^1, H_2L^2, and H_2L^3 were obtained in 60 to 80% yields as colorless oils that slowly crystallized at room temperature in approximately a month. Crystallization of the ligands H_2L^1 and H_2L^3 from acetonitrile gave the corresponding solvates.

N,N'-bis{(1*S*,3*S*,6*R*)-4[(*E*)-hydroxyimino]-3,7,7-trimethylbicyclo[4.1.0]heptan-3-yl}-α,α'-diamino-*meta*-xylene ($H_2L^1 \cdot CH_3CN$). Colorless crystals, $[\alpha]_{578}^{16}$ +247 (*c* 0.87, CH_3OH).

IR (KBr, cm^{-1}): 3288 (O–H), 3232 (N–H), 940 (N–O).

MS (*m*/*z* (I_{rel}, %)): 466 (13, M^+), 431 (25), 390 (26), 284 (62), 219 (52), 185 (39), 120 (100), 105 (58), 104 (73), 91 (36).

^1H NMR ($CDCl_3$, δ, ppm): 0.73 ddd (2H, H(1), *J* = 9.3 Hz, *J* = 9.3 Hz, *J* = 5.1 Hz), 0.80 s (6H, H(8)), 0.84 ddd (2H, H(6), *J* = 8.9 Hz, *J* = 8.9 Hz, *J* = 1.4 Hz), 0.99 s (6H, H(9)), 1.23 s (6H, H(10)), 1.37 dd (2H, $H(2)^{pro\text{-}S}$, *J* = 14.8 Hz, *J* = 5.8 Hz), 2.20 dd (2H, $H(2)^{pro\text{-}R}$, *J* = 14.8 Hz, *J* = 9.3 Hz), 2.29 dd (2H, $H(5)^{pro\text{-}S}$, *J* = 19.0 Hz, *J* = 8.4 Hz), 2.94 dd (2H, $H(5)^{pro\text{-}R}$, *J* = 19.0 Hz, *J* = 1.4 Hz), 3.40 d (2H, H(11a), *J* = 12.6 Hz), 3.68 d (2H, H(11b), *J* = 12.6 Hz), 7.20–7.25 (4H, H(13), H(14), H(15)), 9.6 vbr (2H, =N–OH).

^{13}C NMR ($CDCl_3$, δ, ppm): 14.41 (C(8)), 16.41 (C(1)), 17.86 (C(7)), 18.72 (C(10)), 19.01 (C(5)), 21.81 (C(6)), 27.83 (C(9)), 34.48 (C(2)), 54.98 (C(11)), 140.55 (C(12)), 126.67 (C(13)), 128.48 (C(14)), 128.56 (C(15)), 161.53 (C(4)).

For $C_{30}H_{45}N_5O_2$			
anal. calcd, %:	C, 71.0;	H, 8.9;	N, 13.8.
Found, %:	C, 71.1;	H, 8.7;	N, 13.2.

N,N'-bis{(1*S*,4*R*)-2-[(*E*)-hydroxyimino]-1-methyl-4-(1-methylethenyl)cyclohexyl}-α,α'-diamino-*meta*-xylene (H_2L^2). An amorphous white powder, $[\alpha]_{578}^{16}$ +120 (*c* 1.00, CH_3OH).

IR (2%, CCl_4, cm^{-1}): 3600 (O–H), 3277 (N–H).

MS (*m*/*z* (I_{rel}, %)): 466.33024 (10, $[M]^+$, for $C_{28}H_{42}N_4O_2$ anal. calcd.: $[M]^+$ = 466.33076), 431 (21), 284 (67), 267 (17), 150 (17), 135 (100), 121 (22), 120 (78), 119 (21), 118 (41), 105 (32), 93 (18), 91 (28), 41 (18).

^{1}H NMR ($CDCl_3$, δ, ppm): 1.34 s (6H, H(10)), 1.53–1.63 m (4H, $H(6)^{ax}$ and $H(5)^{eq}$), 1.74 s (6H, H(9)), 1.80 m (2H, $H(5)^{ax}$), 1.92 ddd (2H, $H(6)^{eq}$, *J* = 14.0 Hz, *J* = 3.0 Hz, *J* = 3.0 Hz), 1.95 dd (2H, $H(3)^{ax}$, *J* = 13.0 Hz, *J* = 13.0 Hz), 2.07 dddd (2H, H(4), *J* = 11.8 Hz, *J* = 11.8 Hz, *J* = 3.3 Hz, *J* = 3.3 Hz), 3.32 ddd (2H, $H(3)^{eq}$, *J* = 13.0 Hz, *J* = 3.3 Hz, *J* = 1.8 Hz), 3.41 d (2H, H(11a), *J* = 12.5 Hz), 3.69 d (2H, H(11b), *J* = 12.5 Hz), 4.74 m (2H, H(8a)), 4.75 (dq, 2H, H(8b), *J* = 1.5 Hz, *J* = 1.5 Hz), 7.15–7.33 m (4H, H(13), H(14), H(15)), 9.3 vbr (2H, =N–OH).

^{13}C NMR ($CDCl_3$, δ ppm): 20.52 (C(9)), 23.03 (C(10)), 25.38 (C(5)), 25.90 (C(3)), 40.14 (C(6)), 44.58 (C(4)), 46.55 (C(11)), 56.51 (C(1)), 109.31 (C(8)), 126.56 (C(13)), 128.01 (C(14)), 128.30 (C(15)), 140.80 (C(7)), 148.29 (C(12)), 162.28 (C(2)).

For $C_{28}H_{42}N_4O_2$			
anal. calcd, %:	C, 72.1;	H, 9.1;	N, 12.0.
Found, %:	C, 72.0;	H, 9.0;	N, 11.8.

