New dinuclear palladium complex with a Chinese-lantern structure

M. O. Talismanova,[a]* A. A. Sidorov,[a] G. G. Aleksandrov,[a] Yu. F. Oprunenko,[b]
I. L. Eremenko,[a] and I. I. Moiseev[a]

[a]*N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,*
31 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (095) 955 4835. E-mail: ilerem@igic.ras.ru
[b]*Department of Chemistry, Moscow State University,*
Leninskie Gory, 119992 Moscow, Russian Federation.
Fax: +7 (095) 932 8846. E-mail: oprunenko@nmr.chem.msu.su

The new dinuclear palladium complex $Pd_2(\mu\text{-}S,N\text{-}SC_7H_5N_2)_4$ with a Chinese-lantern structure was synthesized by the reaction of K_2PdCl_4 with 2-mercaptobenzimidazole and structurally characterized by X-ray diffraction analysis.

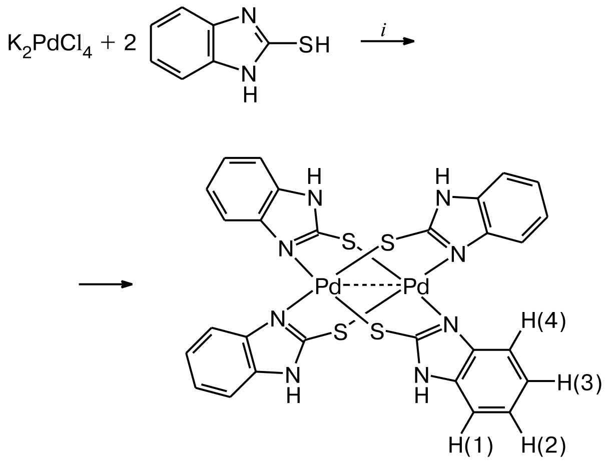
Key words: 2-mercaptobenzimidazole, palladium(II) complexes, dinuclear complexes, X-ray diffraction analysis.

Dinuclear tetrabridged complexes with a Chinese-lantern structure are typical primarily of 3d elements. In the presence of a direct metal—metal bond, such complexes with more heavy d metals (for example, with molybdenum(II), tungsten(II), or rhodium(II)) can also be formed.[1] Platinum(II) carboxylates have tetranuclear structures,[2] whereas a trinuclear core is typical of palladium carboxylates.[3—5] Dinuclear complexes, which have a Chinese-lantern structure and contain four three-atom bridges between d elements (for example, chromium),[1,6,7] were also prepared using deprotonated aminopyridines or other related organic compounds as ligands. However, the dinuclear structures of the latter complexes are stabilized, as a rule, by a strong metal—metal bond.[1] One would expect the formation of dinuclear complexes with a Chinese-lantern structure in systems containing deprotonated 2-mercaptobenzimidazole (**L**^{1}). The geometric characteristics and mobility of the protons in the latter ligand are suitable for the formation of the three-atom S—C—N bridge, which is convenient for the assembly of a dinuclear tetrabridged structure. Unlike carboxylates, the ligand **L**^{1} contains "soft" sulfur and nitrogen atoms, which is favorable for coordination to the platinum metals in oxidation state +2. However, it has recently been demonstrated[8] that the use of the ligand **L**^{1} in the reactions with platinum(II) derivatives leads to the formation of the mononuclear dication $[PtL_4]^{2+}$, in which the metal atom is bound only to the sulfur atoms of four neutral ligands, both nitrogen atoms in the ligand **L**^{1} being protonated and not involved in bonds with the metal center.

Results and Discussion

We found that the reaction of K_2PdCl_4 with **L**^{1} (reagent ratio was 1 : 2) in a THF—water mixture (5 : 1) in the presence of triethylamine afforded the dinuclear complex $Pd_2(\mu\text{-}\mathbf{L}^2)_4 \cdot 6THF$ (**1**, where $\mathbf{L}^2 = \mathbf{L}^1 - H^+$) in 30% yield (Scheme 1).

