LETTERS
TO THE EDITOR

Synthesis and Crystal Structure of Palladium(II) Mononuclear Complex with Thiourea

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At present it is universally recognized that square-planar platinum(II) *cis*-diamines, unlike their *trans*-isomers, are inclined to the formation of linear chains with short distances $\text{Pt}\cdots\text{Pt} < 3.5 \text{ \AA}$, i.e. to the formation of coordination supramolecular constructions [1].

Examination of the X-ray structural data for *cis*- and *trans*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ complexes [2] allows an assumption that the column motive in the mutual arrangement of *cis*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ species provides favorable conditions for the appearance of intermolecular non-covalent interactions between them, which significantly define properties of a complex as a whole. Analogous intermolecular interactions in palladium(II) compounds are poorly investigated because of high propensity of *cis*-isomers to isomerize into *trans*-forms.

The action of thiourea on platinum(II) diaminate *cis*-complexes results in the full substitution of thiourea molecules for all intraspherical ligands [3]. However, according to experimental data, 1,10-phenanthroline (phen) molecules are not replaced by thiourea (tu) molecules. It allows us to study Pd–Pd intermolecular interactions in palladium(II) complexes with thiols.

In the present publication we describe the synthesis and X-ray crystallographic analysis of a new palladium(II) mononuclear complex with thiourea. The complex $[\text{Pd}(\text{phen})(\text{tu})_2](\text{NO}_3)_2$ (**I**) crystallizes in the monoclinic crystal system with the *P*-1 space group, *a* 10.32, *b* 13.29, *c* 15.33 Å, α 92.98, β 94.42, γ 108.64, *V* 1979.97 Å³, *Z* 2, *R* 4.59%. The main structural unit in the crystal structure of complex **I** is the PdNNS square-planar fragment formed by a phenanthroline molecule and two thiourea molecules coordinated to palladium through sulfur atoms (NPdN 81.07, SPdN 95.08 and 95.86, SPdS 87.82°). Molecules of the com-

plex form dimers with the Pd $\cdots$ Pd distance of 3.46 Å and the average interplanar distance of ~3.3 Å. A complicated system of hydrogen bonds including bonds with outer-sphere nitrate ions was found in the crystal structure of the complex.

Bis(*S*-thiourea)(1,10-phenanthroline)palladium(II) nitrate. To a suspension of 150 mg (0.419 mmol) of Pd(phen)Cl₂ in 20 ml of water prepared by the modified procedure [4], 142.5 mg (0.839 mmol) of AgNO₃ dissolved in a minimal amount of water was added. The mixture was homogenized and heated on a water bath over 30 min. A precipitate of AgCl was filtered off, and 31.9 mg (0.419 mmol) of thiourea dissolved in alcohol was added to the reaction mixture. Orange rodlike crystals precipitated from the solution in some days. Yield 30% (with respect to Pd). IR spectrum (KBr), cm⁻¹: 3307, 3131, 3063, 1647, 1516, 1426, 1367, 1331, 851, 820, 716, 485. Found, %: C 30.14; H 3.12; Pd 19.58; N 19.36; S 11.67. C₁₄H₁₆N₈O₆PdS₂. Calculated, %: C 29.87; H 2.87; Pd 18.91; N 19.91; S 11.39.

Crystallographic data of complex **I** are deposited in the Cambridge bank of structural data (CCDC 800840).

REFERENCES

1. Connick, W.B., Marsh, R.E., Schaefer, W.P., and Gray, H.B., *Inorg. Chem.*, 1997, vol. 36, no. 5, p. 913.
2. <http://www.ccdc.cam.ac.uk/deposit> (*Inorganic Crystal Structure Database*; *cis*: no. 26641; *trans*: no. 26642)
3. Grinberg, A.A., *Vvedenie v khimiyu kompleksnykh soedinenii* (Introduction to the Chemistry of Complex Compounds), Leningrad: Khimiya, 1986.
4. Chernyaev, I.I., *Sintez kompleksnykh soedinenii platinovykh metallov. Spravochnik* (Synthesis of Complex Compounds of Platinum Metals. Handbook), Moscow: Nauka, 1964.