Exploring stability of nitrite isomeric forms induced by external stimuli in crystals of a model nickel nitro complex

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In recent years, coordination compounds possessing potential to undergo linkage isomerization under the influence of external stimuli have gained more interest due their applicability in optoelectronics, photonics and photovoltaics [1]. The presence of the ambidentate ligands providing various coordination modes is essential for this reaction to occur. The development of effective switchable materials requires a deep understanding of the processes underlying the desired properties, thus structural studies and theoretical modelling of such systems is of fundamental importance.

As a part of the broader project devoted to the design of effective switchable compounds [2] a nickel complex stabilized with a (N,O,O)-chelating ancillary ligand with a nitrite group as the ambidentate ligand was synthesized. Its photo-switching potential was verified by solid-state spectroscopy and photocrystallography. The occurrence of the nitro-to-nitrito isomerization process due to irradiation with 530 nm LED light was detected by IR measurements, as well as determination of the metastable temperature limit – 200 K, and time of relaxation at these conditions – 1.5h. X-ray diffraction experiments enabled the further study of the structure and properties of the photo-induced species. The results show nearly complete nitro-to-nitrito conversion upon sample irradiation with 530 nm LED. During this process there could be detected exo-nitrito and endo-nitrito isomeric forms. However, their contribution varies depending on temperature and illumination time. The dominance of the endo-nitrito isomer was related to shorter irradiation periods and temperature range close to temperature metastable limit, while the exo-nitrito isomer is formed more efficiently at 150 K and below with an irradiation period exceeding 40 min.

More information regarding the nature of the metastable species was obtained from modelling the photoreaction mechanism and assessment of the stability of each isomeric form in the crystal. The influence of the structural factors such as inter-/intramolecular interactions and reaction cavity was also considered, as their crucial role was established in similar cases [3].

Figure 1. Scheme comparing molecule’s energy of each nitrite isomeric form in crystal structure.


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