

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

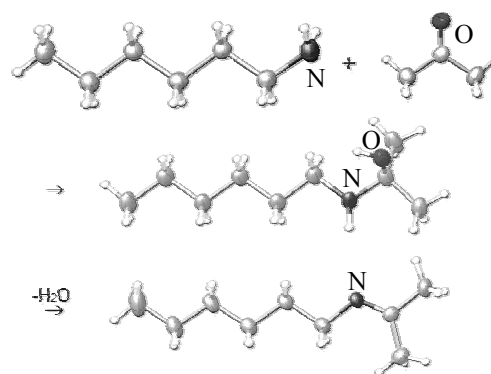
Keywords: X-ray cryocrystallography, unstable compounds, X-ray crystal structure determination

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)