Poster Presentation

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Photocrystallographic and kinetic studies of metastable linkage isomers

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The ability of a molecular system to reversibly convert between two distinct states on photoactivation is desirable for many real-world applications, including photo-switchable device media. When induced in the solid-state, the process can be studied by crystallography and specifically photocrystallographic methods have contributed greatly to this diverse research area. The process of linkage isomerism has proved popular for photocrystallographic study. While the atomic rearrangements involved in the process are large enough to be determined from diffraction data, the changes are also moderate enough that crystal integrity is often maintained. Examples of species studied by these methods include nitrite, sulfur dioxide and nitrosyl coordination complexes [1]. Our research has focused on metal–nitrite complexes displaying nitro–nitrito isomerism and has aimed toward the rational design of new systems to undergo maximum conversion. Recently we have studied a selection of nickel–amine systems, including [Ni(Et4dien)(η2-O,ON)(η1-NO2)]. This complex shows diverse linkage isomeric behaviour on thermal and photochemical treatment [2], with 100% nitro–nitrito conversion achieved on excitation at λ = 500nm. The thermal and photochemical processes have been studied in detail [3] and the results of temperature studies, steady-state and pseudo-steady-state photocrystallographic experiments and solid-state kinetic studies are presented. The findings are discussed in relation to the key information they provide on the steric and kinetic factors that may influence the isomerisation process in the single-crystal.

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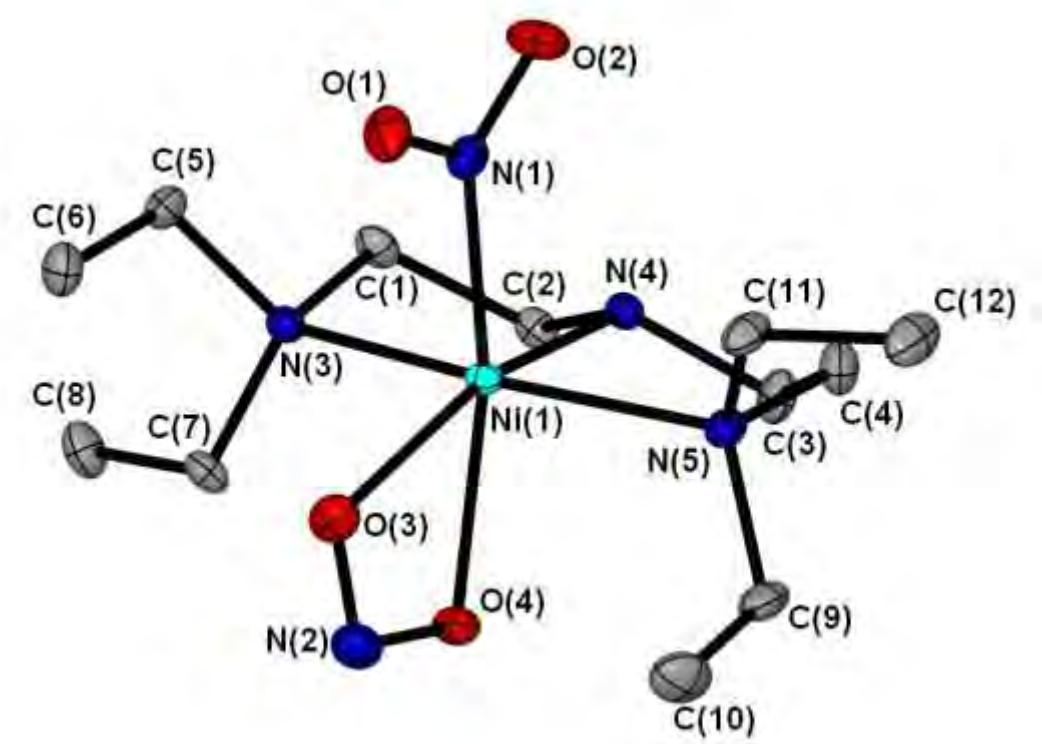

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