8. V. A. Dorokhov, A. V. Komkov, A. M. Sakharov, and V. S. Bogdanov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 177 [*Russ. Chem. Bull.*, 1996, **45**, 168 (Engl. Transl.)].
9. V. A. Dorokhov, L. G. Vorontsova, and M. G. Kurella, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 2541 [*Russ. Chem. Bull.*, 1996, **45**, 2411 (Engl. Transl.)].
10. V. A. Dorokhov and M. F. Gordeev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 1211 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, **38**, 1104 (Engl. Transl.)].
11. V. A. Dorokhov, M. A. Prezent, M. F. Gordeev, and V. S. Bogdanov, *Zh. Org. Khim.*, 1995, **31**, 769 [*J. Org. Chem.*, 1995, **31** (Engl. Transl.)].
12. A. F. Crowther, F. H. So Curd, and F. L. Rose, *J. Chem. Soc.*, 1948, 590.
13. A. K. Bose and Sh. Garratt, *J. Am. Chem. Soc.*, 1962, **84**, 1310.

Received April 8, 1997

Synthesis and structure of the Pd^{II} complex with 3,3-dinitropropylamine

B. S. Fedorov,* N. I. Golovina, G. V. Strukov, V. V. Kedrov, V. V. Arakcheeva, R. F. Trofimova, G. V. Shilov, and L. O. Atovmyan

Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: 007 (096) 515 3588

The reaction of 3,3-dinitropropylamine with $PdCl_2$ gave the previously unknown complex, bis(3,3-dinitropropylaminato-N,C^3)palladium(II). The structure of the complex was established by X-ray diffraction analysis.

Key words: 3,3-dinitropropylamine, reaction with palladium(II) chloride; bis(3,3-dinitropropylaminato-N,C^3)palladium(II), crystal structure; X-ray diffraction analysis.

It is known that complexes of palladium(II) with some organic diamines (diaminocyclohexane, diaminoethane, and diaminopropane), like *cis*-diamminedichloroplatinum(II),[1] exhibit antitumor activity.[2] The synthesis of unconventional complexes with new ligands that differ from known ligands both in composition and molecular design is of interest in the search for weakly toxic antitumor compounds. At this time there is no data on the use of terminal polynitro compounds as ligands in complexes of palladium and platinum. These complexes possess increased oxidation potentials and can serve as a source of nitric oxide, which is known[3—5] to be an endogenic bioregulator that affects vascular tone, the function of blood platelets, the nervous and immune systems, *etc.* It was found that 3,3-dinitropropylamine, which contains two reaction centers (anionic and amine) can act as such a ligand. Like amino acids,[6] this polynitroalkylamine acts as a bidentate ligand in the reaction with palladium(II) chloride to form the previously unknown complex, bis(3,3-dinitropropylaminato-N,C^3)palladium(II) (**1**).

According to the data of X-ray structural analysis, compound **1** is a chelate complex with a distorted planar square coordination about the Pd^{II} ion (Fig. 1). The Pd(1), N(1), N(2), C(6), and C(3) atoms deviate from

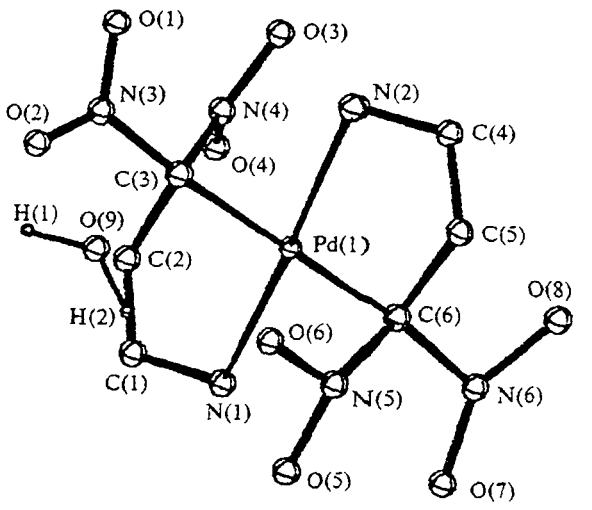

Fig. 1. Molecular and crystal structure of complex **1**.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 9, pp. 1704—1705, September, 1997.

Table 1. Bond lengths (d) and bond angles (ω) in the coordination unit of molecule **1**

Bond	d/Å	Angle	ω/deg
Pd(1)—N(1)	2.03	C(3)—Pd(1)—N(2)	97.1
Pd(1)—N(2)	2.08	C(3)—Pd(1)—N(1)	82.6
Pd(1)—C(3)	2.16	N(1)—Pd(1)—C(6)	97.0
Pd(1)—C(6)	2.09	C(6)—Pd(1)—N(2)	83.1

