ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2009, Vol. 35, No. 3, pp. 210–214. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © E.V. Makotchenko, I.A. Baidina, 2009, published in Koordinatsionnaya Khimiya, 2009, Vol. 35, No. 3, pp. 212–216.

Binuclear Au(III)–Pd(II) Complex with Deprotonated Diethylenetriamine as a Bridging Ligand: Synthesis and Crystal Structure

E. V. Makotchenko and I. A. Baidina

Nikolaev Institute of Inorganic Chemistry, Siberian Division, Russian Academy of Sciences,
pr. akademika Lavrent'eva 3, Novosibirsk, 630090 Russia
E-mail: evm@che.nsk.su

Received March 13, 2008

Abstract—The heterobinuclear complex [AuCl(μ-Dien*)$PdCl_3$] (Dien* is deprotonated diethylenetriamine) was obtained and examined by X-ray diffraction analysis. Crystals are orthorhombic: $a = 13.886(3)$ Å, $b = 7.213(1)$ Å, $c = 11.824(2)$ Å, $V = 1184.3(4)$ Å^3, space group $Pna2_1$, $Z = 4$, $\rho_{calcd} = 3.070$ g/cm^3, $R = 0.02$. The coordination entities of gold and palladium are AuN_3Cl and $PdNCl_3$, respectively. The central N(2) atom of deprotonated diethylenetriamine is the shared vertex of the coordination squares of gold and palladium.

DOI: 10.1134/S1070328409030087

At present, investigations of heterometallic coordination compounds that can be employed as precursors for the preparation of various bimetallic formulations are of increased interest. The first problem in the study of such complexes is to determine their structures.

Complexes with bridging ligands constitute one of the main groups of binuclear compounds. Their structures can be represented as the coordination spheres of complexing metals joined by their vertices, edges, and faces. Such binuclear complexes with tetrahedral, square, and octahedral coordination entities are exemplified in [1]; however, the given examples include no complex containing the coordination squares with a shared vertex. Such an example may be provided by the double complex salt $[Au_2(Dien^*)Cl_4]_2[IrCl_6] \cdot 4H_2O$ (Dien* is deprotonated diethylenetriamine), in which the dimeric cation shows a similar geometry (two squares joined by vertices) [2]. In the dimeric cation of this salt, deprotonated diethylenetriamine serves to bridge two gold atoms. Having three functional groups (N atoms), diethylenetriamine ($H_2NC_2H_4NHC_2H_4NH_2$, Dien) is a tridentate ligand and usually can be coordinated in the (1, 2, 3)-types, in terms of the notation cited in [3]. Only a few complexes with Dien as a bridging ligand have been obtained. For instance, in $[Ag_2(Dien)_2(PMe_3)_2](PF_6)_2$ [4] and $[Hg_2(Dien)_3](ClO_4)_4$ [5], diethylenetriamine is coordinated according to the (1, 2)–(3) type; i.e., one terminal and central N atoms are bound to the metal atom, while the other terminal N atom is bound to the other atom of the same metal. A similar coordination type is found in the cations $[M_2(Dien)_3]^{4+}$ ($M = Cu^{2+}$ and Zn^{2+}) of the complexes with the anionic rhenium chalcocyanide clusters $[Re_4Q_4(CN)_{12}]^{4-}$ (Q = Se and Te) [3]. Another type of (1)–(3) coordination of diethylenetriamine is found in [{(Dien)Cu–Dien–Cu(Dien)}$Re_4S_4(CN)_{12}$] [3] and $[Au_2(Dien)_2](BF_4)_2 \cdot C_2H_5OH$ [6]. Upon proton abstraction from Dien, the central N(2) atom acquire a lone electron pair and can be involved in a donor–acceptor interaction with another metal atom, thus functioning as a bridge [7]. In the dimeric cation $[Au_2(Dien^*)Cl_4]^+$, either Au atom is bound to the central and one terminal N atom; i.e., diethylenetriamine is coordinated in a new (1, 2)–(2, 3) type.

