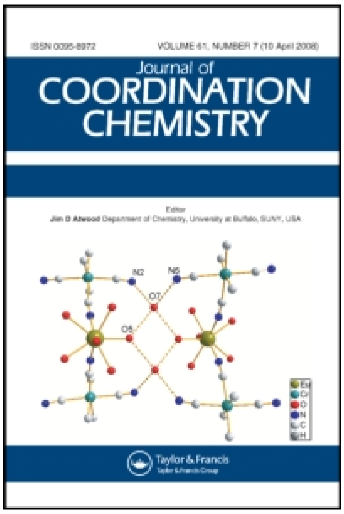

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Palladium(II) Complexes of 1-vinylimidazole

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PALLADIUM(II) COMPLEXES OF 1-VINYLIMIDAZOLE

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Two new co-ordination compounds of Pd^{II} with 1-vinylimidazole of the formulae $[PdL_4]Cl_2 \cdot 3H_2O$ and *trans*-$[PdL_2Cl_2]$, where L is a 1-vinylimidazole molecule, have been obtained. The compounds were characterised by spectroscopic, molar conductivity, thermogravimetric and magnetochemical measurements. Single crystal X-ray structure analyses of the complexes were also carried out. The compounds are diamagnetic with square-planar coordination around the palladium(II) ions. Other physico-chemical properties of the both complexes are compatible with their structures.

Keywords: Palladium(II) complexes; Imidazole derivatives; Crystal structure; Spectra

INTRODUCTION

Derivatives of imidazole represent a class of heterocyclic compounds of great importance. Both imidazole and its derivatives have found widespread applications in pharmacy and industry (*e.g.*, as effective corrosion inhibitors) [1 – 4]. Complexes of 1-vinylimidazole with transition metals have been used as hidden curing agents for epoxy resins [5]. Remarkable also is their biological activity [6]. Previously, coordination of 1-vinylimidazole was studied with Co^{II}, Ni^{II}, Cu^{II}, Zn^{II} and Cd^{II} in aqueous solution together with extractability of these compounds by organic solvents [7]. Reports on complexes of the azole in the solid state have dealt with crystal structures of the chloride complexes of Co^{II} [4, 8] and Cu^{II} [8], as well as with

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spectroscopic and other characteristics [8–10]. In this contribution, spectroscopic characteristics, crystal structures and properties of the chloride complexes of palladium(II) with 1-vinylimidazole are reported.

EXPERIMENTAL

Reagent and Preparation of the Complexes

[PdL$_4$]Cl$_2$ · 3H$_2$O(1)

One mmol of $PdCl_2$ (POCh, Gliwice, Poland) was dissolved in acetone and acidified with a few drops of conc. HCl. To this solution, kept in a water bath, a1-vinylimidazole (Aldrich-Europe) solution in acetone was added to adjust the pH to 10. On the next day, the colourless crystals which had formed were washed with absolute ether and dried under vacuum at room temperature.

Trans-[PdL$_2$Cl$_2$] (2)

This was obtained by thermal degradation of **1** at 120°C. Ochre coloured crystals of the compound were crystallised from an acetone-toluene mixture (1:1 v/v).

Anal. Found (%): **1** C, 39.5; H, 5.1; N, 18.6. Calc. for $[PdL_4]C1_2 \cdot 3H_2O$: C, 39.52; H, 4.98; N, 18.44; **2** C, 33.0; H, 3.4; N, 15.5. Calc. for $[PdL_2Cl_2]$: C, 32.86; H, 3.31; N, 15.33.

Physical Methods

Elemental analyses were run on a Model 240 Perkin Elmer CHN instrument. IR spectra were recorded on a Perkin Elmer 180 ($50-4000\,cm^{-1}$ range) spectrophotometer in KBr pellets. FIR spectra were obtained in Nujol mulls sandwiched between polyethylene plates. Magnetic measurements were carried out at 293 K using $Hg[Co(NCS)_4]$ as calibrant. Corrections for diamagnetism of the constituent atoms were calculated using Pascal's constants.

