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Synthesis of Pd(II) Complexes Containing the Protonated Form or Molecule of 2-(3,5-Dimethylpyrazol-1-yl)-4-Methylquinoline (L). The Crystal Structure of [Pd(HL)Cl_3]

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Abstract—The diamagnetic complexes [Pd(HL)Cl_3] (**I**) and PdLCl_2 (**II**), where L is 2-(3,5-dimethylpyrazol-1-yl)-4-methylquinoline, were obtained. According to X-ray diffraction data, the crystal structure of complex **I** consists of mononuclear acentric molecules. The coordination polygon PdNCl_3 is a distorted square (trapezium) made up of the pyrazole N atom of the monodentate ligand (cation HL^+) and three Cl atoms. Complex **II** seems to contain the square polygon PdN_2Cl_2.

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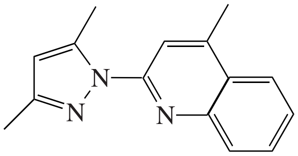
Nitrogen heterocyclic compounds containing two rings with donor N atoms are widely used as ligands in coordination chemistry. Classic representative of such ligands are 2,2'-bipyridyl and 1,10-phenanthroline each containing two identical rings. At present, much research is focused on the synthesis of metal complexes with nitrogen heterocycles containing two different rings, as well as on the study of their structures and properties. For instance, complexes with derivatives of pyrimidinylaminotriazole [1], pyrazolylpyrimidine [2, 3], and pyrimidinylpyridine [4] have been synthesized. Recently, we have obtained complexes of Fe(II), Co(II), and Cu(II) with chiral and achiral pyrazolylquinoline derivatives [5, 6]. The complexes described in [3, 5] are catalytically active in ethene polymerization.

The goal of this study was to obtain and study Pd(II) complexes with the achiral ligand 2-(3,5-dimethylpyrazol-1-yl)-4-methylquinoline (**L**).



(L)

EXPERIMENTAL

Reagent **L** was prepared from 2-hydrazino-4-methylquinoline and acetylacetone as described in [7] for the synthesis of 4-methyl-2-pyrazolylquinolines. The NMR spectra of reagent L were identical with the literature data [8]. Palladium dichloride (high-purity grade), fractionally distilled ethanol, acetonitrile (analytical grade), and dichloromethane (reagent grade) were employed.

Synthesis of [Pd(HL)Cl_3] (I). Ethanol (2 ml) was added at ~50°C to a solution of $PdCl_2$ (0.035 g, 0.2 mmol) in concentrated HCl (~0.2 ml). The resulting solution was filtered, whereupon a solution of reagent L (0.048 g, 0.2 mmol) in a mixture of CH_2Cl_2 (2 ml) and MeCN (10 ml) was added. The reaction mixture was heated to ~50°C and transferred to a closed weighing bottle. After three days, the reddish orange crystalline precipitate that formed was filtered off by suction, washed with ethanol, and dried in air. The yield of complex **I** was 0.047 g (52%).

Found (%):	C 40.6;	H 3.9;	N 9.6;	Cl 23.1.
For $C_{15}H_{16}Cl_3N_3Pd$				
anal. calcd. (%):	C 40.0;	H 3.6;	N 9.3;	Cl 23.6.

^{1}H NMR (DMSO-d_6–$CDCl_3$, 500 MHz), δ (ppm): 2.23 s (3H), 2.72 s (3H), 2.74 s (3H); 6.09 br.s (1H), 7.54 ddd (1H, J = 8.3 Hz, J = 7.0 Hz, J = 0.6 Hz), 7.70 ddd (1H, J = 8.3 Hz, J = 7.0 Hz, J = 1.1 Hz), 7.89 d (1H, J = 8.4 Hz), 7.92 s (1H), 8.02 d (1H, J = 8.3 Hz).

^{13}C NMR (DMSO-d_6–$CDCl_3$, 125 MHz), δ (ppm): 13.26 q, 14.57 q, 18.40 q, 109.32 d, 114.55 d, 123.74 d, 125.53 d, 125.86 s, 128.36 d, 129.62 d, 141.37 s, 145.38 s, 146.85 s, 148.98 s, 151.33 s.

