Integration Of Crystallographic Techniques Into Teaching Labs

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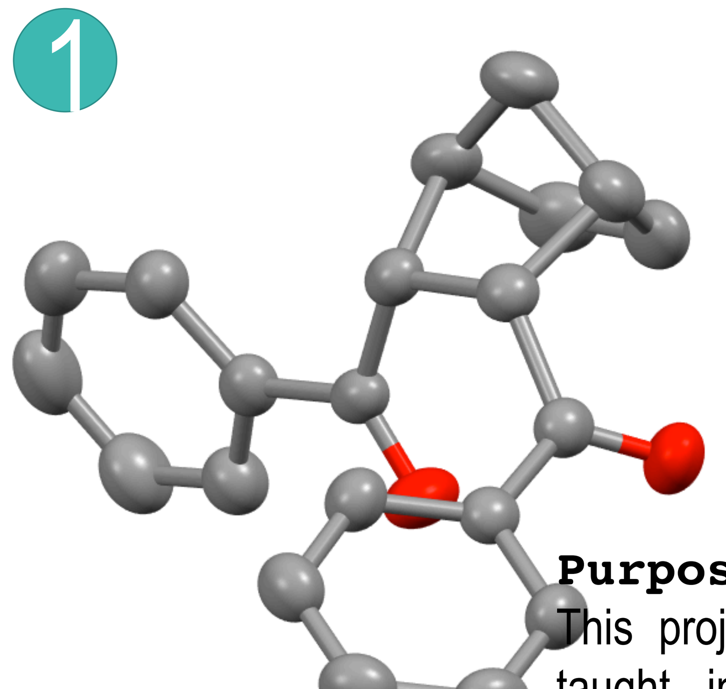


Fig. 1 *endo,endo*-2,3-dibenzoylbicyclo[2.2.1]hept-5-ene (a = 29.725(4)Å, b = 34.105(5) Å, c = 6.1755(6) Å)

Fig. 2 The X2S X-ray diffractometer (XRD) which carries out the analysis of crystal samples.

2014 international year of crystallography

Purpose:
This project seeks to transform the way chemistry is taught in the classroom by providing a hands-on experience to physical chemistry via crystals. Crystallography provides an in-depth look at the nature of molecules from simple to complex. Allowing students to be introduced to crystallographic techniques early in their undergraduate careers will allow for a better understand of concepts such as inter-/intra-molecular forces, bonding, sterics, packing, symmetry, and chirality.

2 How does it work?

1. Harvest
Crystals are checked for purity and polarization under a microscope.

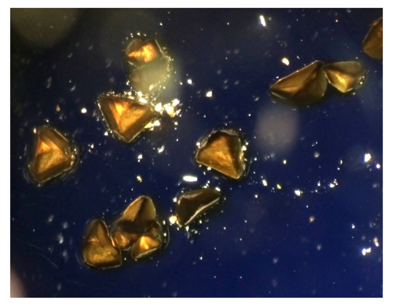


Fig 3. Cu_4I_4[pyridine]$_4$ crystals under 10x magnification.

2. Mount
Using an appropriate adhesive, crystals are mounted to a plastic mount under the microscope.

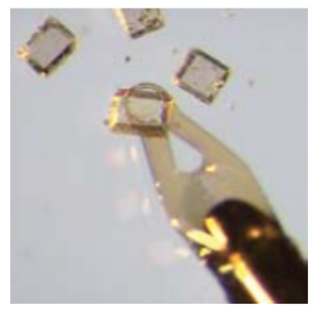
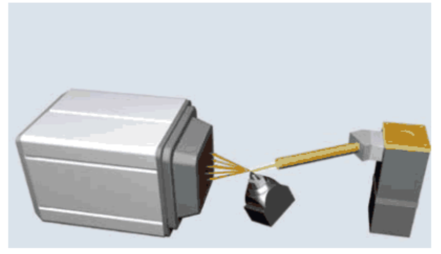


Fig. 4 Crystal being mounted on a point mount in preparation for XRD analysis.

3. Run
The crystal/mount is placed into the X2S and allowed to process for 4-24 hours. The crystal rotates and X-rays diffract through to produce a model.