This study is devoted to the structure of the heterobinuclear gold and palladium complex [AuCl(μ-Dien*)$PdCl_3$] (**I**) with an unexpected and earlier unknown (1, 2, 3)–(2') type of diethylenetriamine coordination (the prime serves to indicate the coordination with a dissimilar metal).

EXPERIMENTAL

The starting complexes [Au(Dien)Cl]Cl_2, $K_2[PdCl_4]$, and $(NH_4)_2[PdCl_4]$ were prepared as described in [8, 9].

Synthesis of complex I. The complex [AuCl(Dien)]Cl_2 (0.0203 g, 0.05 mmol) was dissolved in 0.01 M HCl (5 ml) and then $(NH_4)_2[PdCl_4]$ (0.0142 g, 0.05 mmol) was added. Concentration of this mixture at room temperature gave crystals as dark brown flattened prisms; crystallization began after 20–30 min. After a day, the crystals were filtered off, washed with minimum amounts of 0.01 M HCl, ethanol, and ether, and dried in air. The yield was 0.025 g (~90%). Out of them, a suitable single crystal was used for X-ray diffraction analysis. The same crystals were obtained from the reaction mixture in the presence of NaCl (1.0 mol/l) or when $(NH_4)_2[PdCl_4]$ was replaced by $K_2[PdCl_4]$.

The content of (Au + Pd) was determined gravimetrically: a sample was decomposed in $HClO_4$–H_2SO_4 and the metals were reduced with hydrazine sulfate; elemental analysis for C, H, and N was performed at the Novosibirsk Institute of Organic Chemistry (Siberian Division of the Russian Academy of Sciences).

For $C_4H_{12}N_3Cl_4AuPd$ anal. calcd. (%): C, 8.78; H, 2.21; N, 7.68; (Au + Pd), 55.42.

Found (%): C, 8.9; H, 2.1; N, 7.5; (Au + Pd), 55.5.

X-ray diffraction analysis. The unit cell parameters and experimental reflection intensities for crystal structure **I** were measured at 293(2) K on a Bruker-Nonius X8Apex automated four-circle diffractometer equipped with an XY-detector (MoK_α radiation, λ = 0.71073 Å, graphite monochromator) according to a standard procedure. Crystallographic parameters and a summary of data collection for complex **I** are given in Table 1. The coordinates of the basic atoms have been deposited with the Cambridge Crystallographic Data Collection (no. 679 045).

Structure **I** was solved by the direct method and refined in the anisotropic (isotropic for H atoms) approximation. The hydrogen atoms were located geometrically.

Selected bond lengths and angles in structure **I** are given in Table 2. All calculations were performed with the SHELX-97 program package [10]. The powder diffraction pattern (DRON-3M, CuK_α radiation) was indexed from single-crystal X-ray diffraction data. The diffraction pattern shows no irrelevant lines, which suggests that product **I** consists of one phase.

In pH measurements of the mother liquors, $K_2[PdCl_4]$ was used instead of $(NH_4)_2[PdCl_4]$; the reaction volume was doubled. Measurements were carried out on an ELWRO N5170 pH meter with an ESK-10301/7 glass electrode calibrated against HCl solutions. Electronic absorption spectra were recorded on an UV-VIS spectrophotometer.

RESULTS AND DISCUSSION

A room-temperature reaction of $(NH_4)_2[PdCl_4]$ with $[Au(Dien)Cl]Cl_2$ in 0.01 M HCl gave the heterobinuclear complex [AuCl(μ-Dien*)$PdCl_3$] (**I**), which was proved by elemental analysis and X-ray diffraction data. The formation of this complex was unexpected, because first of all we anticipated growing single crystals of a binary complex salt with the metal-to-metal ratio 1 : 1, as in a reaction between $[Au(Dien)Cl]^{2+}$ and $[MCl_6]^{2-}$ (M = Ir(IV) and Pt(IV)) [11].

