Commission on Crystallographic Teaching
International Union of Crystallography
http://www.iucr.org/iucr-top/comm/cteach/
Newsletter No. 2, November 2007

This issue's theme:
'History of the ORTEP of the Year (OOTY)
Award' and other articles
http://www.iucr.org/iucr-top/comm/cteach/newsletters/

Table of Contents
(This Issue's Editor: Lachlan Cranswick)
(Editors' warning – unless you want to kill 58 pages worth of forest – DO NOT press the "print" button. For hardcopies – you may like to only print out the articles of personal interest.)

THE IUCR COMMISSION ON CRYSTALLOGRAPHIC TEACHING - TRIENNIUM 2005-2008

Chairman: Prof. Paola Spadon
Department of Chemical Sciences
Padua University, Via Marzolo 1
35131 Padova, Italy
Tel: +39049 8275275
Fax: +39049 8275239
E-mail: paola.spadon@unipd.it
WWW: http://www.chimica.unipd.it/

Roberto Baggio
Depto.de Fisica (Lab.TANDAR),
Comision Nacional de Energia Atomica,
Av. Gral Paz 1499, 1650 San Martín,
Pcia. de Buenos Aires,
Argentina
Tel: (54-11-)6772 7109
Fax: (54-11-)6772 7121
E-mail: baggio@cnea.gov.ar

Professor Elena V. Boldyreva
Head of the Chair of Solid State Chemistry,
Novosibirsk State University,
Pirogova, 2,
Novosibirsk 630090,
Russia
Tel: +7-3833-397238
Fax: +7-3833-397845
E-mail: boldyrev@nsu.ru

Professor Susan Bourne
Department of Chemistry,
University of Cape Town,
Rondebosch 7701
South Africa
Tel: +27 21 650 2563
Fax: +27 21 689 7499
E-mail: xraysue@science.uct.ac.za
WWW: http://www.uct.ac.za/depts/cem/academic/sbourne.htm

Professor Gervais Chapuis
Swiss Federal School of Technology,
BSP, CH-1015 Lausanne
Switzerland
Tel/Fax: +41(0)21 693 0630/0634
E-mail: Gervais.chapuis@epfl.ch

Lachlan M. D. Cranswick
Canadian Neutron Beam Center (CNBC),
National Research Council of Canada (NRC),
Building 459, Station 18, Chalk River Laboratories,
Chalk River, Ontario,
Canada, K0J 1J0
Tel: (613) 584-8811 (Ext. 3719)
Fax: (613) 584-4040
E-mail: Lachlan.Cranswick@nrc.gc.ca
WWW: http://neutron.nrc.gc.ca/

K.M. Crennell (UK)
E-mail: KMCrennell@argonet.co.uk

Margaret Kastner (USA)
E-mail: kastner@bucknell.edu

Keichiro Ogawa (Japan)
E-mail: ogawa@ramie.c.u-tokyo.ac.jp

Vinod Kumar Wadhawan (India)
E-mail: wadhawan@barc.gov.in

Consultants

Professor Marek l. Glowka
Institute of General and Ecological Chemistry,
Technical Univ. of Lodz,
ul. Zeromskiego 116
90-924 Lodz, Poland
Tel: +(48)(42)631-31-21
Fax: +(48)(42)631-31-28
E-mail: marekglo@p.lodz.pl

Katherine Kantardijeff (USA)
E-mail: kkantardjieff@fullerton.edu

Reinhard Neder (Germany)
E-mail: reinhard.neder@mail.uni-wuerzburg.de

Prof. Dr. Shigeru Ohba
Department of Chemistry,
Keio University,
Hiyoshi 4-1-1, Kohoku-ku,
Yokohama 223-8521, Japan
Tel: (+81)-45-566-1308
Fax: (+81)-45-566-1314
E-mail: ohba@flet.keio.ac.jp

From the Commission Chair

The XXI International Congress of the IUCr will take place in Osaka in August 2008. In view of this important opportunity, that will gather together crystallographers coming from all over the world, the Commission for Crystallographic Teaching is planning to organize its "traditional" Microsymposium:

MS 11 : Pittfalls and successes in crystallographic teaching
      (chair : David Watkin, UK, and co-chair: Paola Spadon, Italy)

In recognition of the importance of teaching crystallography for the research community, and responding a large interest in the topics related to teaching, the Program Committee has allocated also two more Microsymposia to the Crystallographic Teaching Commission, to be organized in collaboration with the Commission on Crystallographic Computing and with the Commission on Biological Macromolecules:

MS 25 : Crystallographic teaching using new computer and internet based approaches
      (chair : T.N. Guru Row, India and co-chair : A. Le Bail, France)

MS 44 : Teaching macromolecular crystallography
      (chair : Katherine Kantardijeff, USA and co-chair : Bob Blessing, USA)

In addition to the three MS, the Programme Committee has agreed, that a special Workshop (set for the opening day of the Meeting, from 9.00 till 13.00) will be dedicated specially to teaching.

What is good with this Workshop is that all key-note lecturers from the meeting, as well as MS speakers, chairs and co-chairs, as well as the members of the Program Committee are allowed and even welcome to speak at the Workshop. There are no restrictions for the participation in the Workshop also for any of the key-note lecturers from the meeting, as well as MS speakers, chairs and co-chairs, as well as the members of the Program Committee from the previous IUCr Meetings.

In this way we really hope, that a great number of names, who would otherwise be excluded from the list on the formal basis, would contribute.

As tentative topics for the Workshop, we suggest "Teaching crystallography for non-crystallographers" ("Crystallography and Chemical Bonding", "Crystallography and Pharmaceuticals", "Crystallography and New Materials") and "Teaching Advanced Crystallography for Experts" ("Teaching Diffuse Scattering", "Teaching Crystallography of Modulated Structures". Other suggestions are most welcome.

On behalf of the Commission on Crystallographic teaching, I strongly invite all crystallographers to submit contributions for the events organized, making in this way the programme for the Osaka meeting as much exciting as possible.

Looking forward to meet many friends in Osaka.

Paola Spadon (paola.spadon@unipd.it)

The History of the ORTEP of the Year ("OOTY") Award

Richard L. Harlow
Harlow LC, 3837 Tremayne Ter,
Silver Spring, Maryland, 20906, USA
*E-mail: r.harlow@cavtel.net*

My career as a small-molecule crystallographer began in the days of film and manual counter techniques. The importance of the resolution of the data (and subsequent data/parameter ratio) and the accuracy of the intensity data became quickly apparent to this novice as many of the early structural refinements yielded rather bizarre thermal ellipsoids, even some which were non-positive definite. Recording of the intensities by hand and the card-punching the data led to many reflections with large discrepancies between Fobs and Fcalc. These reflections could be dropped from the refinement or the mistakes could be corrected but, in either case, the refined positional and thermal parameter were little changed although the R value, of course, dropped precipitously. Limiting the data to certain 2-theta ranges only made matters worse, and refinements using only the "high-angle" data, for example, gave even more bizarre results. I put the "high-angle" in quotes because, at that time, the data did not extend very far in reciprocal space: most Weissenberg films were taken with Cu radiation and our counter instrument, although using Mo radiation, was very tedious to operate (low intensity tubes, every reflection had to be manually maximized, x-ray exposure issues) so no one took any more data than necessary. Re-collection of the data or re-reading of films often improved the refinement results when the new data was merged with the original set but, generally, the results were still not very satisfying.

I really didn't appreciate how poor these early data sets were until I had the opportunity to collect data on a semi-automatic diffractometer. Much of the tediousness of the data collection was removed and one could extend the 2-theta range without much exertion. I re-collected the data on several of the crystals that I had previous used on the manual instrument. The refinements of the new data gave much more reasonable and consistent bond distances and thermal parameters. With the advent of totally automated diffractometers with low-temperature devices, high quality crystal structures became readily available. Except for bizarre ellipsoids associated with disorder problems. I generally assumed that there should be no further excuse for "bad" (by which I mean chemically unreasonable) ellipsoids as presented in ORTEP drawings.

Enough structures had been reported by the mid 1970's that comparison of bond distances and angles for structures similar to mine was both possible and practical. I then spent a lot of time in the library researching the literature in an attempt to sort out the best structures for a given comparison. One could discount the accuracy of much of the earlier work based on film and manual counter techniques, but I was surprised to find that even many of the recently reported structures had bond distances which were clearly outside of their expected values. I also noted that these structures often had weird-looking ORTEP drawings. Some of these were associated with disorder but, otherwise, the reasons for the chemically unreasonable bond distances and thermal ellipsoids were not discussed. Many of my previous refinements on structures which had space group ambiguities had taught me that strange bond distances were often associated with the high correlations that exist in refinements using space groups of lower than actual symmetry. I therefore assumed that many of the "problem" structures had been refined in the wrong crystal system and/or space group. The point was brought home when I read in one such report that the crystal grew as "hexagonal pillars" but the structure was refined in a monoclinic space group. A quick transformation of the unit cell showed that it was, in fact, hexagonal.

It was at this point that I moved to DuPont. Armed with a brand-new automated diffractometer, I was quickly turning out structures for the hoard of organic and inorganic chemists then present at the company. I was then asked to present a series of short lectures on X-ray crystallography without using mathematics. I was surprised to find the course entitled "Crystallography for Chimpanzees" very well attended, in part because the speed of a structural analysis was now comparable to that of more traditional techniques like NMR and in part because DuPont managers were easily impressed by a molecular

"picture". ORTEP drawings became part of a large number of research presentations and almost everyone wanted one. The course focused on some of the fundamentals but I found that the most common point of interest was around the issue of how a chemist could tell a reliable crystal structure from an incorrect one, especially after I harped on the low reliability of R values for this purpose. I then concentrated on the quantity and quality of the data (data/parameter ratio, resolution, low-temperature data) and on the results of the refinement (chemically reasonable bond distances and angles, inclusion of the hydrogen atoms, the ORTEP drawing). To emphasize the latter, I presented a number of ORTEP drawings of problematic structures. I doubt that the chemists ever really learned much about crystallography, but they remembered the "bad" ORTEPs.
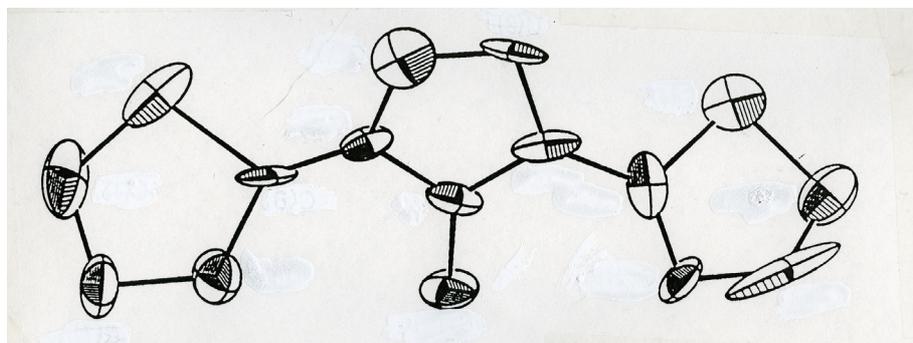

Fig. 1: *ORTEP which is responsible for the OOTY award. Incorrect space group assignment was later corrected by the original authors.*

One such chemist, Joel Miller (now at the University of Utah) came to my office one day with one of the most ugly ORTEPs I have ever seen (Figure 1). It was immediately clear that the structure should have been refined in the alternative centrosymmetric space group. He suggested that I should have an "ORTEP of the Year Award" so that DuPont chemists, as they are combing the literature, would pay more attention to the molecular drawings. At the time, I myself was struggling with literature searches: even though the Cambridge files could now be searched by computer, the stored data did not contain the thermal parameters and so I had to resort to the original literature to check on each questionable structure. With all of my frustrations dealing with "wrong" structures, I decided to adopt Joel's suggestion but it was clear that I needed to go national or international if I was ever to eliminate the plethora of incorrect structures. Thus, I placed the first announcement for the "OOTY" award in the ACA Newsletter: I would pay $100 for the best example of a "bad" ORTEP in the open literature with the prize to be given out at the next ACA meeting. Figure 2 shows a couple of classic ORTEPs which were submitted.
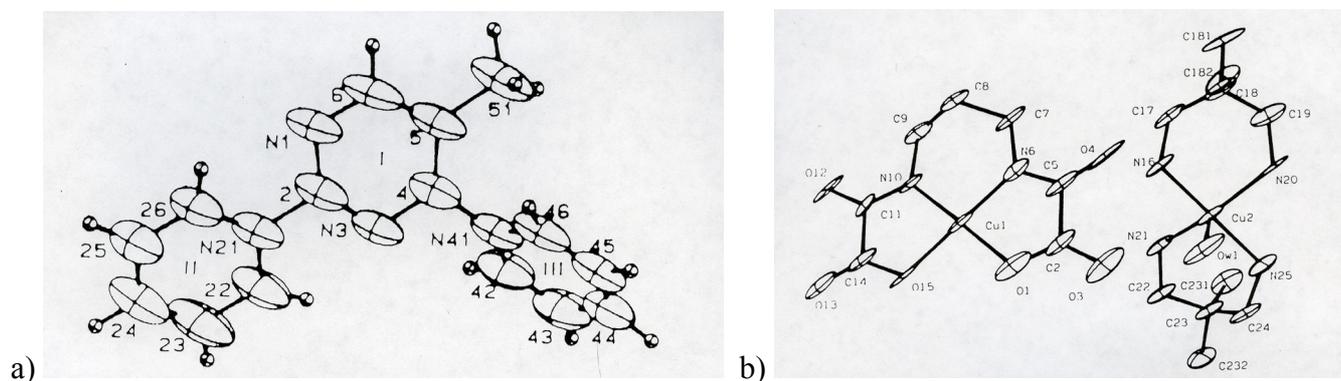

Fig. 2: *(a) Data collected on a windy day and (b). during a "noreaster"? It has been suggested that these folks simply failed to match the output of their least-squares program with the appropriate input for ORTEP. You'd think the reviewers might have said something.*

Over the years, I increased the amount of the prize to $200 but I added the stipulation that the authors had to tell me what was wrong with the original structure. For chemists, just to notice that something "looked" wrong was about all I could ask, but crystallographers should be able to figure out what went wrong. At the same time, I attempted to place an advertisement in the ACS journal, C&E News, in order to reach chemists who did crystallography on the side because I found that they were the source of most of the incorrect structures over the years – Chem. Comm. and JACS proved to be most fertile ground for incorrect structures. However, the ACS totally blew me off. While there had also been attempts over the years by various ACA officials to discourage/eliminate the presentation of the "OOTY" award, I must say that I always had a number of strong supporters who realized the basic educational and awareness value of the award. Although the venue for the award was shifted from the main banquet to the small-molecule/service SIG meetings, it was never suppressed. After all, the protein people were not interested in "bad" ORTEPs and, of course, they hardly ever got a structure wrong.