Scheme 1



1

i. THF/H$_2$O (5 : 1), Et$_3$N

Dinuclear complex **1** was also prepared by the reaction of **L**^{1} with the semiquinonediimine complex $Pd[1,2\text{-}(NH)(NPh)C_6H_4]_2$ (**2**) (reagent ratio was 2 : 1),

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1449—1452, July, 2004.

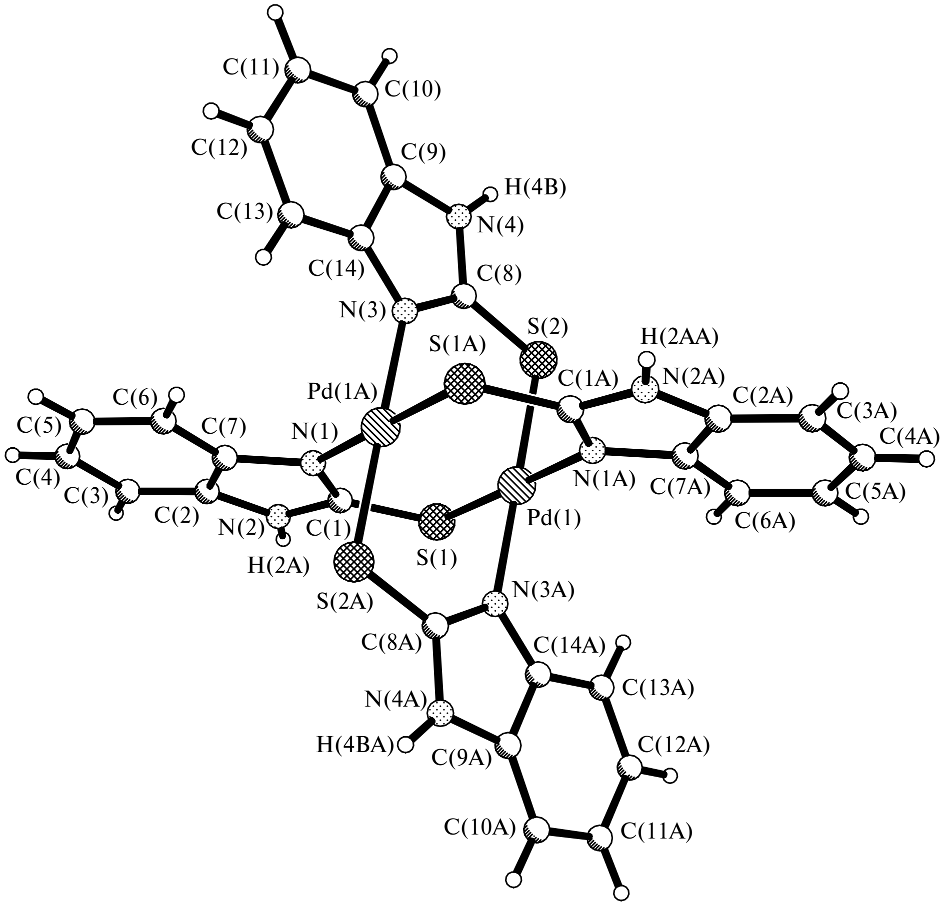


Fig. 1. Molecular structure of the $Pd_2(\mu\text{-}S,N\text{-}SC_7H_5N_2)_4$ complex.

