Poster

Insights into role of non-covalent interactions in achieving pressure-induced linkage isomerism of nitrite ligand.

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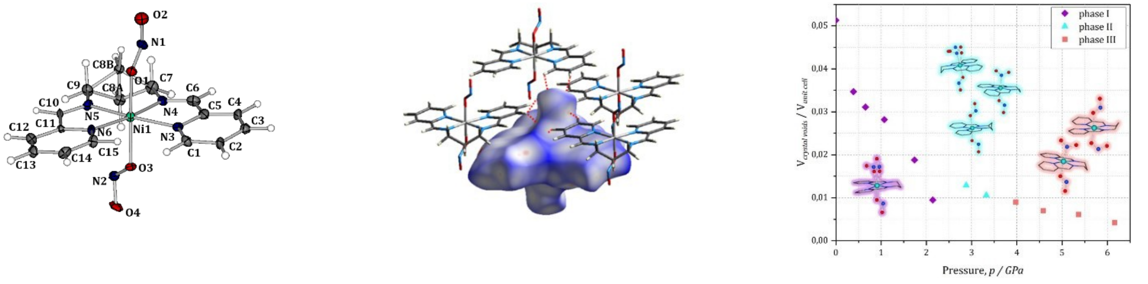
The ability to adapt the crystalline structure to various conditions underpins the stimuli-responsive properties of materials. Such systems often undergo solid-state reactions such as linkage isomerism. While it was shown in numerous studies that small inorganic moieties, such as NO_2, exhibit ability to change the way of bonding to metal centre in response to external stimuli like temperature [1], or electromagnetic radiation [2], the initiation of such structural transformations via high pressure (HP) remains largely unexplored [3]. Here, we present a nickel nitrite complex (Fig. 1*a*) designed by us in such a way that it exhibits an unconventional binding mode of the nitrite ligand in the solid state. Although the *exo*-nitrito isomeric form is not energetically favoured as an isolated molecule, in the case of the studied system it is well-stabilised thanks to intermolecular interactions in the crystal structure, including aromatic interaction and hydrogen bonding. Hirshfeld surface analysis depicted in Fig. 1*b* reveals a compact crystal packing driven by $\pi\cdots\pi$ interactions between aromatic fragments of ancillary ligands. In consequence, each nitrite ligand is compelled into narrow space where it forms numerous hydrogen bonds, stabilizing the *exo*-nitrito bonding mode. Multi-temperature studies highlight the importance of these interactions. Along with the elevated temperature the interatomic interactions weaken which enables some residual isomerisation (~5%) of the nitrite group towards its more energetically preferred *endo*-nitrito configuration. In addition, following our previous computational study [4] the optimal unit cell hosting the *exo*-nitrito isomer is usually elongated *ca.* along the nitrite group, suggesting its greater susceptibility to mechanical stimuli in this case. Indeed, the unit cell was mainly affected along the dimension parallel to the NO_2 fragment according to multi-temperature analysis and HP data. HP crystallographic measurements indicate pressure-induced changes in the nitrite ligand's binding mode, accompanied by two phase transitions (Fig.1*c*) and piezochromic effect. This study sheds light on the interplay between non-covalent interactions and external stimuli in driving novel solid-state transformations, offering insights into the design of responsive materials with tailored functionalities.



(*a*) (*b*) (*c*)

Figure 1. (*a*) Molecular structure of **Ni-diONO** derived from X-ray diffraction collected at 100 K. Atomic thermal motion is represented as ellipsoids at 50% probability (*b*) Hirshfeld surface generated for **Ni-diONO** mapped with d norm, visualising intermolecular interactions responsible for stabilisation of *exo*-nitrito conformation for each nitrate ligand (c) Relationship between the applied pressure and $V_{crystal\ voids} / V_{unit\ cell}$ ratio.

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