

MS16 O1

Functional Molecular Cocrystals Leonard R. MacGillivray, Anatoliy N. Sokolov, Dejan-Kresimir Bucar, and Poonam Kaushik. *Department of Chemistry, University of Iowa, Iowa City, Iowa, USA.*
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Keywords: cocrystal, reactivity, hydrogen bonds

Molecular cocrystals provide an exciting opportunity to apply principles of organic and supramolecular chemistry to construct solids that exhibit tunable properties. The modular nature of the approach means that molecules can be readily replaced to determine affects of molecular size, shape, and functionality on the solid-state assembly process. This can be particularly appealing in a case where a robust structural unit, or supramolecular synthon, is known to affect a bulk physical property. In this presentation, we will demonstrate can molecular cocrystals can be constructed to affect chemical reactivity in the solid state. We will also discuss how molecular cocrystals can be developed to design organic semiconductors and pharmaceutical materials.

MS16 O2

Chemical Reactions on the Diffractometer Roland Boese^a, Sebastian A. Cirkel^a *Institut fuer Anorganische Chemie der Universitaet Duisburg-Essen, 45117 Essen, Germany.* E-mail: roland.boese@uni-due.de

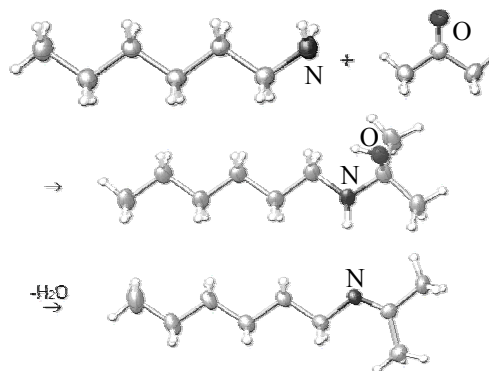
Keywords: X-ray cryocrystallography, unstable compounds, X-ray crystal structure determination

In situ crystallization techniques at low temperature are commonly applied to grow crystals of compounds which are liquids or gases at ambient. Cryocrystallography on the diffractometer in capillaries is nowadays commonplace. The cocrystallization technique for producing multicomponent crystals having new properties is a new field especially for Active Pharmaceutical Ingredients. Here, usually non-covalent bonds are formed between the entities employed.

Producing new compounds by formation of covalent bonds, is common synthesis and there seems to be no reason to perform a chemical reaction on the diffractometer in a capillary.

However, if the reaction can be slowed down by cooling, there is a realistic chance to trap intermediate and instable compounds by crystallization, thus gaining detailed information on the reaction path.

Such an example is the formation of Imines (Schiff Bases) by reaction of amines and ketones. They may form cocrystals with non-covalent bonds, the next step is the formation of the instable semi-aminals which can be trapped and crystallized together with the cleaving water molecules, finally resulting in Imines as shown in figure 1.



A 1:1 mixture of hexylamine and acetone, cooled in a capillary forms the semi-aminal which can be crystallized and subsequently giving the imine. This reaction represents only one of a series where all components on the reaction pathway were crystallized, unfortunately until now we do not have the co-crystal, the semi-aminal and the imine of one pair of compounds.

We believe that here exists a new field of X-ray crystallography which gives a better insight into reaction pathways on the way to new compounds.

MS16 O3

Tuning solid emission by ionic platinum terpyridines John S. Field^a, Lesibana Ledwaba^a, Orde Munro^a, David McMillin^b and Bradley Waldron^a, ^a*School of Chemistry, University of KwaZulu-Natal, Pietermaritzburg, South Africa.* ^b*Department of Chemistry, Purdue University, West Lafayette, IN 4907-1393, USA.*
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Keywords: platinum terpyridine, crystal design, emission.

Ionic platinum terpyridines of the type [Pt{4'-(R)trpy}Cl]Anion where R = Ph, *o*-CH₃C₆H₄, *o*-ClC₆H₄ or *o*-CF₃C₆H₄, trpy = 2,2':6',2''-terpyridine, Anion = SbF₆⁻, BF₄⁻ or CF₃SO₃⁻, are strongly photoluminescent in the solid state [1]. Often the solid emission by materials of this type is quite different from that observed in fluid solution, because of the presence in the crystal of either d_{z²}(Pt)-d_{z²}(Pt) and/or π(trpy)-π(trpy) intermolecular interactions. However, the influence of these interactions on the emission, in particular on the dependence of the wavelength of the emission maximum on temperature, depends on the precise arrangement of the cations and anions in the crystal.

We report here our recent work on the crystal structures and solid state photoluminescent properties of platinum terpyridines where the co-ligand bonded to platinum is either the CN⁻ or NCS⁻ ion. As with the chloride derivatives, the nature of the substituent in the 4'-position of the trpy ligand, as well as the size of the anion, plays a role in determining the crystal structure and hence the emission properties of the compound. Further factors are solvent inclusion and polymorphism, in particular concomitant polymorphism, as exhibited by the orange and yellow forms of [Pt{4'-(*o*-ClC₆H₄)trpy}(CN)]SbF₆. Finally, we have evidence from crystal structure determinations that the NCS⁻ ion bonds linearly to the platinum through the N-atom in the solid state; also that a lone pair on the S-atom can participate in n(S)-π(trpy)

intermolecular interactions that influence the photophysical properties of the material.