Figure 1. ORTEP drawing of the $[ReO(H_2pmen)Cl_2]^+$ cation
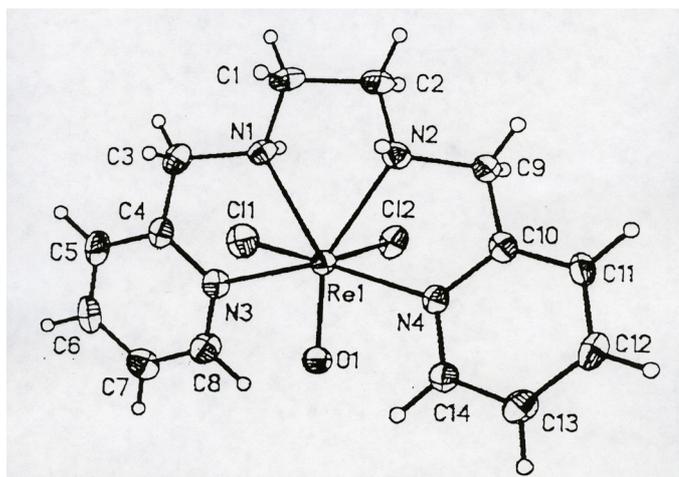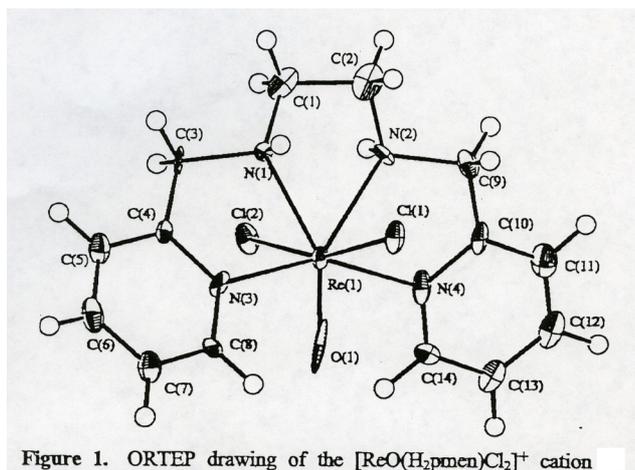
Fig. 3: *a) ORTEP that was about to be published reportedly based on poor data and improper absorption correction. It appears that the oxygen site may have been contaminated with Cl as in the examples of "bond-stretch isomers". (b) Structure based on high quality data and proper absorption correction.*

Since I retired from DuPont seven years ago, most of my OOTY archives have been trashed so I can't produce a list of winners and their contributions. In general, I think it is obvious that missing symmetry is probably the number one cause of "bad" ORTEPs (Figure 3), but missing weak reflections (systematic extinctions and superlattices) and misinterpreting chemical (e.g. bond-stretch isomerism studies) and physical (see Figure 4) disorder follow close behind. Of course, poor data collection precedures and improper absorption corrections may still contribute (Figure 5). One case of clear fraud was discovered, not by viewing the ORTEP directly (because it had been doctored) but by noting that the submitted thermal parameters did not match those shown in the ORTEP diagram.
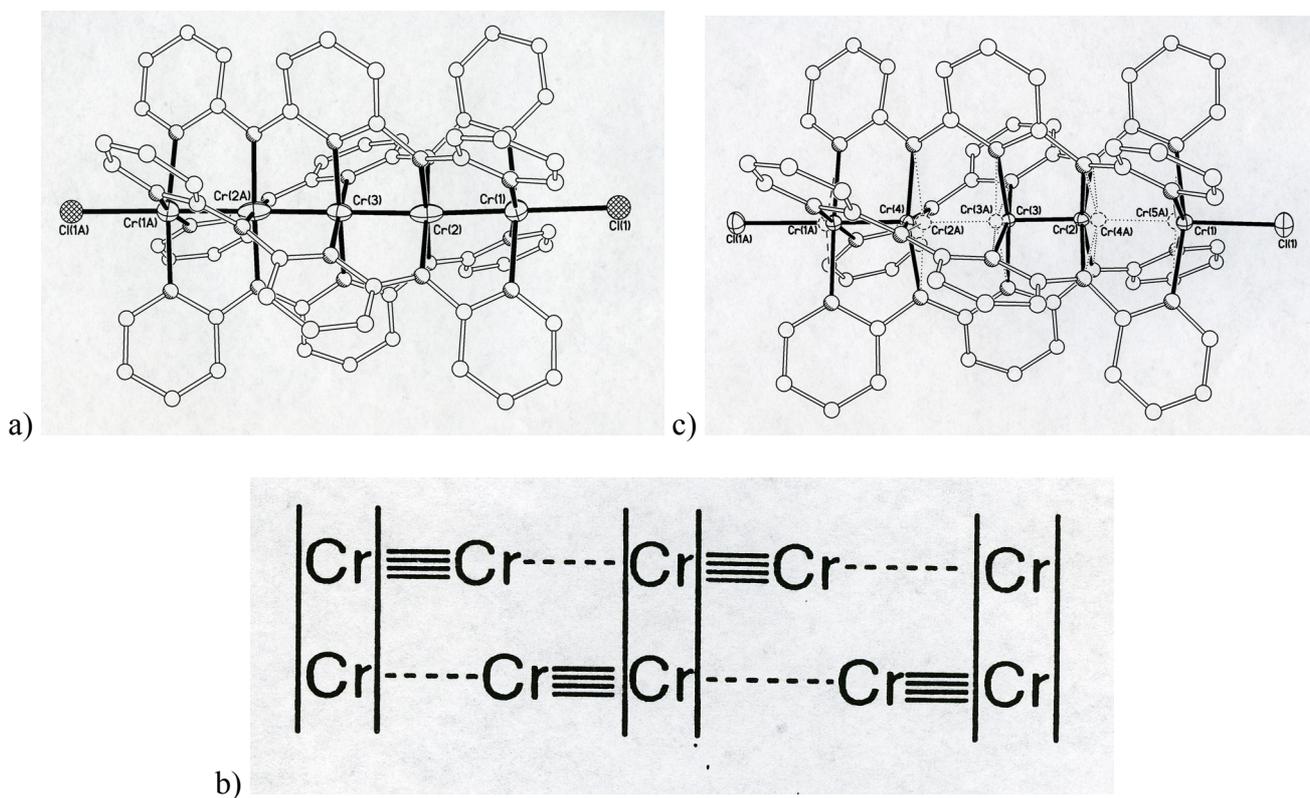
Fig. 4: *The four equivalent Cr-Cr bonds in (a) were corrected using a disordered model (b) with the resulting ORTEP shown in (c).*
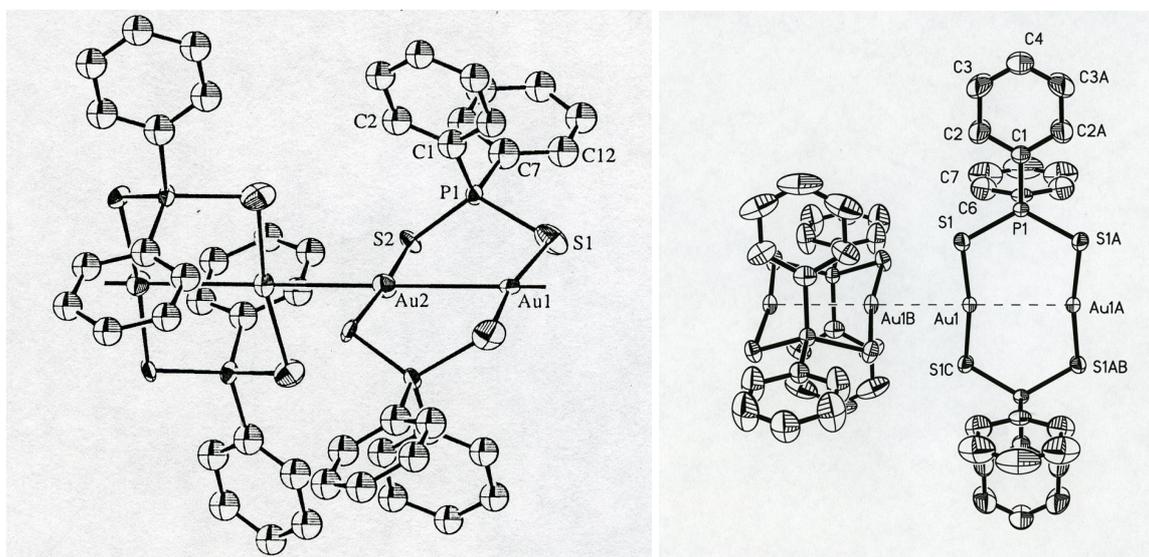
Fig. 5: *a) Structure refined in space group I4. Structure correctly refined in I4/m.*

The Award came to end when I left DuPont (Figure 6). The programs that Joe Calabrese had developed on my behalf to analyze problem structures along with the structural databases and library tools were no longer available to me. One of my biggest concerns was the advent of refinement software which would allow even the most inexperienced people to restrain, constrain, and otherwise control each of the atomic thermal parameters. This clearly pointed to a future where it would be much harder, if not impossible, to detect incorrect structures directly from the ORTEP drawings. Every ORTEP drawing could now be made "perfect".
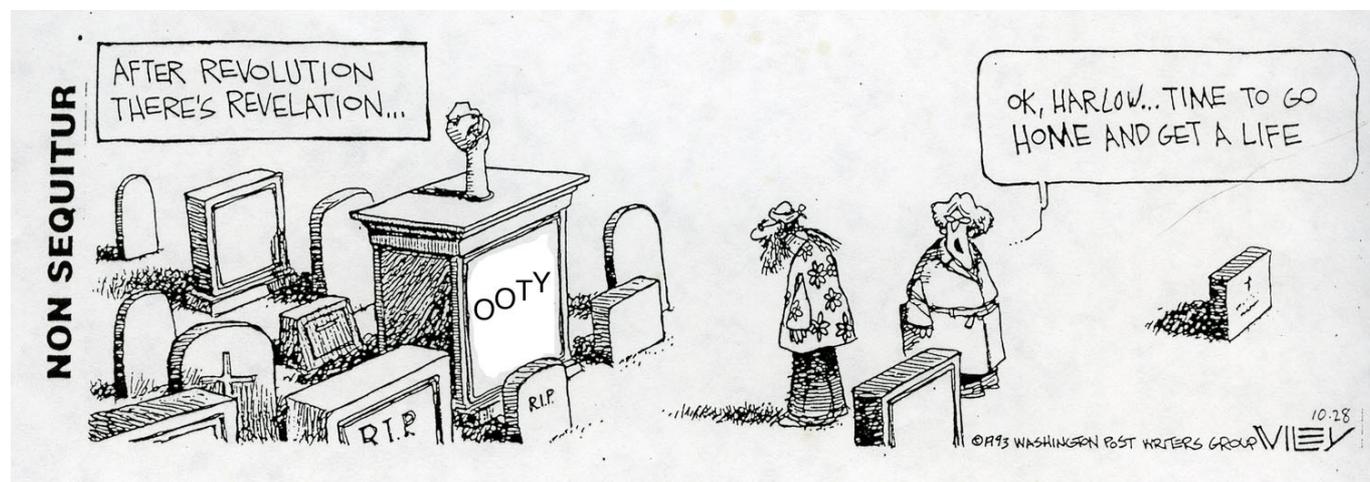

Fig. 6: *It's over.*

So, to end this history, I want to thank Carroll Johnson for developing the ORTEP program, Joel Miller for planting the seed for the OOTY award, Joe Calabrese for developing software to help me analyze structures, all the contributors and winners, and those ACA members, as noted above, who supported the award even risking embarrassment should one of their structures be nominated. Only one structure by a ACA member ever reached even the nomination stage. Finally, I need to thank the infamous R. Harlow Foundation for Disabused Crystallographers for putting up the funds for the prize and the occasional beer money.

Addendum

I would like to add a comment regarding structure validation software and the CIF format that were developed over the last 25 years or so. When I started OOTY "out of frustration", I could pick up any copy of Acta Cryst. and find funny ORTEPs. In fact, I prided myself on being able to show any chemist who showed up at my office door a "bad" ORTEP just by opening up a random copy Acta Cryst. C. When the award ended a dozen years later, I could no longer find any good examples of "bad" ORTEPs in Acta. I'm sure that this had little to do with OOTY award, but I commend the editors for taking a strong stand on structure validation and I thank all those who worked on the CIF format and the software to validate crystal structures. I wish the ACS journals would take validation just as seriously -- if it hasn't already.

Richard L. Harlow
Harlow LC, 3837 Tremayne Ter,
Silver Spring, Maryland, 20906, USA
E-mail: r.harlow@cavtel.net

Place-holder page. Reprint starts on following page.

Troublesome Crystal Structures: Prevention, Detection, and Resolution

Richard L. Harlow

Central Research and Development
E. I. Dupont de Nemours &
Co., Inc.
Wilmington, DE 19880-0228

A large number of incorrect structures is being published today. These structures are proving to be a particular problem to those of us who are interested in comparing structural moieties found in the databases in order to develop structure-property relationships. Problems can reside in the input data, e.g., wrong unit cell or low quality intensity data, or in the structural model, e.g., wrong space group or atom types. Many of the common mistakes are, however, relatively easy to detect and thus should be preventable; at the very least, suspicious structures can be flagged, if not by the authors then by the referees and, ultimately, the crystallographic databases. This article describes some of the more common mistakes and their effects on the resulting structures, lists a series of tests that can be used to detect incorrect structures, and makes a strong plea for the publication of higher quality structures.

Key words: fuzzy structures; incorrect structures; *R* value; single-crystal structures; thermal parameters.

1. Introduction

The determination of crystal/molecular structures by x-ray single-crystal diffraction methods has been blessed with three characteristics that render it absolutely unique as an analytical technique. First, the technique is very robust: structures can be extracted from diffraction data even when they suffer from severe statistical and systematic errors. Second, there are numerous checkpoints along the path of a structure determination which can be used to guide one to the correct structure or, at least, guide one away from an incorrect structural model. Finally, if done correctly, the result is a very cost-effective "picture" of the atomic arrangement with a large amount of information content: bond distances, coordination geometries, thermal motions, intermolecular interactions, etc.

With the automated data collection procedures, low-temperature capabilities and computer analysis packages available today, the conversion of diffraction spots into a crystal structure ought to be perfectly straightfor-

ward for the average molecular crystal and only somewhat more difficult for inorganic structures where problems with absorption, twinning, pseudosymmetry etc., are more common. As it turns out, however, a fair number of "wrong" structures are being published each year which indicates that the authors, the reviewers, and the editors have all failed to recognize one or more symptoms of incorrect structures. My definition of an "incorrect" or "wrong" structure, by the way, is simply that one or more of the critical crystallographic outputs, namely the unit cell, the space group symmetry, the types of atoms and their positional and thermal parameters, have been improperly determined and reported. No one knows how many incorrect structures have been placed in the crystallographic databases but, in spite of repeated reviews on the subject [1,2,3], the number is obviously continuing to grow: each review contains far more examples than the previous one. The purpose of this chapter is to examine even more examples of

troublesome structures in order to understand better how incorrect structures can be detected and hopefully resolved before they get into print and into the databases.

2. Structure Classifications

2.1 Quality Structures

It is useful to point out that crystal structures, in my opinion, fall into one of four classifications. First, there are *quality* structures. These are structures in which all of the atoms, including the hydrogen atoms if present, have been refined to yield reasonable positional and thermal parameters. Hydrogen atoms in organic and organometallic structures are true indicators of the quality of both the data and the structural model. I maintain that if you can refine the hydrogen atoms (isotropic thermal parameters, B, that are less than 6.0 $Å^2$ and all of the C–H bonds are between 0.85 Å and 1.05 Å), the data must be of high quality and the model must be correct. Oxygen atoms in an inorganic oxide can serve the same purpose but the M–O distances can be more variable and the oxygen atoms, in this case, must be refined with anisotropic thermal parameters. Of course, all of the anisotropic thermal parameters should be reasonable, both in magnitude (for organic and organometallic structures, no Beq greater than 5 A^2; for inorganic structures, no Beq greater than 2.5 A^2) and in shape (cigar- and disk-shaped ellipsoids generally eliminate a structure from the quality classification; adjacent atoms vibrating in orthogonal directions is also an unacceptable feature). Chemically-equivalent bonds, particularly C–C bonds, should have equivalent bond distances. Finally, quality structures are, of course, characterized by good R ($R = \Sigma \left| |F_0| - |F_c| \right| / \Sigma |F_0|$) values.

2.2 Fuzzy Structures

The second category, which includes most of the structures being reported today, contains the *fuzzy* structures. These are firstly and primarily characterized by good R values. This group contains most of the organic and organometallic structures which have been solved and refined with "room-temperature" data. Hydrogen atoms, if included at all, refine to poor positions with widely variable, generally high, thermal parameters, or are "idealized." These structures may contain atoms with strange-looking anisotropic thermal parameters, atoms which have been constrained or restrained in some fashion, and/or "disordered" atoms. They also may have considerable variation in their chemically-equivalent bond distances and may even have bond distances which are unreasonable when compared to those in related structures.

2.3 Incorrect Structures

The third category consists of the *incorrect* structures. These, unfortunately, have all of the same characteristics of the *fuzzy* group, including low R values, and so the two are often hard to distinguish at first glance. Generally, however, their problems are more severe: improbable coordination geometries, bizarre bond distances and angles, impossible intra- and intermolecular contacts, and nonpositive-definite anisotropic thermal parameters.

2.4 Junk Structures

The last category includes all the structures with high R values. A low R value, characteristic of correct as well as incorrect structures, obviously has very little meaning, but a high R value sends a clear message that something is very wrong. The adjective "high" is both structure dependent, i.e., what types of atoms are present, and procedure dependent, i.e., were all the data or only the "observed" data used in the refinements? Nonetheless, structures with R values well above 0.15 (based on "observed" reflections!) continue to be published. I have decided to exclude structures in this category from further consideration because there are no useful lessons to be learned from them (unless, of course, you're interested in publishing such a structure and want to know which journals still accept them).

3. Examples of Troublesome Structures

I have tried to select a wide variety of examples which emphasize particular crystallographic problems. The unique symptoms and the ultimate disposal of each case will be described briefly. Most of these examples were not included in the earlier reviews [1,2,3]: in Sec. 4, I will attempt to summarize the lessons that can be learned from all of these sources.

3.1 Incorrect Laue Group/Space Group Symmetry

Probably the most common error in crystal structures relates to incorrect symmetry, particularly cases where the assigned symmetry is too low. Refinements are often done in the wrong space group and sometimes in the wrong Laue group. Marsh [4a] and Baur [4b] have published extensively on this type of mistake and by now there is a clear picture of the kind of symptoms that these structures exhibit. A particularly good example [5] is shown in Fig. 1.