Thermal decomposition of the $[PdL_4]Cl_2 \cdot 3H_2O$ under dynamic conditions was studied using a 951 TGA Thermogravimetric Analyzer (DuPont Instruments). The sample (5.298 mg) was heated in static air at a rate of $5\,deg\,min^{-1}$ in an open standard crucible. The final product of decomposition was identified as palladium metal based on TG curves and X-ray powder diffraction [11]. The X-ray powder diffraction patterns were taken on a DRON-2 (USSR) diffractometer equipped with a scintillation counter linked to an IBM computer by a step by step method over the 2Θ angle range of 4–80°. The electronic spectra (5000–50000 cm^{-1}) were recorded on a Cary 5 instrument.

Crystallography

Measurements of the studied palladium(II) complexes were performed on a Kuma KM4CCD κ-axis diffractometer with graphite-monochromated Mo$K\alpha$ radiation. Data were corrected for Lorentz and polarization effects. No absorption correction was applied. The structures were solved by direct methods using the SHELX-97 [12] computer program package and refined by full-matrix least-squares methods using SHELXL-97 [13]. Crystal data and details of data collection together with the refinement procedures are presented in Table I. Final coordinates of the non-hydrogen atoms are listed in Tables II and III. Full lists of crystallographic data are available from the authors upon request.

TABLE I Crystal data and structure refinement details for complexes **1** and **2**

	1	**2**
Empirical formula	$C_{20}H_{30}Cl_2N_8O_3Pd$	$C_{10}H_{12}Cl_2N_4Pd$
Molecular weight	607.82	365.54
Temperature	100(1) K	100(1) K
Radiation	Mo $K\alpha(\lambda = 0.71073$ Å)	Mo $K\alpha(\lambda = 0.71073$ Å)
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$
a/Å	19.061(4)	7.199(2)
b/Å	10.480(2)	13.462(3)
c/Å	16.057(3)	6.616(2)
β/°	125.80(3)	102.66(3)
V/Å^3	2601.5(9)	625.59(2)
Z	4	2
μ/mm^{-1}	0.956	1.892
Reflections collected	9063	3675
Independent reflections	3169, [R(int) = 0.029]	1340, [R(int) = 0.017]
Final Rl, $wR2$ [$I > 2\sigma(I)$]	0.038, 0.092	0.020, 0.054

TABLE II Atomic coordinates and equivalent isotropic displacement parameters for $[PdL_4]Cl_2 \cdot 3H_2O$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x/a	y/b	z/c	$U(eq)$
Pd	0.0000	0.0000	0.0000	0.02291(11)
Cl	0.09720(5)	0.24438(7)	−0.04334(6)	0.03253(17)
O(1)	0.26958(17)	0.0815(3)	0.0467(2)	0.0516(7)

TABLE II (Continued)

	x/a	y/b	z/c	$U(eq)$
O(2)	0.0000	0.4110(4)	−0.2500	0.100(2)
N(11)	−0.03675(15)	0.1244(2)	0.06181(16)	0.0277(5)
N(12)	−0.1067(2)	0.2105(4)	0.1150(2)	0.0649(12)
N(21)	−0.11305(16)	0.0295(2)	−0.13887(17)	0.0275(5)
N(22)	−0.2512(2)	0.0202(3)	−0.2687(2)	0.0505(9)
C(11)	−0.0941(2)	0.1048(5)	0.0805(3)	0.0504(10)
C(12)	−0.0551(4)	0.3024(4)	0.1188(4)	0.0806(19)
C(13)	−0.0113(3)	0.2488(3)	0.0861(3)	0.0532(10)
C(14)	−0.1574(6)	0.2703(8)	0.1485(6)	0.0454(16)
C(15)	−0.2237(5)	0.2087(9)	0.1215(6)	0.0429(16)
C(21)	−0.1881(2)	−0.0249(3)	−0.1742(3)	0.0382(7)
C(22)	−0.2138(3)	0.1070(4)	−0.2940(2)	0.0504(10)
C(23)	−0.1284(2)	0.1124(3)	−0.2143(2)	0.0373(7)
C(24)	−0.3372(4)	−0.0061(6)	−0.3489(5)	0.0258(11)
C(25)	−0.3804(5)	−0.0659(6)	−0.3209(5)	0.0270(12)
C(14′)	−0.1758(5)	0.1887(6)	0.1292(5)	0.0339(14)
C(15′)	−0.2087(6)	0.2903(7)	0.1450(5)	0.0377(15)
C(24′)	−0.3430(5)	−0.0338(8)	−0.3080(6)	0.0322(14)
C(25′)	−0.4058(4)	−0.0212(7)	−0.4061(5)	0.0379(14)