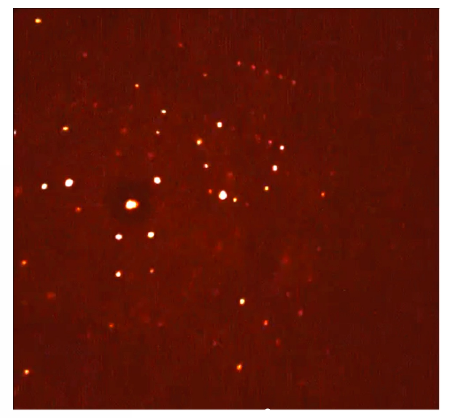


Fig. 5 (top) Analog of the interior of the X2S during a run.
Fig. 6 (bottom) Diffraction pattern of a crystal.

4. Results and Analysis
The X2S does not always spit out a finalized model and therefore may require further refinement through APEX software. The models are used to analyze bond distances and angles of molecules like the Fe(acac)$_3$ to the right.

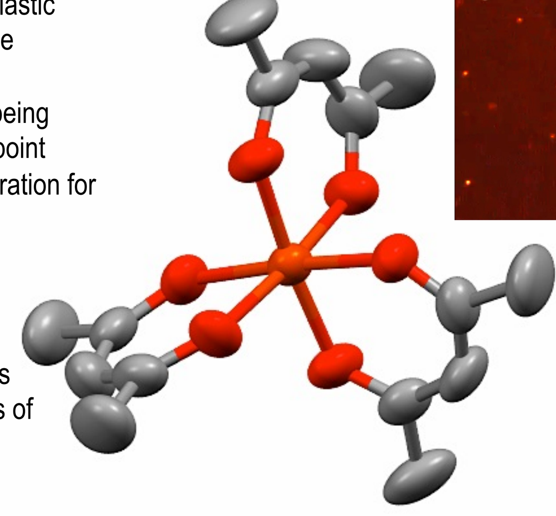


Fig. 7 Fe(acac)$_3$ [R-factor: 3.9%] molecule as viewed in Mercury

3 CHEM 210L: Impurities and Recrystallization

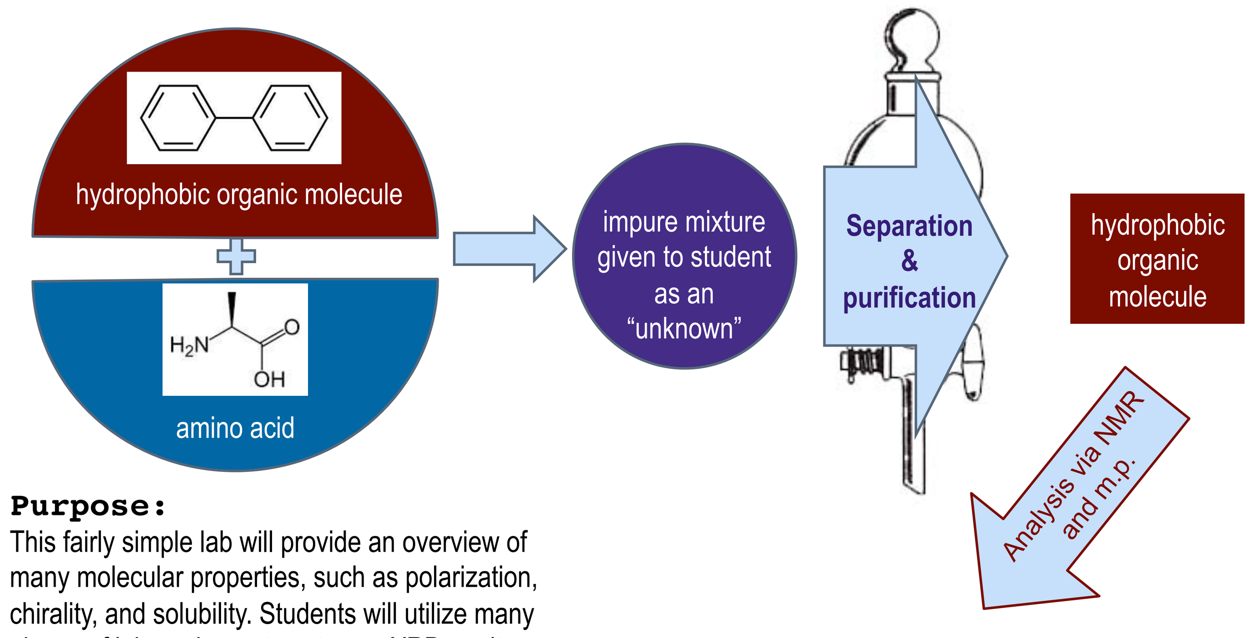


Fig. 8 Glycine crystals under 20x magnification

Purpose:
This fairly simple lab will provide an overview of many molecular properties, such as polarization, chirality, and solubility. Students will utilize many pieces of lab equipment—rotovap, XRD, meltemps—as well as grow and mount their own crystals.

Skillset:
- Miscibility/solvents
- Separation by separatory funnel
- Rotary evaporation to refine solid
- Melting point for identification
- NMR analysis
- Recrystallization & XRD
- Mercury software for molecular analysis
- Chirality centers (enantiomeric pairs)

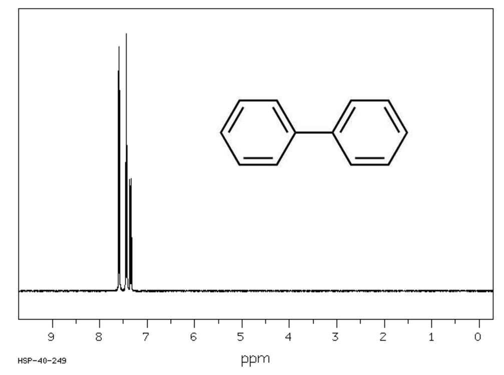


Fig. 9 ^{1}H NMR of biphenyl. The three peaks correspond to the 3 sets of identical hydrogen atoms found on the molecule. Image: http://sdbs.db.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