This structure was refined in noncentrosymmetric space group $Pca2_1$ when it should have been refined in centrosymmetric Pcam (Pbcm). Not only are the
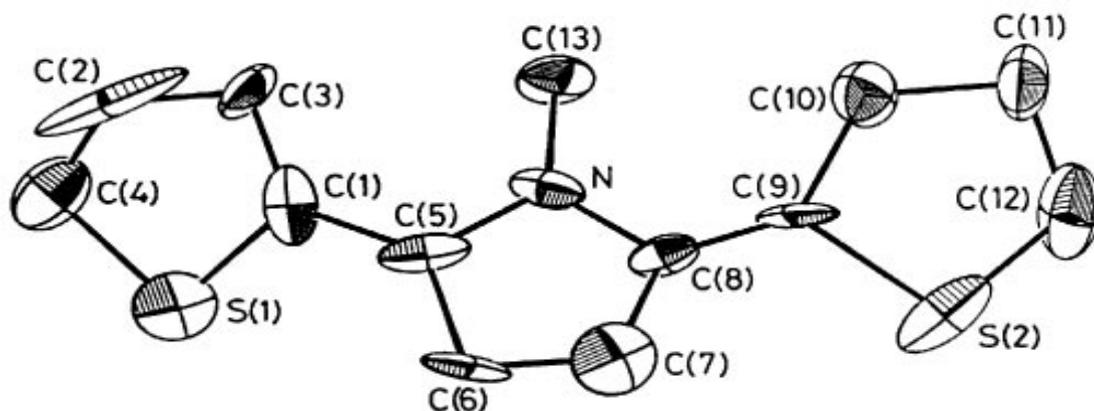
Fig. 1. Thermal ellipsoid drawing of 2,5-*bis* (2-thienyl)pyrrole.

thermal ellipsoids nonsensical, but the chemically-equivalent bond distances such as S(1)–C(1) and S(2–C(9) differ by 0.10 Å. These symptoms are caused by the high correlations between positional and thermal parameters of atoms in the two halves of the molecule which are actually related by a mirror plane in Pcam. Although a re-refinement of the structure has yet to be carried out in Pcam, the mirror planes which are perpendicular to the *c*-axis can be seen quite clearly in a packing diagram.

Cases where the assigned symmetry is too high appear to be rather rare. This is probably true because the *R* values tend to "hang" at unacceptable levels which makes these structures difficult to publish. Lowering the symmetry, generally dropping from a centrosymmetric to a non-centrosymmetric space group, often resolves the problem with the *R* values. If left in the higher symmetry space group, the model is forced to fit the "average" of the two asymmetric units which are only approximately related by the imposed crystallographic symmetry. Experience in our laboratory and elsewhere [6] suggests that such a structure will either contain atoms with enlarged anisotropic thermal parameters or will appear disordered.

3.2 Incorrect Atom Types

The second most common error is the incorrect identification of atom types. The next structure was reported to be the first monomeric rhodium(II) complex containing two phosphine and two chloride ligands [7]. If true, one would have to explain why the Rh–Cl bonds, 2.428 Å, are much longer than expected and why the chloride ligands have large thermal motions parallel to the Rh–Cl bond as shown in Fig. 2.

In addition, rhodium(II) should be paramagnetic and yet the ^{1}H NMR spectrum is quite "normal," indicative of a diamagnetic compound. Both of these anomalies can be explained if the compound is actually a rhodium(I) complex with one Cl and one CO (or N_2) ligand. As a disordered structure (the Rh sits on a crystallographic inversion center), the "thermal" ellipsoid associated with the Cl atom has been forced to fit the three half-occupied C, O, and Cl atoms, necessarily elongating it in the direction of the bond. In addition, the center of the electron density has shifted away from the rhodium atom, lengthening the apparent Rh–Cl bond. This structure was recently re-examined in more detail [8]; a model based on a disordered Cl and CO refined very well. A true dichloride has also been published and is pictured in Fig. 3 [9]. It shows both a normal Rh–Cl bond of 2.298 Å and a thermal ellipsoid elongated perpendicular to the Rh–Cl axis.

In the case just described, the thermal ellipsoid had an usual shape but not an unusual size. This is basically because the CO group has roughly the same number of electrons as the chlorine. If the identity of an atom, especially a "heavy" atom, is mistaken, the thermal ellipsoid will be proportionately larger or smaller, depending on the difference in the number of electrons between the real atom and the atom used in the model. Such was the case in two compounds with the general formula $Ph_3C_6H_2M$, where M = Cu and Ag. These compounds, if correct, would have been unique because the metal atoms have a coordination number of 1! The original paper [10] was published with only a packing diagram with the molecules represented by balls and sticks. Lacking any visualization of the thermal ellipsoids, there was little indication that the atom types were incorrect except for the fact that the Cu–C and Ag–C bond lengths were virtually identical, something not
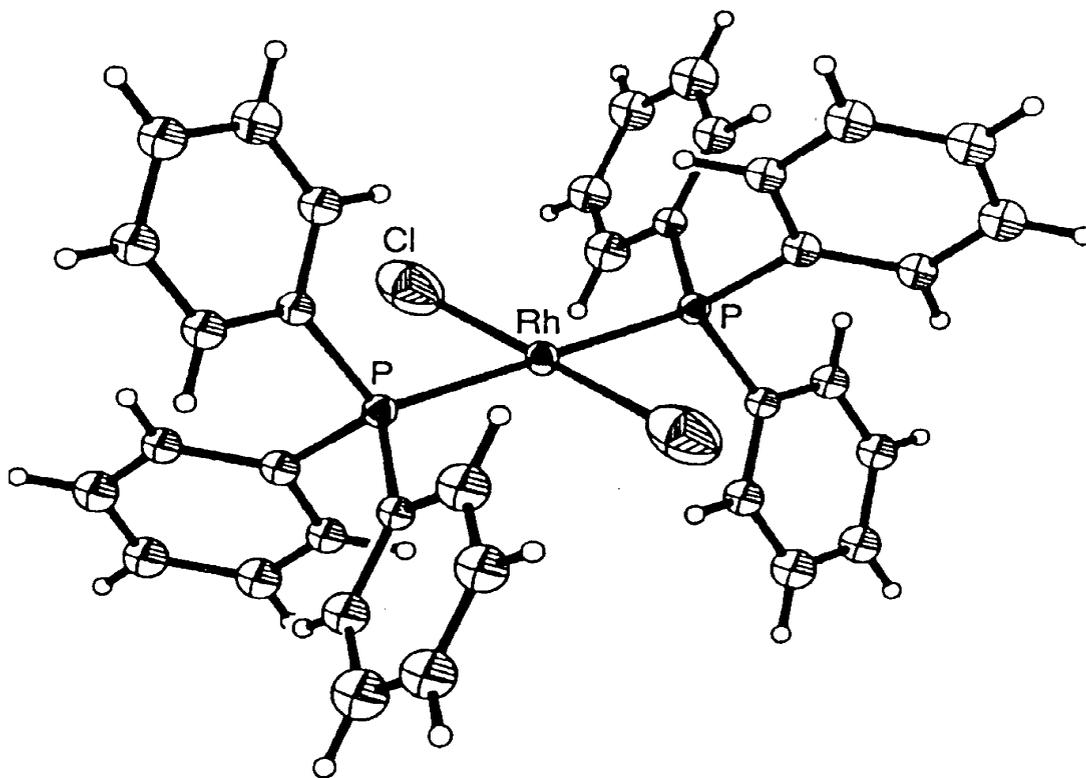
Fig. 2.   Thermal ellipsoid drawing of *trans-bis*-(triphenylphosphine)-rhodiumdichloride.
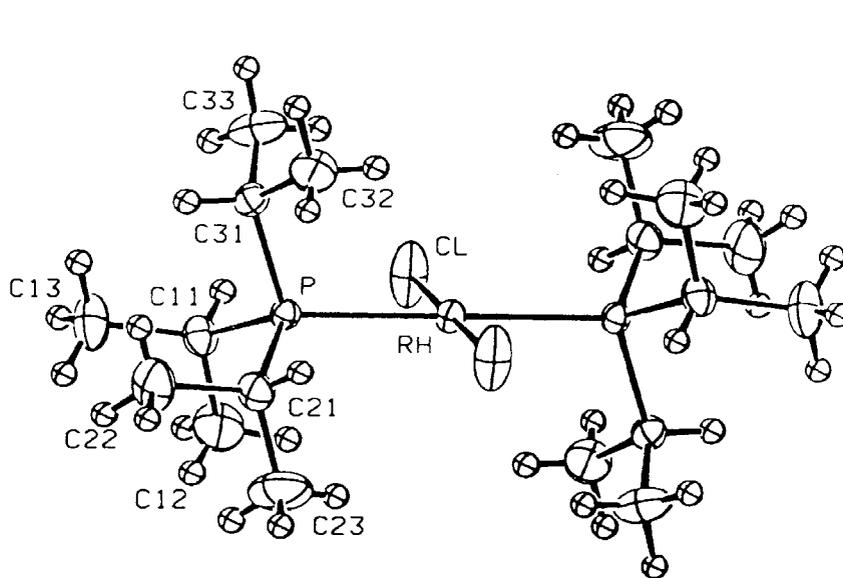

Fig. 3.   *Trans-bis*(tri-isopropylphosphine)rhodiumdichloride.

expected for a first- and second-row transition metal. These structures were ultimately reinvestigated [11] and found to be bromides. Figure 4 shows both the incorrect structure refined as a Ag complex and the correct structure where the atom is refined as a Br. The thermal ellipsoid of the Ag atom, in spite of being the heaviest atom in the structure, is much larger than those of the carbon atoms.
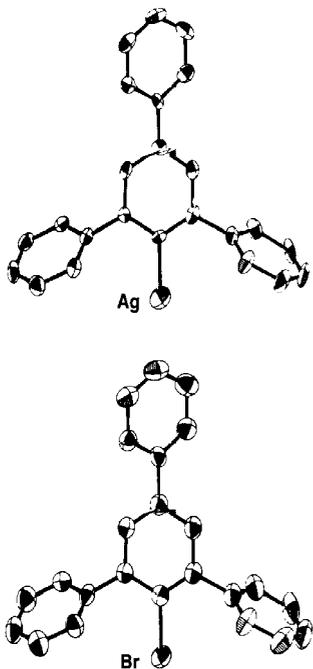
Fig. 4. Thermal ellipsoid drawings of 2,4,6-triphenylbenzene bonded to a single atom of Br in the correct structure, Ag in the incorrect structure.

Perhaps more insidious are the cases where one atom type partially substitutes for another. Crystallization of compounds with the general formula $MoOCl_2(PR_3)_3$ led to both blue and green crystals. Crystal structures for a number of compounds with different R substituents showed the blue form had the expected structure with a short $M = O$ distance while the green form had a much longer $M–O$ bond, more indicative of a single bond rather than a double bond. The term "bond-stretch isomers" was coined for these complexes in which the orbitals of the Mo atom could presumably rehybridize to accommodate either a single or double bond to the oxygen atom. All of this was eventually shown to be incorrect [12]: the oxygen site in the green crystals was partially occupied by a chlorine atom. Since chlorine is a stronger scatterer than oxygen, and since a Mo–Cl bond is much longer than a Mo = O bond, it only takes a small contamination of the site to significantly lengthen the

bond. It is interesting that the thermal ellipsoids of the the oxygen atoms in the green crystals do not show any significant elongation in these cases. In other examples of possible bond-stretch isomerism, in particular the $NbOCl_3(PMe_3)_3$ series, the thermal ellipsoids did give some warning that the oxygen site was contaminated with chlorine [13].

3.3 Incorrect Unit Cells/Bravais Lattices

Automated indexing software on today's diffractometers makes the job of determining a unit cell and its Bravais lattice trivial. Unfortunately, the unit cell which comes out is only as good as the reflections which are put into it. If the reflections are not representative of the true cell, wrong unit cells will result. This is of particular concern when a superlattice is present since only the strong reflections are generally used in the indexing routine. It is equally unfortunate that the autoindexing routine is often not followed up with a series of oscillation photographs to look for weak superlattice reflections or reflections which might alter the Bravais lattice. Missing a superlattice or mistakenly assuming a centered lattice results in an "average" structure in which many of the atoms may have unusually large thermal parameters and/or appear disordered.

Such was the case in the structure of the usual tetramer shown diagrammatically in Fig. 5. Based on "room-temperature" data, the structure was solved and refined in space group I2/m [14].
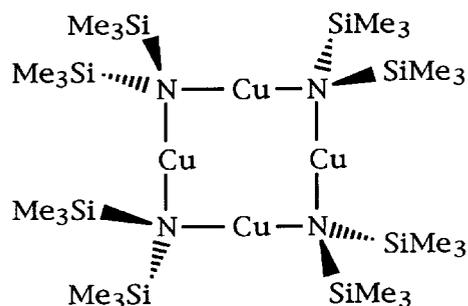
Fig. 5. Chemical structure of a $[CuN(SiMe_3)_2]$ tetramer.

Although the thermal ellipsoids have not been shown, the U_{eq} for many of the methyl carbons are very large. A great deal of effort was expended by the authors to improve the structure by using DIFABS, applying extinction corrections, and attempting refinements in I2 and Im. None of these worked. The real problem with the structure is that the cell is not body-centered but

primitive, P2/n [15]. The weak reflections, which are clearly observable even at room temperature, had been missed by the original authors. A comparison of the ORTEP drawings for the incorrect and correct structures is given in Fig. 6. In the correct structure, the methyl carbons have the expected staggered conformation; in the incorrect structure, their positions are averaged to give an eclipse conformation, the large ellipsoids being required to account for the smeared electron density (actually, this structure probably would have refined better if a disordered model had been used for the methyl carbon atoms).
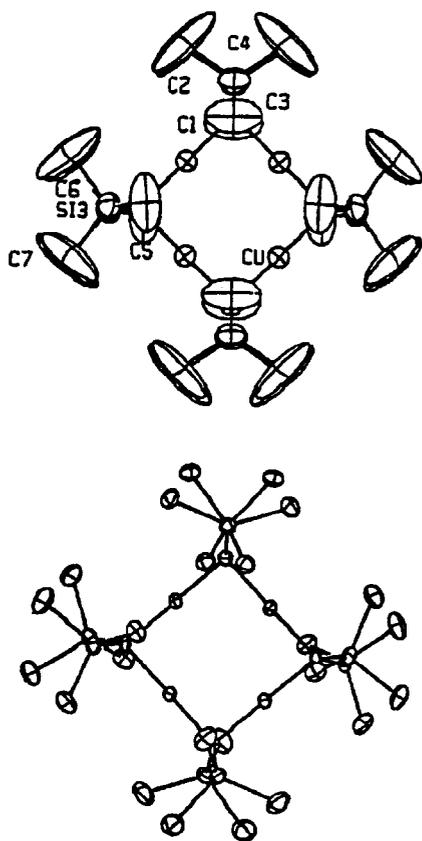
Fig. 6. Thermal ellipsoid drawing of the [CuN(SiMe₃)₂] tetramer as refined in space group I2/m (top). Same structure refined in P2/n (bottom).

As a second example, we have investigated the structure of Sr_2IrO_4 which, on first appearance, crystallizes in a small tetragonal cell: $a = 3.89$ Å, $c = 12.90$ Å [16] with space group I4/mmm. Refinement of the structure showed that it consisted of sheets of IrO_6 octahedra, corner-shared with Ir–O–Ir angles of exactly 180°. Two problems arose, however: the anisotropic thermal ellipsoid of the unique in-plane oxygen atom was severely elongated perpendicular to the Ir–Ir vector and the com-

pound showed ferromagnetic behavior which is not possible if the compound is truly I4/mmm. Careful studies using single-crystal photographic and synchrotron powder-diffraction techniques eventually revealed seven superlattice reflections: the cell, in fact, had a volume four times that of the original cell. An investigation of a single-crystal on an in-house, sealed-tube diffractometer showed that only one of these reflections had a measured intensity above the three sigma level under "normal" operating conditions. The structure, as shown in Fig. 7, was eventually refined using neutron powder diffraction data (where the superlattice reflections were more easily seen) and yielded a structure in which the IrO_6 octahedral layers were rotated by ±11°, making the Ir–O–Ir angle 157.9° [17].
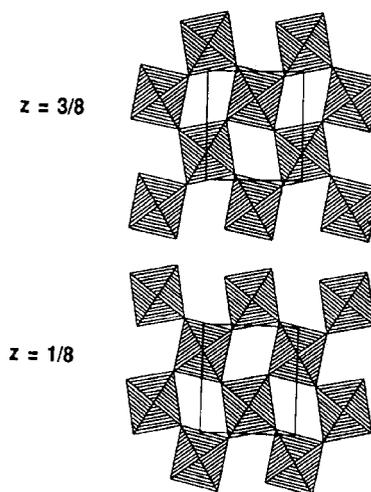
Fig. 7. Two layers of the Sr_2IrO_4 structure showing the rotation of the IrO_6 octahedra. Only the in-plane oxygen atoms contribute intensity to the superlattice reflections.