It is known that $[PdCl_4]^{2-}$ in an aqueous solution rapidly undergoes aquation and that the complex $[Pd(H_2O)Cl_3]^-$ is a weak acid ($pK_a = 7.0$) [12]. The complex cation $[Au(Dien)Cl]^{2+}$ behaves like a weak acid ($pK_a = 4.0$) [13] because of easy proton abstraction from coordinated diethylenetriamine. The crystals of binuclear complex **I** were obtained in an acidic medium (final pH < 2); i.e., deprotonated species were absent almost completely. In an acidic aqueous solution, palladium exists at $[Cl^-]$ = 0.03 mol/l, mainly as $[PdCl_4]^{2-}$ and $[Pd(H_2O)Cl_3]^-$; at $[Cl^-] \geq 1.0$ mol/l, the dominant palla-

Table 1. Crystallographic parameters and a summary of data collection for [AuCl(μ-Dien*)$PdCl_3$]

Parameter	Value
M	547.33
Crystal system	Orthorhombic
Space group	$Pna2_1$
Unit cell parameters:	
a, Å	13.886(3)
b, Å	7.213(1)
c, Å	11.824(2)
V, Å^3	1184.3(4)
Z	4
ρ_{calcd}, g/cm^3	3.070
μ, mm^{-1}	14.754
F(000)	1000
Crystal size, mm	0.22 × 0.07 × 0.04
θ scan range, deg	2.93–32.56
Ranges of h, k, and l	$-20 \leq h \leq 20$, $-10 \leq k \leq 10$, $-8 \leq l \leq 17$
Number of measured reflections	11746
Number of independent reflections	2981 (R_{int} = 0.0343)
Number of reflections with $I > 2\sigma(I)$	2764
Completeness of data collection for θ = 25°, %	99.3
Refinement method	Full-matrix least-squares method on F^2
Number of parameters refined	125
GOOF on F^2	0.934
R factors, $I > 2\sigma(I)$	$R_1 = 0.0211$, $wR_2 = 0.0441$
R factors for all reflections	$R_1 = 0.0247$, $wR_2 = 0.0454$
Absolute parameter	0.005(6)
Extinction coefficient	0.00001(6)
Residual electron density (min и max), e Å^{-3}	–1.375 and 1.031

Table 2. Selected bond lengths and angles in [AuCl(μ-Dien*)$PdCl_3$]

Bond	*d*, Å	Angle	ω, deg
Au(1)–N(2)	2.031(6)	N(2)Au(1)N(1)	85.83(16)
Au(1)–N(1)	2.038(4)	N(2)Au(1)N(3)	85.03(18)
Au(1)–N(3)	2.039(4)	N(1)Au(1)N(3)	168.88(18)
Au(1)–Cl(3)	2.2975(18)	N(2)Au(1)Cl(3)	178.55(14)
Pd(1)–N(2)	2.090(5)	N(1)Au(1)Cl(3)	94.60(12)
Pd(1)–Cl(4)	2.3097(13)	N(3)Au(1)Cl(3)	94.69(14)
Pd(1)–Cl(1)	2.3128(13)	N(2)Pd(1)Cl(4)	91.84(15)
Pd(1)–Cl(2)	2.3395(14)	N(2)Pd(1)Cl(1)	175.04(12)
N(1)–C(1)	1.494(6)	Cl(4)Pd(1)Cl(1)	89.22(5)
C(1)–C(2)	1.519(7)	N(2)Pd(1)Cl(2)	90.34(15)
C(2)–N(2)	1.495(6)	Cl(4)Pd(1)Cl(2)	174.76(5)
N(2)–C(3)	1.479(7)	Cl(1)Pd(1)Cl(2)	89.01(5)
C(3)–C(4)	1.509(8)	C(1)N(1)Au(1)	107.8(3)
C(4)–N(3)	1.501(7)	C(4)N(3)Au(1)	108.1(3)
		N(1)C(1)C(2)	107.4(4)
		N(2)C(2)C(1)	107.3(4)
		C(3)N(2)C(2)	114.8(4)
		C(3)N(2)Au(1)	104.1(4)
		C(2)N(2)Au(1)	103.8(3)
		C(3)N(2)Pd(1)	112.2(3)
		C(2)N(2)Pd(1)	109.9(3)
		Au(1)N(2)Pd(1)	111.5(2)
		N(2)C(3)C(4)	107.1(4)
		N(3)C(4)C(3)	108.5(4)
		N(3)C(4)C(3)	108.5(4)

