# Difficult Crystals
Data Collection, Reduction & Refinement

MS02.01.01 CRYO-CRYSTAL STRUCTURE ANALYSIS AND APPLICATIONS TO REACTION INTERMEDIATES.

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As a major aspect of our work, techniques have been established to handle 'shortlived' intermediates in organometallic synthesis. Key features of this work involved the introduction of new synthetic routes generating the metastable target compounds, and the development of comprehensive cryotechniques to make the solid state structure investigations feasible. Although, many alkali metal species had been characterized by crystal structure analysis in the past 20 years, little was known about the nature of the thermolabile intermediates involved in their reactions. To address this problem, we developed a low temperature crystal handling technique which facilitates the x-ray structural characterization of low melting (down to -80°C) and/or extremely air-sensitive species (T. Kottke, D. Stalke, J. *Appl. Crystallogr.* 1993, 26, 615). In a typical experiment, single crystals are grown at a temperature ranging from 0 to -120°C and - after cryomanipulation under a polarizing microscope - transferred to the diffractometer at the required low temperature. Applying this technique, the 'text book structures' of the classical lithium organometallics [^{n}BuLi]$_6$, [^{t}BuLi]$_4$, and the metastable [^{t}BuLi.Et$_2$O]$_2$ have been determined (T. Kottke, D. Stalke, *Angew. Chem. Int. Ed. Engl.* 1993, 32, 580).
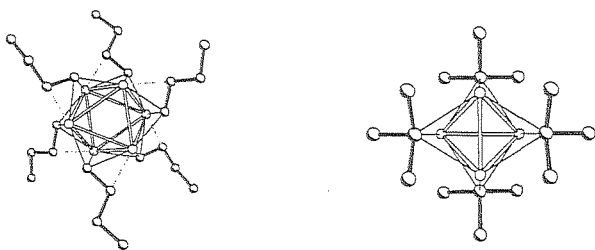
MS02.01.02 SMALL-MOLECULE STRUCTURES WITH LARGE-MOLECULE PROBLEMS.

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The causes and effects of data and model deficiencies in small-molecule structures are explored, with emphasis on problems analogous to those commonly encountered in macromolecular crystallography — poor resolution, weak scattering, and incomplete structural models. Possible methods of treating such problems are discussed, using examples from organic and inorganic chemistry, and with special consideration of the limits of the validity of the results. Although reference is made to specialized methods, the examples presented are taken from problems treated with widely available crystallographic techniques.

Some causes of weak scattering, sometimes inherent and not a result of poor sample quality, are described, with reference to two structure determinations from samples with two quite distinct features leading to deficient data. In one of these examples, a control experiment is used to estimate the validity of the information derived from the defective data set. Another example is used to explore the problems caused by an incomplete structural model. As a means of estimating the limits of common crystallographic techniques for treating small-molecule structures with data or model deficiencies, an unsuccessful structure determination is described.

MS02.01.03 STRUCTURES WITH Z'>1: PROBLEMS AND OPPORTUNITIES.

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Structures with Z'>1 (more than one independent formula unit in the asymmetric unit) frequently present crystallographic difficulties. Such structures are nearly always pseudosymmetric, at least locally. Data-to-parameter ratios are often low and least-squares refinements unstable or slow to converge. Structure solution can be a problem, especially if the molecules are approximately planar. Even if everything goes smoothly there is the nagging worry that additional symmetry has been overlooked and will be found by an alert Editor, Referee, or interested reader.

Examples (some published, some not) will be discussed. In several the use of constraints, including the rigid-group approximation, was very important.

Consideration of structures with Z'>1 may also lead to greater understanding of crystal packing. Only about 7% of the structures in the Cambridge Structural Database have Z'>1; crystallization with $Z' \leq 1$ is the norm. (The tendency to low Z' values may explain why crystals containing two different stereoisomers are rare.) Certain classes of compounds are, however, especially likely to crystallize with Z'>1. Among these are the monoalcohols C_nH_mOH and *vic*-diols $C_nH_m(OH)_2$. Optimization of H-bonding interactions in these compounds often rules out a unit cell having $Z' \leq 1$. Other Z'>1 structures reveal multi-molecule packing units that have internal structure incompatible with translational symmetry. Probably such aggregates exist in solution but are found only rarely in the solid state. Finally, many Z'>1 crystals, especially those grown at one temperature and studied at a lower temperature, can be viewed as having commensurately modulated structures.

MS02.01.04 THE SOLUTION AND REFINEMENT OF STRUCTURES WITH X-RAY DIFFRACTION DATA FROM TWINNED CRYSTALS.

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Precise and accurate crystal structures, including proteins, can be obtained from X-ray diffraction data gathered from twinned crystals. In a twinned crystal, the intensity of each reflection or a subclass of reflections may be represented as $I(hkl) = x*I(hkl) + (1-x)*I(h'k'l')$, where x is the fractional amount of the major component and where the twin law that relates indices hkl and h'k'l' in a systematic manner can be summarized in matrix form. When x is greater that 0.65, the structure usually may be solved and refined without major difficulty. Since the minor component essentially amounts to a random noise on the diffraction intensity data of the major component, the final positional parameters, while often lacking the precision that would be expected from the extent of data collected, do not contain serious systematic error. Poorly behaved thermal parameters can be expected when the extent of twinning is severe (0.5<x<0.75). The values of the discrepancy indices R1(on F, observed data) and, especially, wR2 (on F^2, all data) can be aesthetically displeasing to referees, even when the extent of twinning is small (0.85<x). Several least-squares programs, for example SHELXL93 (G.M. Sheldrick) and CRYSTALS (D.J. Watkin), offer the user the capability to enter a twin law, to flag twin-affected data, and to refine the twin component x (or twin components, if more than two twin components exist). In addition, the refined value of the twin component is used to "detwin" the data for subsequent electron density Fourier syntheses.

Even as x approaches 0.5, direct methods may still reveal an interpretable, albeit noisy, electron density map, since phases more