although in lower yield (19%). The structure of complex **1** as a 1 : 6 solvate with THF was established by X-ray diffraction analysis. In complex **1**, two palladium atoms are linked through four three-atom S—C—N bridges of the ligand **L²** (Pd—S, 2.272(2)—2.280(2) Å; Pd—N, 2.045(7)—2.059(6) Å; S—C, 1.703(10)—1.714(10) Å; C—N, 1.311(11)—1.317(11) Å). The metal atoms in the PdS_2N_2 fragment retain a square-planar environment formed by the *cis*-arranged sulfur and nitrogen atoms (S—Pd—S and N—Pd—N angles are 90.62(9) and 90.4(3)°, respectively) (Fig. 1, Table 1). The THF solvate molecules are not involved in coordination to the metal atoms, but four of them are linked to the bridging ligands through the N(2)—H(2)...O(2)S and N(4)—H(4)...O(3)S [$-x + 1$, $-y$, $-z + 2$] hydrogen bonds between the oxygen atoms of THF and the protons of the NH groups of the imidazole fragments (Fig. 2). These hydrogen bonds are characterized by virtually identical geometric parameters (O...H, 1.890(2) Å; O...N, 2.772(1) Å; N—H...O, 175°).

Table 1. Selected geometric characteristics of complex **1**

Bond	*d*/Å	Angle	ω/deg
Pd(1)...Pd(1A)	2.739(2)	N(1)—Pd(1)—N(3)	90.4(3)
Pd(1)—S(1)	2.272(2)	N(1)—Pd(1)—S(1)	178.9(2)
Pd(1)—S(2)	2.280(2)	N(3)—Pd(1)—S(1)	89.15(19)
Pd(1)—N(1)	2.045(7)	N(1)—Pd(1)—S(2)	89.9(2)
Pd(1)—N(3)	2.059(6)	N(3)—Pd(1)—S(2)	179.5(2)
S(1)—C(1)	1.703(10)	S(1)—Pd(1)—S(2)	90.62(9)
S(2)—C(8)	1.714(10)	N(1)—Pd(1)—Pd(1A)	85.1(2)
N(1)—C(1)	1.311(11)	N(3)—Pd(1)—Pd(1A)	86.5(2)
N(1)—C(7)	1.417(12)	S(1)—Pd(1)—Pd(1A)	93.92(7)
N(2)—C(1)	1.337(11)	S(2)—Pd(1)—Pd(1A)	93.13(7)
N(2)—C(2)	1.355(13)	C(1)—S(1)—Pd(1)	103.0(3)
N(3)—C(8)	1.317(11)	C(8)—S(2)—Pd(1)	104.0(3)
N(3)—C(14)	1.345(11)	C(1)—N(1)—Pd(1)	128.4(6)
N(4)—C(8)	1.349(11)	C(7)—N(1)—Pd(1)	124.2(6)
N(4)—C(9)	1.386(12)	C(8)—N(3)—Pd(1)	127.0(6)
		C(14)—N(3)—Pd(1)	125.0(6)
		N(1)—C(1)—S(1)	129.2(7)
		N(3)—C(8)—S(2)	129.4(7)

The distance between the palladium(II) atoms in complex **1** (2.739(2) Å) is substantially smaller than the sum of the covalent radii. However, the direct metal—metal interaction in this complex is highly unlikely. In this connection, it should be noted that such short distances between the metal atoms in structures of this type (for ex-