Synthesis of $PdLCl_2$ (II). Ethanol (3 ml) was added at ~50°C to a solution of $PdCl_2$ (0.035 g, 0.2 mmol) in concentrated HCl (~0.2 ml). Then a solution of reagent L (0.048 g, 0.2 mmol) in a mixture of CH_2Cl_2 (7 ml) and MeCN (7 ml) was added. Heating was required to dissolve the resulting precipitate. On cooling, a yellow precipitate formed. The mixture was left overnight. The precipitate was filtered off by suction, washed with ethanol, and dried in air. The yield of complex **II** was 0.053 g (65%).

Found (%):	C 43.8;	H 3.7;	N 10.2;	Cl 17.5.
For $C_{15}H_{15}Cl_2N_3Pd$				
anal. calcd. (%):	C 43.5;	H 3.6;	N 10.1;	Cl 17.1.

Microanalyses of the complexes obtained were performed on Hewlett Packard 185 and Carlo Erba 1106 analyzers. Static magnetic susceptibility was measured by the Faraday method at room temperature. IR spectra were recorded in the 4000–400 cm^{-1} range on a Scimitar FTS 2000 FTIR spectrometer for samples of complex **II** in a fluorinated oil and reagent L in Nujol. ^1H and ^{13}C NMR spectra (500 and 125 MHz, respectively) were recorded on a Bruker DRX 500 instrument for solution with the concentration $c = 5–10$ mg/ml at 30°C. The signals of the solvent (DMSO-d_6) at δ_H 2.50 and δ_C 39.50 ppm were used as the internal standards.

X-ray diffraction analysis was performed for orange single crystals of complex **I** obtained in its synthesis. Unit cell parameters and reflection intensities were measured on a Bruker X8 Apex automated diffractometer fitted with a CCD area detector at room temperature according to a standard procedure (MoK_α radiation, graphite monochromator). Crystallographic parameters and a summary of data collection for structure **I** are given in Table 1. Structure **I** was solved by the direct method and refined by the full-matrix least-squares method in the anisotropic approximation for the non-hydrogen atoms with the SHELXL-97 program package [9]. The hydrogen atoms were located geometrically and refined in the isotropic approximation.

Comprehensive tables of the atomic coordinates and the bond lengths and angles have been deposited with the Cambridge Crystallographic Data Collection (no. 691946) and can be made available from the authors upon request. Selected bond lengths and angles in structure **I** are given in Table 2.

An experimental X-ray powder diffraction profile obtained for polycrystals of complex **I** was identical with that calculated from single-crystal X-ray diffraction data.

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

Parameter	Value
FM	451.06
Crystal system	Monoclinic
Space group	$P2_1/n$
a, Å	7.4340(10)
b, Å	8.8203(16)
c, Å	25.431(5)
β, deg	90.193(4)
V, Å^3	1667.5(5)
Z; ρ_{calcd}, g/cm^3	4; 1.797
μ, mm^{-1}	1.592
Crystal size (mm)	0.12 × 0.10 × 0.06
θ Scan range, deg	2.44–25.00
Number of measured reflections	9608
Number of independent reflections	2742
R_{int}	0.0475
Number of reflections with $I > 2\sigma(I)$	2151
Number of parameters refined	218
GOOF on F^2	1.061
R factor, $I > 2\sigma(I)$	
R_1	0.0478
wR_2	0.0950
R factor (for all reflections I_{hkl})	
R_1	0.0680
wR_2	0.1003
Residual electron density, max/min, e Å^{-3}	0.597/–0.630

