STRUCTURE OF PALLADIUM COMPLEXES WITH TRIDENTATE THIOSEMICARBAZONES

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Reaction of K₂[PdCl₄] with N₄-substituted thiosemicarbazones of 8-quinolinaldehyde (HLR) in water-dimethylformamide (DMF) solutions, gives rise to the formation of the complexes of the general formula [Pd(LR)Cl] where R is H (I), C₂H₅ (II) or C₆H₂(CH₃)₃ (III) and [Pd(LR)Cl]·DMF (IV), where R is C₆H₅. The X-ray investigation of II – IV structure shows a tridentate coordination of the thiosemicarbazones *via* N,N,S set of donor atoms and the coordination number of the palladium is supplemented up to four by chlorine ion. The structure of the complexes II-IV is N,N,S,Cl square-planar. In the figure the structure of III is presented as an example.

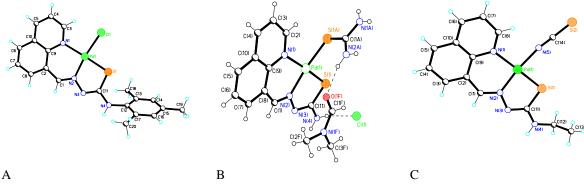


Fig. Structure of the complex III (A), V (B) and VII (C)

The ionic structure can be obtained when the chlorine anion is substituted by neutral thiourea molecule (Tu). After treatment of I with Tu and slow evaporation of waterdimethylformamide solutions a compound of the composition $[Pd(LH)Tu]Cl\cdot DMF(V)$ were obtained. The X-ray investigation of the structure showed that the complex is formed by the cation $[Pd(LH)(Tu)]^+$, anions Cl^- and solvating DMF molecule. The coordination mode of the thiosemicarbazone in these complexes is the same as was found in II-IV, but the fourth position in the square-planar coordination surrounding is occupied by the sulfur atom of the Tu molecule (Fig. B). Interaction of V with Ag₂SO₄ gives rise to the formation of [Pd(LH)Tu]₂·SO₄·2DMF (VI). The chlorine ion can be substituted from the inner sphere too. The treatment of **II** with KNCS in water-DMF solutions is accompanied by the dissolution of the products and precipitation after a slow vaporization of a compound of the formula $Pd(LC_2H_5)NCS$ (VII). The complex $Pd(L-C_6H_4(CH_3))NCS \cdot H_2O$ (VIII) was obtained in the same mode. The structures of the both complexes are molecular with a square-planar configuration formed by N,N,S donor set of the thiosemicarbazones and coordinated NCSanion. It is interesting to note that, nevertheless the palladium(II) ion is a thiophylic species, in these complexes the coordination of the NCS-ion via nitrogen atom is accepted (Fig. C).

The common peculiarity of the complexes **I-VIII** is the stabilization of the anionic form of coordinated N₄-substituted thiosemicarbazones of 8-quinolinaldehydes.