dium species in solution is $[PdCl_4]^{2-}$ [14]. The formation of binuclear complex **I** can be represented by the equations:

$$[Au(Dien)Cl]^{2+} + [PdCl_4]^{2-} = [AuCl(\mu\text{-}Dien^*)PdCl_3](\mathbf{I}) + Cl^- + H^+, \quad (1)$$

$$[Au(Dien)Cl]^{2+} + [Pd(H_2O)Cl_3]^- = [AuCl(\mu\text{-}Dien^*)PdCl_3](\mathbf{I}) + H_2O + H^+. \quad (2)$$

Essentially, the chloride ion in $[PdCl_4]^{2-}$ or water in $[Pd(H_2O)Cl_3]^-$ are replaced in solution by $[Au(Dien)Cl]^{2+}$ with proton abstraction from coordinated Dien. Process (1) may be regarded as a version of "the Anderson rearrangement" extensively studied for ammonium complexes with various metals in both solutions and the solid state [7]. It can be seen in Eqs. (1) and (2) that the formation of binuclear complex **I** should be accompanied by an increase in the concentration of the hydrogen ions in solution. Indeed, pH measurements of the solution after the removal of the crystals detected excess H^+ ions (a mole of H^+ per mole of product **I**).

The resulting complex **I** is insoluble in water, acetonitrile, carbon tetrachloride, chloroform, and hexane and is poorly soluble in DMF. Apparently, the very low solubility of binuclear complex **I** in water favors its formation. The electronic absorption spectra of complex **I** (~2 mg) in an aqueous solution (incomplete dissolution, pH ~ 6) and in 0.01 M $HClO_4$ (V = 50 ml, 5-h stirring) show either distinct peaks or inflections characteristic of $[Pd(H_2O)Cl_3]^-$, $[Pd(H_2O)_2Cl_2]$ [14] and either $[Au(Dien^*)Cl]^+$ [15] (in the former case) or $[Au(Dien)Cl]^{2+}$ [15] (in the latter case). Obviously, the dissolution of binuclear complex **I** in aqueous solution is accompanied by cleavage of the bridging bond.

According to X-ray diffraction data, structure **I** is built from the neutral binuclear complexes [AuCl(μ-Dien*)$PdCl_3$] (Fig. 1). The intramolecular Au···Pd distance (3.407 Å) is substantially shorter than the Au···Au distance (3.52 Å) in the dimeric cation $[Au_2(Dien^*)Cl_4]^+$ [2]. In binuclear structure **I**, the coordination polygons of the Au and Pd atoms are distorted squares. The Au atom coordinates three N atoms of the chelating tridentate ligand Dien* and the Cl atom. The coordination square of the Pd atom is made up of three Cl atoms and the N atom of Dien*. Thus, deprotonated diethylenetriamine fulfils a double function: chelation of the Au atom and bridging of the Au and Pd atoms. The bridging N(2) atom is bound to the metal atoms and two C atoms. The R'–N(2)–R" bond angles (103.8°–112.2°) are close to tetrahedral ones. Also note that the sums of the same angles at the N(2) atom in complexes **I** and [Au(Dien*)Cl](ClO_4) (**II**) [8] are comparable (322.7° and 321(3)°, respectively) and are much smaller than that in [Au(Dien)Cl]Cl(ClO_4) (**III**) (332(4)°) [8]. The N–C and C–C bond lengths in complex **I** have standard values (on average, 1.492 and 1.514 Å, respectively). On the whole, the geometry of the ligand Dien* in structure **I** is similar with that found in complex **II**.

