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Experimental Organometallic Chemistry

A Practicum in Synthesis
and Characterization

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For some experiments using this spectrophotometric cell, one may need to know the volume of solvent. This can be determined by first transferring the solvent into the modified graduated centrifuge tube shown in Figure 2 followed by vacuum transfer of the solvent into the bulb of the spectrophotometric cell. The centrifuge tube (15 mL capacity, Pyrex, Corning 8100 from VWR Scientific) is fitted with a 14/20 standard taper female ground glass joint. This tube is then used in conjunction with a right angle Teflon vacuum valve (Kontes K-826610, size 4) fitted with a 14/20 standard taper male ground glass joint and 24/40 standard taper female ground glass joint that can be attached to a vacuum line.

Acknowledgment

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Chapter 10

Handling of Reactive Compounds for X-ray Structure Analysis

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Methods have been developed that allow simple handling of highly reactive crystalline compounds in preparation for x-ray analysis. The essence of the method consists in protecting the crystals with a layer of hydrocarbon oil during manipulation. Crystals can be prepared by handling can be carried out in the open. Routine use of gas stream cooling (<140 K) during x-ray data collection has allowed long-term exposure with retention of crystal integrity, without the use of protective capillaries. Use of fast data acquisition methods allows determination of new structures in 24 hrs, or less, without use of other analytical techniques.

The most reliable and informative method of structure determination is a single-crystal x-ray study. However, x-ray measurements can require hours or days of radiation exposure, with attendant problems in maintaining the chemical integrity of the sample under study. Many important and intriguing compounds are highly reactive, and cannot be exposed to the atmosphere without catastrophic consequences. Sometimes even relatively stable compounds cause problems when their crystals contain incorporated solvent which escapes when the crystals are removed from the mother liquor. Loss of this solvent can cause collapse of the crystal structure. Annoying problems can also occur simply because the substance is hygroscopic.

A commonly used answer to the incompatibility of chemical properties and method of preferred structure determination has been to protect the crystal by sealing it in a glass capillary. Many otherwise inaccessible, but important structures have been determined by use of this method. However, the procedure is far from simple, and requires relatively elaborate equipment for maintaining an inert atmosphere during manipulation of the specimen.

In response to this situation a much simplified technique for the handling of reactive materials has been developed. The essence of the method consists in protecting the sample from the atmosphere

with a layer of inert, viscous oil, and in maintaining the crystal at low temperature during data collection.

The Case for Low Temperature

Cooling systems designed for routine use on x-ray diffractometers are almost exclusively based on the gas-stream principle, where the sample temperature is controlled with a stream of gas, usually dry nitrogen. Contemporary commercial low-temperature attachments allow reasonably easy temperature control in the range from near liquid nitrogen temperature to about room temperature.

Practically all crystals will be perfectly stable when kept in a nitrogen stream around 100 K. No solvent will escape, and reaction with oxygen or other atmospheric components is virtually impossible. This is the main reason for carrying out x-ray experiments on reactive samples at low temperature. However, consideration of the effect of cooling on atomic thermal parameters reveals another significant advantage. The intensity of a diffraction maximum is modified by a temperature factor, or damping factor, D , which in its simplest form is given by $D = \exp(-2B/(\sin\theta/\lambda)^2)$. The coefficient B is to a good approximation proportional to the Kelvin temperature. Common values of B for atoms in molecular crystals fall in the range 3 to 6 Å². Lowering of the temperature from 300 K to 100 K will reduce these to 1 to 2 Å². For $\sin\theta/\lambda$ around 0.5-0.6 Å⁻¹ this results in intensity enhancement by a factor of around 5, indicating that a fivefold increase in data collection speed can be realized without loss of data quality. For groups or ions such as ClO₄⁻ or PF₆⁻ that are notorious for large B values (15 Å² at 300 K is not uncommon), lowering the temperature can make the difference between a clean structural description and an intractable one.

The question of the effect of rapid cooling on the crystal is often raised, mainly with the concern that phase transitions or thermal stress may destroy the crystal. From experience with hundreds of compounds it can be stated with confidence that damage from cooling is rare. Perhaps about 1% of the crystals will undergo a phase transition under the conditions described here. Most of these cases can be handled by raising the temperature to a few degrees above the transition temperature. In practically no case is slow cooling of value; more frequently it will cause problems.