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

Bond	d, Å	Bond	d, Å
Pd(1)–N(2)	2.059(5)	C(3)–C(4)	1.412(8)
Pd(1)–Cl(3)	2.277(2)	C(3)–C(10)	1.505(8)
Pd(1)–Cl(2)	2.283(2)	C(4)–C(5)	1.399(8)
Pd(1)–Cl(1)	2.330(2)	C(4)–C(9)	1.442(8)
N(1)–C(1)	1.323(7)	C(5)–C(6)	1.405(8)
N(1)–C(5)	1.370(7)	C(6)–C(7)	1.356(9)
N(2)–C(11)	1.324(7)	C(7)–C(8)	1.389(9)
N(2)–N(3)	1.373(6)	C(8)–C(9)	1.361(9)
N(3)–C(13)	1.390(7)	C(11)–C(12)	1.390(8)
N(3)–C(1)	1.406(7)	C(11)–C(14)	1.491(8)
C(1)–C(2)	1.377(8)	C(12)–C(13)	1.359(8)
C(2)–C(3)	1.383(8)	C(13)–C(15)	1.479(8)
Angle	**ω, deg**	**Angle**	**ω, deg**
N(2)Pd(1)Cl(3)	178.8(1)	C(4)C(3)C(10)	122.5(5)
N(2)Pd(1)Cl(2)	88.7(2)	C(5)C(4)C(3)	120.0(5)
Cl(3)Pd(1)Cl(2)	90.54(8)	C(5)C(4)C(9)	117.0(5)
N(2)Pd(1)Cl(1)	89.6(2)	C(3)C(4)C(9)	123.0(5)
Cl(3)Pd(1)Cl(1)	91.22(8)	N(1)C(5)C(4)	118.1(5)
Cl(2)Pd(1)Cl(1)	176.31(7)	N(1)C(5)C(6)	120.0(5)
C(1)N(1)C(5)	122.7(5)	C(4)C(5)C(6)	121.9(5)
C(11)N(2)N(3)	106.3(4)	C(7)C(6)C(5)	119.4(7)
C(11)N(2)Pd(1)	125.9(4)	C(6)C(7)C(8)	120.2(7)
N(3)N(2)Pd(1)	127.5(3)	C(9)C(8)C(7)	122.2(6)
N(2)N(3)C(13)	110.3(4)	C(8)C(9)C(4)	119.3(6)
N(2)N(3)C(1)	123.4(5)	N(2)C(11)C(12)	110.0(5)
C(13)N(3)C(1)	125.9(5)	N(2)C(11)C(14)	122.1(5)
N(1)C(1)C(2)	120.5(5)	C(12)C(11)C(14)	127.9(5)
N(1)C(1)N(3)	117.2(5)	C(13)C(12)C(11)	108.2(5)
C(2)C(1)N(3)	122.2(5)	C(12)C(13)N(3)	105.2(5)
C(1)C(2)C(3)	120.4(5)	C(12)C(13)C(15)	129.5(6)

RESULTS AND DISCUSSION

A reaction of $PdCl_2$ with reagent L in the presence of HCl gives different complexes **I** and **II**, depending on the reaction conditions. Both complexes are diamagnetic, which indicates the low-spin configuration d^8 of the Pd^{2+} ion. With an excess of acetonitrile, the reaction yields complex **I** containing ligand L in the protonated form (elemental analysis data). With an increase in the CH_2Cl_2, we obtained complex **II** containing a neutral molecule of L. It is known that quinoline is a stronger base ($pK_\alpha = 4.94$) than pyrazole ($pK_\alpha = 2.53$) [10]. Therefore, complex **I** could be expected to contain the cation HL^+ resulting from the protonation of L at the N atom of the quinoline fragment. This assumption was confirmed by X-ray diffraction data for complex **I**.

The structural unit of complex **I** is a mononuclear acentric molecule (Fig. 1). The Pd atom is coordinated to the pyrazole N atom of the monodentate ligand cation HL^+ (Pd–N 2.059(5) Å) and three Cl atoms (Pd–Cl 2.277(2)–2.330(2) Å). The coordination polygon $PdNCl_3$ can be regarded as a distorted square (trapezium); the N···Cl distances are 3.038(6) and 3.100(5) Å and the Cl···Cl distances are 3.240(3) and 3.292(3) Å. The symmetry of the coordination polygon in complex **I** is consistent with its diamagnetism. The average deviation of the N and Cl atoms from the plane NCl_3 is 0.038(1) Å; the Pd atom deviates from this plane only by 0.020(1) Å. The Pd–N and Pd–Cl bond lengths and the bond angles in structure **I** are close to those in a Pd(II) complex with a pyrazole derivative also containing the $PdNCl_3$ polygon [11].