The Au–Cl distance in structure **I** (2.297 Å) is intermediate between analogous distances in complexes **II** (2.33(1) Å) and **III** (2.273(8) Å). The lengths of three Au–N bonds in structure **I** are close; their average (2.036 ± 0.005 Å) is the same as in complex **II**.

The Pd–Cl bond lengths in structure **I** (on average, 2.321 ± 0.019 Å) are close to those in $K_2[PdCl_4]$ (2.298 Å) [16]. The Pd–N bond length in complex **I**

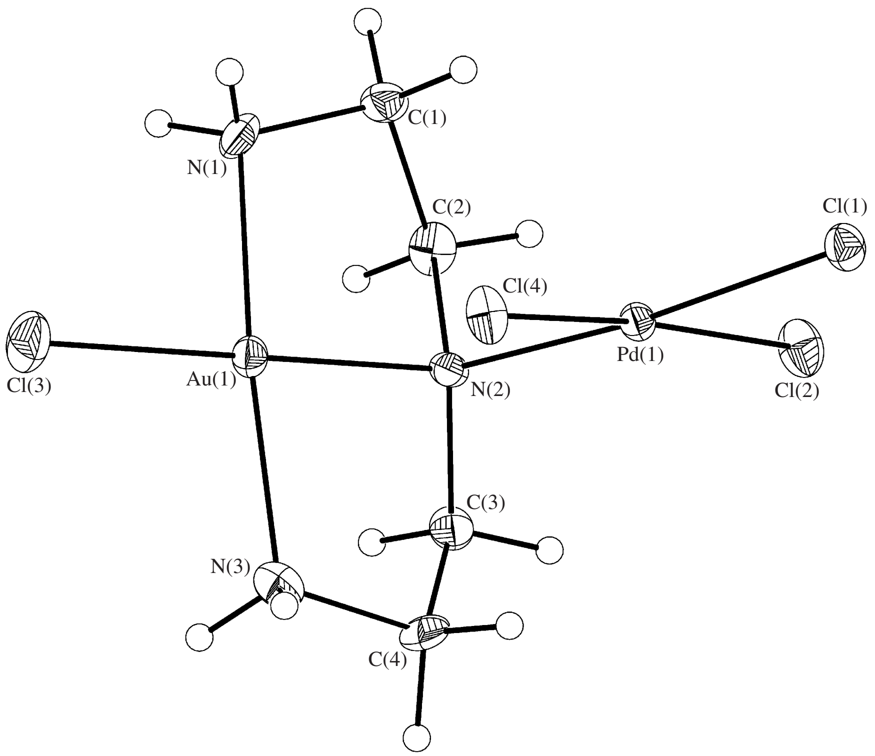

Fig. 1. Binuclear structure **I** with atomic numbering.

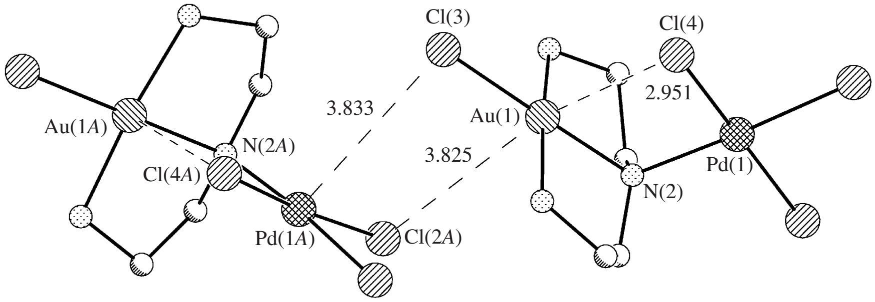

Fig. 2. Fragment of crystal structure **I** and additional contacts of the central metal atoms (symmetry operation code for the atoms in molecule A is $0.5 - x$, $0.5 + y$, $0.5 + z$).

(2.090 Å) is somewhat longer than that in $[Pd(Dien)NO_2]^+$ (2.047 Å) [17].

The bond angles at the central Au and Pd atoms in structure **I** differ from perfect values (90°) by no more than 5°. The coordination squares are planar to within ±0.08 Å. The angle between the normals to these planes is 89.6°; i.e., the planes of the coordination squares AuN_3Cl and $PdNCl_3$ are virtually perpendicular to each other.

