Brief Communications

Synthesis and structure of the complex of 2-(2-pyridyl)-2-oxazoline with $PdCl_2$

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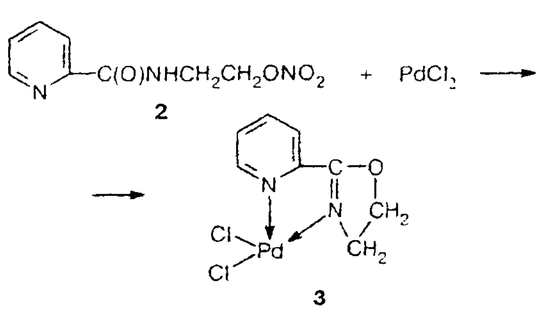
The reaction of *N*-2-nitroxyethylpicolinamide with $PdCl_2$ afforded the new complex *cis*-[2-(2-pyridyl)-2-oxazoline-*N,N'*]dichloropalladium(II). The structure of this complex was established by X-ray diffraction analysis.

Key words: *N*-2-nitroxyethylpicolinamide, reaction with palladium(II) chloride, *cis*-[2-(2-pyridyl)-2-oxazoline-*N,N'*]dichloropalladium(II), crystal structure, X-ray diffraction analysis.

Previously,[1] we have demonstrated that the reaction of *N,N'*-bis(2-nitroxyethyl)pyridine-2,6-dicarboxamide (**1**) with $PdCl_2$ in an acidic aqueous-alcoholic medium afforded a crystalline molecular compound as a cocrystallizate of *cis*-(*N*-2-nitroxyethylpicolinamide-*N,N'*)dichloropalladium(II) with *cis*-[2-(2-pyridyl)-2-oxazoline-*N,N'*]dichloropalladium(II). It was suggested that the complexation proceeded with the participation of *N*-2-nitroxyethylpicolinamide (**2**), which was formed as a result of hydrolytic elimination of one nitroxyethylamide group from the initial diamide **1**.

To confirm this suggestion, we studied the reaction of $PdCl_2$ with amide **2** under conditions analogous to those reported previously.[1] In this case, the complex of 2-(2-pyridyl)-2-oxazoline with $PdCl_2$ (**3**) was obtained in 84% yield.

Therefore, the formation of complexes containing the oxazoline ring in the reactions of $PdCl_2$ with pyridine-2,6-dicarboxamides containing the nitroxyethyl group is, apparently, the major direction of these reactions and has a general character.



Since pyridinecarboxamides containing nitroxylethyl substituents are used as medicines, considerable study has been given to their reactivities in recent years. It was shown[2] that *N*-(2-nitroxyethyl)nicotinamide (the effi-

