

MS40-1-1 The effect of auxiliary ligands on nitrite group linkage isomerization reaction in a series of nickel(II) complexes

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Abstract

Molecular switches are materials that undergo chemical transformation (isomerization, cyclisation etc.) upon some external stimuli (light pulse, temperature, high pressure). Such systems can be used in many ways, for example in optoelectronics, medicine or solar energetics. A good example of compounds of this kind are transition-metal complexes with ambidentate ligands, such as: -NO₂, -SO₂, -DMSO, that undergo photoisomerisation reaction. Switchable systems' behaviour upon light irradiation can be readily examined photocrystallographically. Understanding of factors governing such processes in crystals and their mechanisms will contribute to later conscious design of efficient molecular switches, and further to development of new technologies.

The current study is a part of our wider project dedicated to design and thorough investigations of novel photoswitchable transition-metal systems with small ambidentate ligands [1]. The series of compounds presented here differ by the type of the chelating N,N,O-donor ligand (different amine fragment or aliphatic substituents), which affects the Ni-NO₂ bond strength. This effect along with crystal packing and intermolecular interaction influence on the photo-induced isomerization were deeply investigated. The examined compounds switch from nitro to nitrito binding mode under 405 nm - 530 nm LED light irradiation, with good conversion rates close to 100%, and the generated linkage isomers are stable in a wide temperature range. The reaction is proven reversible, the systems relax back to the ground state around 220 K. The isomerization reactions were examined using solid-state photoIR spectroscopy and photocrystallography, which also enabled structural evaluation of the light-induced metastable-state species. Intermolecular interactions were characterized using DFT calculations and Hirshfeld surface approach. Theoretical calculations were also used to determine relative stability of various linkage isomers under consideration.

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References

[1] Kutniewska, S. E., Krowczynski, A., Kaminski, R., Jarzemska, K. N., Pillet, S., Wenger, E. & Schaniel, D. (2020). IUCrJ 7, 1188-1198.