TABLE III Atomic coordinates and equivalent isotropic displacement parameters for [PdL_2Cl_2]. *U*(eq) is defined as one third of the trace of the orthogonalized *Uij* tensor

	x/a	y/b	z/c	$U(eq)$
Pd	0.0000	0.0000	0.0000	0.00880(9)
Cl	−0.19238(6)	0.05052(3)	0.21639(7)	0.01407(12)
N(1)	0.1303(2)	0.13300(11)	0.0322(2)	0.0109(3)
N(2)	0.3539(2)	0.24657(12)	0.0856(2)	0.0114(3)
C(1)	0.3157(3)	0.14783(14)	0.0734(3)	0.0120(3)
C(2)	0.1814(3)	0.29681(14)	0.0480(3)	0.0127(4)
C(3)	0.0455(3)	0.22550(15)	0.0162(3)	0.0125(4)
C(4)	0.5406(3)	0.28649(15)	0.1267(3)	0.0145(4)
C(5)	0.5798(3)	0.38232(16)	0.1447(3)	0.0191(4)

RESULTS AND DISCUSSION

The Structure of Complex (1)-[PdL_4]$Cl_2 \cdot 3H_2O$

Selected interatomic distances and angles of complex **1** are shown in Table IV. Its molecular geometry and the numbering of the atoms is shown in Figure 1. The palladium(II) ion is situated at a centre of symmetry of a square planar complex. The Pd—N bond lengths are 1.997(2) and 2.022(3) Å. The angles in the coordination plane are 90.5(1) and 89.5(5)°. The *trans* angles are each 180°. In the first ligand molecule, the plane of the

TABLE IV Selected bond lengths [Å] and bond angles [°] for complexes **1** and **2**

1	**2**
Bond lengths (*Å*)	
Pd N(11) 1.997(2)	Pd N(1) 2.011(2)
Pd N(21) 2.022(3)	Pd Cl 2.302(1)
N(11) C(11) 1.308(4)	N(1) C(1) 1.318(2)
N(11) C(13) 1.366(4)	N(1) C(3) 1.381(3)
N(12) C(11) 1.322(6)	N(2) C(1) 1.356(3)
N(12) C(12) 1.353(7)	N(2) C(2) 1.388(2)
N(12) C(14) 1.490(8)	N(2) C(4) 1.417(2)
C(12) C(13) 1.343(5)	C(2) C(3) 1.354(3)
C(14) C(15) 1.251(12)	C(4) C(5) 1.320(3)
Bond angles (°)	
N(11) Pd N(11$^{\mathrm{i}}$) 180.0	N(1) Pd N(1$^{\mathrm{i}}$) 180
N(11) Pd N(21$^{\mathrm{i}}$) 90.5(1)	N(1) Pd Cl 90.1(1)
N(11) Pd N(21) 89.5(1)	N(1$^{\mathrm{i}}$) Pd Cl 89.9(1)
N(21$^{\mathrm{i}}$) Pd N(21) 180	Cl Pd Cl$^{\mathrm{i}}$ 180
C(11) N(11) C(13) 106.8(3)	C(1) N(1) C(3) 106.9(2)
C(11) N(11) Pd 126.5(3)	C(1) N(1) Pd 125.8(1)
C(13) N(11) Pd 126.6(2)	C(3) N(1) Pd 127.4(1)
C(11) N(12) C(12) 108.0(3)	C(1) N(2) C(2) 107.8(2)
C(11) N(12) C(14) 145.0(5)	C(1) N(2) C(4) 123.7(2)
C(12) N(12) C(14) 107.0(5)	C(2) N(2) C(4) 128.6(2)
N(1l) C(11) N(12) 110.2(4)	N(1) C(1) N(2) 110.1(2)
C(13) C(12) N(12) 106.7(4)	C(3) C(2) N(2) 105.7(2)
C(12) C(13) N(11) 108.2(4)	C(2) C(3) N(1) 109.6(2)
N(12) C(14) C(15) 113.2(9)	N(2) C(4) C(5) 124.2(2)