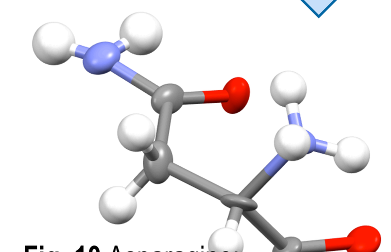


Fig. 10 Asparagine; Zwitterion configuration

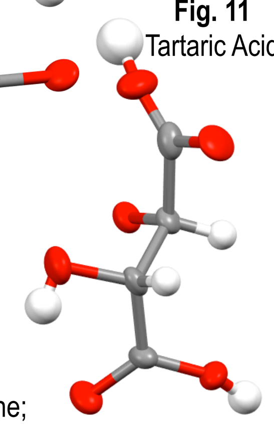


Fig. 11 Tartaric Acid

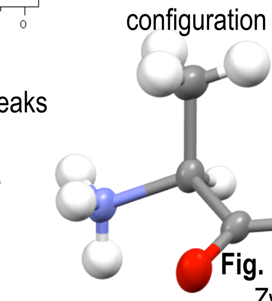


Fig. 12 Alanine; Zwitterion configuration

4 CHEM 366: Suzuki-Miyara Cross-Coupling Lab

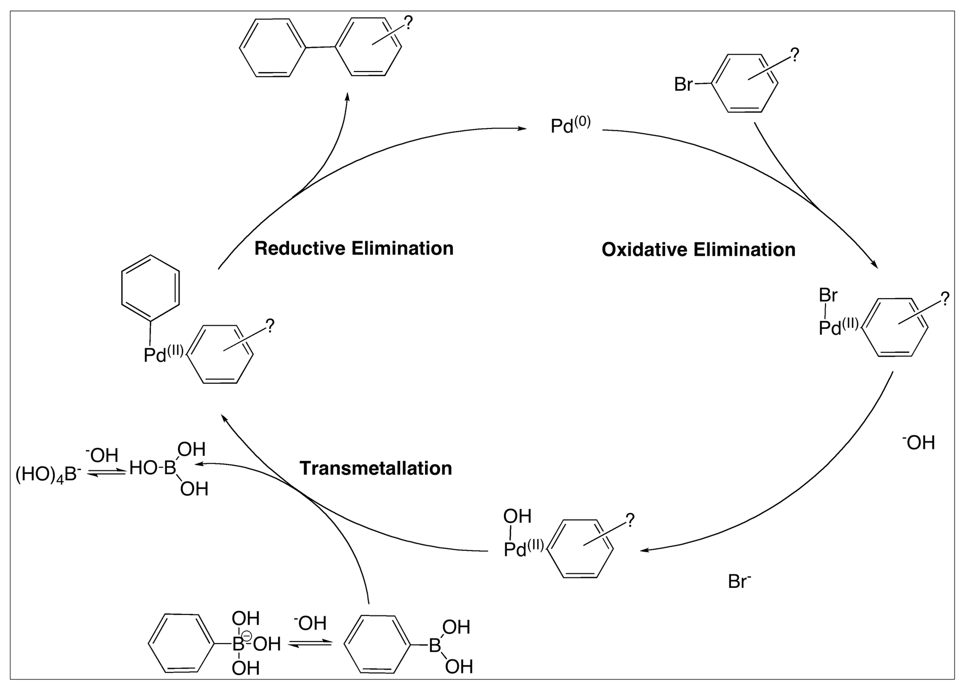


Fig.13 The Catalytic Cycle of a Suzuki-Miyaura Cross-Coupling Reaction Featuring an Unknown Aryl
Adapted from: Miyaura, N.; Suzuki, A. Palladium-Catalyzed Cross-Coupling Reactions of Organoboron Compounds *Chem. Rev.* **1995**, 95, 2457-2483

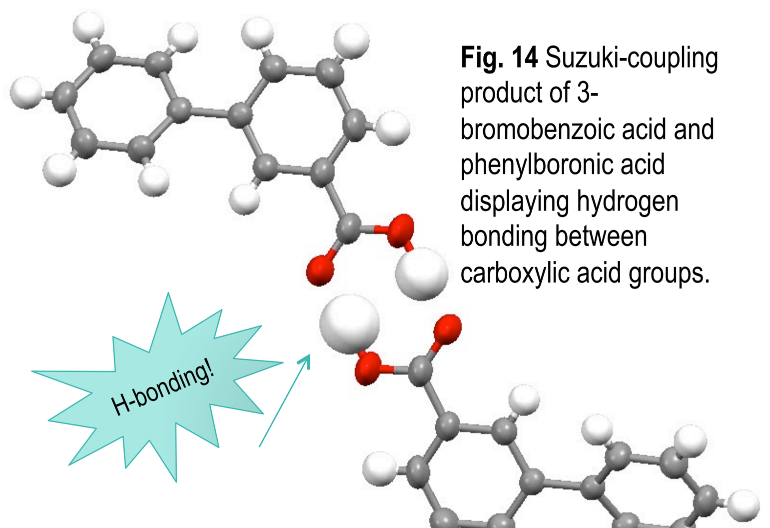


Fig. 14 Suzuki-coupling product of 3-bromobenzoic acid and phenylboronic acid displaying hydrogen bonding between carboxylic acid groups.

Skillset:
- Green chemistry: Use of a water soluble/air stable catalyst
- Aryl Coupling—carbon bond formation
- NMR Analysis
- SciFinder navigation

Purpose:
Carbon—carbon bond formation is a widely applicable synthesis, used in pharmaceuticals, polymerization and agrochemicals, making this technique one of merit to introduce in the classroom. However, the crystallization of products proved to be difficult. Therefore, this lab will be formatted as an unknown lab, with the possibility of crystallization.

Each student will couple an unknown aryl to phenylboronic acid by an inorganic catalyst. Students will use resulting NMR and melting point data to back reference SciFinder and identify the unknown. Aside from analytical aspects, this lab is also important due to its sustainability. The reaction is run in water, under air, with a minimal amount of catalyst (1mL of 0.025mmol [Pd] catalyst).

Acknowledgements:
Lisa Holmes
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Alan Younis

5 CHEM 366: Copper-iodide-pyridine Cubane Structures

Purpose:
This lab serves a an advanced inorganic look at luminescence thermochromism. Students are asked to synthesize the copper cubane structures—which yield gorgeous crystals—and observe the change in luminescence at room temperature and in liquid nitrogen.