N,N'-bis{(1*R*,2*R*,5*R*)-3-[(*E*)-hydroxyimino]-2,6,6-trimethylbicyclo[3.1.1]heptan-2-yl}-α,α'-diamino-*meta*-xylene ($H_2L^3 \cdot 0.5\ CH_3CN$). Colorless crystals, $[\alpha]_{578}^{17}$ –106 (*c* 0.87, CH_3OH).

IR (KBr, cm^{-1}): 3298 (O–H), 3300 (N–H).

MS (*m*/*z* ($I_{rel.}$, %)): 466.3285 (1, $[M]^+$, for $C_{28}H_{42}N_4O_2$ anal. calcd.: $[M]^+$ = 466.3302), 431 (2), 391 (3), 390 (9), 336 (11), 284 (29), 243 (17), 189 (29), 172 (11), 135 (16), 122 (19), 120 (100), 119 (12), 118 (25), 106 (23), 105 (12), 104 (12), 91 (30), 79 (14), 77 (18), 69 (12), 53 (11), 41 (26).

^{1}H NMR ($CDCl_3$, δ, ppm): 0.90 s (6H, H(8)), 1.29 s (6H, H(9)), 1.47 s (6H, H(10)), 1.65 d (2H, H(7a), *J* = 10.4 Hz), 1.94 dddd (2H, H(5), *J* = 5.6 Hz, *J* = 5.6 Hz, *J* = 2.7 Hz, *J* = 2.7 Hz), 2.04 dd (2H, H(1), *J* = 5.6 Hz, *J* = 5.6 Hz), 2.23 dddd (2H, H(7a), *J* = 10.4 Hz, *J* = 6.1 Hz, *J* = 6.1 Hz, *J* = 2.7 Hz), 2.55 dd (2H, H(4a), *J* = 18.4 Hz, *J* = 2.4 Hz), 2.84 ddd (2H, H(4b), *J* = 18.4 Hz, *J* = 2.3 Hz, *J* = 2.3 Hz), 3.49 d (2H, H(11a), *J* = 12.2 Hz), 3.74 d (2H, H(11), *J* = 12.2 Hz), 7.10–7.17 m (3H, H(13), H(14)), 7.20 br.s (1H, H(15), 9.1 vbr (2H, =N–OH).

^{13}C NMR ($CDCl_3$, δ, ppm): 22.56 (C(8)), 24.01 (C(10)), 27.67 (C(9)), 27.89 (C(7)), 29.65 (C(4)), 37.79 (C(5)), 38.97 (C(6)), 46.24 (C(11)), 50.06 (C(1)), 60.24 (C(2)), 126.92 (C(13)), 128.18 (C(14)), 128.59 (C(15)), 140.56 (C(12)), 161.55 (C(3)).

For $C_{29}H_{43.5}N_{3.5}O_2$			
anal. calcd, %:	C, 71.5;	H, 9.0;	N, 12.9.
Found, %:	C, 71.4;	H, 8.7;	N, 13.1.

Synthesis of $Pd_2(H_2L^1)Cl_4$ (I). A solution of $H_2L^1 \cdot CH_3CN$ (0.047 g, 0.09 mmol) in ethanol (1.5 ml) and a solution of $PdCl_2$ (0.035 g, 0.2 mmol) in ethanol (1.5 ml) were acidified with two drops of concentrated HCl and mixed. The resulting solution was left in a closed beaker in air for three days. The yellow crystalline precipitate that formed was filtered off under suction, washed with ethanol and hexane, and dried in air. The yield was 0.067 g (89%), $[\alpha]_{578}^{15}$ + 92 (*c* 0.35, CH_2Cl_2).

For $C_{28}H_{42}N_4Cl_4O_2Pd_2$			
anal. calcd, %:	C, 40.9;	H, 5.1;	N, 6.8.
Found, %:	C, 40.6;	H, 5.4;	N, 6.8.

Synthesis of $Pd_2(H_2L^2)Cl_4$ (II). The ligand H_2L^2 (0.047 g, 0.1 mmol) was dissolved under heating in ethanol (1.5 ml). Palladium dichloride (0.035 g, 0.2 mmol) was dissolved under heating in a mixture of ethanol (1.5 ml) and concentrated HCl (1.5 ml). The resulting solutions were mixed and cooled. After several hours, the yellow precipitate that formed was filtered off under suction, washed with ethanol and hexane, and dried at 80°C. The yield was 0.051 g (62%), $[\alpha]_{578}^{23}$ – 57.6 (*c* 1.18, CH_3OH–CH_2Cl_2).

For $C_{28}H_{42}N_4Cl_4O_2Pd_2$			
anal. calcd, %:	C, 40.9;	H, 5.1;	N, 6.8.
Found, %:	C, 40.7;	H, 5.4;	N, 6.5.

Synthesis of $Pd_2(H_2L^3)Cl_4$ (III). Palladium dichloride (0.035 g, 0.2 mmol) was dissolved under heating in concentrated HCl (0.2 ml). Then ethanol (2 ml) was added. The resulting solution was filtered through a filter paper and mixed with a solution of $H_2L^3 \cdot 0.5CH_3CN$ (0.047 g, ~0.1 mmol) in ethanol (2 ml). A yellow precipitate formed immediately upon the mixing. After an hour, the precipitate was filtered off under suction, washed with cooled ethanol, and dried in air. The yield

was 0.030 g (43%), $[\alpha]_{578}^{23}$ –71.4 (*c* 0.28, CH_3OH–CH_2Cl_2).

