

Influence of sulfur⋯oxygen, π ⋯ π /C-H⋯ π and other intermolecular interactions on molecular switching of the NO₂ ligand in polymorphic forms of a nickel(II) complex

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This study explores how subtle differences in non-covalent interactions—specifically sulfur⋯oxygen contacts, π ⋯ π stacking, and C-H⋯ π interactions—influence the molecular switching behaviour of the NO₂ ligand in a triplet octahedral nickel(II) complex. These types of systems are capable of undergoing linkage isomerism in the solid state, triggered by external stimuli, such as temperature[1], electromagnetic radiation[2], or pressure[3]. The molecular switching behaviour is conditioned by the presence of ambidentate ligands—small inorganic moieties with multiple free electron pairs that allow them to alter their coordination modes.

In addition to the two N-bound nitrite (NO₂) ligands capable of undergoing linkage isomerism, the nickel(II) metal centre in the studied system is coordinated by a large, planar ancillary ligand containing thiazole rings. These thiazole rings are engaged in numerous non-covalent interactions that stabilize the respective crystal structure. Crystallization of the compound into either the monoclinic (P2₁/c) or orthorhombic (Pnma) form critically depends on the presence of water molecules. Both polymorphs have unit cells with comparable dimensions, each containing four molecules of the nickel(II) complex. The water content directly influences which polymorphic form is obtained. In the monoclinic form (Form_1), number of water molecule is equal to the number of complex molecules. Reduction of the water content by half leads to a structural rearrangement so as to optimize intermolecular interactions which induces a transition to the orthorhombic crystal form (Form_2).

The compound's photoswitching properties in both polymorphic forms were examined using photocrystallographic and spectroscopic methods. While both forms respond to the same range of UV-Vis radiation, the structural transformations they undergo differ. In the Form_2, both NO₂ ligands undergo isomerization: the N1-site nitro isomer converts to the *endo*-nitrito form, and the N2-site NO₂ converts to the *exo*-nitrito form, each exhibiting maximum conversion at different wavelengths. The Form_1 displays isomerization only at the N1-site, which switches to the *exo*-nitrito isomer. This asymmetric transformation induces a phase transition involving reduced symmetry and twinning.

The aim of this study is to rationalize how subtle variations in intermolecular interactions between the two polymorphic forms can lead to significantly different photoproducts, despite originating from the same switchable molecule. Through a detailed structural analysis supported by computational methods, the research highlights the importance of weak interactions in directing linkage isomerism pathways.

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[3] Potempa, K., Paliwoda, D., Jarzemska, K. N., Kamiński, R., Krówczyński, A., Borowski, P., Hanfland, M. (2024). *Chem. Commun.* **60**, 9194-9197.

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