The square coordination of the Au atom in structure **I** is extended to an asymmetrically elongated tetragonal bipyramid (4 + 1 + 1) with two Cl atoms from the Pd environment. The Cl(4) atom in the same binuclear complex is at a distance of 2.951 Å from Au (intramolecular contact); the Cl(2*A*) atom in an adjacent complex is substantially more distant (Au···Cl 3.825 Å, intermolecular contact) (Fig. 2). The angle Cl(4)AuCl(2*A*) is 167.4°. The square coordination of the Pd atom is extended to an elongated tetragonal pyramid (4 + 1) with the Cl(3) atom from the Au environment in the adjacent complex (Pd···Cl 3.833 Å). Through such additional contacts, the molecules in structure **I** are united into chains. The Au···Pd distance in a chain is 4.558 Å.

The general character of molecular packing in crystal structure **I** is shown in Fig. 3. Apart from the aforementioned additional contacts of the central atoms, the binuclear molecules are united through N–H···Cl and C–H…Cl hydrogen bonds (the shortest N···Cl and C···Cl distances are 3.23 and 3.47 Å, respectively).

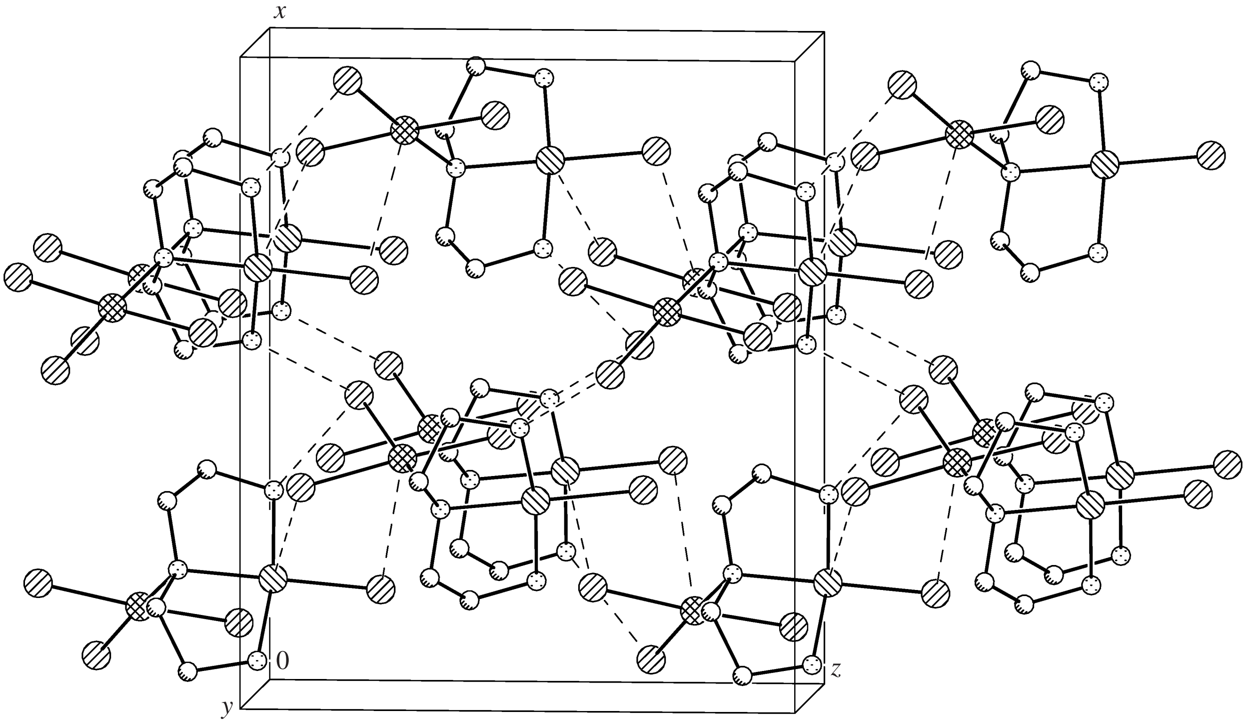

Fig. 3. General packing of the structural units in the crystal of complex **I** along axis *y*.