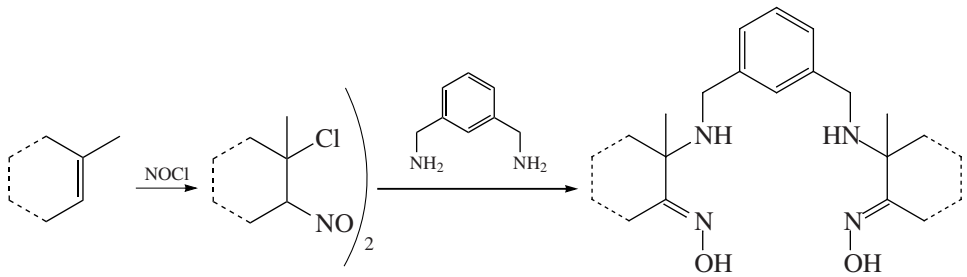
For $C_{28}H_{42}N_4Cl_4O_2Pd_2$				
anal. calcd, %:	C, 41.0;	H, 5.2;	N, 6.8;	Cl, 17.3.
Found, %:	C, 41.3;	H, 5.1;	N, 6.7;	Cl, 17.4.

Elemental analysis was performed on Hewlett Packard 185 and Carlo Erba 1106 instruments. The magnetic susceptibilities of the polycrystalline complexes were measured by the Faraday method at room temperature. ^1H and ^{13}C NMR spectra (500 and 125 MHz, respectively) were recorded on a Bruker DRX 500 instrument at 25 to 40°C in $CDCl_3$ and CD_2Cl_2 (*c* = 40–60 mg/ml for the ligands and 5–10 mg/ml for the complexes). The chemical shifts are referenced to tetramethylsilane (δ_H 0.00 ppm, δ_C 0.00 ppm). Signals of the solvent at δ_H 7.24 and δ_C 76.90 ppm (in $CDCl_3$) and at δ_H 5.32 ppm (in CD_2Cl_2) 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. Prepared Silufol plates with a fixed SiO_2 layer were used for TLC. To visualize spots, the plates were covered by spraying with a 0.4% solution of ninhydrin in ethanol and heated. Preparative column chromatography was carried out on glass columns packed with KSK silica gel (grain size 0.10–0.04 mm).

X-ray diffraction analysis of complex **I** was carried out for a yellow single crystal (prismatic habitus, 0.15 × 0.12 × 0.07 mm). The unit cell parameters and reflection intensities were measured according to a standard procedure on a Bruker X8 APEX automated four-circle diffractometer equipped with a CCD area detector (MoK_α radiation, λ = 0.71073 Å, graphite monochromator) at room temperature. Crystallographic parameters and a summary of data collection and refinement for complex **I** are given in Table 1. The acentric space group chosen after a quenching analysis of the collected array of reflection intensities was supported by calculations. Structure **I** was solved by the direct method and refined by the full-matrix least-squares method on F^2 in the anisotropic approximation for nonhydrogen atoms with the SHELXL-97 program package [13]. Hydrogen atoms were located geometrically and refined in the rider model. Selected bond lengths and angles in structure **I** are given in Table 2. Comprehensive tables of the atomic coordinates and the bond lengths and angles have been deposited with the Cambridge Crystallographic Data Collection (CCDC No. 679 485) and can be made available from the authors upon request.

RESULTS AND DISCUSSION

Ligands H_2L^1–H_2L^3 were obtained by a reaction previously employed for the synthesis of bis(α-amino oximes) [14]:



First, the starting monoterpene hydrocarbons (+)-3-carene, (+)-limonene, and (–)-α-pinene were converted into crystalline dimeric nitrosochlorides. The latter were treated with α,α'-diamino-*meta*-xylene to give the corresponding diamino dioximes: the ligands H_2L^1, H_2L^2, and H_2L^3, respectively (H_2L^1 and H_2L^3 as solvates).

Reactions of $PdCl_2$ with H_2L^1–H_2L^3 afforded complexes **I**–**III** similar in composition to $Pd_2(H_2L)Cl_4$ [12]. In the synthesis of complex **II**, the precipitate that formed was dried at 80°C because of a possible impurity of ethanol. The complexes obtained are diamagnetic, which suggests the low-spin configuration d^8. The [α] values for H_2L^1–H_2L^3 and complexes **I**–**III** show that only complex **II** has the sign of [α] opposite to that of the free ligand.

According to X-ray diffraction data, structure **I** consists of acentric binuclear molecules. Structure **I** with all atoms in general positions is shown in Fig. 1. Either Pd atom coordinates two N atoms of the tetradentate bridging cyclic ligand H_2L^1 and two Cl atoms. Coordination of H_2L^1 results in ring closure of two five-membered chelate rings PdN_2C_2 with somewhat different Pd–N distances: 2.000(3) and 2.069(3) Å and 1.994(3) and 2.086(3) Å (the shorter bonds refer to the oxime N atoms). Four Pd–Cl distances differ less (2.276(1)–

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

Parameter	Value
Empirical formula	$C_{28}H_{42}N_4Cl_4O_2Pd_2$
M	821.26
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a, Å	10.6269(2)
b, Å	13.7980(2)
c, Å	24.1388(4)
V, Å^3	3539.47(10)
Z; ρ_{calcd}, g/cm^3	4; 1.541
μ, mm^{-1}	1.348
Crystal size, mm	$0.15 \times 0.12 \times 0.07$
θ scan range, deg	2.09–25.67
Number of measured reflections	32557
Number of independent reflections	6686
R_{int}	0.0429
Number of reflections with $I > 2\sigma(I)$	5668
Number of parameters refined	410
GOOF for F^2	0.993
R factor, $I > 2\sigma(I)$	
R_1	0.0257
wR_2	0.0562
R factor (for all I_{hkl})	
R_1	0.0369
wR_2	0.0597
Absolute structural parameter	–0.05(2)

Table 2. Selected bond lengths and angles in structure **I**

Bond	d, Å	Bond	d, Å
Pd(1)–N(2)	2.000(3)	Pd(2)–N(4)	1.994(3)
Pd(1)–N(1)	2.069(3)	Pd(2)–N(3)	2.086(3)
Pd(1)–Cl(1)	2.2800(9)	Pd(2)–Cl(3)	2.276(1)
Pd(1)–Cl(2)	2.2926(9)	Pd(2)–Cl(4)	2.316(1)
N(1)–C(11)	1.486(4)	N(3)–C(11a)	1.509(5)
N(1)–C(3)	1.506(4)	N(3)–C(3a)	1.522(4)
O(1)–N(2)	1.385(4)	O(2)–N(4)	1.385(4)
N(2)–C(4)	1.278(4)	N(4)–C(4a)	1.286(5)
C(1)–C(2)	1.500(5)	C(1a)–C(2a)	1.486(6)
C(1)–C(6)	1.523(5)	C(1a)–C(6a)	1.522(5)
C(1)–C(7)	1.523(5)	C(1a)–C(7a)	1.533(6)
C(2)–C(3)	1.555(5)	C(2a)–C(3a)	1.544(5)
C(3)–C(4)	1.519(5)	C(3a)–C(4a)	1.510(6)
C(3)–C(10)	1.537(5)	C(3a)–C(10a)	1.525(6)
C(4)–C(5)	1.494(4)	C(4a)–C(5a)	1.494(6)
C(5)–C(6)	1.505(5)	C(5a)–C(6a)	1.504(5)
C(6)–C(7)	1.524(5)	C(6a)–C(7a)	1.510(6)
C(7)–C(9)	1.515(7)	C(7a)–C(9a)	1.493(6)
C(7)–C(8)	1.525(7)	C(7a)–C(8a)	1.513(6)
C(11)–C(12)	1.501(5)	C(11a)–C(16)	1.489(5)
C(12)–C(17)	1.382(5)	C(14)–C(15)	1.392(6)
C(12)–C(13)	1.395(5)	C(15)–C(16)	1.388(5)
C(13)–C(14)	1.367(5)	C(16)–C(17)	1.394(5)
Angle	**ω, deg**	**Angle**	**ω, deg**
N(2)Pd(1)N(1)	78.84(10)	N(4)Pd(2)N(3)	79.04(12)
N(2)Pd(1)Cl(1)	171.00(9)	N(4)Pd(2)Cl(3)	175.8(1)
N(1)Pd(1)Cl(1)	95.06(8)	N(3)Pd(2)Cl(3)	97.01(9)
N(2)Pd(1)Cl(2)	92.30(8)	N(4)Pd(2)Cl(4)	91.3(1)
N(1)Pd(1)Cl(2)	169.97(8)	N(3)Pd(2)Cl(4)	168.1(1)
Cl(1)Pd(1)Cl(2)	94.27(4)	Cl(3)Pd(2)Cl(4)	92.81(6)
C(11)N(1)C(3)	114.1(3)	C(11a)N(3)C(3a)	115.3(3)
C(11)N(1)Pd(1)	111.2(2)	C(11a)N(3)Pd(2)	121.8(2)
C(3)N(1)Pd(1)	105.0(2)	C(3a)N(3)Pd(2)	105.9(2)
C(4)N(2)O(1)	117.3(3)	C(4a)N(4)O(2)	117.3(4)
C(4)N(2)Pd(1)	117.0(2)	C(4a)N(4)Pd(2)	118.3(3)
O(1)N(2)Pd(1)	125.7(2)	O(2)N(4)Pd(2)	123.5(3)

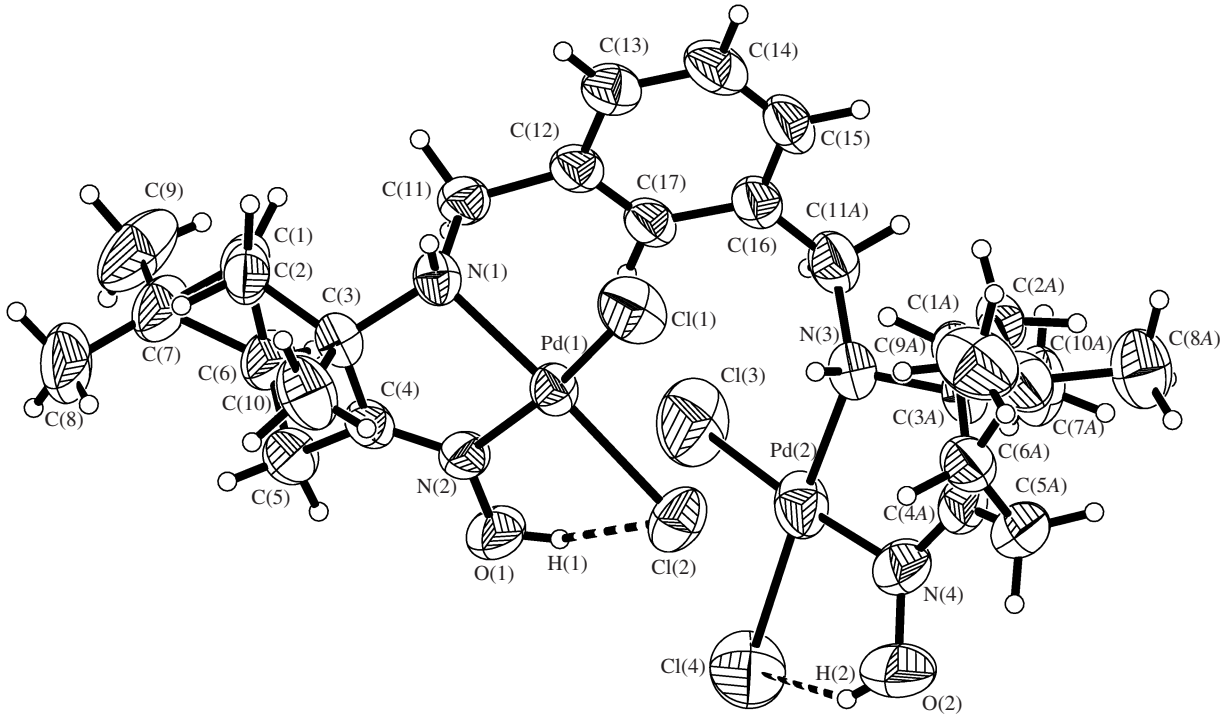


Fig. 1. Structure of the acentric binuclear molecule in complex **I** with numbering of the non-hydrogen atoms.