[1] Field, J. S., Haines, R. J., McMillin, D. R., Summerton, G. C., *J. Chem. Soc., Dalton Trans.*, 2002, 1369.

MS16 O4

Single-Crystal to Single-Crystal Photochemical Reactions in Inclusion Compounds. Menahem Kaftory, Tali Lavy, *Schulich Faculty of Chemistry, Technion-Israel Institute of Technology, Haifa 32000, Israel*
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Keywords: Photochemistry, Inclusion Compounds, Solid-State Reaction

We have found that single-crystal to single-crystal photochemical reaction takes place when we irradiated inclusion compounds with a regular mercury lamp.

Photochemical reaction of reactant guest molecules in inclusion compounds results in changes in the volume of the product guest molecules. In cases where the size of the reaction core is large enough to accommodate the substrate and the product (not simultaneously), the reaction is expected to be homogeneous (single-crystal to single-crystal) [1]. Voids are expected to be created if the volume of the product is significantly smaller than that of the pre-reacted guest molecules. In such cases either the single crystal will be destructed or?

In this paper we describe the photodimerization of two compounds 2(1H)-pyridone or 6-methyl-2-(1H)-pyridone, present as guest molecules in inclusion compounds. In each of these compounds, the volume of the dimer is smaller than the volume of the separated monomers, and as a result voids are created. In both cases water molecules that penetrate into the crystal occupy these voids in an ordered fashion. It was found that the water penetration occurs only at a late stages of the conversion suggesting that a critical amount of voids are necessary for the penetration to take place. After dimerization, voids are generated forming discontinuous channels. The discontinuity comes about from plugs of unreacted monomers. Only when all the monomers have dimerized the pieces of channels can merge to become continuous allowing for the penetration of water. After a period of several months the water diffuses out leaving single crystals. In both cases significant rotation induced by the dimerization occurs and is in association with hydrogen bond breakage and formation. [2]

[1] T. Lavy, Y. Sheinin, M. Kaftory, *Eur. J. Org.Chem.* 2004, 4802.

[2] T. Lavy, M. Kaftory, *CrystEngComm*, 9, 2007, 123.

MS16 O5

Novel Acetylpenanedionato Complexes for MOF Construction Daniel M. Töbrens^a, Michael Hummel^b, Herwig Schottenberger^b, Volker Kahlenberg^a, Reinhard Kaindl^a, ^a*Institute of Mineralogy and Petrography,*

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Keywords: Metal-Organic Complexes; Structure Analysis of small Molecules; Framework Structures

Symmetrically functionalized β -diketonate complexes, bearing linkable terminal substituents like the acetylpenanedionato complexes presented herein, hold the potential for the synthesis of new coordination polymers, namely metal-organic frameworks (MOFs). This class of porous materials is attracting continuous attention due to their large and adjustable cavities, high apparent surface areas, and selective uptake of small molecules. Acetylpenanedionato as a ligand forms exceptionally stable complexes and allows for a wide variety of linkable terminal substituents. It thus represents an inviting challenge to investigate its use in secondary building units. The novel compounds based on this complex and presented herein encompass four- and bi-ligand complexes and a variety of linear ligand-forming molecules.

The crystal structures of the complexes were determined from laboratory X-ray powder diffraction data. A comprehensive characterisation by a variety of spectroscopic and physico-chemical methods reflects the molecular and crystallographic differences between the compounds. The divalent metals palladium and magnesium both form linear bi-ligand complexes with plane-square coordination of the central cation. The Pd(II) complex forms a crystal structure of isolated molecules, in which the molecular conformation does not show any significant deviation from the expected ideal state. The use of this complex in MOF construction is promising for catalytic applications. In contrast, the Mg(II) complex crystallises in a way to complete the octahedral coordination of the central cation, resulting in strong inter-molecular bonds and a significant distortion of the ligands. This is reflected by vibrational band shifts and low solubility of the compound. Zr(IV) is coordinated by four chelating ligands [2], forming a square-antiprismatic oxygen coordination polyhedron. The geometry of this complex makes it capable to form network nodes. High pseudo-symmetry of the complexes is observed in all cases. The oxygen coordination polyhedron of the central metal in all cases is of very high regularity. The molecules symmetry is generally broken by orientational order of the free acetyl groups only. In $[\text{Zr}(\text{C}_4\text{H}_9\text{O}_3)_4]$ and $[\text{Pd}(\text{C}_4\text{H}_9\text{O}_3)_2]$ the symmetry of the molecule is retained on Wyckoff positions of lower site symmetry, indicating the absence of any significant inter-molecular forces.

From these components, a large variety of MOFs could be constructed. Experiments to this end are in progress.

[1] Hummel M. *Diploma thesis. University of Innsbruck, Faculty of Chemistry and Pharmacy.* 2006.

[2] Töbrens D. M. et al. *Crystal Growth & Design* 6(2), 1720, 2006.