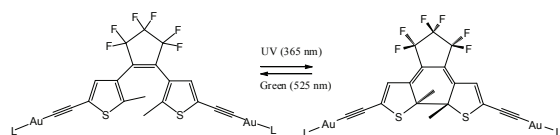


**FA4-MS05-O1**

**Photocrystallography: Time Resolved Studies on Coordination Complexes.** Paul R. Raithby<sup>a</sup>, Simon K. Brayshaw<sup>a</sup>, Stefanie Schiffrers<sup>a</sup>, John E. Warren<sup>a</sup>, Mark R. Warren<sup>a</sup>, Simon J. Teat<sup>b</sup>. <sup>a</sup>*Department of Chemistry, University of Bath, Bath, UK.* <sup>b</sup>*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  $\mu\text{s}$  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

**FA4-MS05-O2**

**Structure and Reactivity of Derivatives of the Mo(allyl)(CO)<sub>2</sub> 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 <sup>1</sup>H 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.

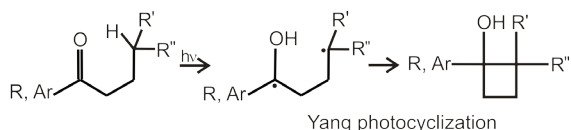
[1] Alonso J.C., Neves P., Pires da Silva M.J., Quintal S., Vaz P.D., Silva C., Valente A.A., Ferreira P., Calhorda M.J., Félix V., Drew M.G.B., *Organometallics* **2007**, *26*, 5548. [2] Martinho P.N., Quintal S., Costa P., Losi S., Félix V., Gimeno M.C., Laguna A., Drew M.G.B., Zanello P., Calhorda M.J. *Eur.J. Inorg. Chem.* **2006**, 4096. [3] Costa P.M.F.J., Mora M., Calhorda M.J., Félix V., Ferreira P., Drew, M.G.B., Wadepl H., *J. Organomet. Chem.* **687**, 57-68, **2003**.

**Keywords:** molybdenum complexes; intermolecular interactions; density functional theory

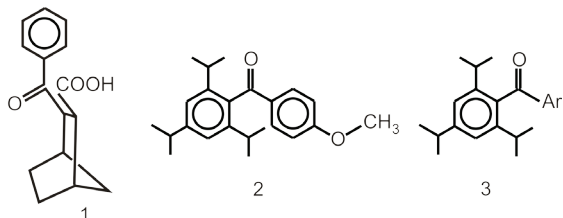
**FA4-MS05-O3**

**Monitoring Structural Changes in Crystals During Physical and Chemical Processes.** Julia Bąkowicz<sup>a</sup>, Ilona Turowska-Tyrk<sup>a</sup>. <sup>a</sup>*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:



In this poster the results of monitoring photo-induced structural changes in crystals of three compounds will be presented:



Crystals of compounds **1** and **2** are photochemically inert at ambient temperature, however undergo a photo-induced physical process. This process is partially reversible with time for **1**, however the reverse path is different (Fig. 1).

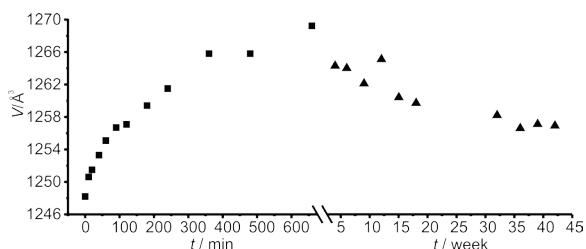


Fig. 1. Variation in the cell volume with time of crystal irradiation and time for the reverse process.

Compound **3** is photosensitive, however contrary to compounds **1** and **2**, it undergoes the Yang photocyclization. There are statistically significant differences between crystal structures determined for different stages of the photoreaction, *i.e.* characterized by different amounts of reactant (and product) molecules. The variations in the cell constants, geometry of the reaction centre and orientation of molecules during the studied reaction were observed and analyzed.

[1] Turowska-Tyrk I., Trzop E., Scheffer J.R., Chen S., *Acta Cryst.*, **2006**, B62, 128. [2] Turowska-Tyrk I., Bąkiewicz J., Scheffer J.R., Xia W., *CrystEngComm*, **2006**, 8, 616. [3] Turowska-Tyrk I., Łabecka I., Scheffer J.R., Xia W., *Pol. J. Chem.*, **2007**, 81, 813. [4] Turowska-Tyrk I., Bąkiewicz J., Scheffer J.R., *Acta Cryst.*, **2007**, B63, 933. [5] Trzop E., Turowska-Tyrk I., *Acta Cryst.*, **2008**, B64, 375. [6] Turowska-Tyrk I., *Chem. Phys.*, **2003**, 288, 241. [7] Bąkiewicz J., Turowska-Tyrk I., *Acta Cryst B.*, submitted.

**Keywords:** structural change; photochemistry; physics of solids

#### FA4-MS05-O4

##### Combining X-ray Diffraction and Spectroscopy to Study (Photo)dynamic Processes. Panče Naumov<sup>a,b</sup>.

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Techniques which have been traditionally employed to study photoinduced, thermally induced or other dynamic processes are electronic (absorption and emission UV-vis) spectroscopy, vibrational (IR and Raman) and NMR spectroscopies, which are now readily available with commercial experimental setups in steady-state or time-resolved mode. While the spectroscopic techniques are an excellent approach to deduce details on the energy profiles, they provide only limited and, occasionally, ambiguous information on the spatial atomic arrangement and the geometrical changes related to dynamic processes. On the other hand, the X-ray diffraction provides precise information on molecular geometry, but it is not informative about the potential energy profile and the reaction kinetics. In practice, because of the different time-scales between the spectroscopic and X-ray diffraction methods, the information obtained by spectroscopy can be very useful to support diffraction data, for at least the following reasons:

(a) Spectroscopic data can be correlated to structural data to establish spectra-structure correlations;

(b) Spectroscopic data can be used to supplement X-ray results in clearing out details within the “grey zones” of the X-ray crystallography (e.g. hydrogen positions, difficult cases of disorder, crystalline-to-amorphous phase transitions, etc.);

(c) Spectroscopic data can be employed to check or even to correct inaccurate X-ray diffraction data.

In this presentation, the importance of using spectroscopic data for structure elucidation will be illustrated with several examples from our laboratory and from other authors. The results are of broad significance for the fields of structural chemistry and materials science because they demonstrate that the combination of spectroscopic and diffraction methods can provide a more complete and accurate chemical information than either of these methods alone. The development of single crystal and powder X-ray photodiffraction (photocrystallography), as a complementary technique to the spectroscopy and a very convenient analytical tool for direct study of dynamic solid-state phenomena, will be also elaborated.

**Keywords:** reactive intermediates; solid-state photochemistry; spectroscopy and molecular structure

#### FA4-MS05-O5

##### Structural Similarity and Reoccurring Hydrogen Bonding Patterns in Acylanilides. Susanne Huth<sup>a</sup>,

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Small molecule X-ray crystallography has become an important tool for the detailed investigation of the solid state with the ultimate aim to understand the (supra)molecular assemblies in crystal structures. The systematic study of crystal packing patterns together with the application of