2.316(1) Å). The Pd–N and Pd–Cl bond lengths and angles in structure **I** are close to those in $[Pd_2(H_2L)Cl_4]$ [12]. In addition, complex **I** contains two five-membered H rings Pd(1)N(2)O(1)H(1)Cl(2) and Pd(2)N(4)O(2)H(2)Cl(4) by means of the intramolecular H bond O–H···Cl (O(1)···Cl(2) 3.155(2), O(2)···Cl(4) 3.075(5) Å)). The angles O(1)H(1)Cl(2) and O(2)H(2)Cl(4) are 126.8° and 133.1°, respectively.

The coordination environment of either Pd atom can be regarded as a square distorted in a tetrahedral manner (trapezium) with the following distances: N···N 2.584(4) and 2.597(5) Å, Cl···Cl 3.3326(2) and 3.351(1), N···Cl 3.091(3)–3.269(3) Å. This geometry of the coordination environment of the Pd atoms correlates with the diamagnetism of complex **I**. The largest deviations of the N and Cl atoms from the two planes N_2Cl_2 are 0.112(1) and 0.086(1) Å, respectively. The Pd(1) and Pd(2) atoms deviate from these planes by –0.020(1) and –0.054(1) Å, respectively. It should be emphasized that in contrast to $Pd_2(H_2L)Cl_4$ [12], the fragments $PdCl_2$ in complex **I** are *cis* to each other and the angle between the planes N_2Cl_2 in the coordination entities PdN_2Cl_2 is ~30.9°. The Pd···Pd distance is 4.669(2) Å. Therefore, introduction of an aryl group into the bridge linking the carbocyclic fragments of H_2L^1 fixes the *cisoid* coordination of $PdCl_2$.

Calculations of the planes passing through the atoms of the chelate rings PdN_2C_2 and the six-membered carbocycles in structure **I** showed that all of them are noticeably deformed. Both five-membered chelate rings PdN_2C_2 comprising the N atoms of the oxime and amino groups exist in the envelope conformation: the N(1) and N(3) atoms deviate from the planes of the other four atoms by –0.725(4) and 0.669(5) Å. The conformation of both six-membered carbocycles is a distorted boat: the C(2) and C(5) atoms in one and the C(2a) and C(5a) atoms in the other carbocycle are on the same side of the planes C(1)C(3)C(4)C(6) and C(1a)C(3a)C(4a)C(6a), deviating by 0.455(6), 0.655(6), 0.553(5), and 0.675(6) Å, respectively. The dimethylcyclopropane fragments share the C(1)–C(6) and C(1a)–C(6a) edges with the six-membered carbocycles and their dihedral angles with the planes C(1)C(3)C(4)C(6) and C(1a)C(3a)C(4a)C(6a) are 139.6° and 142.5°, respectively.

The projection of crystal structure **I** onto the plane (001) is shown in Fig. 2. The intermolecular distance in structure **I** are within van der Waals interactions and weak H bonds. The Cl atoms form most contacts: the shortest Cl···N and Cl···C distances are 3.363(3) and 3.555(5) Å, respectively. Binuclear molecules are united through these contacts into a three-dimensional framework.

Complexes **II** and **III** are similar in composition to complex **I** and are also diamagnetic. Apparently, their solid-state structures look like structure **I**.

