

Oral Contributions

[MS31 - 04] Photocrystallographic Studies of Novel Metal – Nitrite Compounds.

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The technique of photocrystallography has developed rapidly alongside the dramatic advancements in X-ray methods and instrumentation seen in recent decades.[1] Photocrystallographic studies allow the full, three-dimensional structures of transient and metastable photoactivated species to be conclusively determined from diffraction data, and the technique has been successfully employed in both MX [2] and small molecule [3] disciplines. The current challenges of both achieving faster and faster time resolution, whilst also obtaining the highest possible level of photo-conversion, have continued to attract much interest in this research area. Our work has centred on small molecule metal – nitrite complexes that are found to undergo linkage isomerism upon photoactivation in the single crystal, producing metastable nitrito-(11-ONO) isomers. In particular, our research has been targeted at the rational design of systems allowing very high levels of conversion, and we have reported the complex $[\text{Ni}(\text{dppe})(\text{NO}_2)\text{Cl}]$ (dppe = diphenylphosphinoethane) as the first system to undergo 100 % nitro – nitrito conversion.[4] More recently, we have also reported interesting thermal and photo-isomerisation behaviour in the complex $[\text{Ni}(\text{Et}_4\text{dien})(\text{NO}_2)_2]$, (Et_4dien = N,N,N',N'-tetraethyldiethylenetriamine). [5] Steady-state photocrystallographic studies with this system will be discussed. Excitation with 500 nm LED light produces a metastable endo-nitrito isomer at low temperature (100 K), with 100 % photo-conversion in the single crystal. Additionally, pseudo-steady-state experiments conducted at Diamond Light Source will be described. These studies indicate that another,

short-lived exo-nitrito isomer can be induced in the system, between 150 and 180 K. The photo-isomerism behaviour in a number of analogous metal – nitrite compounds has also been studied, including palladium and platinum systems and nickel complexes with different amine ancillary ligands. Comparisons will be made between these complexes, to provide insight into the key steric, electronic and kinetic factors that potentially affect the solid state linkage isomerisation process.

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