3.4 Wrong Site Symmetry

Many space groups offer the possibility of placing an atom on more than one type of site symmetry. On discovering that cis-$(C_6H_{13}N)_2PtCl_2$ crystallizes in space group Pbcm with $Z = 4$, it was quite natural to assume that the Pt atom must sit on a 2-fold axis rather than on an inversion center. The structure of this complex was subsequently solved, refined ($R = 0.054$) and published [18]. A thermal-ellipsoid drawing was not provided but the structure, as shown in Fig. 8, is quite unusual in the sense that the Pt atom adopts a flattened tetrahedral coordination rather than a square-planar geometry found for virtually all other 4-coordinate Pt(II) complexes.
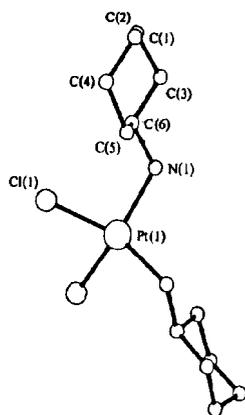
Fig. 8. Ball-and-stick model of the presumably *cis-bis*(cyclohexylamine)-platinum dichloride when the complex was placed on a crystallographic 2-fold axis.

A year later, the structure of the trans-complex was reported [19] with no reference to the earlier work on the *cis*-complex. Its structure ($R = 0.041$) is shown in Fig. 9 and appears quite normal, at least in terms of the Pt coordination.

Several years later, the two structures were compared [20] and it was noted that they had identical lattice parameters and space groups. Clearly, the *cis*-complex was incorrect: apparently, the compound underwent an isomerization to the trans form during the recrystallization process.

3.5 Hydrogen Atoms

It is often claimed that hydrogen atoms are sometimes difficult to locate and refine. If authors insist on relying on "room-temperature" data, I might agree. With "low-temperature" data, however, there is very little excuse unless absorption or disorder effects cannot be ade-

quately dealt with. Hydrogen atoms are not only important from a structural point of view (omitting them causes some shift in the positions of the atoms that they are bonded to) but also from a chemical viewpoint in terms of establishing the exact chemical formula: hydrogen bonded dimers, hydride formation, etc. One example of the latter is the structure of $Cp*Co(H)_3CoCp*$ which recently made headlines when it was reported as $Cp*Co=CoCp*$, the first true example of a metal-metal multiple bond in which there were no bridging atoms [21]. The structure was met with some skepticism and, almost immediately, a reinvestigation showed that there were three bridging hydrides which had been missed in the original study [22].

3.6 Polar Space Groups

Structural solutions and refinements of compounds which crystallize in polar space groups have been known for a long time to be problematic. Choosing the wrong polarity can lead to incorrect bond lengths whenever atoms with significant anomalous scattering are present. I have no specific examples where structures with the wrong polarity have been published but the nature of the problem was clearly pointed out some years ago [23]. Besides the polarity issue, these structures are often plagued with elements of pseudosymmetry. This is particularly true whenever the compound contains a single "heavy" atom which dominates the scattering. The basic problem stems from the fact that placing *one* atom, heavy or otherwise, in a general position in a unit cell with polar symmetry often generates additional symmetry elements.

Recent examples of this phenomenon include the structures of two tungsten complexes, $W(PMe_3)_4H_2Cl_2$ and $W(PMe_3)_4H_2F_2(H_2O)$ [24], the former having been corrected before publication and the latter being a reinvestigation of an incorrect structure [25]. The space group in both cases was $Cmc2_1$ and wrong structures were readily obtained and refined to reasonable R
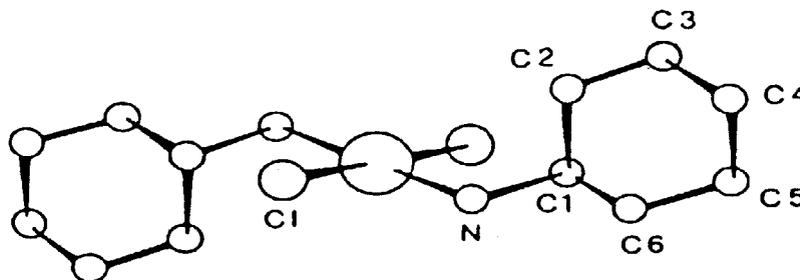
Fig. 9. Structure of *trans-bis*(cyclohexylamine)platinumdichloride when the complex was placed on a crystallographic inversion center. The size of the atoms is arbitrary; the spheres are not thermal ellipsoids.

values. The incorrect structures in these cases contained some atoms from the "real" structure and some from the "pseudosymmetric" structure, in this case produced by a pseudo mirror plane perpendicular to the c-axis. The real structure is produced when the axial phosphine ligands tilt towards the equatorial chloride ligands; the incorrect structure has them tilting toward the equatorial phosphines. When refined, both structures will converge very nicely with the incorrect structure converging to a false minimum. Even if one atom is placed in an incorrect position which differs from the correct position by only an Å or so, the least-squares technique will fail to shift the atom to the correct position. This was clearly demonstrated for the structure of $W(PMe_3)_4H_2Cl_2$ where the axial phosphorus atoms (related by a real mirror plane) were manually translated from their incorrect to their correct positions as shown in Fig. 10 [26].

What is particularly worrisome about the incorrect structures in these cases is that neither the thermal parameters nor the bond distances gave any strong indication that the structures were wrong. Close contacts between the hydrogen atoms (if calculated in assumed positions) gave the only warning that something was amiss.

We have found, however, that both the bond distances and the thermal parameters may be quite telling if the data are collected at low-temperature where the high-angle reflections are well represented. We have recently encountered another "problematic" structure involving one heavy atom, Hg, in the same polar space group, $Cmc2_1$: $[(C_5H_8N_2)_2Hg]Cl_2$ [27]. Whenever atoms from both the real and pseudosymmetric images were included in the refinement, some of the bond distances and thermal parameters associated with "light" atoms (carbons and nitrogens) of the organic ligands became unreasonable. Also, the hydrogen atoms could not be refined properly when the model contained atoms from each image. When the correct model using all atoms from the same image was refined, not only were the bond distances and thermal parameters reasonable but the refinement of the hydrogen atoms was also possible.

3.7 Disorder

As I have already noted, disorder can have a variety of origins: wrong unit cell, wrong Bravais lattice, partial occupancies, etc. Sometimes, however, a structure can be truly disordered (multiple atomic sites) and the problem be misinterpreted. One such case was the crystal
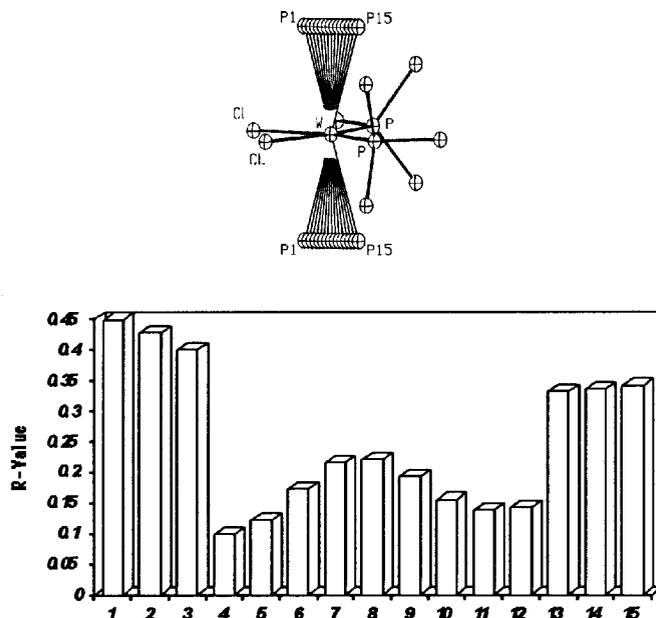
Fig. 10. Partial structure of $W(PMe_3)_4H_2Cl_2$ (top). The two axial phosphorus atoms (without the methyl groups) were placed at a series of positions from P1 to P15, with the pseudo-mirror being located at P8. The resulting R value for each of these positions is shown in the (bottom) graph. In the correct structure, these phosphorus atoms refine to position P4, the real minimum. In the incorrect structure, they refine to position P12, a false minimum. Thus, once an atom is placed at a pseudo-image position, it is trapped there.

structure of *trans*-4-chloro-2,4,6-*tris*(trichloromethyl)-1-*oxa*-3,5-dithiane [28]. This compound was made by adding Cl_2 across a C=C of a precursor molecule. Its structure has two molecules per asymmetric unit, one of which appeared quite normal: the $C=CCl_2$ moiety had been converted to $Cl-C-C-Cl_3$ with typical C–Cl distances of 1.79 Å and a C–C bond length of 1.55 Å The second molecule, however, appeared to have been caught mid-stream in its reaction with the Cl_2 to give a $Cl-C=CCl_2-Cl$ moiety where the C–Cl bonds were now greater than 2.07 Å and the central carbon-carbon bond was 1.28 Å. These authors either didn't look at the thermal ellipsoids or ignored them. Shown in Fig. 11 are the ORTEP drawings of the molecules given as part of a reinvestigation of this structure [29].
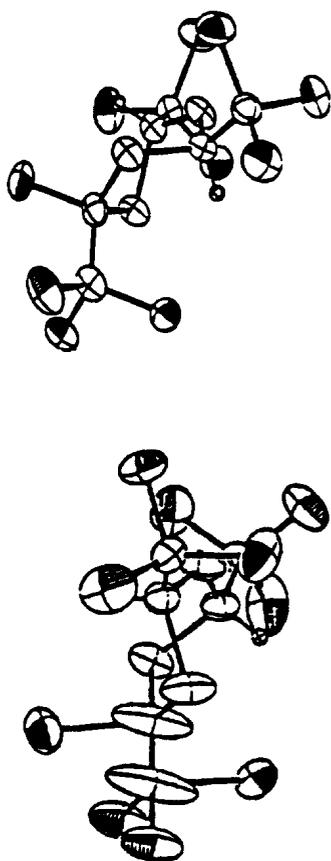
Fig. 11. Thermal ellipsoid drawings of the two molecules of *trans*-4-chloro-2,4,6-*tris*(trichloromethyl)-1-*oxa*-3,5-di-thiane. The –CCl-CCl₃ moieties are located at the bottom left of each drawing. The molecule at the top refined normally; the abnormal molecule on the bottom has severely elongated ellipsoids especially for the two central carbon atoms.

The large ellipsoids of the carbon atoms in the second molecule are clearly indicative of a disorder. When modeled correctly, as shown in Fig. 12, all the bond distances are close to their expected values.

3.8 Decomposition

I have always had the impression that crystallographers generally consider decomposition to be a rather benign source of intensity errors, errors that are easily corrected by using a set of intensity standards that are measured periodically during the data collection process. When a crystal decomposes, it is the high-angle reflections, and hence the "resolution" of the structure which suffer most. Invariably, the standards used to correct for the loss of intensity are low-angle reflections. Thus, the correction is generally inappropriate. Even if reflections from all angles are selected as standards, the assumption that all reflections within a small range of two-theta are affected equally by the decomposition is only roughly valid. An example of the problems that can arise is shown in Fig. 13, a structure which as originally reported, refined to $R = 0.168$ after correcting for a 15.1 % loss in intensity [30]. Chemically-equivalent bond lengths are quite disparate: N(1)–N(2), 1.359 Å; N(2)–N(3), 1.299 Å: N(7)–C(9), 1.348 Å; N(4)–C(8), 1.268 Å.

These same authors later collected data with the crystal cooled to 153 K [31]. At this temperature, there was no decomposition and the structure refined reasonably well ($R = 0.069$): all of the chemically equivalent bond distances differed by less than 3 sigma.

3.9 *Fuzzy* Structures

The problem with *fuzzy* structures is that it is difficult to decide whether they are interesting structures or wrong structures. I would like to present two examples to illustrate the point. The first is the structure of $[P(t\text{-Bu})_3]_2Rh(CO)Cl$ in which the rhodium(I) should have square-planar coordination. As first reported [32], however, the geometry about the Rh atom was that of a flattened tetrahedron. In addition, the Rh–C=O angle was bent, 164.7°, and the C=O distance was ridiculously short: 0.987 Å (Cl contamination?). Since this structure was interesting to me as part of a general study of rhodium compounds, I decided to have a second look at it. The resulting structure, refined with "low-temperature" data, is shown in Fig. 14 [33]. The coordination about the rhodium is, without question, that of a flattened tetrahedron. The Rh–C=O angle is indeed bent, 167.3°, although the C=O distance is now far more reasonable at 1.150 Å. Because the positions of the hydrogen atoms could be refined, it is now clear that the
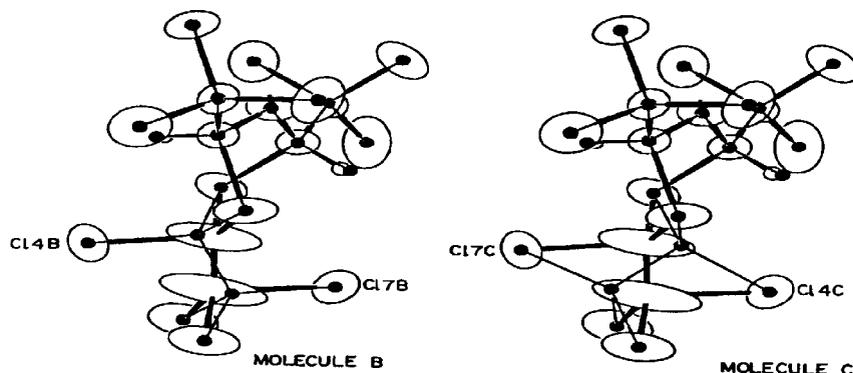
Fig. 12. The disordered model, represented by the dots (atom positions) and thin lines (bonds), used to refine the second molecule.
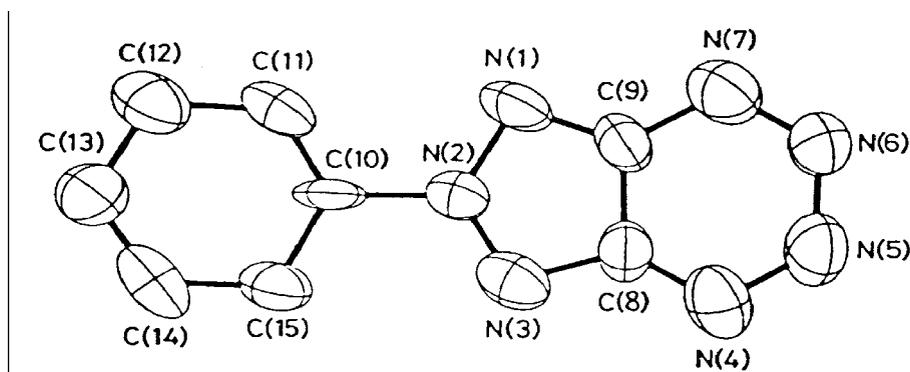

Fig. 13. Thermal ellipsoid drawing of 6-phenyl[1,2,3]triazolo[4,5-e]-1,2,3,4-tetrazine.
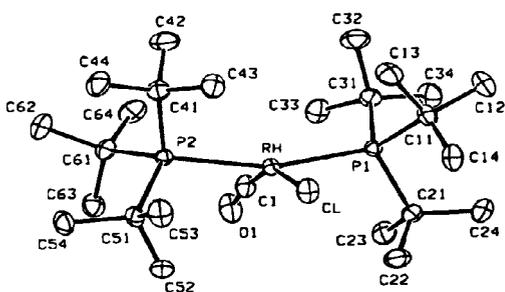
Fig. 14. Distorted structure of [P(t-Bu)$_3$]$_2$Rh(CO)Cl.

the severe distortion in this complex is simply the result of steric interactions between the bulky *tris*(*t*-butyl)phosphine ligands and the CO and Cl ligands. Where unusual structures are concerned, only a *quality*

structure gives one the level of confidence needed to proclaim that it indeed has unique features.

It is very common to rush through the data collection process either by using high scan speeds or by limiting the data collection to the low-angle reflections. Both of these limit the resolution of the structure since the weaker high-angle reflections are then not included in the refinement. Even those who advocate using all of the data in their refinements are deluding themselves if the high-angle intensities all have near zero values. One example of a low-resolution structure is that of 3,4-dimethoxy-cinnamic acid which was originally solved and refined using only 725 reflections [34]. The structure is triclinic, P$\bar{1}$, with a Z value of 4. With two molecules per asymmetric unit, a refinement using anisotropic thermal parameters would have produced a data/parameter ratio of something less than 3. In addition, a close inspection of the structure showed that the

two crystallographically independent molecules were related by a pseudo-center of symmetry. As a result, the refinement was unstable, characterized by high correlations and nonpositive-definite thermal parameters. Many of the resulting bond lengths were unreasonable.