Two quinoline rings, as well as the pyrazole ring, are virtually planar. The average deviation of the pyrazole atoms and two methyl C atoms is 0.008(4) Å. The average deviation of the quinoline atoms and the methyl C(10) atom from the root-mean-square plane is 0.017(6) Å. The pyrazole ring makes an angle of 98.7° with the coordination polygon $PdNCl_3$ and is rotated about the N(3)–C(1) bond through 41.0° relative to the quinoline fragment. In the ring $\overline{\mathrm{Pd(1)N(2)N(3)C(1)N(1)H(1N)Cl(1)}}$, the Cl(1)···N(1) distance is 3.101(5) Å and the angle N(1)HCl(1) is 170°, which suggests the presence of an intramolecular H bond.

The packing of mononuclear molecules in crystal structure **I** is shown in Fig. 2a (projection onto the plane (010)). The conjugated rings of the quinoline fragments have a center of symmetry (0.5, 0, 0.5); the distance between their centers is $r = 3.73$ Å and the distance between the rings is $d = 3.52$ Å (Fig. 2b). These data suggest π–π-interactions between the quinoline molecules (Fig. 3a) [12]. When the same rings are about the center of symmetry (0, 0, 0.5) ($r = 5.025$, $d = 3.52$ Å), peripheral overlap results in only one short contact (C(9)···C(9') 3.52 Å) (Fig. 3b). Therefore, a distinctive

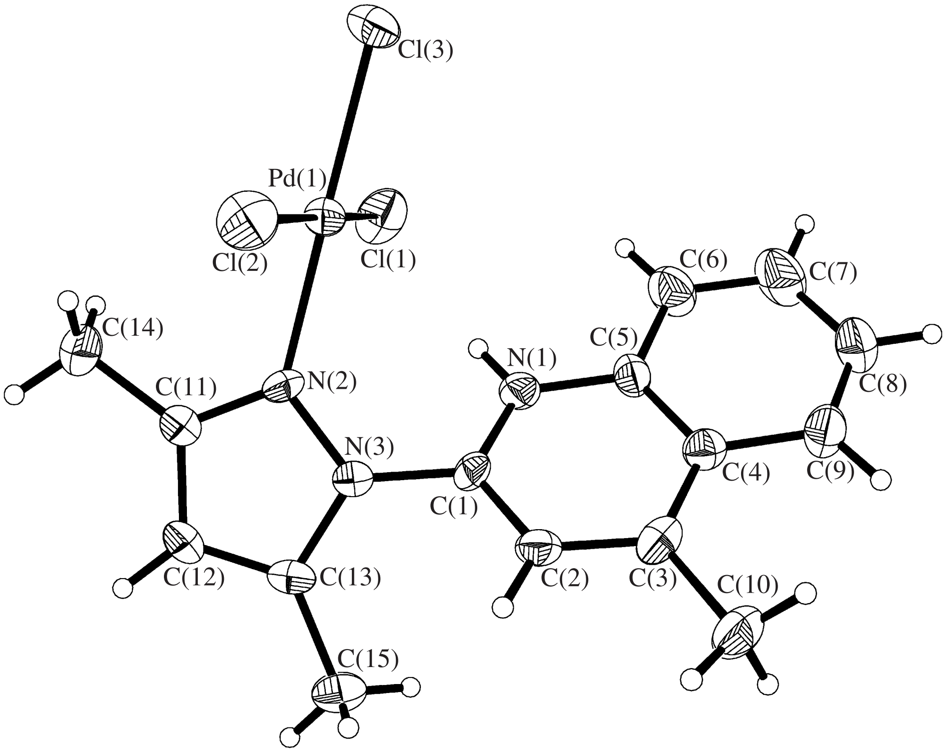


Fig. 1. Acentric structure **I** with numbering of the non-hydrogen atoms.

feature of structure **I** is the formation of dimeric ensembles stabilized by π–π-interactions between the rings of two parallel quinoline fragments. Similar interactions were noted in [6].

