Photocrystallography of switchable palladium and rhodium nitro complexes

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Abstract

The properties of photoinduced linkage isomers (PLIs) in complexes [Pd(NH3)4][Pd(NH3)3NO2][CrOx3]?yH2O (Ox = oxalate) and [Rh(NH3)5NO2](NO3)2?0.5H2O were investigated using XRD and spectroscopic techniques. XRD analysis revealed that irradiation at 365 nm at 150 K of the single crystals of the palladium complex led to the formation of endo-ONO isomers PLI1 and PLI2.[1] PLI1 and PLI2 differ in their intermolecular surroundings, where the partial occupation of a neighboring site by a solvate water molecule prevents the photoinduced formation of PLI2. Photocrystallographic analysis of the palladium complex at 10 K revealed the formation of exo-ONO isomers PLI3 and PLI4, which are not sufficiently stable at 80 K. Thus, four different PLIs can be photogenerated in [Pd(NH3)3NO2]+. Moreover, the type and population of PLIs could be influenced by the amount of solvent H2O molecules and by the temperature of the photogeneration. In the octahedral rhodium complex [Rh(NH3)5NO2](NO3)2?0.5H2O, the generation of exo-ONO isomer is possible even at room temperature, which is explained by a high activation barrier of the exo-ONO to NO2 reaction. The obtained data allowed us to propose possible mechanisms of isomerization-relaxation of PLIs in both complexes.

[1] A. Mikhailov, K. A. Konieczny, M. Gladysheva, P. Plyusnin, S. Pillet, D. Schaniel, Inorg. Chem. 2023, 62, 5531–5542.