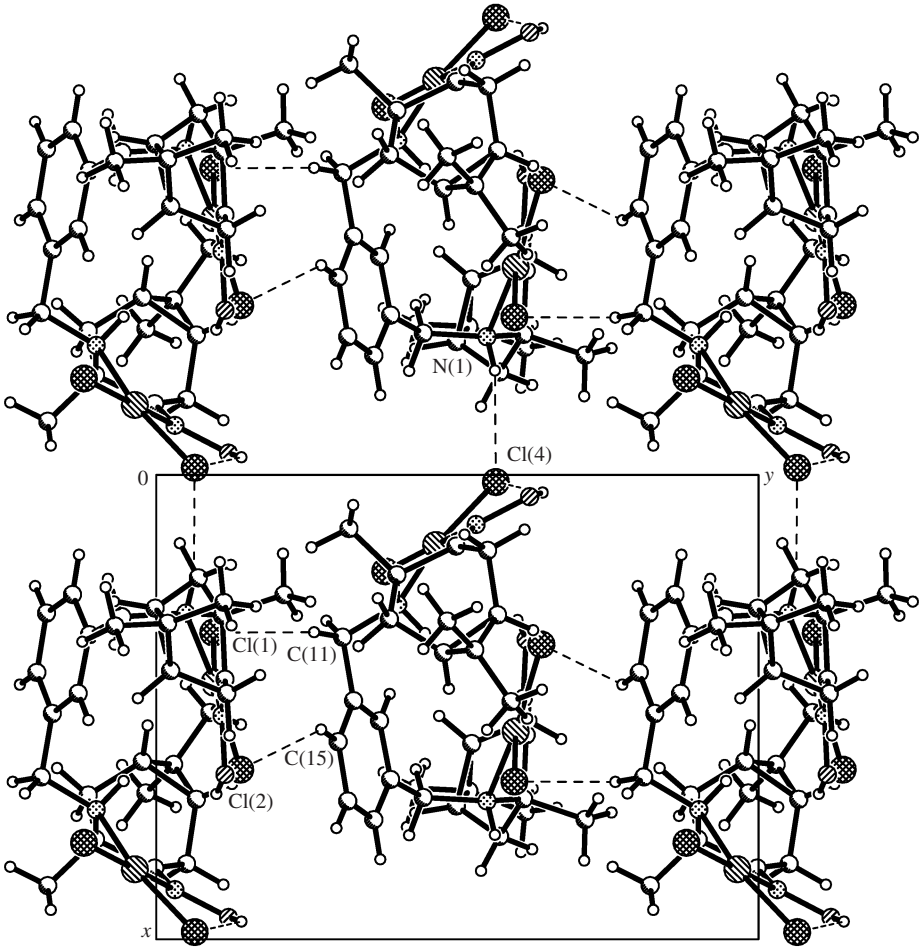


Fig. 2. Projection of crystal structure **I** onto the plane (001). Hydrogen bonds and intermolecular contacts are indicated with dashed lines.

Complexes **I–III** are moderately soluble in $CDCl_3$. The ^1H NMR spectra of the resulting solutions (Figs. 3–5) suggest the presence of similar structures. The changes in the spectra of the complexes (compared to the starting ligands H_2L^1–H_2L^3) are most dramatic for the signals of the H atoms of those ligand fragments that are in close vicinity of the coordinated N atoms (methyl geminal to the amino group, benzyl H atoms, and hydroxyl proton). Therefore, the way of coordination of the ligands in the solid-state complexes is the same as in their solutions. The NMR spectra of all the complexes studied exhibit several sets of signals that can relate to their different forms undergoing interconversions in solution. This is most pronounced with complex **I**.

Complex **I** is well soluble in $CDCl_3$ at room temperature. However, several minutes after its complete dissolution, a crystalline precipitate forms in the solution. This precipitate is virtually insoluble in $CDCl_3$. The ^1H NMR spectrum of the supernatant liquid (Fig. 3b) shows more than one set of signals and their ratio changes upon 1-h heating at +40°C (Fig. 3c). Further heating at this temperature for 6 h produces no changes in the spectrum. The crystalline precipitate formed in $CDCl_3$ is soluble in CD_2Cl_2. However, according to the ^1H NMR spectrum of the resulting solution (Fig. 3d), the crystalline precipitate and the supernatant liquid contain identical forms of the same complex (different chemical shifts in the spectra (Figs. 3b–3d) are due to the solvent effect). Most likely, complex **I** forms a crystalline solvate with one or more $CDCl_3$ molecules and this solvate is poorly soluble in $CDCl_3$ but is well soluble in CD_2Cl_2. The possibility of forming a solvate with $CDCl_3$ molecules has been proved for a binuclear complex of $PdCl_2$ with a bis(α-thiooxime) derivative of (+)-3-carene in [12]. In the crystal, complex **I** exists as a single form. When dissolved in CD_2Cl_2 or $CDCl_3$, this form is transformed into an equilibrium mixture of forms undergoing slow interconversions (on the time scale of the NMR experiment).

Most likely, the interconvertible forms of the complexes are conformers that are stable enough because of