Setting up a low-temperature x-ray laboratory requires a certain investment of resources, and without a serious commitment the results are likely to be disappointing. Unfortunately, one cannot expect all cooling units to perform well as delivered by the vendor, although at least the more commonly sold models are basically sound. Up to this time the real responsibility for good performance has been left with the customer. Common problems are proneness to icing, excessive coolant consumption, and inadequate temperature stability. Solutions to the problems depend on model and make, and are beyond the scope of this book. Many unnecessary difficulties can be avoided by seeking advice from laboratories with successful low-temperature installations.

Preparation and Transfer of Crystals

The overall aim of the crystal handling technique is to keep

10. HOPE *Handling of Reactive Compounds*

operations as simple as possible, without undue risk to the sample. There are important practical and psychological reasons for this.

As is well enough known, it is rather common that a number of crystals must be examined on the diffractometer before a satisfactory specimen is found. Simple procedures that can be quickly executed will save much precious time. They are also more likely to result in a good crystal than are time-consuming, difficult methods, since there will be less resistance to discarding a marginal sample.

In general, it is desirable to prepare the crystals in a container with a relatively narrow mouth, and with the possibility of admitting an inert gas (typically N₂) through a separate inlet (a Schlenk tube is an example). In that way a reasonable overpressure of the gas is sufficient to prevent intrusion of atmospheric contaminants when the container is uncapped. With such a setup it is usually possible to carry out transfer of the crystals without use of a separate controlled atmosphere chamber.

Crystal growing techniques that are generally applicable to stable compounds can of course also be used with reactive compounds, provided adequate precautions are taken to avoid contamination. A large number of highly reactive crystals have been grown simply by placing a Schlenk tube with the appropriate solution (or reaction mixture) in a freezer at about -20°C.

Since more detailed accounts of preparative methods can be found elsewhere in this book, this section will not contain further discussion of that topic.

Retrieval of Crystals

General. As soon as crystals of appropriate size have been obtained it is time to transfer a specimen to the diffractometer. This is usually a two-step operation. First a sizable portion of the crystalline product is transferred to a flat-bottomed dish to which has been added a protective oil to a depth of a few mm, the amount depending on the expected reactivity of the compound. This laboratory has obtained excellent results with Paratone-N (Exxon), either neat, or mixed about 1:1 with mineral oil. For many compounds the resin part of epoxy glue has also worked well. The main requirements for the protective oil are fairly high viscosity (for slow diffusion of atmospheric gases and slow dissolution of the crystals), transparency to light (for convenience when working with a microscope), and inertness toward the compound in question.

Detailed Procedure. Two alternative, detailed procedures for transfer of crystals that decompose slowly or melt above room temperature are given.

First Procedure:

- (a1) Add a 3 - 5 mm deep layer of the protective oil to a 5 - 10 cm petri dish.
- (a2) Tilt the sample container so that a portion of the crystals moves to the neck of the flask, then tilt it back slowly so that these crystals remain in the neck. (At times it may be better to skip step (a2)).
- (a3) Attach a gas supply hose to the flask, and apply a reasonable overpressure.

- (a4) Open the flask, and with a spatula quickly scoop up a portion of the crystals, and stir them into the oil already prepared. The distance the sample is to be moved through air should be as short as practicable.

Second Procedure:

- (b1) Is the same as (a1).
 (b2) Obtain a Pasteur pipette with a tip wide enough to suck up the crystals (1 - 2 mm) and flush it with inert gas.
 (b3) Is the same as (a3).
 (b4) Open the flask, and withdraw a generous sample with the pipette. Avoid excessive amounts of solution.
 (b5) Position the pipette with its opening in the oil and expel the crystals.

Sample Selection and Mounting. The sample should now be safe for a few minutes, and one can proceed to selection and mounting of a crystal. Selection of a suitable crystal is similar to procedures commonly used for chemically stable samples. A sewing needle held with a pin vice, and a sharp razor blade are useful tools. The binocular microscope should have a polarizing attachment to assist in judging quality of crystallinity.

Under the microscope a crystal with desirable attributes (size, apparent crystallinity) is selected and cleaned. The crystal is then removed from the oil by lifting it out with a prepared mounting fiber (see below for description), and immediately transferred to the cold stream on the diffractometer. This step can often be simplified if the crystal is moved toward the surface of the oil before one attempts to pick it up.

The distance between microscope and diffractometer should be short, no more than two or three meters. The transfer process can then be completed in about ten seconds. Because of the viscosity of the oil the crystal will be encased in a drop that will protect it during the transfer. At the low temperature in the cold stream the oil will become glass hard, and thus ensure a perfectly stable mounting.

Optical effects associated with the drop can interfere with the visual centering of the crystal, so that the amount of oil should be kept as small as possible, commensurate with the stability of the crystal.