Desiraju brought this structure to my attention because he was interested in resolving whether the refinement was unstable because of the lack of data, the presence of pseudo-centers, or both. Data were collected with the crystal cooled to –100 °C and at room temperature. Refinements using both data sets (2543 and 1893 reflections, respectively, with 367 variables including isotropic hydrogen atoms) converged rapidly with no high correlations between the two molecules [35] Clearly, the original problem with the structure was not the pseudosymmetry, just the lack of data, in particular the high-angle data. Shown in Fig. 15 is the asymmetric unit of this structure refined with data collected at –100 °C.

3.10 Structures That Don't Exist At All

While investigating a series of strontium iridium oxides, one crystal which appeared to have the composition $Sr_5Ir_3O_{11}$ was studied [36]. The c-axis of this tetragonal cell suggested that it was composed of alternating single and double layers of IrO_6 octahedra as shown in Fig. 16. Via direct methods and subsequent electron-density maps, the structure solved quite nicely to yield the "expected" model ($R = 0.050$). However, two of the atoms, one iridium and one oxygen, had nonpositive-definite thermal parameters. Subsequently, a careful inspection of the data collection profiles showed that many peaks were not well centered and that the c-axis

dimension had an unreasonably large esd. Photographic techniques were then employed to show that the crystal was not truly "single": there were in fact many bizarre reflections, some of which were sharp, some broad, and some of which appeared to be split. These characteristics are commonly found in materials where random stacking of more than one type of layer occurs. Indeed, a high-resolution electron microscopy image showed that the crystal actually consisted of separate regions of single-layered Sr_2IrO_4 and double-layered $Sr_3Ir_2O_7$, randomly interleaved to produce an approximate 50:50 mixture. I have every reason to believe, however, that the "incorrect" structure could easily have been published.

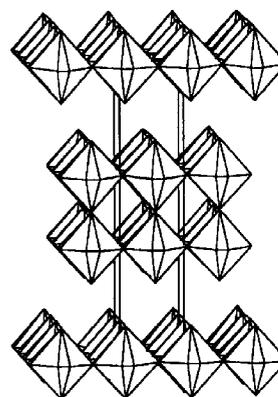**Fig. 16.** "Ordered" structure of $Sr_5Ir_3O_{11}$ showing only alternating single and double layers of IrO_6 octahedra.
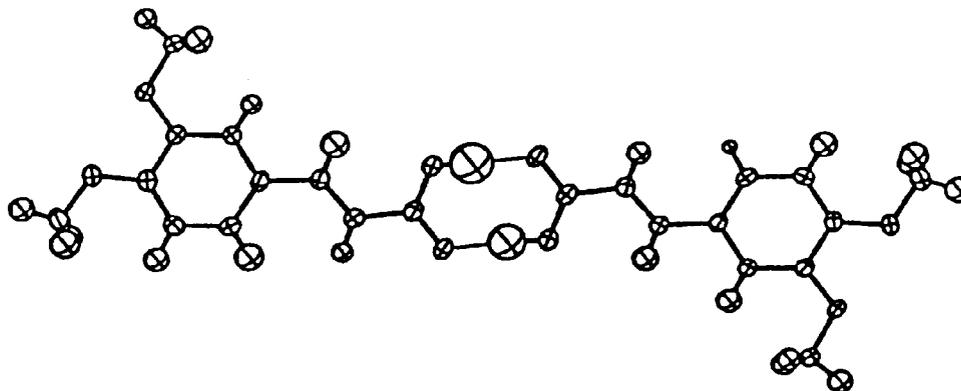

Fig. 15. Two molecules of 3,4-dimethoxycinnamic acid which form a hydrogen-bonded pair via a pseudo-center of symmetry. The hydrogen atoms have been drawn with their refined isotropic thermal spheres.

4. Conclusions

There are several types of "incorrect" structures that I have not listed among the examples here, although there may be some in my treasure-trove of "improbable structures" culled from the literature over a 25 year period. "Twinned" crystals, for example, that weren't recognized as such. Cases where serious absorption problems were ignored or improperly corrected for; Diffractometer misalignments; Unrecognized phase transitions during data collections; Misuse of programs like DIFABS; Problems I haven't even thought of. Anyone interested in learning more about "wrong" structures should not only read Refs. [1, 2, 3, 4 and 29], but should also peruse the titles of crystallographic papers for keywords such as reinvestigation, redetermination and pitfalls. One should also be wary of words such as new, novel and unique when applied to crystal structures; with tens of thousands of structures in the databases (even if I believe that most of them are *fuzzy*), hardly anything is really "new."

After examining a large number of "wrong" structures, I have come to a number of (sometimes interrelated) conclusions:

(1) Wrong structures generally have good *R* values. While the *junk* group is expected to have a large number of incorrect structures, wrong structures are found, more often than I believe is generally recognized, in the *fuzzy* group.

(2) Wrong organic and organometallic structures, almost without exception, are based on "room-temperature" intensity data where the high-angle reflections, if measured at all, are largely "unobserved." These are basically low-resolution structures, particularly with respect to the "light" atoms which have large vibrational amplitudes and which contribute little to the intensity of the high-angle reflections.

(3) Wrong structures usually exhibit one or more of three symptoms: unusual bond distances, unreasonable thermal ellipsoids, and/or impossible intra- and interatomic nonbonded contacts.

No *quality* structure has ever been shown to be incorrect. Hydrogen atoms, for example, simply don't refine well if either the data or the model contain even modest errors. Organic and organometallic structures must generally be refined using "low-temperature" data in order to be placed in this category. The other advantage of cooling crystals is that unreasonable thermal parameters become much more obvious and, thus, wrong structures are much easier to spot and correct. In fact, I am so confident in my concept of a *quality* structure that I would like to challenge readers to find an example of a *quality* structure that is wrong!

There is little excuse for incorrect structures today. Programs exist to check the metric symmetry of unit cells, to average raw data under a variety of symmetry conditions (although absorption effects may still lead to difficulties here) and to look for additional symmetry elements once the structure is complete. The consistency of chemically-equivalent bond distances, particularly among the "lighter" elements, is easily checked. Databases can be used to see if any of bond distances fall out of the expected ranges or if any of the atoms have unknown coordination geometries. Inorganic structures can be analyzed via the bond-valence model [37]. Strange thermal ellipsoids should not be ignored—they signal that something is wrong with the data, the model, or both. By the way, once you become sensitized to strange ellipsoids, you will see them everywhere! Finally, the structure should be checked for close intra- and interatomic distances, particularly among the hydrogen atoms.

5. Acknowledgments

6. References

[1] J. A. Ibers, Critical Evaluation of Chemical and Physical Structural Information: D. R. Lide and M. A. Paul, eds., National Academy of Sciences, Washington, DC (1974) pp. 199–218.

[2] P. G. Jones, Chem. Soc. Rev. **13**, 157–172 (1984).

[3] G. Parkin, Chem. Rev. **93**, 887–911 (1993).

[4a] R. E. Marsh has numerous publications related to symmetry corrections, the most recent of which is R. E. Marsh and I. Bernal, Acta Cryst. **B51**, 300–307 (1995).

[4b] W. H. Baur and E. Tillmanns, Acta Cryst. **B42**, 95–111 (1986); W. H. Baur and D. Kassner, Acta Cryst. **B48**, 356–369 (1992); W. H. Baur, Acta Cryst. **B50**, 141–146 (1994).

[5] J. P. Ferraris, R. G. Andrus, and D. C. Hrncir, J. Chem. Soc., Chem. Commun., 1318–1320 (1989).

[6] M. C. Kuchta, H. V. R. Dias, S. G. Bott, and G. Parkin, personal communication on a re–evaluation of the structure of [Tp^{t-Bu}]In.

[7] C. A. Ogle, T. C. Masterman, and J. L. Hubbard, J. Chem. Soc., Chem. Commun., 1733–1734 (1990).

[8] K. R. Dunbar and S. C. Haefner, Inorg. Chem. **31**, 3676–3679 (1992).

[9] R. L. Harlow, D. L. Thorn, R. T. Baker, and N. L. Jones, Inorg. Chem. 31, 993–997 (1992).

[10] R. Lingnau and J. Straehle, Angew. Chem. Int. Ed. Engl. **27**, 436 (1988).

[11] A. Haaland, K. Rypdal, H. P. Verne, W. Scherer, and W. R. Thiel, Angew. Chem. Int. Ed. Engl. **33**, 2443–2445 (1994).

[12] K. Yoon and G. Parkin, J. Amer. Chem. Soc. **113**, 1437–1438 (1991).

[13] There are very good general discussions of bond stretch isomerism given in the Ref. 3 and in V. Gibson and M. McPartlin, J. Chem. Soc. Dalton Trans. 947–956 (1992).

[14] P. Miele, J. D. Foulon, N. Hovnanian, J. Durand, and L. Cot, Eur. J. Solid State Inorg. Chem. **29**, 573–583 (1992).

[15] R. K. Laxman, A. M. James, F. R. Fronczek, and A. W. Maverick, Inorg. Chem., submitted.

[16] Unit cell dimensions agree with those reported by J. J. Randall, L. Katz, and R. Ward, J. Amer. Chem. Soc. 266–267 (1957).

[17] M. K. Crawford, M. A. Subramanian, R. L. Harlow, J. A. Fernandez-Baca, Z. R. Wang, and D. C. Johnston, Rhys. Rev. **B49**, 9198–9201 (1994).

[18] J. Iball and S. N. Scrimgeour, Acta Cryst. **B33**, 1194–1196 (1977).

[19] G. Zanotti, A. Del Pra, G. Bombieri, and A. M. Tamburro, Acta Cryst. **B34**, 2138–2141 (1978).

[20] C. J. L. Lock, R. A. Speranzini, and M. Zvagulis, Acta Cryst. **B36**, 1789–1793 (1980).

[21] J. J. Schneider, R. Goddard, S. Werner, and C. Krueger, Angew. Chem. Int. Ed. Engl. **30**, 1124–1126 (1991).

[22] K. H. Theopold, J. L. Kersten, A. L. Rheingold, C. P. Casey, R. A. Wiedenhoefer, and C. E. C. A. Hop, Angew. Chem. Int. Ed. Engl. **31**, 1341–1343 (1992).

[23] D. W. J. Cruickshank and W. S. McDonald, Acta Cryst. **23**, 9–11 (1967).

[24] V. J. Murphy, D. Rabinovich, and G. Parkin, J. Amer. Chem. Soc. **117**, 9762–9763 (1995).

[25] C. Minqin and K. Prout, J. Struct. Chem. **5**, 23–27 (1986).

[26] R. Harlow, comments and graphs for "False Minima Can Cause Crystal Structure Errors," Science/technology article, by S. Borman, Chem. & Eng. News, October 2, 27–29 (1995).

[27] W. J. Marshall and R. L. Harlow, manuscript in preparation.

[28] A. Irving and H. M. N. H. Irving, J. Crystallogr. Spectrosc. Res. **18**, 439–446 (1988).

[29] M. Kapon and F. H. Herbstein, Acta Cryst. **B51**, 108–113 (1995).

[30] T. Kaihoh, T. Itoh, K. Yamaguchi, and A. Ohsawa, J. Chem. Soc. Chem. Commun., 1608–1609 (1988).

[31] K. Yamaguchi, T. Kaihoh, T. Itoh, and A. Ohsawa, Acta Cryst. **C47**, 590–592 (1991).

[32] H. Schumann, M. Heisler, and J. Pickardt, J. Chem. Ber. **110**, 1020–1026 (1977).

[33] R. L. Harlow, S. A. Westcott, D. L. Thorn, and R. T. Baker, Inorg. Chem. **31**, 323–326 (1992).

[34] G. R. Desiraju, R. Kamala, B. H. Kumari, and J. A. R. P. Sarma, J. Chem. Soc. Perkin Trans. **2**, 181–189 (1984).

[35] G. R. Desiraju, J. C. Calabrese, and R. L. Harlow, Acta Cryst. **B47**, 77–86 (1991).

[36] R. L. Harlow, Z. G. Li, W. J. Marshall, M. K. Crawford, and M. A. Subramanian, Mat. Res. Bull. **30**, 217–223 (1995).

[37] A complete discussion of the history, theory, and experiences, as well as a list of useful references on the bond–valence model, can be found in I. D. Brown, Acta Cryst. **B48**, 553–572 (1992). As an example of its usefulness in separating correct from incorrect structures, see R. L. Withers, J. G. Thompson, and A. D. Rae, J. Solid State Chemistry **94**, 404–417 (1991).

About the author: *Richard Harlow, as an employee of the DuPont Company, has worked in the field of x-ray and neutron diffraction for the last 18 years. Presently, he is a senior Research Associate within the Corporate Center for Analytical Sciences and is partially responsible for the single-crystal structure determination laboratory. As a founder of the R. Harlow Foundation for Disabused Crystallographers, he actively seeks out problem structures through his "ORTEP of the Year" award, donating $100 per year to anyone who locates the best example of an incorrect structure as determined from its ill-defined thermal ellipsoids.*

Crystallographic Data Validation - Ten Years On

Anthony Linden
Institute of Organic Chemistry,
University of Zurich
Winterthurerstrasse 190
CH-8057 Zurich
Switzerland
E-mail: alinden@oci.uzh.ch

The introduction of the Crystallographic Information File (CIF) standard for archiving and transmitting crystal structure results (Hall *et al*., 1991) opened the way for electronic publication and easy submission of results to the crystallographic databases. This had the immediate advantage that errors arising from retyping data into manuscripts or other formats could be eliminated almost entirely. One just has to see how often older entries in the Cambridge Structural Database (CSD, Allen, 2002) are flagged with a remark that digits had possibly been interchanged or a negative sign was missing. Nonetheless, by the mid 1990s, it was evident that other errors or deficiencies in reported crystal structures were still common and the CIF format, love it or hate it, opened the possibility for checking for many of these errors and shortcomings automatically. The validation of crystal structures became a formal procedure in late 1997 with the introduction of the *checkCIF* software by the *IUCr* journals. This was an initiative of Syd Hall who was Section Editor of *Acta Crystallographica Section C* at the time. Together with Mike Hoyland of the *IUCr* Chester office and Ton Spek from Utrecht University, author of *PLATON*, the Chester *checkCIF* suite was developed and augmented with additional tests incorporated in *PLATON*. Today, the *PLATON* validation tests are an integral part of the *checkCIF* suite. An excellent paper describing the *PLATON* validation tool was published a few years ago (Spek, 2003). Procedurally, little has changed since then and the rationale and need for validation still apply today. The *PLATON* validation tests continue to become more comprehensive as experiences with manuscripts submitted to *Acta Crystallographica Section C* suggest new tests to help authors avoid recurring problems and oversights.

The initial version of *checkCIF* was designed to check for syntax errors in the CIF, that all required information (data items) was present, that the data items were self-consistent (e.g. that the atomic coordinates did actually generate the given bond lengths or that the density corresponded to the cell parameters and contents), and that there were no obvious indicators that the structure model might be incorrect or inadequately developed. Such tests are applicable to all crystal structure determinations, regardless of where they might be published or deposited. In addition, data and structure quality tests were added that are perhaps more specific to the acceptance criteria of *IUCr* journals. The initial aim of *checkCIF* was to give authors a tool for self-evaluation of their results, so as to hopefully reduce revision cycles, and to give co-editors of *IUCr* journals a "heads-up" to help them with their checking and assessment of manuscripts and ease their increasing workload. The idea is that if you ease the burden of having to check manually for mistakes, you can concentrate more on the most important part of the paper - the science being presented and discussed. We are all familiar with the workload issue for journal editors and referees alike as a direct consequence in the explosion in the number of determined and reported crystal structures subsequent to the dawn of the CCD detector era.

Some critics of *checkCIF* feel that the procedure is too rigid, that many of the parameter values used to trip alerts are chosen arbitrarily and without justification, and that the freedom of practitioners to do things in the way that they feel is appropriate has been replaced by a "do it this particular way or else..." dictum. People should not feel uncomfortable with changes or evolution in the way of doing things. Data validation is meant as a tool to assist people with their work, to help them get the best out of their efforts and avoid accidental errors and oversights, as well as to maintain standards. Data validation was not conceived to be an ever higher hurdle being put in people's way to make life difficult. The validation tests are based on many years of experience by *Acta Crystallographica* Co-editors and their assessment of what standards should readily be achievable for *most routine* small molecule crystal structure analyses given good crystals, properly adjusted equipment and well considered and planned experimental and

refinement procedures. The rationale for most of the validation tests is incorporated into *PLATON* (in the file *check.def*) or on the *checkCIF* web site, where the each alert in an online *checkCIF* report has a link to this information. A full listing of the information, as well as some explanations or suggestions to alleviate the problem, can also be seen at *http://journals.iucr.org/services/cif/datavalidation.html*.