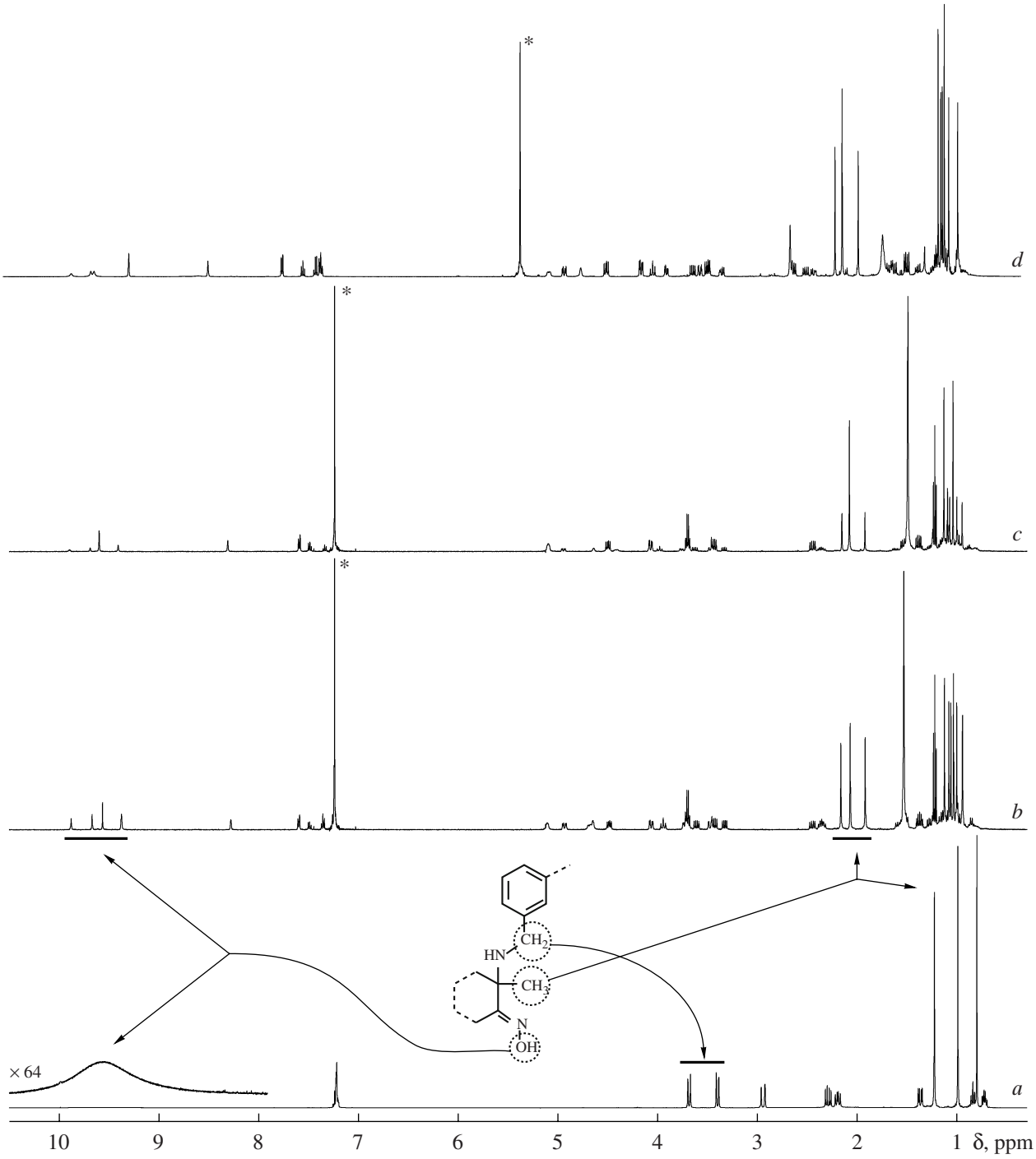


Fig. 3. ^1H NMR spectra of (*a*) ligand H_2L^1 and complex **I** (*b*) immediately after the dissolution in $CDCl_3$ at 30°C, (*c*) after the heating of its solution in $CDCl_3$ to 40°C and keeping at this temperature for 1 h, and (*d*) after the dissolution of the crystalline precipitate in CD_2Cl_2 at 25°C. The signals for the solvent are asterisked.

possible intramolecular interactions between two Pd-containing fragments and because of high energy barriers to conformational transitions by means of rotation about the single bonds NH–CH_2–Ar–CH_2–NH near the *meta*-substituted benzene ring.

The major result obtained in [12] and in this study was the synthesis of a group of binuclear complexes of $PdCl_2$ with chiral dioximes derived from naturally occurring terpenoids. The change in the composition of the bridge linking the terpenoid fragments leads to the

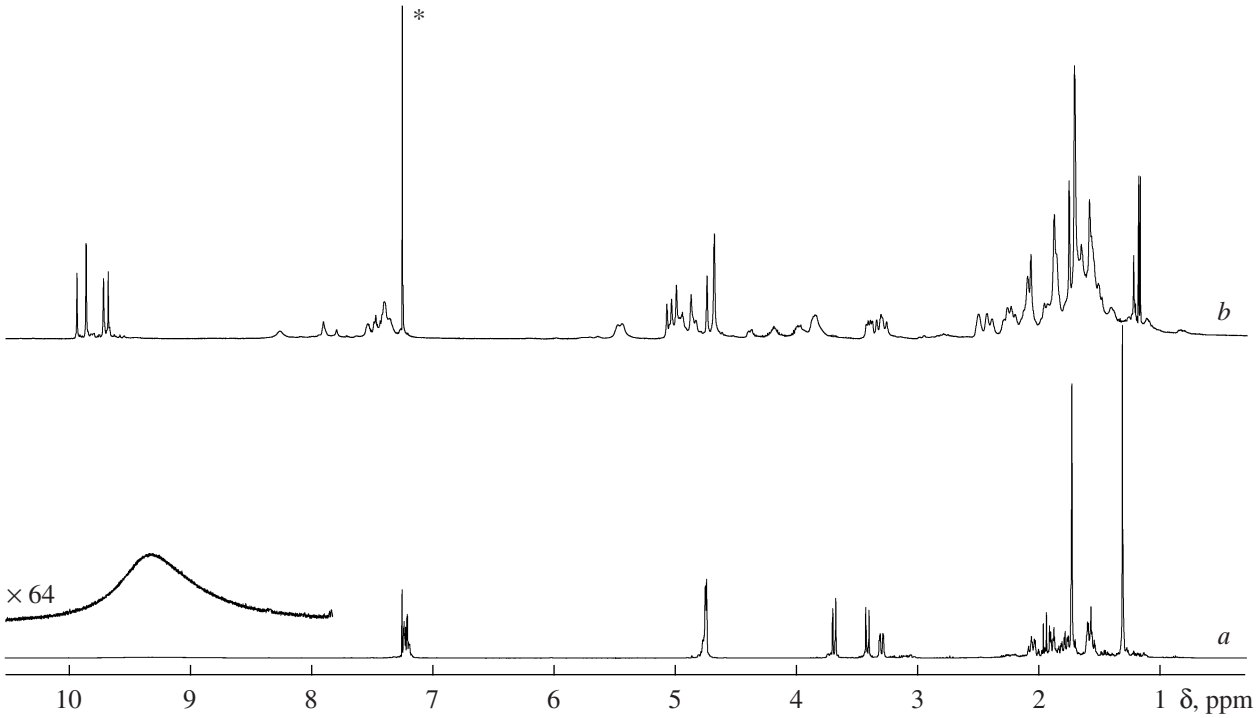


Fig. 4. ^{1}H NMR spectra of (*a*) ligand H_2L^2 and (*b*) complex **II** in $CDCl_3$ at 30°C. The signal for the solvent is asterisked.