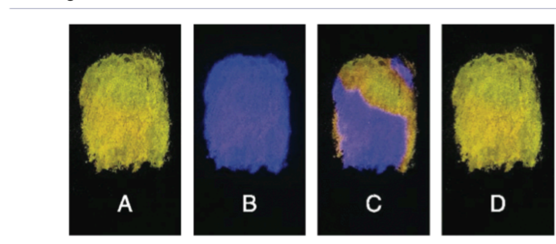


Fig. 15 Luminescence thermochromism of Cu_4I_4[pyridine]$_4$ exposed to λ_{max} = 366 nm UV light: (A/D) 25ºC; (B) -196ºC; (C) warming
From: Parmeggiani, F. and A. Sacchetti (2012). "Preparation and Luminescence Thermochromism of Tetranuclear Copper(I)-Pyridine-Iodide Clusters." Journal of Chemical Education **89**(7): 946-949. **2a** corresponds to the Cu_4I_4[pyridine]$_4$ structure.

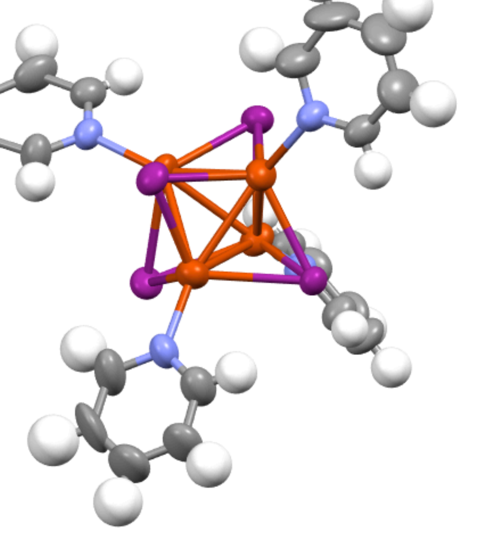


Fig. 16 Cu_4I_4[pyridine]$_4$ molecular structure solved after raw powder was crystallized in EtOH over DMSO at room temperature.

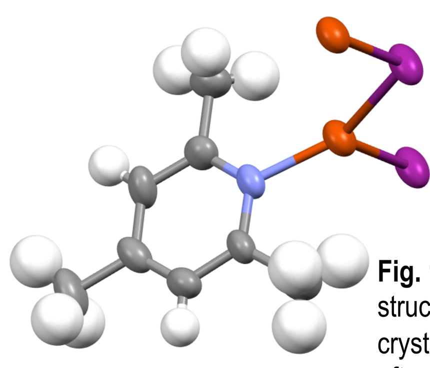


Fig. 17 CuI[2,4,6-trimethylpyridine] molecular structure solved after raw powder was crystallized from slow evaporation from acetone after overnight in vacuo.

Discussion:
In researching this lab, previous research suggested that decreasing bond distances contributed to the change in luminescent color at different temperatures. However, after the Cu_4I_4[pyridine]$_4$ was analyzed via XRD from temperatures 90K-240K, we saw no change in bond distances or angles. There was, however, an increase in unit cell volume as the temperature increased. Therefore we believe the color change to come from some aspect of a change in packing.

Skillset:
- Thermochromism discussion and analysis
- Crystal growth techniques and XRD protocol
- Mercury software use/navigation
- APEX use/navigation
- Inorganic synthesis

6 CHEM 366: Diels-Alder and Polymerization Lab

Purpose:
This lab serves to demonstrate the Diels-Alder reaction, a common reaction studied in CHEM 220, between a furan and maleic anhydride. The second step of the lab involves a ring-opening reaction, eventually yielding a diester. This portion of the yields gorgeous, large crystals for each step. This lab also allows for the product of the reaction to be polymerized in an inorganic synthesis that must be carried out in an oxygen-free environment. Students will learn how to appropriately operate a dry box/glove box.