Having said this, it should be made clear that it is very well recognised that there will always be non-routine or unusual features in some crystal structures, that special non-standard procedures are needed to handle certain cases, or that the quality of the data, while the best available, is lower than par, but that the result serves its purpose, is not over analysed and is unambiguous. Data validation is not intended as a means of blocking the publication of such cases. All that is required is that the authors justify scientifically the reasons leading to the validation alerts. This justification need not be onerous and can often be achieved within a sentence or two, although it is important that the arguments be based on logic and science and not on emotion. After all, the basis of scientific reasoning and presentation of results is that all aspects of the experiment should be properly documented and conclusions justified. While the reporting of routine crystal structures these days has often been reduced to the contents of the CIF, as a result of space saving policies of many journals, it is essential to highlight any unusual features or procedures used in the analysis, so that another person understands what has been done. If this reporting is done properly and routinely, it becomes second nature to the authors, so is not seen as a big bug-bear at the time of validation, while editors and referees immediately have the explanation of validation alerts at their fingertips and so are able to make an informed assessment without having to ask the authors for more information, or even immediately reject the paper, which is usually when authors get their backs up.

Some people feel that the now very extensive validation suite highlights some items that are thought to be unimportant if the work is being published as supporting results in a non-crystallographic journal, yet the editors and referees query these validation alerts or use them to reject the paper. That is unfortunate, but perhaps points more to the need to educate the editors and referees of such journals about the meaning of the *checkCIF* items and the flexibility that should be given if the alerts are properly justified. In any case, no item assessed by *checkCIF* is entirely unimportant. Many alerts suggest niggly little things that can easily be rectified with little effort. The validation tests should be comprehensive. Then, any work that passes all tests is (hopefully) of a very high standard, while practitioners and journals alike should be able to decide for themselves if they wish to accept lower levels of compliance and what these levels might be. Crystallography journals will naturally require higher standards than might a general chemistry journal. However, if one constantly aims to do the best and has the tools to assist in the achievement of that goal, the average output will probably be of a higher quality than if no "encouragement" was being provided at all.

Finally comes the question: do we still need a "big brother" style validation, or have we learnt our lesson and can now be self-sufficient or self-controlling in this regard? Having easy to use validation tools is always useful, so there is a continued need for them for this reason alone. More importantly, as any co-editor of *Acta Crystallographic Section C* or *E* will tell you, there are still, frustratingly, many mistakes or oversights being made or strange procedures being used in crystal structure determinations, and some of these are still getting through into published papers in some journals. One of the reasons for this is the explosion in the number of groups determining crystal structures in some countries and the subsequent dramatic rise in the number of manuscripts submitted to journals in all fields, yet those scientists, while trying hard, are apparently not always receiving proper instruction from experienced practitioners. It appears that some of those doing crystal structure analyses are often learning things by word of mouth, trial and error, following manuals and "blindly" using automated instrumentation and software. Consequently, the validation tools are more important than ever, both as a tool for the authors, and to enable journal editors and referees to maintain constant vigilance, while still being able to cope with the surge in manuscripts. Anyone who doubts these comments is invited to volunteer to be a regular referee for *Acta Crystallographic Section C* or *E* where first hand experience will quickly reveal the sort of work often being submitted for publication.

The following examples illustrate two recent cases of related, incorrect structures being published. This anecdote highlights the failure of authors and referees to recognise the meaning of the validation alerts which, albeit possibly obscure, should have drawn their attention to the existence of a problem. However, even in the absence of validation, just looking at the ORTEP drawing in one paper should have revealed the problem instantly to the referee, even if he or she was a chemist who had little idea about crystallography, yet the mistake was not detected. In light of the preceding article in this newsletter by Richard Harlow, I can only say: Richard, the first example may be deserving of just one more OOTY award.

The first example comes from a recent paper in *Helvetica Chimica Acta* by *Baysal et al*. (2007). The reported compound, **4**, was claimed to possess an exocyclic C=N–H (imine) group. Even without running *checkCIF*, a glance at the ORTEP image in Fig. 1 of their paper immediately shows that the H-atom of this group has been positioned incorrectly as a linear C=N–H arrangement is depicted! It is disappointing that this was not noticed by a referee. I suspect most non-crystallographer referees believe that crystal structures are always right, so do not even bother to look at the ORTEP properly.
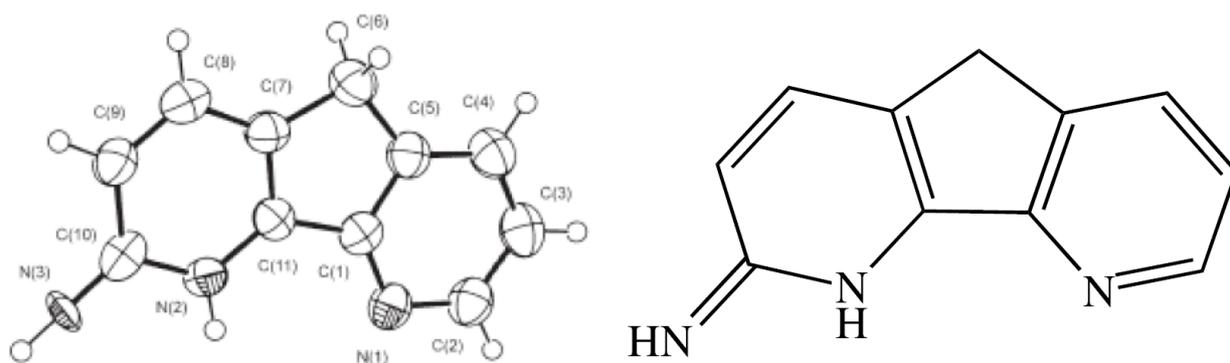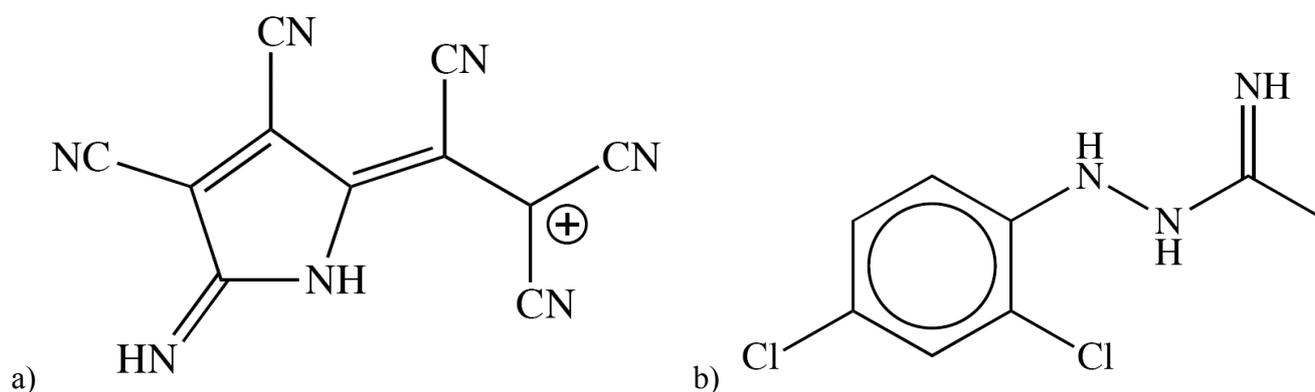

Fig. 1. *The molecular structure of compound **4**, as published by Baysal et al. (2007). Reproduced with permission of Verlag Helvetica Chimica Acta.*

The authors then went on to analyse intermolecular hydrogen bonds emanating from the imine H-atom and their Fig. 2 clearly shows impossibly short H···H contacts as a result of the "mis-positioned" H-atom. No-one noticed this, either. The authors actually remarked that the C=N bond of 1.199(5) Å was considerably shorter than the other C–N bonds in the molecule, (although none of these are true C=N double bonds), but failed to note that this would be exactly right for C=O. A precursor molecule that they had synthesised, their compound **3**, was actually the carbonyl compound! All of this evidence immediately suggested that instead of an imine group, the group was carbonyl. When I contacted the authors about their structure, they responded that they agreed the H-atom was in the incorrect position, but could do nothing about it because that is where the refinement program (SHELXL97!!) had placed it. They have since worked out how to correct that mistake. However, they are still confident that the structure does contain an imine group, because of other spectroscopic data and the fact that the crystals were red, whereas those of **3** were yellow. I asked them to try a test refinement with N–H replaced with O and see what happened to the *R*-factor, but they have not advised me of the results of such a test. I suspect that they are being misled by their faith in the other chemical evidence, which is based on their *bulk* material. I have asked them if they would be willing to send me their reflection data, but so far they have not done so.
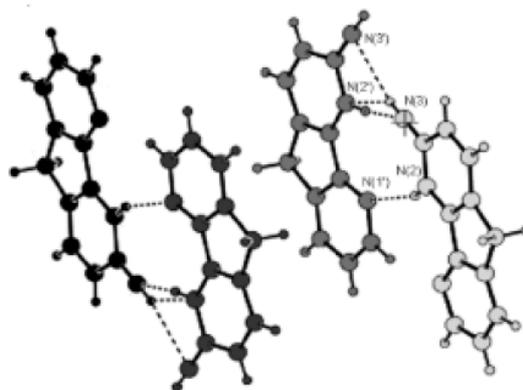
Fig. 2. *The reported hydrogen-bonding in **4**. Reproduced with permission of Verlag Helvetica Chimica Acta.*

To investigate the matter further, I conducted a search of the CSD for terminal imines in an environment similar to that in **4** in order to ascertain the C=N bond length which was usually observed, and if there was a precedent for unusually short C=N imine bonds. The CSD revealed 66 entries, with most C=N bond lengths in the range of 1.25–1.32 Å. Notably, apart from the above-mentioned structure, there were two other structures with bond lengths less than 1.22 Å and these clearly seemed to be outliers. One structure was reported in *Angew. Chem.* in 1985, so it is difficult to test that further without access to the raw data (*Dessy et al.*, 1985). However, the reported imine C=N bond length of 1.17(7) Å seems too short to be reasonable, even in the environment of the somewhat special cation (Fig. 3a) The second structure (Fig. 3b) was reported in *Acta Crystallographica Section E* by *Heng et al.* (2006) and has an imine C=N bond length of 1.215(5) Å. With access to the archived structure factors, it was possible to refine their structure again with the imine group changed to a carbonyl group and the *R*-factor decreased from the reported 0.070 to 0.064. In addition, a contoured difference *Fourier* map centred about the imine group showed significant "dirty" features representing a small amount of residual electron density in the vicinity of the imine N-atom, whereas the corresponding map for the carbonyl model was completely featureless. Clearly, this is another case of a carbonyl group modelled incorrectly as an imine. Another search of the CSD for terminal imines with no restriction on the environment revealed several more examples of unusually short C=N bonds and some of them may indeed be misinterpreted structures that actually possess carbonyl groups (for example, as part of an ester function), but I have not investigated these in any detail.

Fig. 3. *The molecules reported by (a) Dessy et al. (1985) and (b) Heng et al. (2006).*

The next question is: what does *checkCIF* have to say about the incorrect structures described above?

For the structure of compound **4** by *Baysal et al.* (2007), *checkCIF* reports that the imine H-atom is too close to another H-atom (A alert), that the imine N-atom has a displacement ellipsoid that is inconsistent with that of its neighbour (B alert concerning the Hirshfeld test), and another C alert concerning a

possible missing hydrogen bond acceptor for the imine H-atom. The A and B alerts should have told the authors that there was something wrong with the imine group in their model, provided that they had actually used *checkCIF*. However, it might have been difficult for them to interpret the meaning of the Hirshfeld alert if they were firmly convinced for chemical reasons that they were indeed analysing the imine compound.

For the structure by *Heng et al.* (2006), the only relevant alert generated by the submitted CIF is a C alert that the N–H group does not have an appropriately positioned hydrogen bond acceptor. Such alerts are always worth considering carefully, but, except for the more astute, may not be enough to point many practitioners to the fact that the imine group should be carbonyl. The absence of a Hirshfeld alert for the submitted CIF is interesting. A new refinement of the incorrect structure using the deposited structure factors actually generated a Hirshfeld C alert for the N–C bond involving the imine N-atom. This suggests that the authors may have used an undocumented procedure during their refinement, such as a DELU restraint, although the submitted CIF does not contain any refinement flags or additional parameters which might indicate that this has been done. Note that the results reported by *Heng et al.* (2006) are based on data whose quality was not optimal – even the correct model has a poorish *R*-factor of 0.064. Thus, ambiguities concerning the correctness of structures with high *R*-factors cannot be excluded, or detected reliably and point further to the need for practitioners to ensure that they obtain the highest quality data possible, and preferably at low-temperature.

The take-home message from these examples is that it is important that data validation continues to be applied routinely for all crystal structure determinations. This means that authors, journal editors and referees need to be educated that *checkCIF* and *PLATON* validation are tools to be used not only when publishing in a crystallographic journal, but for every structure. It would be a welcome development if the editors of all journals insisted that authors provide an annotated copy of the *checkCIF* report with every submission, even if only to ensure that authors have actually used the facility – as a result of which they might discover and rectify a problem before submission. Using *checkCIF* and addressing any issues before submission of the paper, then responding in the accompanying *checkCIF* report to remaining alerts is the simplest way that authors have of ensuring a speedy passage of crystallographic results through the publication process. Furthermore, practitioners perhaps need to be better educated about the meaning of some of the more obscure alerts like the Hirshfeld test and how various combinations of alerts might be interpreted. Nonetheless, the *Baysal et al.* (2007) example shows that even if data validation does not detect all model errors, the problem should have been immediately obvious to the authors and the referees by visual inspection of the ORTEP and hydrogen-bonding diagrams. That such a blatantly obvious error in the model remained undetected prior to publication is baffling. Authors and referees should use data validation software conscientiously, but should not blindly rely on it as a replacement for simply looking at a structure and thinking about it logically. Our eyes often reveal things to us that numerical data may not. In this regard, one should not underestimate the value of generating and viewing contoured difference *Fourier* maps in regions of interest and/or uncertainty. This facility is available in *PLATON* and is very easy to use.

References

Allen, F. H. (2002). *Acta Cryst*. B**58**, 380–388.
Baysal, D., Gümgüm, B., Yildirim, L. T. Ülkü, D., Boga, A. D. & Özkar, S. (2007). *Helv. Chim. Acta*, **90**, 1211–1217.
Dessy, G., Fares, V., Flamini, A. & Giuliani, A. M. (1985). *Angew. Chem. Int. Ed. Engl*. **24**, 426–427.
Hall, S. R., Allen, F. H. & Brown, I. D. (1991). *Acta Cryst*. A**47**, 655–685.
Heng, J., Wu, W.-Y., Wu, Y.-M. & Zhu, H.-J. (2006). *Acta Cryst*. E**62**, o4359–o4360.
Spek, A. L. (2003). *J. Appl. Cryst*. **36**, 7–13.

An Online Course in X-ray Crystallography

Patrick J. Carroll
Director, X-ray Crystallography Facility
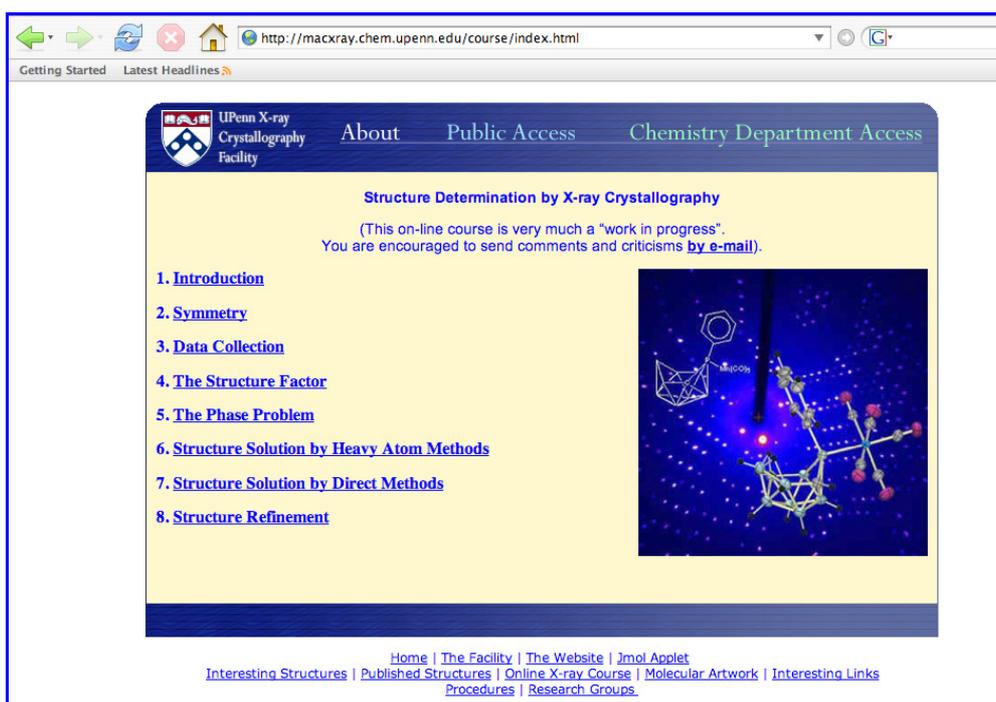*Department of Chemistry*
University of Pennsylvania
Philadelphia, PA, USA
W-mail: carrollp@sas.upenn.edu
Web: http://macxray.chem.upenn.edu/

Introduction

Recently I've been developing an online course in the fundamentals of X-ray crystallography. It was conceived as a supplement to a traditional lecture-type course I've taught for about a dozen years. The purpose of the original course was to provide an introduction to crystallographic structure determination to, particularly, inorganic chemistry students pursuing a Ph. D. in the Penn Chemistry Department. At that time, it was realized that there were very many structure determinations magically appearing in Ph.D. theses and the students should at least become acquainted with the language of crystallography. The lecture course attempted to provide an introduction to theory while at the same time using a large number of actual structures determined in Penn's X-ray Facility as real world examples. The new online course is located at macxray.chem.upenn.edu/course/. Below is the first page of the course, which displays an outline of the major topics covered:

The target audience for both the traditional lecture course and the online course are first year graduate students who are just in the process of choosing their thesis advisor. I have tried to keep the focus on the kind of small molecule structure determination important to synthetic organic and organometallic/inorganic chemists. Most of the examples presented are "medium sized" small molecules of 20 to 50 atoms. The development of the theoretical background is approximately chronological in order to provide some historical perspective; thus, for example, the early introduction of heavy atom methods. Likewise, there is a section on precession photography both to illustrate early methods of data collection and to use as a tool to teach about reciprocal space. In the heavy atom example, there is also a print-out of a Fourier electron density map that the student can contour by hand; this also shows how things "used to be done" at the same time that it provides a real illustration of Fourier theory.