Diamagnetic complex **II** seems to contain the square polygon PdN_2Cl_2 due to coordination of the donor N atoms of the chelating bidentate ligand L to $PdCl_2$. This results in closure of the five-membered chelate ring $PdCN_3$.

The IR spectrum of reagent L shows absorption bands at 1601, 1581, and 1510 cm^{-1} (C=C andC=N stretches). The corresponding bands in the spectrum of complex **II** appear at 1594, 1555, and 1516 cm^{-1}. The shifts of the bands confirm the coordination of the heterocyclic fragments of L through the N atoms. We found that complex **II** can be converted into complex **I** by keeping its yellow crystals for a long period of time in $HCl–EtOH–CH_2Cl_2–CH_3CN$ (the composition of this mixture is identical with that used in the synthesis of complex **II**). As the result, we obtained reddish orange crystals of complex **I**.

Since complexes **I** and **II** are negligibly soluble in common inert solvents employed in NMR studies (CCl_4, $CHCl_3$, and CH_2Cl_2), samples were prepared by dissolving the complexes in pure DMSO-d_6 for **II** or DMSO-d_6-$CDCl_3$ for **I**. The ^{1}H NMR and ^{13}C NMR spectra of both complexes are virtually identical (for this reason, we present here only the spectrum of complex **I**), differing only slightly from the spectrum of free L. The observed subtle distinctions can be attributed to the different concentrations of the solutions and the different conditions of the NMR experiment. When the complex contains the protonated N atom of the quinoline fragment (as in **I**), the signals for the quinoline C atoms in the ^{13}C NMR spectrum should be characteristically shifted compared to those for the nonprotonated form of L. In addition, if the coordination polygon $PdNCl_3$ is retained in solution, the spectrum should show characteristic shifts of the signals for the C atoms of the coordinated pyrazole ring. Since the above effects are not observed and the NMR spectra of reagent L and complexes **I** and **II** in solutions are very similar, one can conclude that structures **I** and **II** are probably unstable in the presence of DMSO.

Our data for Pd(II) complexes suggest that similar complexes containing not only the molecule L but also the cation HL^+ can be obtained from other *d* metals.

