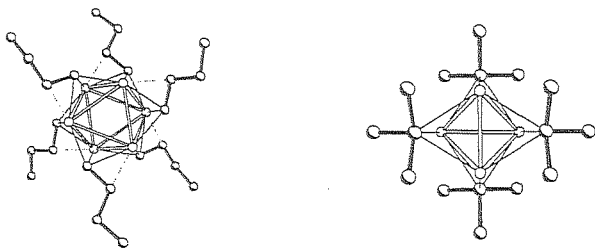


Difficult Crystals

Data Collection, Reduction & Refinement

MS02.01.01 CRYO-CRYSTAL STRUCTURE ANALYSIS AND APPLICATIONS TO REACTION INTERMEDIATES. Dietmar Stalke, Inst. für Anorg. Chem., Am Hubland, D-97074 Würzburg, Germany

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 $[\text{BuLi}]_6$, $[\text{BuLi}]_4$, and the metastable $[\text{BuLi} \cdot \text{Et}_2\text{O}]_2$ 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. Larry R. Falvello, University of Zaragoza, Department of Inorganic Chemistry, Faculty of Science, Plaza San Francisco, E-50009 Zaragoza, Spain.

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. Carolyn Pratt Brock, Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055, USA

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 $\text{C}_n\text{H}_m\text{OH}$ and vic-diols $\text{C}_n\text{H}_m(\text{OH})_2$. 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.

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MS02.01.04 THE SOLUTION AND REFINEMENT OF STRUCTURES WITH X-RAY DIFFRACTION DATA FROM TWINNED CRYSTALS. Geoffrey B. Jameson, Department of Chemistry, Massey University, Palmerston North, New Zealand

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 $I(\text{hkl}) = x \cdot I(\text{hkl}) + (1-x) \cdot I(\text{h}'\text{k}'\text{l}')$, where x is the fractional amount of the major component and where the twin law that relates indices hkl and $\text{h}'\text{k}'\text{l}'$ in a systematic manner can be summarized in matrix form. When x is greater than 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 R_1 (on F , observed data) and, especially, wR_2 (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

so than amplitudes determine the form of electron density maps. Vector (Patterson) maps contain images related by the twin law. There appear to be no circumstances where least-squares refinements should be made with detwinned data, since the process of detwinning unavoidably introduces considerable noise into what might have been an excellent data set. Various examples will be used to illustrate strategies for the identification of twinning (pre- and post-data collection), derivation of the twin law, and solution and optimal refinement of structures.

MS02.01.05 THE APPLICATION OF SHAKE AND BAKE TO UNSOLVED STRUCTURES. R. Curtis Haltiwanger, Drake S. Eggleston, SmithKline Beecham Pharmaceuticals, UW-2950, P.O. Box 1539, King of Prussia, PA 19406

Shake and Bake (SnB)¹, an ab initio dual-space, multiple-solution direct-methods procedure is a powerful addition to the suite of modern structure solution packages. We have successfully applied it to several previously unsolved structures of varying complexity. These vary from a 220 atom structure in space group $P2_1$ to a 120 atom structure in space group $P1$. Details of the implementation and successful application of SnB in our laboratory will be presented.

¹ R. Miller, S. M. Gallo, H. G. Khalak, and C. M. Weeks, *J. Appl. Cryst.* **27**, 613-621 (1994)

MS02.01.06 STRUCTURE DETERMINATION USING CCD AREA DETECTOR - HOW SMALL A CRYSTAL IS TOO SMALL? Nigam P. Rath, Department of Chemistry, University of Missouri-St. Louis, 8001 Natural Bridge Road, St. Louis, MO 63121-4499, USA.

A Siemens CCD area detector system has been used to collect data on several "very small" crystals and their structure solution and refinement achieved by using SHELXTL 5.0 programs for structure determination. In some cases, structure has been re-determined using a bigger crystal and a comparison of results will be presented.

Diffraction data has been collected on the same crystal for organic and organometallic compounds using point detector diffractometer (Siemens P4) and CCD area detector system for comparison of structural results. Advantages and disadvantages of both the detector types will be discussed. Efforts are underway to develop data collection strategies for small crystals and weak diffractors for use with CCD area detector system. Our experience with the area detector system for small molecule structure determination, both high-points and pitfalls, will be presented.