Symmetry transformations used to generate equivalent atoms: $^{\mathrm{i}} = -x, -y, -z$.

imidazole ring (N(11), N(12), C(11), C(12), C(13)) is inclined at an angle of 77.2(2)° to the coordination plane. The respective angle of the second molecule is 85.7(2)°. Carbon atoms C(14), C(15) as well as C(24) and C(25) of the vinyl substituent have half occupancy factors (G = 0.5). The chloride anions are not directly linked to the palladium(II) ion. They are situated on the symmetry axis of the coordination plane, at a distance of 3.461(2) Å from the central ion.

The anions are linked to the water molecules by hydrogen bonding. The lengths and angles of these bonds are compiled in Table V.

The Structure of Complex 2-[PdL$_2$Cl$_2$]

The molecular structure of complex **2** shown in Figure 2 together with the atom numbering scheme. Pd(II) is situated in the centre of the *trans* symmetry of the complex. Within the coordination plane, Pd-N(1) is 2.011(2) Å, thus being almost identical with those in complex **1**. The bonds

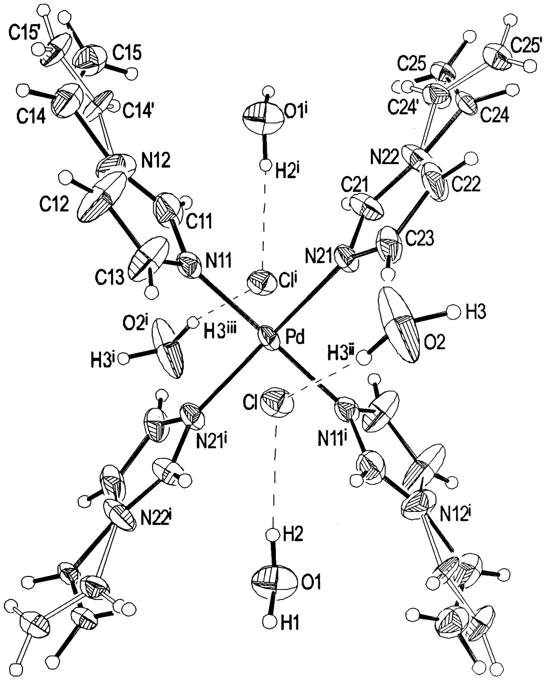

FIGURE 1 The molecular structure of $[PdL_4]Cl_2 \cdot 3H_2O$ (**1**).

TABLE V Hydrogen bond lengths (Å) and bond angles (°) for complex **1**

D—H···A	*D—H*	*H···A*	*D···A*	*DHA*
O(1)—H(1)···Cl(1^{ii})	0.95	2.21	3.152(3)	171
O(1)—H(2)···Cl(1)	0.96	2.27	3.200(3)	163
O(2)—H(3)···Cl(1^{iii})	0.96	2.27	3.209(3)	167

Symmetry transformations used to generate equivalent atoms: $^{i} = -x, -y, -z$, $^{ii} = -x+1/2, -y+1/2, -z$, $^{iii} = -x, y, -z-1/2$.