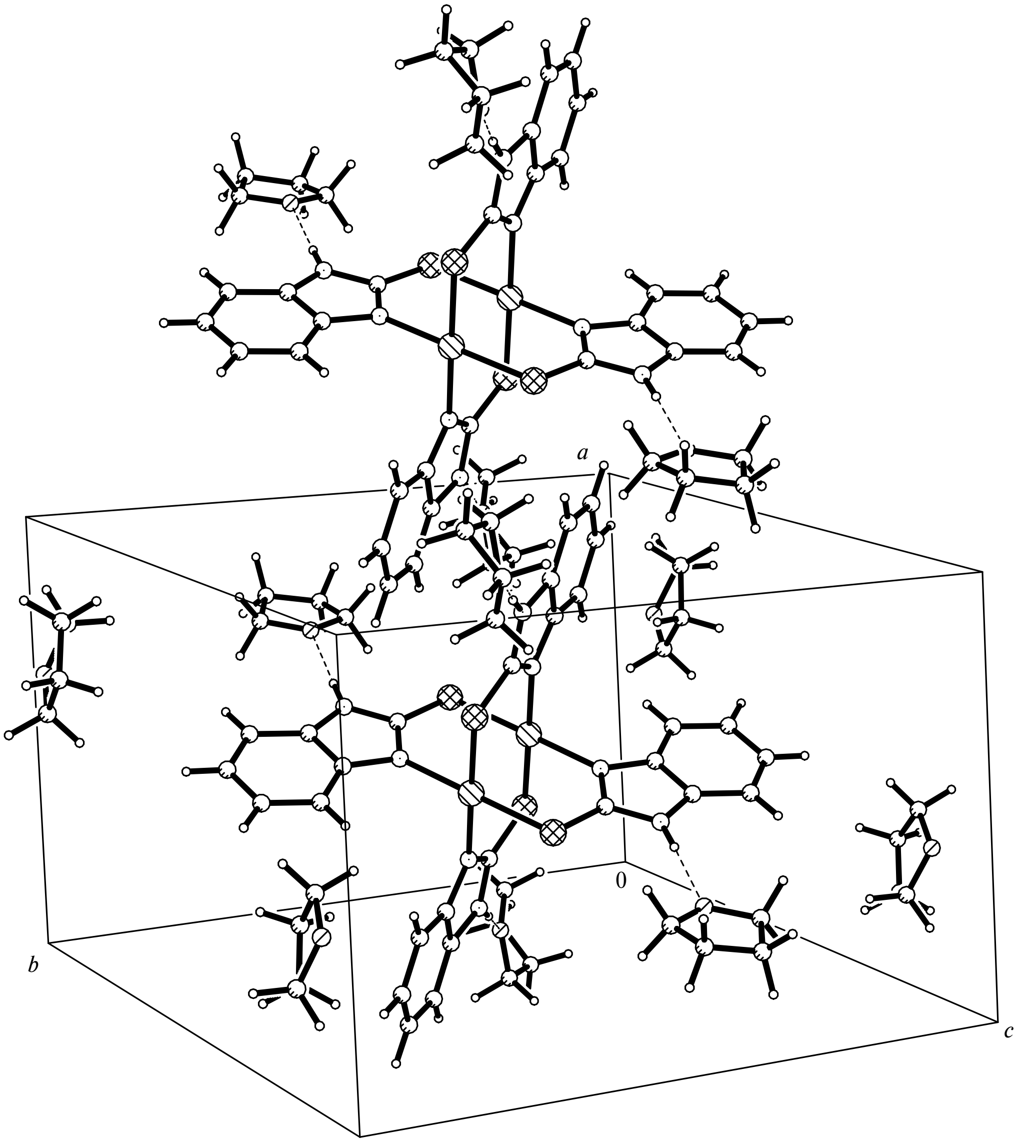


Fig. 2. Fragment of the molecular packing in the crystal of the $Pd_2(\mu\text{-}S,N\text{-}SC_7H_5N_2)_4 \cdot 6THF$ complex (**1**).

ample, in carboxylates) is not necessarily indicative of the presence of a direct bond between these atoms. This statement can be exemplified by dinuclear complexes with high-spin ions having a Chinese-lantern structure. For example, the $Ni_2[(\eta^1\text{-}o\text{-}C_6H_4(NH_2)(NHPh)]_2(\mu\text{-}OOCCMe_3)_4$ complex containing nickel(II) atoms at a very short distance (2.4967(4) Å) exhibits antiferromagnetic properties. The upper value of the magnetic moment at 300 K (2.12 μB per Ni atom) is indicative of the presence of two unpaired electrons on the metal atom.[9] Apparently, in the absence of half-filled orbitals on the metal centers (as was observed for the Pd^{II} atoms in dinuclear complex **1**), direct interaction between these atoms can formally occur only in the case of overlapping of the filled and unfilled orbitals of different metal atoms, which is very unusual for a symmetric tetrabridged dimeric structure.