Skillset:
- Use of glove box and working with air sensitive materials
- Crystal growth techniques and XRD protocol
- Organic and inorganic applications in a singular lab
- Reinforces carboxylic acid chemistry form CHEM 220

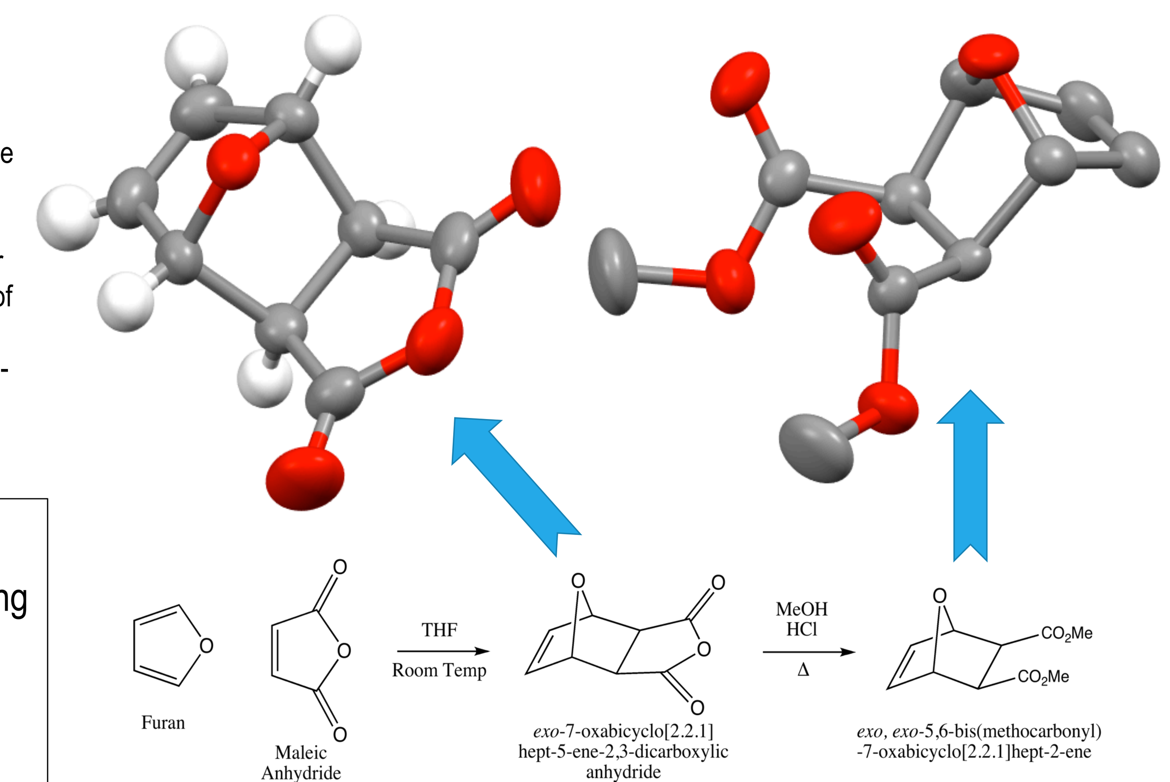
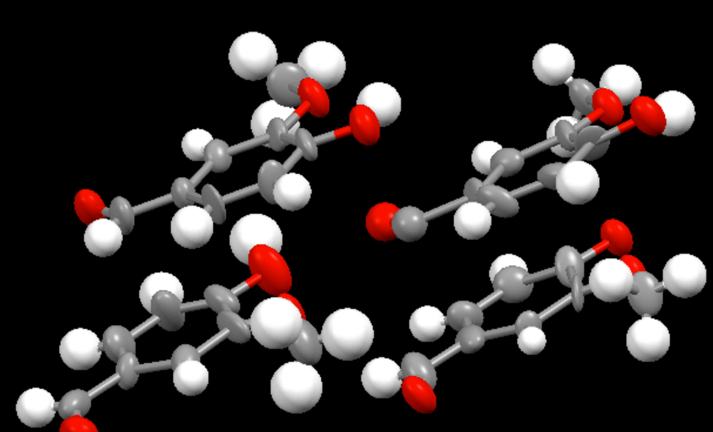
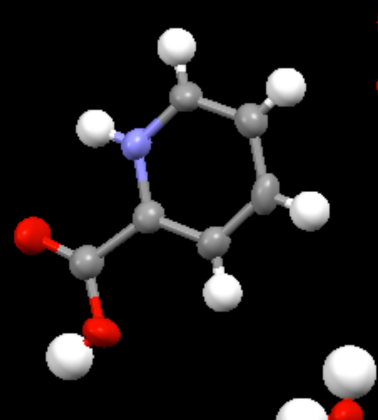