A compound in crystalline form usually takes longer to suffer damage than one might be tempted to infer from its solution reactivity. Therefore it is good practice to determine the amount of air exposure a crystal will tolerate, and adjust the thickness of coating accordingly. Excess oil can be removed by sliding the crystal over a glass plate.

The Mounting Pin. In this laboratory the best results have been obtained with a specially designed mounting pin, illustrated in Figure 1. The pin is a hollow copper rod with a diameter corresponding to the adaptor hole in the goniometer head (normally 3 mm or 0.125 in.). The tip of the pin is tapered down to 0.5 mm. The bore diameter near the tip is 0.5 mm; the rest of the bore is 1.5 mm. In preparation for use the fine bore hole is filled with standard electronic solder (by capillary action). A glass fiber of

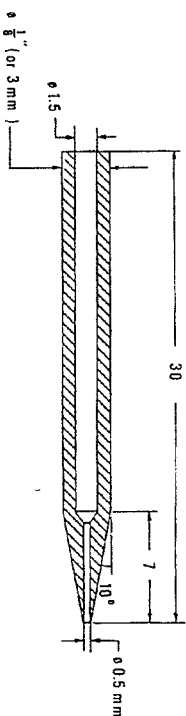


Figure 1. Dimensions of mounting pin. The overall length will depend on diffractometer and goniometer head dimensions. Material: Copper.

appropriate thickness is inserted into the molten solder, which is then allowed to cool. This results in a very stable assembly, with no tendency to drift with temperature changes. The glass fiber should extend 2-3 mm beyond the tip of the copper pin. It is critical that the glass does not extend outside the cold part of the cooling stream. The metal tip should be free of solder lumps, in order to prevent turbulence, which can cause icing. Copper, rather than brass, is used for its much better thermal conductivity.

Data Collection

In a paper from this laboratory it was shown that x-ray data collection can be substantially sped up without loss of significant information (1). With a Nicolet P2 diffractometer we collect 12,000 to 14,000 ω scan reflections in 24 h. Presumably, newer diffractometers can work at higher speeds. If crystals of reasonable quality are available, a 50-atom (non-H) structure should therefore be determined in less than 24 h. Once the crystal structure has been established, spectroscopic and other physical measurements can be planned and executed in a more rational manner than can be done with unknown samples. An x-ray structure determination should therefore normally be the first analytical procedure performed on a newly synthesized compound.

Limitations

The techniques described here are generally useful for compounds that melt near room temperature or higher. The author is developing a procedure for handling of low-melting crystals. Although initial experiments have been successful, the procedures are still fairly complicated, and further development is desirable.

Experience with the Method

The techniques described here were first developed in order to carry out x-ray data collection for phenyllithium etherate (2). More recently the structures of several extremely reactive organocuprates were determined in similar manner (3). A large number of other reactive compounds have also been prepared in the laboratory of Professor P.P. Power, and subsequently structurally characterized. The methods can be readily taught to new students, often requiring only a single demonstration for success. However, it should again be emphasized that good results depend on a properly working low-temperature apparatus, and a certain investment in equipment and acquisition of technique will therefore be required of those who want to take advantage of the methods described here.

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Chapter 10: Application 1

In Situ Crystal Growth for X-ray Diffraction Studies

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A technique for growing crystals *in situ* in a diffractometer enabling the x-ray structural determination of compounds that readily loose solvent upon harvesting is described.

Crystals of $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+[\text{C}_2(\text{CN})_4]^-$ in MeCN readily lose solvent upon collection and although appear nicely formed (ca. $1 \times 1 \times 10$ mm) they diffract like powders. To obtain the crystal structure a method for *in situ* growth of the crystals in the diffractometer was utilized.^{1,2}

A saturated solution of $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+[\text{C}_2(\text{CN})_4]^-$ in MeCN was placed in a capillary and after initially sealing it with grease it was removed from the glove box³ and flame sealed. The capillary was mounted into a diffractometer outfitted with FTS IT14 refrigeration device. The tube was then shock cooled via application of a cotton swab soaked with liquid nitrogen. A myriad of crystals formed⁵. The temperature of the capillary was warmed to just below the dissolution point of the crystals. A tiny hot wire⁶ was then utilized to locally heat specific areas enabling the selective dissolution of undesired crystals. After reducing the number of crystals to 10-20 the temperature was lowered enabling these remaining crystals to grow larger. The warning, hot wire, cooling cycle was repeated until a single crystal remained which was then allowed to grow large enough to enable x-ray analysis. The temperature was then lowered to freeze the remaining supernate as an amorphous matrix.

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