Experimental

Complex **1** was synthesized in air and an inert atmosphere using freshly distilled solvents. The starting complexes K_2PdCl_4 and **2** were prepared according to known procedures.[10,11] The IR spectrum of complex **1** was recorded on a Specord M80 instrument in KBr pellets. The ^1H NMR spectrum of complex **1** was measured on a Varian VXR-400 spectrometer operating at 400 MHz using DMSO-d_6 (Fluka) as the solvent and HMDS as the internal standard.

Hexasolvate of tetrakis[μ-*S*,*N*′-(2-mercaptobenzimidazole)]dipalladium(II) with tetrahydrofuran, $Pd_2(\mu\text{-}S,N\text{-}SC_7H_5N_2)_4 \cdot 6THF$ (1). ***A.*** A solution of 2-mercaptobenzimidazole (0.130 g, 0.87 mmol) in THF (25 mL) and triethylamine (0.5 mL) were added to a solution of K_2PdCl_4 (0.142 g, 0.435 mmol) in H_2O (5 mL). The red-orange reaction solution was stirred at ~20 °C for 15 min, concentrated at 0.1 Torr (20 °C) to 20 mL, and kept in air at ~20 °C for 72 h. The yellow finely crystalline precipitate of compound **1** that formed was filtered off from the mother liquor, washed with cold hexane, and dried in air. The yield was 0.08 g (30% with respect to K_2PdCl_4). Found (%): C, 50.4; H, 5.6; N, 9.0. $C_{52}H_{68}N_8O_6Pd_2S_4$. Calculated (%): C, 50.28; H, 5.48; N, 9.02. IR, ν/cm^{-1}: 3387 m, 3196 w, 2964 m, 2914 w, 2870 w, 1612 w, 1556 w, 1520 w, 1488 w, 1436 v.s, 1416 s, 1388 s, 1356 m, 1296 m, 1276 s, 1260 m, 1224 w, 1180 w, 1096 s, 1048 m, 1016 w, 1000 w, 804 m, 736 s, 684 w, 624 w, 608 w, 512 w, 428 w, 416 m. ^{1}H NMR (DMSO-d_6), δ: 7.02 (t, 4 H, H(2), J = 7.5 Hz); 7.07 (d, 4 H, H(1), J = 7.5 Hz); 7.13 (t, 4 H, H(3), J = 7.5 Hz); 8.02 (d, 4 H, H(4), J = 7.5 Hz); 8.17 (br.s, 4 H, NH) (see Scheme 1).

The crystals suitable for X-ray diffraction analysis were grown by slow cooling of a solution of complex **1** in THF, which was saturated at 50 °C, to room temperature.

B. 2-Mercaptobenzimidazole (0.064 g, 0.424 mmol) was added to a solution of compound **2** (0.1 g, 0.212 mmol) in THF (20 mL). The reaction mixture was stirred at 65 °C for 3 h under argon. Then the crimson-red solution was cooled to ~20 °C, concentrated at 0.1 Torr (20 °C) to 15 mL, and kept at –18 °C for 24 h. The yellow crystals of complex **1** thus prepared were suitable for X-ray diffraction study. The crystals were filtered off, washed with hexane, and dried under a stream of argon. The yield was 0.025 g (19 % with respect to **2**).

Crystals of **1** were studied by X-ray diffraction analysis.