One of the advantages of a web-based presentation, of course, is that the user can follow links that provide additional information. For example, on the following page, which presents von Laue's X-ray experiment, the user can choose to see more information about "X-rays" or "diffraction". Clicking on "Max von Laue" leads to the online version of P.P. Ewald's *Fifty years of X-ray Diffraction* and a recap of von Laue's work (again, one of the peripheral objectives of this webpage is to provide some historical perspective to the people and times involved in the development of the discipline). I am hoping to expand the number of such historical links; presently, there are only a few such references.

This ability to "self-customize" a website enables the novice to obtain the fundamentals he needs while allowing the more experienced user to scan the material quickly. As the site grows, I hope to include examples of structure determinations that are useful to the practicing crystallographer, beyond just their pedagogical value. Many of the symmetry-teaching and unit cell examples are actual structures that have been determined in the Facility at Penn. I think it is very helpful to include real examples from the research area in which the student will be participating. I also plan on including links to other web presentations of crystallography; seeing a principle re-explained from a different viewpoint can add to a student's understanding.

I have tried to present the many equations of crystallographic structure determination clearly and concisely without, perhaps, including every detail of their derivations. Personally, I have difficulty following a detailed mathematical derivation on the computer screen; perhaps this is due to my being over the age of fifty and therefore having grown up during the age of the printed page. My offspring don't seem to have any problems reading a computer screen. I've also tried to keep specialized shorthand notation to a minimum; this can lead to some extensive lines of equations but is clearer for the non-specialist. Of course, it would be possible to include additional links to more substantial derivations for the user who is interested in greater detail; that may be the next layer of webpage development. (Actually, when I first started the page, it was just a test to see if I could present small pieces of the information and compose useful but simple illustrations; after that, it just grew). This next page, which summarizes some of the important definitions and equations involving the concept of the structure factor, is an example of presentation of equations.

Getting Started Latest Headlines

If the summation over discrete atoms in the structure factor expression:

$$\vec{F}_{hkl} = \Sigma f_j \, e^{2\pi i(hx_j + ky_j + lz_j)}$$

is replaced by an integration of a continuous, cyclic electron density function, ρ, an expression is obtained that is of the form of a Fourier Transform:

$$\vec{F}_{hkl} = \int_V \rho(x,y,z) \, e^{2\pi i(hx_j + ky_j + lz_j)} dV$$

This implies that the electron density is the Fourier Transform of the Structure Factor. Likewise, the Structure Factor is the Fourier Transform of the electron density:

$$\rho(x,y,z) = \int_V \vec{F}_{hkl} \, e^{-2\pi i(hx + ky + lz)} dV$$

While this equation is a useful depiction of the relationship between electron density and the structure factor, it is usually used in the form of a summation:

$$\rho(x,y,z) = \frac{1}{V}\Sigma_h \Sigma_k \Sigma_l \vec{F}_{hkl} \, e^{-2\pi i(hx + ky + lz)}$$

This equation says that the electron density, ρ, can be calculated at any point (x, y, z) by constructing a **Fourier Series** which has coefficients that are equal to the Structure Factors.

I've tried to keep the mathematical rigor at about the level of Stout and Jensen's *X-ray Structure Determination - A Practical Guide* (which was a major resource in both the original lecture-type course and the online course). The equations are accompanied by simple drawings when they are helpful to explaining a mathematical conclusion. This course is meant to provide an all-in-one overview of the topic while retaining some semblance of the progressive march through mathematical derivation with the expectation that the user is not a hard-core mathematician. Below is a page that summarizes one of the major ideas about Direct Methods.

Getting Started Latest Headlines

If the results for all three reflections are superimposed:

a
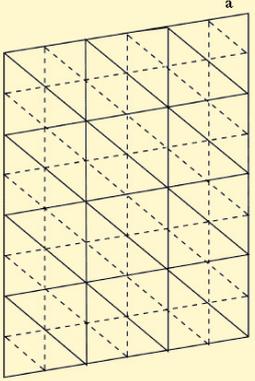
Again, solid lines locate electron density maxima when the phase is 0° (+|F_{hkl}|) and dashed lines locate electron density maxima when the phase is 180° (-|F_{hkl}|). Where three of these maxima intersect, there must be a large amount of electron density, especially if the amplitudes of the three waves are all large (large |F_{hkl}|). At these triple intersection points, in fact, there must be an atom!

Inspection of this figure indicates that there are only two types of triple intersection points: when all three phases are positive or when two phases are negative and one is positive. This observation can be summarized as:

$$s_{300} \cdot s_{004} \cdot s_{30\bar{4}} \sim +1$$

where s_{hkl} represents the sign of $|F_{hkl}|$ and $\sim$ means "is probably equal to".

This is a general relationship and can be applied to other reflection triplets:

$$s_{hkl} \cdot s_{h'k'l'} \cdot s_{h-h'k-k'l-l'} \sim +1$$

c

Another major motivation for using the web to present crystallography is the availability of the Jmol applet. Jmol is a free, open source molecular visualization tool that can be imbedded in a webpage as an applet. (See the Jmol website, jmol.sourceforge.net, for more information). For several years, I had been using Jmol on the Penn X-ray Facility website to archive structural results. A researcher who has had a structure done can log on to his group's page and display his molecule (see macxray.chem.upenn.edu/public.html for archive examples). Being able to rotate a molecule (or unit cell) in real-time affords a better sense of the three dimensionality of the object than can be realized on paper. Jmol does a very good job of rendering molecular objects in color and manipulation of the display is very intuitive and responsive even for large collections of molecules. Jmol is fully scriptable and the construction of various-style buttons is easy for the non-programmer (like myself); it has the capability to measure various geometric parameters (bond distances and angles, torsion angles) using mouse clicks and

to display unit cell contents and resulting packing diagrams so it is ideal for teaching space group symmetry. Jmol reads a large variety of file types (PDB, CML, GAUSSIAN, MOL, MOPAC, etc.). For the display of unit cells, Jmol requires the CIF or SHELXL file. The user can rotate the applet display in real time and by the use of a mouse-button accessible pop-up menu, various display parameters can be changed (atom and bond color and size, van der Waals or covalent radii, etc.). Jmol is in a continuous process of upgrade and the developer community is very responsive to the needs and wants of users (I am hopeful that in the future, Jmol will be able to display s.u.'s on geometric parameters and will incorporate thermal ellipsoids into the molecular display). The screenshot below displays a page showing the c-glide in space group P2$_1$/c.

Future plans for the online course are to increase the number of historical links, to include more real-world examples, to include links to more detailed derivations of important equations, and to develop a general unit cell manipulation page that can handle any user-input space group. Using already completed example structures, I hope to address topics like disorder, absolute structure determination, ambiguous space group assignment, twinning and other topics encountered by the practicing crystallographer. I am also starting to investigate ways for the user to actually "do a structure" online.

X-ray Safety for Analytical Instrumentation:
It's what you cannot see or feel that will hurt you!

Joseph H. Reibenspies
Department of Chemistry, Texas A & M University, USA. E-mail: j-reibenspies@tamu.edu ;
Web: http://www.chem.tamu.edu/xray/

X-rays are high-energy electromagnetic radiation that will ionize material that it illuminates and as such can be very hazardous to unprotected skin, organs and tissue. For scientific instrumentation, the X-rays are restricted to short linear paths between the X-ray source, the specimen and the detector. These paths have a high degree of directionality and are the most dangerous areas of the X-ray instrument that the ordinary user can access. It is thus wise to educate oneself on where the X-ray beam path is and how to avoid exposure (Cook and Oosterkamp, 1962; Martin, 1983).

X-rays are invisible and if they come into contact with your skin they cannot be seen or felt directly. In some instances the X-rays will ionize the air and a tingling sensation will be felt when one comes near the X-ray beam path, however this indicator is unreliable and cannot be trusted as a warning sign before exposure. It is therefore necessary to take every precaution to avoid accidental exposure, rather then rely on some outside stimulation. It is what you cannot see or feel that will hurt you!

The goal of the X-ray safety program is to keep the radiation exposure of any individual occupational worker to be **A**s **L**ow **A**s **R**easonably **P**ossible or **ALARA.** For X-ray instrumentation workers, in general, this is achieved by reducing the time you can be exposed to the radiation source, increasing the distance between you and the radiation source and increasing the shielding between you and the radiation source. Instrumentation design and *Operational Safety Procedures* (OSP) specifically written for each instrument and laboratory can help accomplish these goals.

Modern analytical X-ray instruments are very safe but are still considered to be ultra hazardous equipment. The manufacture and use of these instruments is regulated by federal and state agencies and require the incorporation of a variety of "fail safe" devices that will prevent accidental exposure. Even with the high degree of built in safety features; it is still wise for the occasional user to limit their access to the X-ray beam path and specimen area of the instrument. The less time spent in harm's way the lower the probability of exposure and if exposed the less time spent in direct contact with the X-ray radiation.

The units used when discussing radiation exposure are the Roentgen (**R**), radiation absorbed dose (**rad**) and the radiation equivalent dose (**rem**). The Roentgen is the amount of radiation that produces one unit of ions/cm^3 where 1m**R**/hr is considered a low rate and 100m**R**/hr is considered high. The **rad** is the energy imparted to matter in volume (**V**) divided by the mass and the **rem** is the product of the absorbed dose and the relative biological effect (RBE) necessary to express on a common scale (in SI units : 100 **rad** = 1 gray, **Gy,** and 100 **rem** = 1 sievert, **Sv**). For X-ray radiation the RBE = 1 and 1 **rad** x (RBE) = 1 **rem**. In fact, for X-ray radiation of 10-20Kev one **R**/hr = one **rad** = one **rem**.

The Maximum Permissible Dose (radiation) for occupational users has been defined by the Department of Energy (10 CFR Part 835 : http://www.hss.energy.gov/healthsafety/) as 5 **rem**/yr for the whole body, 15 **rem**/yr for the eyes and 50 **rem**/yr for the hands. Minors and non-occupational workers (custodians, plumbers etc) are allowed only 0.1 **rem**/yr, while a declared pregnant occupational worker is allowed less than 0.5 **rem**/9-month. The highest background radiation in the world is 5 **rem**/yr located at Kerala, India, while in the USA the highest background radiation of 0.2 **rem**/yr is located around Leadville, Colorado. The lowest background radiation (0.07 **rem**/yr) is located along the Atlantic and Gulf coast while the average background radiation is 0.09 **rem**/yr. For comparison it should be noted that a single dental X-ray would deliver about 0.3 **rem** of radiation, which means that two exams per year will accumulate about 1.2 **rem**/yr.

The radiation sources for most analytical X-ray instruments are the sealed tube, the normal focus rotating anode and the micro-focus rotating anode tube. The X-rays are generated by the deacceleration of high velocity electrons by a metallic target in the tube. In practice thousands of watts of electricity are required to accelerate the electrons and circulating water is required to cool the target. From a safety standpoint, the radiation produced by these tubes (measured at the window of the tube where the X-rays exit) is approximately 10^7 **R**/hr for the sealed tube, 10^8 **R**/hr for the normal focus rotating anode and about 3×10^8 **R**/hr for the micro-focus rotating anode (Honkimski et al., 1990; Lubenau, 1971). For safety reasons, it is important for the user to know which tube the X-ray instrument employs and what the tube's power consumption is.

The three most important X-ray safety features for modern analytical X-ray instruments are the primary (safety) shutter, the instrument enclosure and the beam stop. The primary shutter is a mechanical device that can be inserted in the X-ray path to completely attenuate the X-ray beam. The primary shutter is actuated by an electronic solenoid and an open and closed sensor will determine its position. Normally if the command to open the shutter is made and the open shutter sensor does not register a physically open shutter than the X-ray generator will deactivate. The same is true when a close command will not result in the closure of the shutter. This safety feature cannot be overridden.

The instrument enclosure keeps stray X-ray radiation from leaking out and keeps the user from accidentally coming into contact with the X-ray beam. Sensors normally monitor the doors and the panels to the enclosure. If the door or panel is open the shutter will immediately close and cannot be opened unless the door or panel is secured (See figure below). For some instruments the doors and panels are directly linked to the X-ray generator so that opening them while the shutter is open, will result in deactivation. Expert users can override the door sensors by activating a keyed switch, which is necessary for routine instrument alignment but is not intended for everyday instrument use.
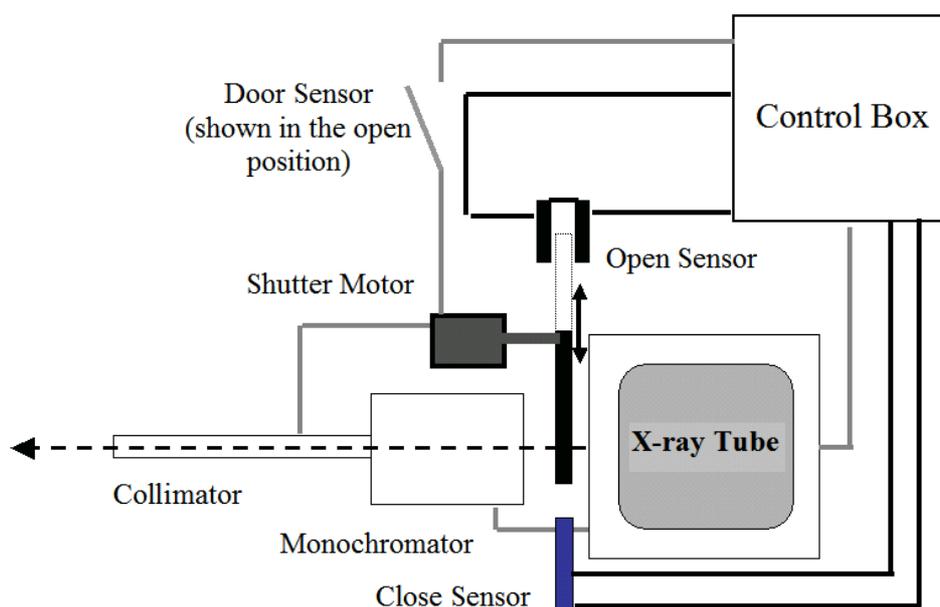
The beam stop is also an important safety device; however it is not as important on modern instrument where shutters and instrument enclosures limit the ordinary user from access to open X-ray beams. The beam stop on an instrument set up in the reflection mode is the specimen itself, while transmission instruments rely on small metallic devices that are positioned after the specimen and before the detector. The main safety feature of the beam stop is to shorten the pathway of the X-ray beam and to attenuate X-rays that are not employed in the experiment.

Air will attenuate X-rays as well as monochromators, slits, filters and other instrument attachments. The attenuation of radiation by air for <u>sealed tube</u> X-ray sources can be estimated by the equation (Lubenau, 1971):

$$R\!\!\!/_{hr} \cong 2432 \times \frac{kV \times mA}{d^2} \times Z$$

where kV x mA is the power applied to the X-ray tube, Z is the atomic number of the target element of the tube and d is the distance, in cm, from the source. Monochromators that are positioned in the X-ray path will attenuate the radiation by about 25% for multi-layer mirrors, 50% for Nickel Filters (0.015mm thick) and about 75% for pyrolytic graphite crystals. Collimators and slits that are positioned in the X-ray path, will effect its direction, separate the users from the source and reduce the area of the X-ray beam.

