AN INEXPENSIVE TECHNIQUE FOR HANDLING SOLVENT-DEPENDENT CRYSTALS.

By Simon R. Drake, Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY, England

(Received 12 May 1993; accepted 29 June 1993)

Abstract

A new method of handling solvent-dependent crystals is described. This involves using a bubble of hexadecane to reduce solvent diffusion. The capillary tube is sealed with araldite resin.

X-ray crystallography is a widely used and very powerful tool for the unambiguous assignment of inorganic and organic compounds. However, the collection of X-ray data may take hours or even weeks, depending on the amount of data to be collected, and during this time period it is quite common for the crystal to decompose. The sensitivity to both air and moisture is a frequent problem encountered with organometallic complexes of both main-group and transition-metal elements and has led to a variety of different approaches to overcome the problem of sample handling. A widely used approach has been to mount and seal single crystals in glass capillary tubes under an inert atmosphere. This simple technique has enabled many landmark molecular structures to be determined.

There are many instances, though, when working in either a dry box or a glove bag, when it is not possible or even desirable to use a naked flame to seal thin-walled glass capillaries containing single crystals suitable for X-ray crystallography. Previous researchers have used a heating element attached to an electrical cord, with the temperature controlled by an external variac (Meyer, 1973; Milledge, 1969). A limitation with this technique is that even with the utmost care there is still the strong possibility of a thermal gradient along the capillary tube and subsequent loss of integrity of the single crystals.

In our research studies, we have found that a major problem consistently arises with crystals containing incorporated solvent. This is facile solvent loss when the crystals are removed from their mother liquor. This loss of lattice-bound solvent generally causes loss of integrity in the crystals. Previous researchers have also made use of a hydrocarbon-oil technique, which is extremely versatile, providing a low-temperature liquid-nitrogen gas-stream source (<140 K) is available for X-ray data collection (Hope, 1987). An elaborate apparatus has also been described for mounting temperature-sensitive crystals using high-molecular-weight alkanes as adhesives (Seebach, Amstutz, Laube, Schweizer & Dunitz, 1985). Given that such equipment is not universally available and very expensive to set up, we have devised a low-cost cold-sealing solution to this problem. In addition, we have also found that addition of high-boiling alkane solvents to the X-ray capillaries can effectively stop solvent loss, which, if it is very volatile, may permeate out through the glue.

Our aim with this technique is to keep the operation as simple as possible, with minimal risk to the sample. The operations may routinely be carried out in an inert-gas-flushed glove box with the minimum of inconvenience. We have also found, by taking in a small amount of the dry solvent, for which the crystals exhibit a solvent-dependent nature, that solvent loss does not occur while manipulating the samples in the glove bag or glove box.

To a suitable capillary (0.5 mm i.d.) held by tweezers (with a notch cut into them to ensure they hold the capillary securely) was added ca 0.3 µl of the mother liquor via a microsyringe at the base of the capillary. A glass fibre (ca 0.3 mm wide and 10 cm long) was dipped lightly into hexadecane and used to pick up a suitable crystal, which was quickly placed into the capillary as near to the sealed end as possible. A small amount of hexadecane (~1 µl) was then added to the tube via a microsyringe and allowed to move down the tube slowly to form a bubble approximately 0.5–1 cm above the crystal. The capillary was then broken to the required size of ca 1.5 cm and the end carefully dressed with the tweezers. Finally the open end was carefully filled with rapid-setting araldite resin using a thin metal spatula. The capillary was then left to stand in a small block of beeswax (5 x 5 cm) that had several 1 mm holes drilled in it to the depth of 1 cm.

Alternatively, we have found that the Prentice-Hall model kits (Lange & Haendler, 1972) are also useful because of the internal ridges running the length of the tubing, which support the X-ray capillary tube while the glue sets. After ca 3–4 h the araldite has cured and the X-ray capillary tube may be handled in the atmosphere for several weeks with no visible decomposition of the crystals.

The use of the hexadecane solvent reduces the possibility of solvent diffusion through the araldite and ensures that the crystal stays in an atmosphere of the solvent. If solvent loss is severe, then the crystal may be mounted directly into hexadecane (2 µl) and the tube sealed as described above. This may then be cooled to 253 K or below in a cold stream and X-ray diffraction data collected. The crystal is then held rigid in the frozen alkane solvent. This technique works very well if the crystals are coloured because the hexadecane becomes slightly cloudy on freezing. There is a possibility that optical problems associated with the hexadecane may create difficulties in aligning the crystal, hence it is imperative that the alkane volume should be kept as small as possible.
The apparatus required is inexpensive and is also useful when manipulating moisture-sensitive crystals. We have found that even badly desolvating crystals may be manipulated using this relatively straightforward technique. By following the operation outlined above, we have obtained structures of very sensitive materials. This approach is well within the capability of any laboratory that is interested in the determination of single-crystal X-ray structures of highly solvent dependent crystals.

References


**Crystallization in a laboratory chamber furnace.** By B. ČABRić, Faculty of Sciences, PO Box 60, 34000 Kragujevac, Yugoslavia, T. PAVLOVIć, Faculty of Philosophy, Niš, Yugoslavia, and B. Žižić, Faculty of Physics, Beograd, Yugoslavia

(Received 16 July 1993; accepted 31 August 1993)

Abstract

An apparatus for crystal growth from the melt, based on Stöber's method and realized in our laboratory, is described.

The apparatus for growing crystals from the melt constructed in our laboratory represents a modification of Stöber's method (Vilke, 1977); it is schematically shown in Fig. 1. The apparatus is simple and consists of one or several crucibles (1), an electroresistant chamber furnace (2), an air cooler (3), an adjustable transformer (4) and a thermocouple (5). The air cooler and crucibles are made of quartz glass. The growth of crystals is carried out by increasing the voltage slowly until the substance in the crucible is completely melted and then a flow of air is allowed to pass through the air cooler (Fig. 1) so that the crystallization starts on the surface of the melt. After increasing the air flow through the cooler for several hours, the solidification front reaches the bottom of the crucible. This method was applied to the crystallization of substances with a layered crystal structure (Čabric, Žižić, Napijalo & Pavlović, 1990).

By this method, several substances can be crystallized simultaneously at different crystallization rates.

References