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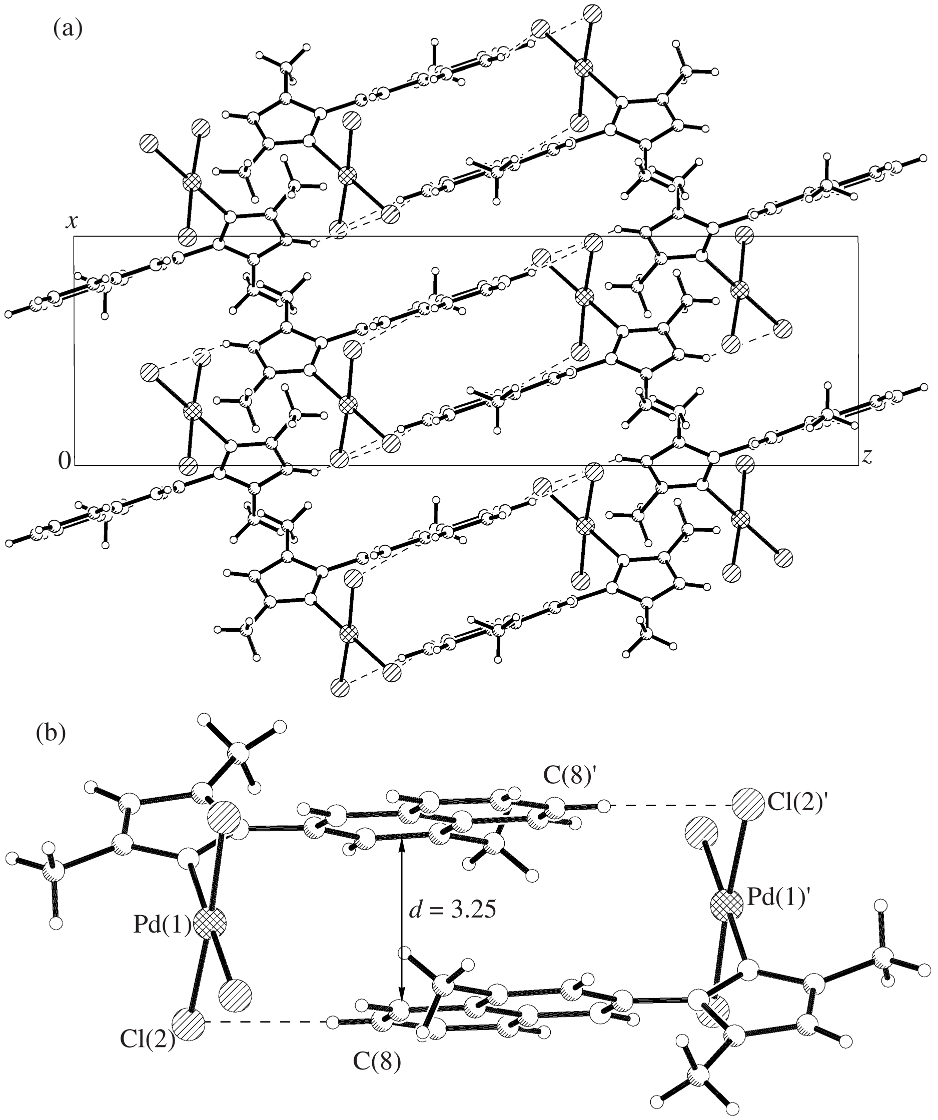

Fig. 2. (a) Projection of crystal structure **I** onto the plane (010) and (b) a fragment of the packing of two adjacent molecules of complex **I**.

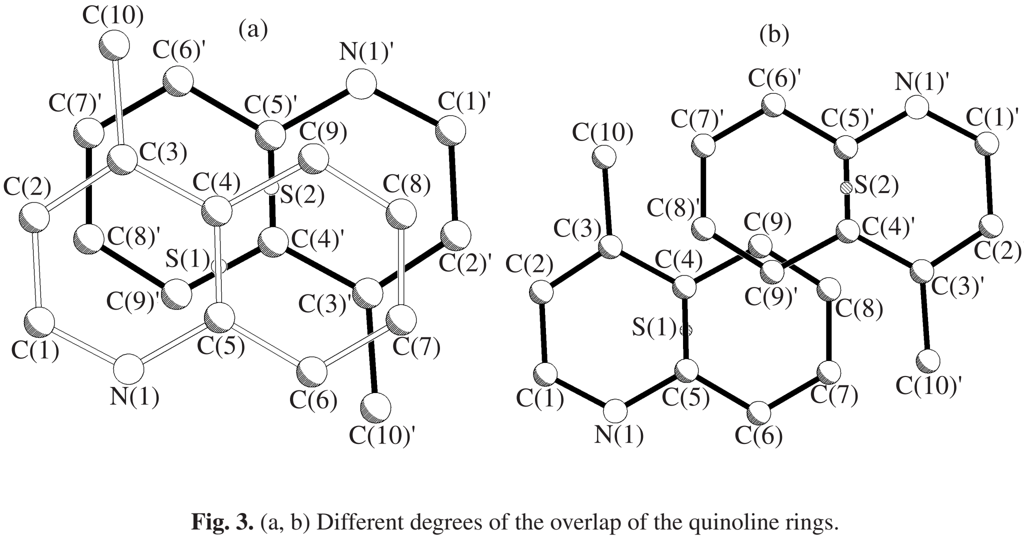

Fig. 3. (a, b) Different degrees of the overlap of the quinoline rings.

powder diffraction analysis, and V.A. Daletskii for magnetochemical measurements.

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