PS02.01.07 MODELING CRYSTAL STRUCTURES WITH DISORDER USING THE SHELXTL 5.0 SOFTWARE PACKAGE. Izya F. Burshtein and Charles F. Campana, Siemens Energy and Automation, Inc., Analytical Instrumentation, 6300 Enterprise Lane, Madison, Wisconsin 53719-1173, USA.

In the past, the existence of disorder in crystal structures has often prevented investigators from successfully completing the refinement of such structures, even though the X-ray intensity data were of very high quality. As single-crystal X-ray diffraction is utilized to solve increasingly large numbers of important real-world structural analysis problems, the ability to recognize and solve such problems becomes even more essential. The SHELXTL 5.0 Software Package includes a number of useful tools which allow complex disorder problems to be analyzed, modeled and successfully refined.

We intend to show more than a dozen examples in which the SHELXTL package has been used to model a variety of interesting disorder problems. We will present primarily structures where

the successful modeling of disorder played the key role in the correct interpretation of the diffraction data. Successful modeling and refinement of a disordered structure not only improves R-values but provides a chemically reasonable description of the structure.

We will describe some of the clues that allow disorder problems to be recognized and graphical methods which may be employed to interpret the disorder mechanism and to construct the model. Specific examples of SHELXTL refinement files illustrating new features will be provided.

PS02.01.08 A NEW EXTENSION OF THE 'LEARNT-PROFILE' METHOD. By Ewa Galdecki, Institute of Low Temperature and Structure Research, Polish Academy of Sciences, ul. Okólna 2, 50-950 Wrocław, Poland

As proved by the author, the use of 'learnt profiles' as models of measured X-ray single-crystal diffraction peaks rather than selected 'shape functions' leads to a very effective data processing. The 'learnt profile' can be determined and used in such a way as in appropriate original papers [Clegg, W. (1981), *Acta Cryst.* **A37**, 437, and references quoted therein], but the idea may also be extended. In a system of data-processing computer programs written by the author one may learn the shape(s) of either

- (i) the double peaks (for various ranges of ϑ values), or
- (ii) the single peak (one of the components of the $K\alpha$ doublet), or
- (iii) the crystal profile, that is one of factors of the physical convolution model (the other ones being the spectral distribution for given source of X-rays, and some aberration functions).

In the case (i) of the 'simple learnt-profile' method, one should collect models of the double-peak shapes within a number (say 25-50) of ϑ ranges (the strongest peaks are selected and averaged), the models are stored in their real angular scale. Thus the widths of the peaks are given. These may be adjusted in the next stage. Using the 'basic learnt-profile' method, described in the original papers, case (ii), it is necessary - apart from learning the single-peak shape (stored by the present author in a standardized form, as a spline function) - to derive some information on the width of such single peaks, that is treated as a function of ϑ and the direction cosines. In the case (iii) of the 'convolution' or 'learnt crystal-profile' method, the spectral distribution of the given $K\alpha_1 - K\alpha_2$ line must be known. It should be expressed as a function of angle for respective ϑ values. The function is used for both the crystal-profile determination - via a deconvolution of the observed profile in relation to the spectral distribution - and, in the next stage, for syntheses of the profiles. As results from the author's tests, the efficiency of the methods is very good. Their properties and possibilities will be discussed in detail.

PS02.01.09 COMMENSURATE STRUCTURES DESCRIBABLE IN TERMS OF DEGENERATE IRREDUCIBLE REPRESENTATIONS. By A. David Rae, Research School of Chemistry, Australian National University, Canberra, ACT, Australia, 0200

When trying to understand problems in structure solution and refinement, many structures are best described as commensurate modulations of parent structures with a smaller unit cell. The diffraction pattern may then be described in terms of parent reflections \mathbf{g} and satellite reflections $\mathbf{g} + \mathbf{k}$ where \mathbf{k} has a limited number of values, in the simplest case just one. The Fourier transform of the parent reflections describes a parent structure which is a disordered version of the true structure and is often quite easy to obtain, especially when the inherent disorder is recognised. The satellite reflections then define a modulation of the parent structure and possible resulting symmetries can be