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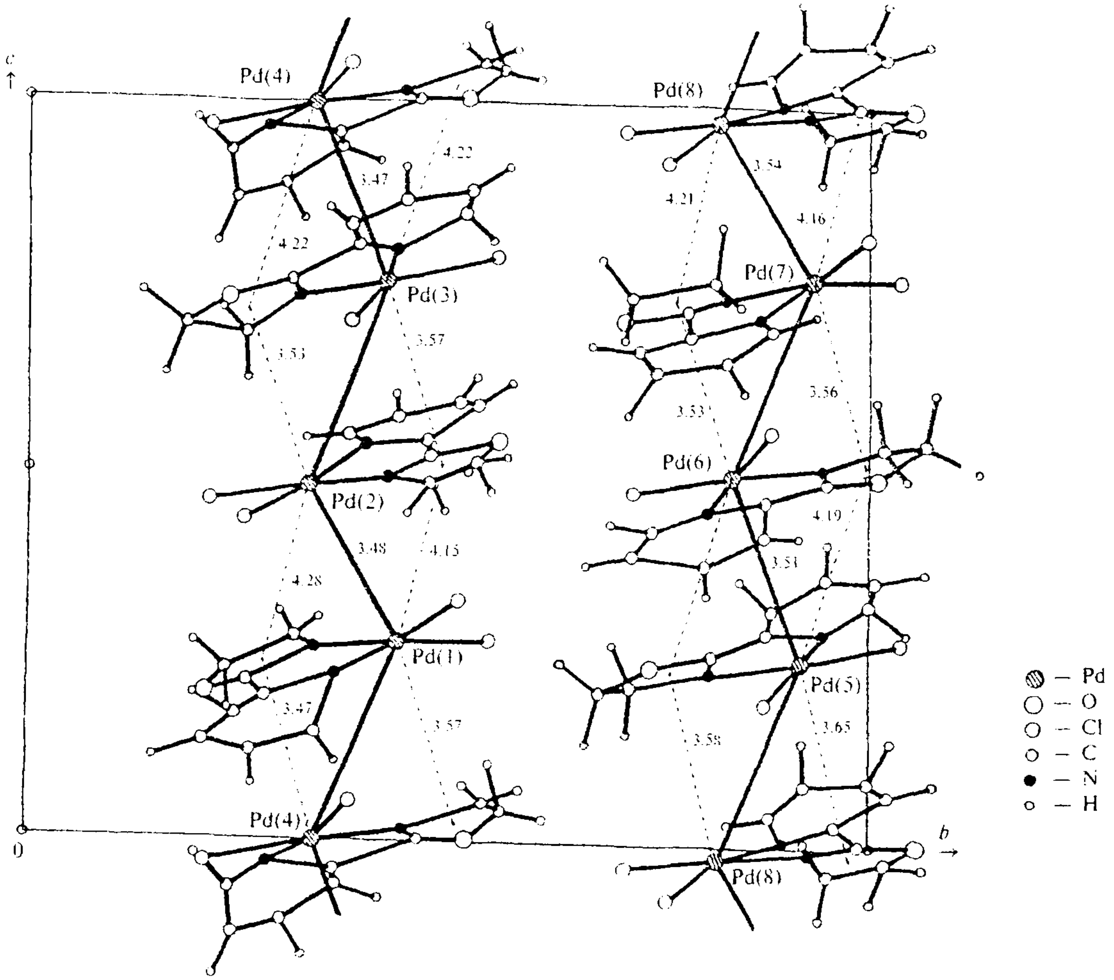

Fig. 1. Crystal structure of complex **3**.

cient cardiological medicine Nicorandil[3,4]) is converted into 2-(3-pyridyl)-2-oxazoline. However, this conversion proceeds only upon prolonged heating in aqueous alkali. The formation of the oxazoline ring was not observed in the synthesis of Nicorandil complexes with copper, platinum, and rhodium salts.[5,6] Apparently, this is associated with the fact that the presence of a substituent at position 3 of the pyridine ring prevents the amide nitrogen atom from participating in chelate formation with the transition metal atom. Complexation of compounds which contain the same substituents at positions 2 and 6 of the pyridine ring and can be involved in chelate formation with the participation of the amide nitrogen atom, universally leads to the formation of the oxazoline ring. Interestingly, this conversion occurs under mild conditions.

The Pd^{II} atom in complex **3** (Fig. 1) has a planar coordination. The molecule contains three fused rings, *viz.*, the pyridine, chelate, and oxazoline fragments. The N atoms, which are *cis*-coordinated to the Pd atom, are involved in the chelate ring. The structure of **3**, though similar to one of the complexes of the cocrystallizate,[1] is distinguished by the fact that the unit cell contains four crystallographically independent complexes linked in infinite chains. There are four chains per asymmetric unit; only crystallographically independent atoms are shown in the *bc* projection for clarity (see Fig. 1). In all the studied complexes, the atoms of the ligands directly bound to the Pd(1), Pd(2), Pd(3), Pd(4), Pd(5), Pd(6), Pd(7), and Pd(8) atoms are located in the corresponding planes, and the deviations of the atoms of the ligands from these planes are, on the average, at most ±0.08 Å. The average deviations of the N and Cl atoms from the plane of the coordination unit are ±0.03 Å. Note an important distinguishing feature of the arrangement of the planar complexes in the crystal. In each infinite chain, the complexes are arranged in a planar-parallel fashion; the deviations are no more than 3°. The arrangement of the *cis* ligands in each complex provides conditions for interactions of the d_{XZ} and d_{YZ} orbitals of the Pd^{II} atom with the π^* orbitals of the pyridine and oxazoline rings. However, these interactions do not affect the interatomic distances. In the crystal, the planar-parallel complexes are linked in zigzag chains, which are apparently stabilized by weak intermolecular interactions between the Pd^{II} atoms and the oxazoline ligands of the adjacent complexes. Thus, the Pd(1), Pd(2), Pd(5), and Pd(6) atoms interact with the ligands coordinated to the Pd(4), Pd(3), Pd(8), and Pd(7) atoms, respectively. The distances between the pairs of the interacting complexes are <3.6 Å, whereas the distances between the pairs of the complexes which are not involved in these interactions along the $Pd^{II}—Pd^{II}$ direction, are also <3.6 Å.