To sum up, we obtained for the first time the heterobinuclear complex [ClAu(μ-Dien*)PdCl$_3$] (**I**) and determined its structure by X-ray diffraction analysis. In complex **I**, the central N atom of deprotonated diethylenetriamine (Dien*) binds the Pd and Au atoms; structure **I** can be described as the coordination squares of the metals joined by their vertices.

ACKNOWLEDGMENTS

We are grateful to N.V. Kurat'eva and I.V. Korol'kov for their assistance in X-ray diffraction and X-ray powder diffraction analyses.

REFERENCES

1. Kostromina, N.A., Kumok, V.N., and Skorik, N.A., *Khimiya koordinatsionnykh soedinenii* (The Chemistry of Coordination Compounds), Moscow: Vysshaya Shkola, 1990.
2. Makotchenko, E.V., Baidina, I.A., and Korenev, S.V., Abstracts of Papers, *XVIII Mezhdunar. Chernyaevskoi konf. po khimii, analitike i tekhnologii platinovykh metallov* (XVIII Int. Chernyaev. Conf. on the Chemistry, Analysis, and Technology of Platinum Metals), Moscow, 2006, p. 184.
3. Efremova, O.A., Mironov, Yu.V., and Fedorov, V.E., *Eur. J. Inorg. Chem.*, 2006, no. 13, p. 2533.
4. Plappert, E.C., Mingos, D.M.P., Lawrence, S.E., and Williams, D.J., *J. Chem. Soc., Dalton Trans.*, 1997, p. 2129.
5. Patra, G.K. and Goldberg, I., *Polyhedron*, 2002, vol. 21, p. 2195.
6. Yau, J., Mingos, D.M.P., Menzer, S., and Williams, D.J., *J. Chem. Soc., Dalton Trans.*, 1995, p. 2575.
7. Kukushkin, Yu.N., *Reaktsionnaya sposobnost' koordinatsionnykh soedinenii* (Reactivity of Coordination Compounds), Leningrad: Khimiya, 1987.
8. Nardin, G., Randaccio, L., Annibale, G., et al., *J. Chem. Soc., Dalton Trans.*, 1980, p. 220.
9. *Sintez kompleksnykh soedinenii metallov platinovoi gruppy* (The Synthesis of Complex Compounds of Platinum Group Metals), Chernyaev, I.I., Ed., Moscow: Nauka, 1964.
10. Sheldrick, G.M., *SHELX-97. Program for Crystal Structure Solution*, Göttingen (Germany): Univ. of Göttingen, 1997.
11. Korenev, S.V., Makotchenko, E.V., Plyusnin, P.E., et al., *Izv. Akad. Nauk, Ser. Khim.*, 2006, no. 3, p. 416.
12. Bekker, P.Z. and Robb, W., *J. Inorg. Nucl. Chem.*, 1975, vol. 37, p. 829.
13. Baddly, W.H., Basolo, F., Gray, H.B., et al., *Inorg. Chem., 19*63, vol. 2, no. 5, p. 921.
14. Buslaeva, T.M. and Simanova, S.A., *Koord. Khim.*, 1999, vol. 25, no. 3, p. 165 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 25, no. 3, p. 151].
15. Gladkaya, A.Sh., Don, G.M., Evstaf'eva, O.N., and Golovaneva, I.F., *Zh. Neorg. Khim.*, 1991, vol. 36, no. 5, p. 1202.
16. Gromilov, S.A., Alekseev, V.I., Baidina, I.A., et al., *Zh. Neorg. Khim.*, 1994, vol. 39, no. 12, p. 2017.
17. Bresciani, Pahorn., Callgaris, M., and Randaccio, L., *J. Chem. Soc., Dalton Trans.*, 1976, p. 725.