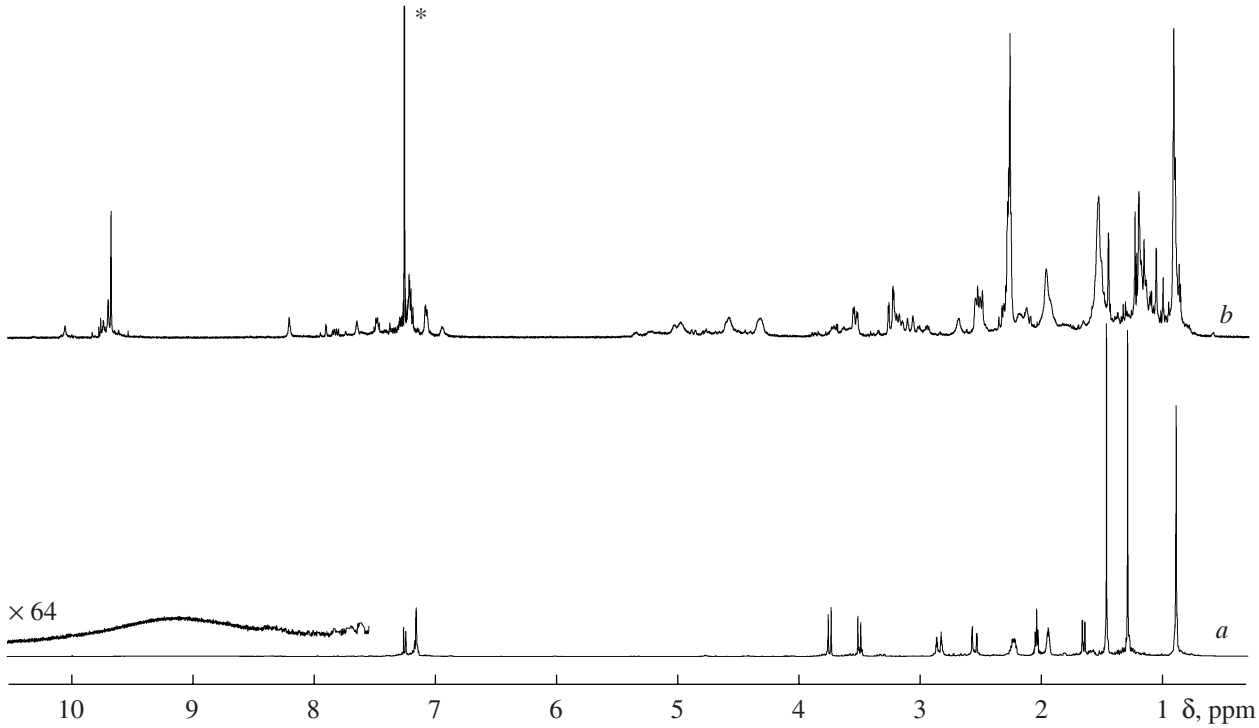


Fig. 5. ^{1}H NMR spectra of (*a*) ligand H_2L^3 and (*b*) complex **III** in $CDCl_3$ at 30°C. The signal for the solvent is asterisked.

addition of two $PdCl_2$ molecules in the *trans*- or *cis*-position relative to the dioxime molecule.

ACKNOWLEDGMENTS

We are grateful to V.A. Daletskii for measuring the static magnetic susceptibility.

REFERENCES

1. Von Zelewsky, A. and Mamula, O., *Dalton Trans.*, 2000, no. 3, p. 219.
2. Mamula, O. and von Zelewsky, A., *Coord. Chem. Rev.,* 2003, vol. 242, nos. 1–2, p. 87.
3. Tkachev, A.V., *Ross. Khim. Zh.,* 1998, vol. 42, nos. 1–2, p. 42.
4. Larionov, S.V. and Tkachev, A.V., *Ross. Khim. Zh.*, 2004, vol. 48, no. 4, p. 154.
5. Larionov, S.V., Myachina, L.I., Glinskaya, L.A., et al., *Koord. Khim.*, 2003, vol. 29, no. 11, p. 857 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 29, no. 11, p. 795].
6. Larionov, S.V., Myachina, L.I., Savel'eva, Z.A., et al., *Koord. Khim.*, 2004, vol. 30, no. 12, p. 888 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 30, no. 12, p. 837].
7. Larionov, S.V., Savel'eva, Z.A., Glinskaya, L.A., et al., *Zh. Strukt. Khim.,* 2005, vol. 46, no. 3, p. 558.
8. Larionov, S.V., Tkachev, A.V., Savel'eva, Z.A., et al., *Koord. Khim.*, 2006, vol. 32, no. 4, p. 261 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 32, no. 4, p. 250].
9. Larionov, S.V., Savel'eva, Z.A., Glinskaya, L.A., et al., *Koord. Khim.*, 2006, vol. 32, no. 5, p. 365 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 32, no. 5, p. 350].
10. Savel'eva, Z.A., Bizyaev, S.N., Glinskaya, L.A., et al., *Koord. Khim.,* 2006, vol. 32, no. 10, p. 754 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 32, no. 10, p. 723].
11. Savel'eva, Z.A., Klevtsova, R.F., Glinskaya, L.A., et al., *Koord. Khim.*, 2006, vol. 32, no. 11, p. 816 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 32, no. 11, p. 784].
12. Kokina, T.E., Myachina, L.I., Glinskaya, L.A., et al., *Koord. Khim.*, 2008, vol. 34, no. 2, p. 120 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 34, no. 2, p. 115].
13. Sheldrick, G.M., *SHELX-97. Program for the Refinement of Crystal Structures*, Göttingen (Germany): Univ. of Göttingen, 1997.
14. Petukhov, P.A., Bizyaev, S.N., and Tkachev, A.V., *Izv. Akad. Nauk, Ser. Khim.*, 2001, no. 11, p. 2013.