Table 2. Atomic coordinates ($\times 10^4$) in the structure of complex **1**

Atom	x	y	z
Pd(1)	7368(2)	460(2)	2452(2)
O(1)	11250(6)	1690(6)	4054(6)
O(2)	10059(6)	3277(5)	2378(6)
O(3)	10819(5)	−1146(5)	4044(6)
O(4)	10849(6)	−1494(6)	1909(6)
O(5)	3995(6)	2112(5)	635(5)
O(6)	4713(6)	3253(6)	2581(5)
O(7)	3490(5)	−412(6)	655(6)
O(8)	4155(5)	−1650(6)	2807(6)
O(9)	7034(6)	4834(6)	2805(5)
N(1)	6840(7)	663(7)	306(7)
N(2)	7922(7)	445(7)	4668(7)
N(3)	10404(8)	1948(7)	2999(8)
N(4)	10491(7)	−927(8)	2792(8)
N(5)	4253(8)	2018(8)	2050(8)
N(6)	4345(7)	−905(8)	1855(7)
C(1)	8294(9)	832(9)	−101(9)
C(2)	9529(9)	550(8)	801(9)
C(3)	9655(9)	525(9)	2263(9)
C(4)	6547(9)	145(9)	5102(9)
C(5)	5159(9)	460(8)	4213(9)
C(6)	5155(8)	516(9)	2629(9)
H(1)	7909(12)	4830(15)	2357(15)
H(2)	5960(15)	4830(15)	2357(15)
H(3)	8051(14)	−452(15)	5100(15)
H(4)	8252(14)	650(14)	5501(15)
H(5)	6751(14)	−503(14)	5902(14)
H(6)	6352(15)	−511(15)	4303(15)
H(7)	5107(14)	−251(15)	3802(14)
H(8)	4851(14)	450(14)	5054(15)
H(9)	6502(15)	502(14)	−701(15)
H(10)	6652(15)	1650(15)	351(15)
H(11)	8251(14)	1253(14)	750(14)
H(12)	8650(15)	1251(14)	−852(15)
H(13)	9481(14)	1253(14)	1051(15)
H(14)	10102(15)	421(15)	−11(15)

the plane through the chelate unit by −0.054, +0.029, +0.028, −0.002, and −0.002 Å, respectively.

The bond lengths and bond angles in the coordination unit are given in Table 1. The planes of the nitro groups are inclined at the angles of 82.8°, 57.5°, 80.6°, and 63.4° to the central plane of the complex. Water molecules are involved in hydrogen bonding with the N(5)O(5)O(6) nitro group. The O(9)...O(6) and Pd(1)...O(9) distances are 2.5 and 3.84 Å, respectively.

Experimental

Bis(3,3-dinitropropylaminato-N,C^3)palladium(II) (1). A solution of $PdCl_2$ (4.55 mL, 39.02 mg mL^{-1}, ~1 mmol) was added with stirring to a solution of 3,3-dinitropropylamine[7] (0.292 g, ~2.5 mmol) in water (150 mL) at 40—50 °C. Then a dilute aqueous solution of NaOH was added until the pH became 7.0. The reaction mixture was kept at ~20 °C for 14 h. The precipitate of **1** was filtered off and washed with ice water. Crystallization from MeCN gave compound **1** as plates in a yield of 0.19 g (46.1%), decomp.p. >300 °C. Found (%): C, 17.01; H, 3.16; N, 19.79. $C_6H_{12}N_6O_8Pd \cdot H_2O$. Calculated (%): C, 17.13; H, 3.35; N, 19.98. IR (KBr), ν/cm^{-1}: 1265 (C—N); 1310, 1350, 1505, 1530 ($C(NO_2)_2$); 1590, 3270, 3315, (NH_2); 1465, 1475, 2900, 2960 (CH_2); 3430 (H_2O).

Crystals of the $Pd[NH_2(CH_2)_2C(NO_2)_2]_2 \cdot H_2O$ complex (**1**) are monoclinic, M = 420.61, a = 9.187(3) Å, b = 8.700(2) Å, c = 9.774(4) Å, β = 105.93(3)°, V = 751.2(5) Å, d_{calc} = 1.858(5) g cm^{-3}, λ = 0.709 Å, space group $P2_1$, Z = 2. Intensities of 1380 independent reflections were measured on a four-circle KM-4 (KUMA-Diffraction, Poland) diffractometer in the range $0.02 < \sin\theta/\lambda < 0.50$ with the use of the $\omega/2\theta$ scanning technique. The structure of **1** was solved by the direct method on a PC computer using the SHELX-86 program package. Atomic coordinates in the structure of **1** (Table 2) were refined by the full-matrix least-squares method to R_1 = 0.086. Thermal parameters of nonhydrogen atoms were refined anisotropically. Absorption correction was applied using the DIFABS program. The error in the Pd—L bond lengths, the lengths of the bonds between the light atoms, and the bond angles are ±0.03 Å, ±0.05 Å, and ±1°, respectively.

References

1. A. Sigel and H. Sigel, *Metal Ions in Biological Systems*, Marcel Dekker, Inc., New York, 1996.
2. US Pat. 4584316, 1986.
3. J. F. Kerwin, J. R. Lanauster, and P. L. Feldman, *J. Med. Chem.*, 1995, **38**, 4343; *Science*, 1992, **258**, 1862.
4. A. R. Butler and D. L. H. Williams, *Chem. Soc. Rev.*, 1993, **22**, 233.
5. A. R. Galla, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 378.
6. N. V. Sidgwick, *The Chemical Elements and Their Compounds*, Clarendon Press, Oxford, 1950, 1553 pp.
7. L. T. Eremenko, R. G. Gafurov, D. A. Nesterenko, A. G. Korepin, and N. S. Natsibullina, *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1969, 2562 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1969, **18** (Engl. Transl.)].

Received April 9, 1997