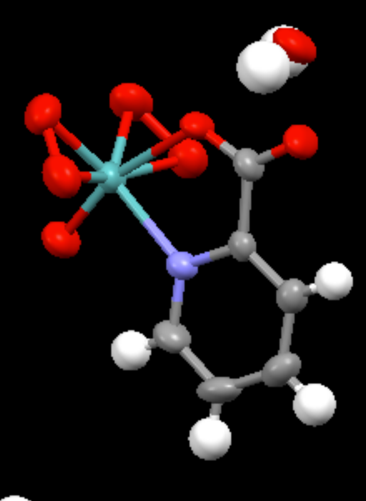
Fig. 18 *Top: exo*-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride *(left)*; *exo, exo*-5,6-bis(methocarbonyl)-7-oxabicyclo[2.2.1]hept-2-ene *(right)* crystal structures. *Below:* scheme of the synthesis of the monomer with two steps.

Other solved structures:

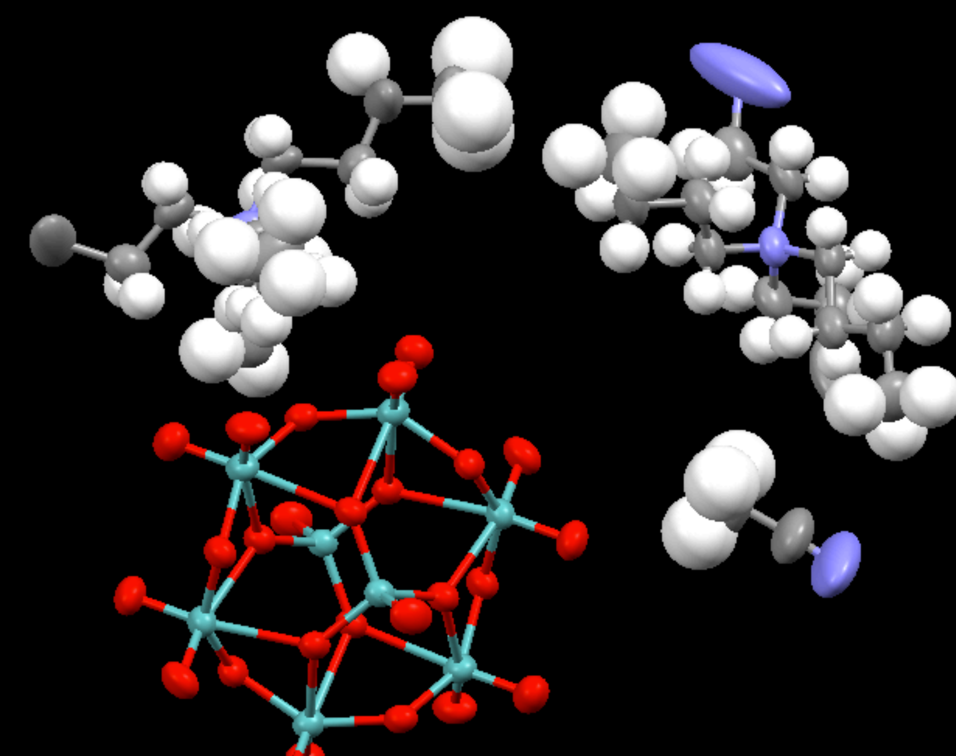


Vanilline

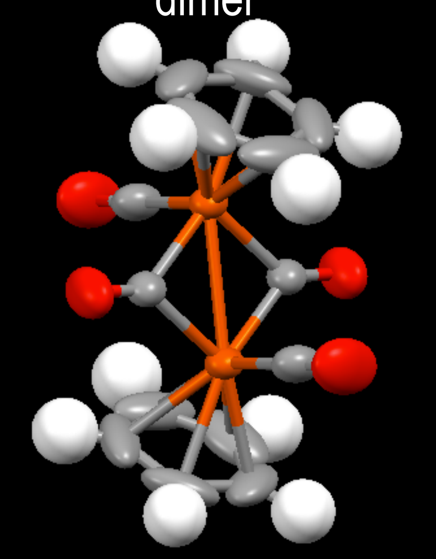




Molybdnum diperoxo-pyridine



Mo_8O_{26} + *tert*-bytul anion



Trans-cyclopentadienyl(dicarbonyl)iron dimer