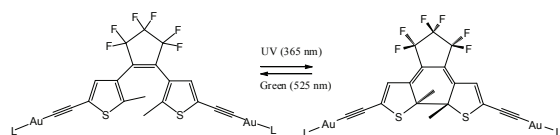


FA4-MS05-O1

Photocrystallography: Time Resolved Studies on Coordination Complexes. Paul R. Raithby^a, Simon K. Brayshaw^a, Stefanie Schiffrers^a, John E. Warren^a, Mark R. Warren^a, Simon J. Teat^b. ^a*Department of Chemistry, University of Bath, Bath, UK.* ^b*Advanced Light Source, Berkeley CA94720, USA.*
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Single-crystal X-ray crystallography has long been thought of as a static, “time averaged” technique that provided information on the three-dimensional structures of reaction products but which gives no information on reaction intermediates. Over the last decade this situation has changed with the development of photocrystallographic [1] methodologies. In these experiments single-crystal X-ray diffraction techniques are combined with photochemical techniques so that the structures of photoactivated species with lifetimes as low as μs can be determined or that photoactivated reactions in the solid-state can be monitored in as they occur.

Here, we present the results of two series of photocrystallographic studies. Firstly, we describe the methodologies used to establish the structures of a series of metastable metal-sulphur dioxide [2] and metal-nitrite complexes which exhibit linkage isomerism. Secondly, we describe formation of [2+2] cycloaddition products and the ring closure reaction of di(thiophenyl)ethene complexes within a single crystal.



[1] P. Coppens, I. I. Vorontsov, T. Graber, M. Gembicky, A. Yu. Kovalevsky, *Acta. Crystallogr. Sect. A* **2005**, *61*, 162. [2] K. F. Bowes, J. M. Cole, S. L. G. Husheer, P. R. Raithby, T. L. Savarese, H. A. Sparkes, S. J. Teat and J. E. Warren, *Chem. Comm.* **2006**, 2448.

Keywords: photocrystallography; coordination complex; metastable

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Structure and Reactivity of Derivatives of the Mo(allyl)(CO)₂ Fragment. Maria José Calhorda. *Department of Chemistry and Biochemistry, University of Lisbon, Lisbon, Portugal.*
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Complexes $[\text{M}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2\text{X}(\text{NCMe})_2]$ (M = Mo, W; X = halide) are very useful to prepare a wide variety of derivatives. Some of them have been applied as catalysts, both homogeneous and heterogeneous, after being immobilized in an appropriate support, or as anti tumor agents.[1,2] The two nitrile ligands are easily substituted by different kinds of bidentate nitrogen ligands, while anionic species tend to substitute X (monodentate) or X and the

nitrile. When suitable functional groups, such as NH, are present in a ligand (dipyridylamine, for instance), N-H...X hydrogen bonds link neighbor molecules into chains that may be observed in the crystal structure. Other ligands, namely 4,4'-bipyridyl, which acts as a bridge between two metal centers, have led to two dimensional arrangements consisting of the binuclear cationic complexes and hexafluorophosphate anions. While the two carbonyls and the centroid of the allyl group always form a facial arrangement in the pseudo octahedral environment around Mo(II), the halide may occupy a position trans (equatorial isomer) or cis (axial isomer) to the allyl. The preferences for each isomer are not very clear, though bulky ligands such as 1,4-(4-chloro)phenyl-2,3-naphthalenediazo-butadiene and related species stabilize the axial isomer. Complexes with small ligands usually exhibit several fluxional isomers in their ¹H NMR spectra. The bis(nitrile) precursor is a good example of this behavior. [3] Interestingly, both isomers were found simultaneously in the same crystal structure for a particular ligand. The axial isomer has no symmetry and in one example the complex has crystallized in a non centrosymmetric group. Mixed polynuclear Fe-Mo complexes based on this Mo(II) system and ferrocenyl derivatives have also been synthesized, and their properties studied. Several of the complexes mentioned above will be described, their structures analyzed, and some aspects of their reactivity and electrochemistry reported. DFT calculations were performed in order to rationalize several aspects of their behavior.

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Keywords: molybdenum complexes; intermolecular interactions; density functional theory

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Monitoring Structural Changes in Crystals During Physical and Chemical Processes. Julia Bąkiewicz^a, Ilona Turowska-Tyrk^a. ^a*Faculty of Chemistry, Wrocław University of Technology, Wrocław, Poland.*
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Photochemical and photophysical processes in crystals studied by means of X-ray structure analysis are the main subject of our interest [1-7]. In particular we monitor structural changes brought about by photo-induced intramolecular cyclization reactions and amorphization. Such studies demand determination of crystal structures for many steps of a photoprocess for one compound. Additionally, in the case of photochemical reactions those structures are characterized by reactant-product disorder. The Yang photocyclization is one of the reactions studied by us very often: