

Light- and temperature-induced linkage isomerism in a series of Ni^{II}, Cu^{II} and Co^{III} complexes in the solid state

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Investigations of long-lived reaction intermediates and metastable species generated upon external stimuli, such as light or heat, in chemical and biological systems are of utmost importance in the context of our understanding of the processes' mechanisms and related phenomena. Linkage isomers can be formed by coordination compounds that contain ambidentate ligands capable of binding to a metal centre through various donor atoms. Such metastable species may exhibit lifetimes as long as hours or days and revert back to the ground state at elevated temperature. Thanks to their properties, photoswitchable materials may find various technological applications, including renewable energy solutions, biosensors or data storage.

The aim of this project was to thoroughly and systematically investigate conditions and dynamics of light-induced nitro group isomerisation reactions which occur in crystals of either designed or literature-reported 4th-row transition-metal complexes. The examined series of compounds consists of coordination compounds of nickel(II), copper(II) and cobalt(III). Metal centres in these systems are coordinated by the nitrite ligand and either (N,N,O) chelating species, NHC group, or amino ligands.

The studied complexes were thoroughly examined crystallographically, spectroscopically and computationally. In the case of Ni(II) and Co(III) nitro complexes partial conversion to metastable endo-nitrito isomers is achieved after irradiation of respective single crystal samples with adjusted UV-Vis LED light at temperatures above 100 K. The metastable-state form is usually stable up to relatively high temperatures, e.g. 240 K, while the maximum conversion may reach 100% for powder samples as indicated by solid-state IR measurements. Instead, copper systems analogous to the above-described nickel coordination compounds exist as the nitrito form in the ground state and work best at 10 K, whereas the metastable nitro form is usually stable only up to 60 K. Such behaviour makes them more difficult to be experimentally analysed and less applicable as functional photoactive materials.

In turn, a very significant 90% nitro-to-nitrito conversion was reported for single-crystals of the Ni(II) nitrite system [Ni(η^5 Cp)(IMes)(η^1 -NO₂)]. The studied compound crystallizes with two symmetry-independent molecules comprising the asymmetric unit. Although the two moieties are geometrically very much alike, their behaviour upon irradiation or temperature appeared to be somewhat different depending on the exact experimental conditions. At 190 K the metastable species reverted back to their ground state.

Trinitrocobalt(III) coordination compounds constitute another interesting group of photoswitchable systems. For instance, Co(Medpt)(NO₂)₃ complex contains three different NO₂ groups in its molecule, which form different intermolecular interactions in the crystal structure, including hydrogen bonds (one is strongly bound, the second one moderately, whereas the third group does not participate in any hydrogen-bond-type contacts). After irradiating of the sample with the UV-Vis light only one of them switches to the nitrito linkage isomer, which shows the importance of crystal packing and intermolecular interactions effects.

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Keywords: IUCr2020; photoisomerization, photocrystallography, NO₂-complexes

The authors thank the PRELUDIUM grant (2017/25/N/ST4/02440) of the National Science Centre in Poland and the Inter-Faculty of Individual Studies in Mathematics and Natural Sciences, University of Warsaw, for financial support. The Wrocław Centre for Networking and Supercomputing (grant No. 285) is gratefully acknowledged for providing computational facilities. The in-house X-ray diffraction experiments were carried out at the Department of Physics, University of Warsaw, on Rigaku Oxford Diffraction SuperNova diffractometer, which was co-financed by the European Union within the European Regional Development Fund (POIG.02.01.00-14.122/09)