Experimental

N-2-Nitroxyethylpicolinamide (**2**) was prepared according to a known procedure,[7] m.p. 54—56 °C. The IR spectrum was recorded on a Specord M-80 spectrophotometer in KBr pellets. The ^1H NMR spectrum was measured on a Bruker 200 spectrometer.

***cis*-[2-(2-Pyridyl)-2-oxazoline-*N*,*N*′]dichloropalladium(II) (3)**. An aqueous solution of $PdCl_2$ (5.3 mL, 40 mg mL^{-1}, 1.13 mmol) was added with stirring to a solution of *N*-2-nitroxyethylpicolinamide (0.211 g, 1 mmol) in 50% ethanol (60 mL) at 25—30 °C. Then the reaction mixture was stirred for 2 h and kept at ~20 °C for 10 h. The precipitate that formed was filtered off, washed with water (3×150 mL) and alcohol (3×100 mL), and dried in air. Yellow-beige crystals were obtained in a yield of 0.274 g (84.3%), m.p. >210 °C. Found (%): C, 29.39; H, 2.41; Cl, 21.64; N, 8.47; Pd, 32.73. $C_8H_8Cl_2N_2OPd$. Calculated (%): C, 29.52; H, 2.48; Cl, 21.78; N, 8.61; Pd, 32.69. IR (KBr), ν/cm^{-1}: 1090, 1628 (2-oxazoline ring); 705, 740, 1395, 1490, 1556, 1578 (2-pyridyl); 2924 (CH_2); 3090 (CH). ^1H NMR (DMSO-d_6), δ: 8.97 (br.d, 1 H, C(6)H, J = 5.6 Hz); 8.36 (ddd, 1 H, C(4)H, J = 7.6, 7.6, and 0.6 Hz); 7.98 (br.d, 1 H, C(3)H, J = 7.6 Hz); 7.94 (ddd, 1 H, C(5)H, J = 7.6, 5.6, and 0.6 Hz); 4.93 (t, 2 H, $CH_2—O$, J = 9.6 Hz); 3.94 (t, 2 H, $CH_2—N$, J = 9.6 Hz).

Crystals for X-ray diffraction study were prepared by slow crystallization of compound **3** from a 1 : 1 $CH_3CN—CH_3NO_2$ mixture.

X-ray diffraction analysis of single crystals of complex **3** was performed on a four-circle KM-4 diffractometer (KUMA—Diffraction, Poland). Crystals of **3** are triclinic, M = 325.47, a = 18.090(10), b = 16.975(12), c = 14.637(15) Å, α = 92.68(8), β = 112.56(8), γ = 77.03(5)°, V = 4041.3(5) Å^3, d = 2.141 g cm^{-3}, λ-Kα = 0.710 Å, space group $P1$, z = 2, μ = 2.33 mm^{-1}.

A total of 8451 reflections were measured in the angle range of $2\theta \le 60.15°$ using the $\omega/2\theta$ scanning technique. The structure was solved by the direct method with the use of the SHELX-97 program package. The atomic coordinates of all components of the unit cell were refined by the full-matrix least-squares method using the SHELX-97 program; the thermal parameters of the nonhydrogen and hydrogen atoms were refined anisotropically and isotropically, respectively; R = 0.055 for 2468 $F_0 > 4\sigma(F_0)$.

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