

**MS40-2-3 Photocrystallographic studies on linkage isomers using an ensemble of complementary methods
#MS40-2-3**

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Abstract

We present results on the structure and properties of photoinduced linkage isomers (PLI), corresponding to nitrosyl (GS) and isonitrosyl (MS1) configurations of the NO ligand, in ruthenium nitrosyl compounds using in situ X-ray diffraction (XRD) and NMR [1]. The solid-state NMR investigations of the PLI in trans-[Ru(py)₄(¹⁵NO)¹⁹F](ClO₄)₂ were performed at temperatures below T = 250 K using a dedicated setup [2]. The results are analyzed in combination with periodic DFT calculations and compared to the results of XRD [3]. The obtained results show the applicability of solid-state multinuclear NMR technique for the investigation of PLI in nitrosyl complexes. The sensitivity and resolution of the NMR technique provides clearly resolved signals from two chemically identical but structurally independent complex cations in both ¹⁹F and ¹⁵N NMR spectra. These measurements allow determining independently both achieved populations of PLI and the rates of reverse transformation for two crystallographic sites. Measurement of ¹⁹F T₁ relaxation show that the compounds are diamagnetic in MS1 as well as in GS. Structural details and changes of the electron density were obtained by measuring the chemical shift tensors of ¹⁵N, ¹⁹F as well as the two bond 2J(¹⁹F-Ru-¹⁵N) and three bond 3J(¹⁹F-Ru-O-¹⁵N) couplings in GS and MS1. Analysis of the NMR results by DFT calculations allowed the assignment of the NMR signals and showed the consistency of the results with the X-ray based structural models. Calculation of the spin-spin ¹⁵N-¹⁹F J-couplings showed that the relative direction of the nuclear spins on ¹⁵N and ¹⁹F are the same in GS and MS1 after the rotation of the NO-ligand, and charge density analysis indicates that there is only a small re-distribution of the charges going from GS to MS1. Globally, these results show that the solid-state NMR technique well complements other photocrystallographic methods such as in situ X-ray diffraction, IR spectroscopy, and calorimetry in the investigation of solid-state light-induced isomers. In that respect the approach presented here opens the door to new NMR studies of such photo-commutating complexes. This should allow the comparison of commutation activation energies of different sites within the same crystals, and open new perspectives on future studies with different ligands and counterions in order to understand the effect of structure and electrostatic interactions on the photocommutation properties.

References

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