

MS37-O5 Photo-induced NO linkage isomerism in nitrosyl complexes : A photocrystallographic and infrared analysis

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Photoinduced metastable linkage NO isomers have been known for a long time in mono-nitrosyl transition metal complexes. The NO ligand can adopt three bonding modes: the linear (or bent) geometry of the ground state (GS), the metastable (MS1) isonitrosyl, as well as the metastable (MS2) side-on configuration. Each metastable state can be populated, up to 100% in some compounds, using laser illumination with the suitable wavelength.

The discovery of photoinduced linkage NO isomers in the complex $[\text{Fe}(\text{CO})_2(\text{NO})_2]$, which exhibits two NO ligands, raises the question whether two different NO ligands on the same metal center can form linkage isomers jointly or independently, opening up for a combination of several metastable states for the dinitrosyl complex.

Light-induced reversible metastable NO linkage isomers are explored in the dinitrosyl compounds $[\text{RuCl}(\text{NO})_2(\text{PPh}_3)_2]\text{BF}_4$ and $[\text{RuBr}(\text{NO})_2(\text{PCy}_3)_2]\text{BF}_4$ by a combination of photocrystallographic and infrared analysis.

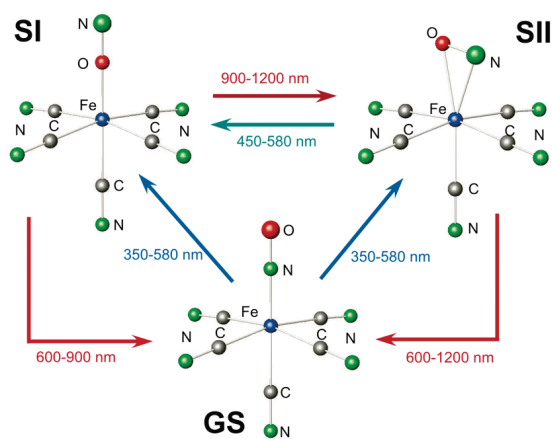


Figure 1. Photo-isomerism of the nitrosyl ligand in $\text{Fe}(\text{NO})(\text{CN})_5$

Keywords: Photo-isomerism, Nitrosyl complexes, Photo-crystallography, Infrared spectroscopy

MS38. Combining crystallographic information with other methods

Chairs: Marco Milanese, Poul Norby

MS38-O1 *In crystallo* optical spectroscopy at synchrotron beamlines - where we are at?

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While a powerful tool for structure determination, the depth of information yielded by X-ray diffraction techniques is somewhat limited. Especially when it comes to verification of chemical characteristics of the sample, a means of gaining additional, complementary data is invaluable. For macromolecular crystallography, for example, this additional information might include, but is not limited to, redox states of metal cofactors, identification of bound ligands and onset and strength of undesired photochemistry. A particular useful approach to harvest this data is the integration of optical spectroscopies, including UV-visible absorption, fluorescence or Raman spectroscopy, into synchrotron beamlines, allowing for (quasi) simultaneous collection of spectroscopic information and diffraction data. Several synchrotron teams, from various fields and all over the world, have thus taken great effort to integrate the necessary instrumentation into their (typically already crowded) beamline stations. This integrated approach results in the possibility to gain the complementary information under identical experimental conditions, using the same sample, thus minimizing any systematic errors that might result from sequential measurements. However, *in crystallo* spectroscopy, especially when performance has to be compromised to allow *in situ* measurements, poses a very special set of challenges, even to the experienced spectroscopist. Here we will present the current state of some instruments, and showcase some of the challenges and success along the way, both in the area of hard- and software development as well as scientific achievements.

Keywords: in crystallo, in situ, Raman, UV/Vis, spectroscopy, synchrotron instrumentation, macromolecular crystallography