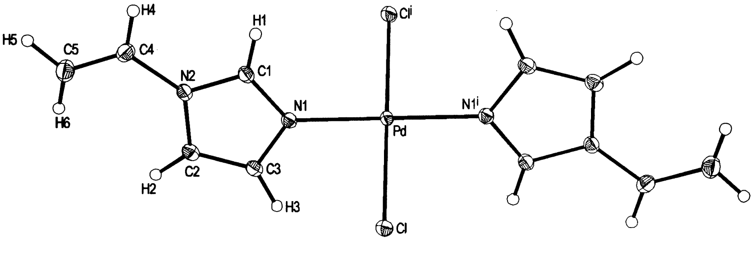

FIGURE 2 The molecular structure of $[PdL_2Cl_2]$ (**2**).

with the chloride ligands are longer than those with nitrogen (2.302(1) Å). The *trans* angles in the coordination plane are 180° each, whereas those between nitrogen atoms and the chloride ligands differ only slightly from 90° (89.9(1) and 90.1(1)°). The plane of the imidazole ring forms an angle of 47.7(1)° with the coordination plane. The inclination of the ring of the azole ligand is thus smaller than in complex **1**.

Physico-chemical Properties of the Complexes

IR spectra of the both complexes are compatible with their structures. It follows that "pyridinic" nitrogen atom of the imidazole ring takes part in coordination with the central ion. In the IR spectra of the complexes, bands resulting from C=N bonds conjugated with C=C of the imidazole ring are displaced by 9 cm^{-1} towards higher frequencies, relative to that of 1-allylimidazole (1504 cm^{-1}) [14–17]. The basic difference between the spectra of the two complexes concerns the far IR. In the spectrum of the complex **2** the ν(Pd—Cl) band is present at 366 cm^{-1}, so that the halogens take part in the coordination sphere. The presence of only one peak is in accordance with a *trans* square planar arrangement around the palladium(II) ion [18, 19]. The determined, molar conductivity in aqueous solution, of complex **1** of 228 $ohm^{-1}cm^{3}mol^{-1}$ is typical for an electrolyte dissociating into three ions. Conductivity of complex **2**, measured in DMF solution, is 13 $ohm^{-1}cm^{3}mol^{-1}$, and is consistent with that of a non-electrolyte [20].

The electronic spectrum of the ochre-coloured compound $[PdL_2Cl_2]$ is typical of square planar complexes of metal ions with d^8 configuration [22]. The onset of the band is located at 18100 cm^{-1}. It is broad and extends far over the UV range. Three peaks at 20 000, 25 000 and 42000 cm^{-1}, can be distinguished within this band. Their positions were determined by assuming Gaussian distributions. In the spectrum of the colourless $[PdL_4]Cl_2 \cdot 3H_2O$ complex there are two charge transfer bands at 27800 and 39400 cm^{-1} that are missing in the spectrum of free 1-vinylimidazole. As expected, compounds **1** and **2**, are diamagnetic.

A study of thermal stability of the complex **1** gave interesting results. Inspection of the TG curve showed that degradation of the molecule occured in the following steps

$$[PdL_4]Cl_2 \cdot 3H_2O \xrightarrow{40-150^\circ C} PdL_2Cl_2 \xrightarrow{190-230^\circ C}$$

$$PdL_{1.5}Cl_2 \xrightarrow{290-350^\circ C} PdLCl_2 \xrightarrow{350-450^\circ C} Pd$$

Our attention was focussed on the product of the first step, because its formula suggested the formation of a new complex in which two 1-vinylimidazole molecules in the coordination sphere have been substituted by two chloride ions. This fact was utilized to prepare complex [PdL_2Cl_2] by thermal degradation of complex **1**. Both TG curve and the X-ray powder diagram show that the final product is palladium metal, similar to the case with other palladium(II) complexes [23].

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