X-ray diffraction study. Experimental X-ray diffraction data for complex **1** were collected on an automated Bruker AXS SMART diffractometer equipped with a CCD detector (graphite monochromator, 110 K, ω scanning technique with a step of 0.3°, $2\theta_{\max}$ = 27.24°, R_{int} = 0.1118) using a standard procedure.[12] The structure was solved by direct methods using the SHELXS97 program package[13] and refined anisotropically by the full-matrix least-squares method using the SHELXL97 program package.[14] Complex **1**, $C_{52}H_{68}N_8O_6Pd_2S_4$, M = 1241.61, monoclinic system, space group $P2_1/c$, a = 10.353(3) Å, b = 16.668(5) Å, c = 15.665(5) Å; α = 90°, β = 97°, γ = 90°, V = 2682.6(15) Å^3, Z = 2, d_{calc} = 1.528 g cm^{-1}, μ = 0.883 mm^{-1}, $\theta/2\theta$-scan range is 1.79—27.24, a total of 10465 reflections were measured, of which 4713 reflections were with $I > 2\sigma$, 324 parameters were refined, R_1 = 0.0847, wR_1 = 0.1993.

We thank the Head and staff of the Center of X-ray Diffraction Studies (A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences) for giving us the possibility to collect X-ray diffraction data on a Bruker AXS SMART diffractometer with the financial support by the Russian Foundation for Basic Research (Project No. 00-03-32807).

This study was financially supported by the Russian Foundation for Basic Research (Project Nos. 02-03-32453 and 04-03-32883) and the Grant from the President of the Russian Federation (Federal Program for the Support of Leading Scientific Schools, Grant NSh-1764.2003.03).

References

1. F. A. Cotton and R. A. Walton, *Multiple Bonds Between Metal Atoms*, A Wiley-Interscience Publication, New York—Chichester—Drisbane—Toronto—Singapore, 1981, 331 pp.
2. M. Carrondo and A. C. Skapski, *Chem. Commun.*, 1976, 410.
3. N. Yu. Kozitsina, M. V. Martens, I. P. Stolyarov, S. E. Nefedov, M. N. Vargaftik, I. L. Eremenko, and I. I. Moiseev, *Zh. Neorg. Khim.*, 1999, **44**, 1920 [*Russ. J. Inorg. Chem.*, 1999, **44** (Engl. Transl.)].
4. A. C. Skapski and M. L. Smart, *Chem. Commun.*, 1970, 658.
5. F. A. Cotton and S. Han, *Revue de Chimie Minerale*, 1983, **20**, 496.
6. F. A. Cotton, R. H. Niswander, and J. C. Sekutowski, *Inorg. Chem.*, 1978, **17**, 3541.
7. F. A. Cotton, R. H. Niswander, and J. C. Sekutowski, *Inorg. Chem.*, 1979, **18**, 1152.
8. J. Jolley, W. I. Cross, R. G. Pritchard, Ch. A. McAuliffe, and K. B. Nolan, *Inorg. Chim. Acta*, 2001, **315**, 36.
9. A. A. Sidorov, I. G. Fomina, A. E. Malkov, A. V. Reshetnikov, G. G. Aleksandrov, and V. M. Novotortsev, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 1915 [*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 1887].
10. *Sintez kompleksnykh soedinenii metallov platinovoi gruppy, Spravochnik* [*Synthesis of Complex Compounds of Platinum Metals. Handbook*], Ed. I. I. Chernyaev, Moscow, 1964, p. 173 (in Russian).
11. I. L. Eremenko, S. E. Nefedov, A. A. Sidorov, M. O. Ponina, P. V. Danilov, T. A. Stromnova, I. P. Stolarov, S. B. Katser, S. T. Orlova, M. N. Vargaftik, I. I. Moiseev, and Yu. A. Ustynyuk, *J. Organomet. Chem.*, 1998, **551**, 171.
12. SMART(Control) and SAINT (Integration) Software, Version 5.0, Bruker AXS Inc., Madison, WI, 1997.
13. G. M. Sheldrick, *SHELX97, Program for the Solution of Crystal Structures*, Göttingen University, Göttingen (Germany), 1997.
14. G. M. Sheldrick, *SHELXL97. Program for the Refinement of Crystal Structures*, University of Göttingen, Göttingen (Germany), 1997.

Received December 17, 2003;
in revised form February 13, 2004