For the user it is critical to evaluate the X-ray pathway and to know the radiation exposure limits. The figure below is an estimate based on the known X-ray flux for a Copper sealed tube (at its maximum power rate), the inverse rate law and the attenuation factor for the X-ray monochromators (Jenkins and Haas, 1975; Shapiro, 2002). The real radiation doses will vary with the age of the X-ray tube, the specific monochromators, slits and filters.
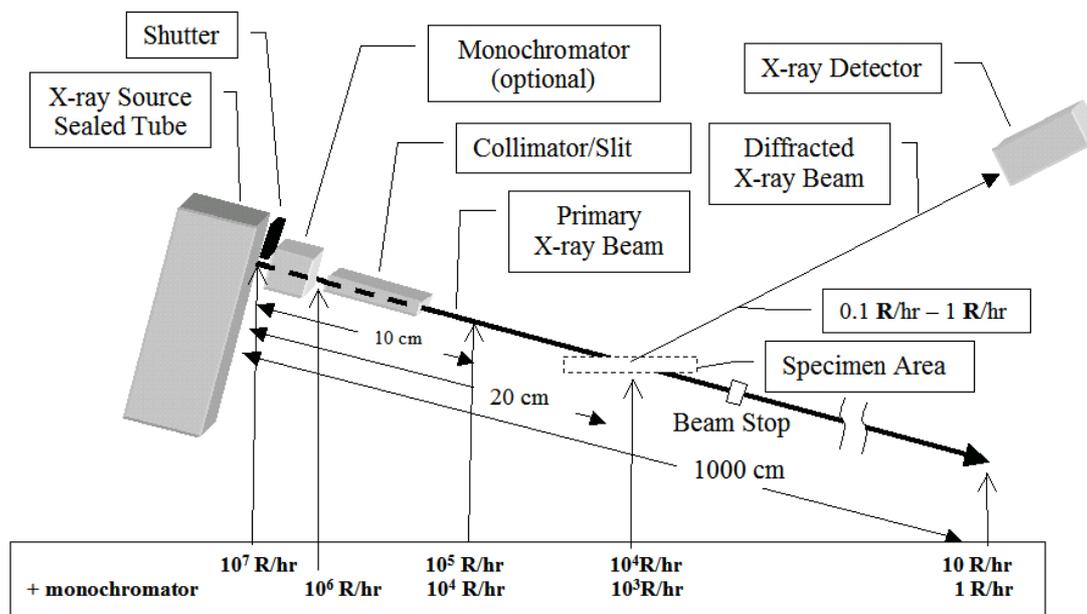
In some localities users are required to wear personal dosimetery in the form of Thermo-Luminescence Devices (TLD) that will detect accidental radiation exposure. The active area of a TLD consists of a small Lithium Fluoride material that can detect radiation doses between .002 to 10^5 **rad**. TLDs are used in both lapel and extremity badges. The lapel badge is normally worn at the level of the X-ray beam while the extremity badge is normally a ring that can be worn on your finger.

The advantage of the badges is that they are often the first documented indication of accidental exposure. The disadvantage of such devices is their usefulness in analytical X-ray instrumentation where the directionality of the primary beam and the size of the badge itself reduce the chance that an accident will be detected. For example given the area of possible X-ray exposure (the upper torso), the size of the X-ray beam and the size of the dosimeter, the likelihood of a stray X-ray photon striking a lapel badge is about 1 in 10,000 and for the extremity badge it increases to 1 in 100. Given these odds and the few accidental exposures for normal usage, the personal dosimeters have been discontinued in many analytical X-ray laboratories.

The health risk of exposure to X-ray radiation is roughly proportional to the square of the dose. Exposures less than 0.1 **rem** are not considered significant while exposures greater than 3000 **rem** will cause cell sterilization. No visible skin damage is seen for X-ray exposures below 300 **rem**, however the cancer risks for such exposures are unknown. For most radiation workers a 100 **rem**/life shows only a statistical decrease in life expectancy of about 1%. On average one will lose one day of life for each **rem** of exposure (Lindel, 1968; Lubenau et al., 1969; Steidley et al., 1981).

Given these facts exposures greater than 1000 **rem** will produce noticeable physiological effects. For soft tissue the depth of exposure of 10-20 keV X-rays is 1.3-4.3 mm ($t_{l/2}$). In the first hour some tingling is experienced. In the first week swelling, blistering, pain, erythema, hair loss (epilation), skin loss (desquamation) is seen. In the first month ulcers (sores that will not heal) and gangrene can occur. In the first year, a 1000 **rem** exposure could lead to loss of digits or skin graphs and cardiacs in the eyes. Any radiation dose greater than 0.1 **rem** is considered significant and should be documented.

If you believe you have been exposed do not ignore it. If you are exposed you may not feel any pain for at least 1 to 6 hours and by then it will be too late. You should stop what you are doing and deactivate the instrument. Leave the instrument *as is*, a radiation safety officer will need to investigate the sight and to ascertain the extent of the radiation exposure. You must contact your supervisor, the laboratory manager and the radiation safety officer for your institution. You must immediately document where, when and how you were exposed to the radiation, in the instrument log, not only for yourself but also for anyone else that may use that particular instrument (or procedure) in the future. Immediately return any personal dosimeters (if any) to your radiation safety officer. Finally, you should take a complete physical as soon as possible to document your current health status. It is important to know what to do in case of such emergences and how to secure the instrument to prevent future accidental exposures.

Modern analytical X-ray instruments are amongst the safest machines of their type in the laboratory. Still these devices are classified as "ultra hazardous" and as such strict liability, use-of-tools and assumption of risk arguments are all valid. In the end, the procedures set forth by your national, state and local radiation safety offices must be followed by the user exactly, any deviations are not legal. You are the first radiation safety officer when it comes to prevention of accidental radiation exposure and your own good health.

References

COOK, J. & OOSTERKAMP, W. (1962) Protection Against Radiation Injury, International Tables for Crystallography.

HONKIMSKI, V., SLEIGHT, J. & SUORTTI, P. (1990) Characteristic X-ray Flux from Sealed Cr, Cu, Mo, Ag, W Tubes, *Journal of Applied Crystallography,* **23,** 412-417.

JENKINS, R. & HAAS, D. (1975) Incidence, Detection and Monitoring of Radiation from X-ray Analytical Instrumentation, *X-ray Spectrometry***,** 33-42.

LINDEL, B. (1968) Occupational Hazards in X-ray Analytical Work. *Health Physics,* **15,** 481-486.

LUBENAU, J. (1971) Radiation Safety Procedures in X-ray Diffraction and Spectroscopy, US Department of Health Education and Welfare (SRDB: RefID: 32635) p 192.

LUBENAU, J., DAVIS, J., MCDONALD, D. & GERUSKY, T. (1969) Analytical X-ray Hazards: A Continuing Problem, *Health Physics,* **16,** 739-746.

MARTIN, E. (1983) A Guide to the Safe Use of X-ray Diffraction and Spectrometry Equipment. Ash Drive, Leeds, LS 17 8RA U.K., Science Reviews Ltd.

SHAPIRO, J. (2002) Radiation Protection: A guide for the scientist, regulators and physicians, Cambridge, Harvard University Press.

STEIDLEY, K., STABILE, R. & SANTILLIPPO, L. (1981) A Case History of Severe Radiation Burns from 50 kVC X-rays, *Health Physics,* **40,** 399-405.

Validation of a Complex Inorganic Crystal Structure using Bond Valence Restraints

Ivana Radosavljević Evans

Department of Chemistry, University of Durham, Science Site, South Road, Durham DH1 3LE, U.K. Fax: +44 191 384737; Tel: +44 191 334 2004 ; E-mail: ivana.radosavljevic@durham.ac.uk

1. Introduction

Inorganic oxides represent a large class of important functional materials. High temperature superconductivity, colossal magnetoresistance, negative thermal expansion, ionic conductivity, ferroelectricity and catalytic activity are among their technologically exploitable properties. These and other physical properties of solid state materials are intimately linked to their crystal structures. There have been numerous cases where early structural characterisations of inorganic oxides resulted in reports of simple, high-symmetry crystal structures. As huge advances in both instrumentation and crystallographic software allow non-ambient (in particular variable temperature) diffraction work to be carried out routinely both at large central facilities and at home laboratories[1], more and more cases are being discovered where the originally reported high-symmetry structure of an inorganic oxide is found to be only an approximate substructure at ambient conditions (although it may be the true structure of a higher temperature form of the material). Examples of relatively recently discovered large oxide superstructures previously incorrectly reported in the literature as high-symmetry phases and/or with smaller unit cells include, for example, ZrP_2O_7, $La_2Mo_2O_9$ and $Mo_2P_4O_{15}$. Some of these oxides possess truly remarkable complexity in terms of the number of crystallographically unique atoms (Figure 1). Originally reported as a cubic material with a = 8.23 Å, at room temperature ZrP_2O_7 crystallises in the orthorhombic space group Pbca, with unit cell parameters a = 24.7437(4) Å, b = 24.7258(3) Å and c = 24.7507(4) Å and 136 atoms in the asymmetric unit[2]. $Mo_2P_4O_{15}$ was first described as monoclinic P2$_1$/c, with a = 8.3068(8) Å, b = 6.5262(6) Å, c = 10.7181(11) Å and β = 106.705(8) with 11 unique atoms, but a more recent single crystal study showed the true unit cell to be about 21 times larger in volume, with a = 24.1134(6) Å, b = 19.5324(5) Å, c = 25.0854(6) Å and β =100.015(1)^o and space group Pn; this corresponds to 441 crystallographically independent atoms[3]. Preliminary investigations of SnP_2O_7 and GeP_2O_7 suggest that their superstructures can be even more complex and contain as many as 540 and 1080 unique atoms, respectively.

In this article, we focus on the important oxide-ion conductor $La_2Mo_2O_9$. When it was first synthesized by Fournier et al.[4] , $La_2Mo_2O_9$ was described as a cubic material with the unit cell parameter a = 7.155 Å. Its exceptional oxide ion conductivity was reported by Lacorre et al.[5], who associated the rise in conductivity of almost two orders of magnitude with a phase transition from the room temperature α-form to a high temperature β-form at 580°C. They showed by powder neutron diffraction that β-$La_2Mo_2O_9$ is in fact a cubic material with a = 7.2014(5) Å and suggested on the basis of neutron and electron diffraction data that the true crystal symmetry of the room temperature phase is monoclinic. Full structural characterisation of α-$La_2Mo_2O_9$ and its correlation with the highly conductive beta-form, however, was not achieved until single crystals became available[6].

2. α-La$_2$Mo$_2$O$_9$ Structure Determination and Description

Polycrystalline $La_2Mo_2O_9$ was prepared from stoichiometric amounts of La_2O_3 and MoO_3, by heating an intimate mixture of the reactants at 900°C for 3 days with intermediate grinding. A small amount of the powder obtained was melted, cooled at a rate of 3°/min to 300°C and furnace cooled to room temperature. Very small crystals were isolated from the cooled melt. Single crystal X-ray diffraction was carried out on a Bruker SMART three-circle diffractometer equipped with an APEX CCD detector and a Bede Microsource$^®$ X-ray source of Mo K$_α$ radiation. A cube-shaped crystal of approximate dimensions 0.04 ×

0.04×0.04 mm^3 was used. A full sphere of data was collected with a counting time of 40 seconds per frame. A multiscan absorption correction was applied to the raw data and it gave R$_{int}$ of 2.8%. The structure was solved by a combination of direct methods implemented in the program SIR92 [7] which gave the metal sites, and difference Fourier maps that revealed the oxygen atom positions. It was refined by full-matrix least squares against F in the Crystals [8] suite. The final model was obtained by anisotropic refinement of cations and isotropic treatment of oxygen atoms and gave agreement factors of R = 8.80 % and wR = 8.78 %. Crystallographic details are given in Table 1.

Table 1: Crystallographic details for α-La$_2$Mo$_2$O$_9$

Formula	La$_2$Mo$_2$O$_9$
MW	613.69
Space group	P2$_1$
a (Å)	14.325(3)
b (Å)	21.482(4)
c (Å)	28.585(6)
β (°)	90.40(3)°
V (Å^3)	8796(3)
Z	48
Density (g/cm^{-3})	5.561
μ (mm^{-1})	14.8
# unique reflections	27496
# observed reflections	19233
# parameters refined	1730
R (%)	8.80
wR (%)	8.78

The key conclusion of the elucidation of the α-La$_2$Mo$_2$O$_9$ structure is that the 48 unique Mo atoms are found in three different coordination types: 15 are tetrahedral, 15 trigonal bipyramidal and 18 octahedral (typical local coordinations are shown in Figure 2a). The 6-coordinate Mo atoms in α-La$_2$Mo$_2$O$_9$ typically contain one bond significantly longer than the others, as commonly seen in some other d^0 systems. A polyhedral representation of the structure of α-La$_2$Mo$_2$O$_9$ is shown in Figure 2b.
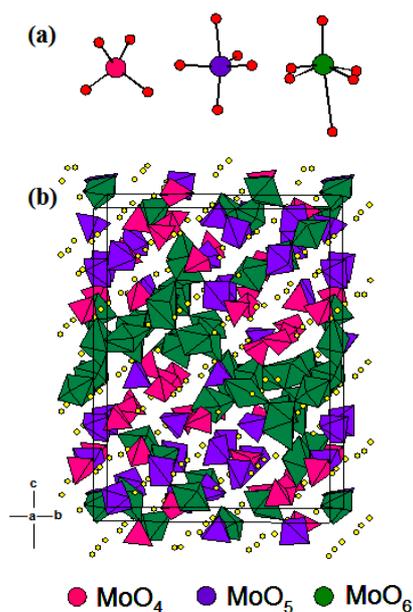
Figure 2: *(a) Three Mo coordination geometry types observed in α-La$_2$Mo$_2$O$_9$. (b) Polyhedral representation of α-La$_2$Mo$_2$O$_9$: tetrahedral groups shown in pink, trigonal bipyramidal in purple, octahedral in green; yellow spheres represent La atoms. (Figure reproduced from Evans et al. [6], by permission from the ACS).*

A comparative analysis of the oxygen atom distribution in the α-La$_2$Mo$_2$O$_9$ structure and in the high temperature β-form provides insight into the oxide-ion conduction mechanism in this material (Figure 3).
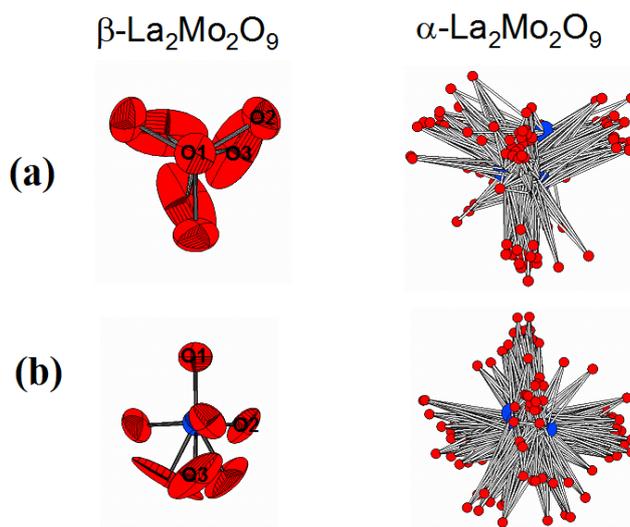
Figure 3: Comparison of Mo site coordination in β-La$_2$Mo$_2$O$_9$ and α-La$_2$Mo$_2$O$_9$; (a) and (b) show two mutually perpendicular views. For α-La$_2$Mo$_2$O$_9$ the picture represents a superposition of all independent Mo atoms and their coordination spheres, obtained by transformation of the monoclinic superstructure into the underlying cubic subcell. (Figure reproduced from Evans et al. [6], by permission from the ACS).

There is a clear correlation between the distribution of dynamically disordered oxygen atoms in β-La$_2$Mo$_2$O$_9$ and the static oxygen atom distribution in α-La$_2$Mo$_2$O$_9$. This is illustrated qualitatively by the positions and numbers of unique oxygen atoms in α-La$_2$Mo$_2$O$_9$ relative to the shapes of oxygen atomic displacement parameters and site fractional occupancies in β-La$_2$Mo$_2$O$_9$ found in the powder neutron diffraction study. To quantify this relationship, the 216 unique oxygen atoms in the α-La$_2$Mo$_2$O$_9$ structure can be subdivided into those that lie closest to each of the three crystallographic sites O1, O2 and O3 used to model the disordered β structure. It is found that there are 47, 116 and 53 oxygen atoms that lie nearest to O1, O2 and O3 sites of β-La$_2$Mo$_2$O$_9$ respectively, which, taking site multiplicities into account, corresponds to fractional site occupancies in a simple cubic model of 0.33, 0.81 and 0.37; these are remarkably close to the O1, O2 and O3 oxygen site occupancies for β-La$_2$Mo$_2$O$_9$ of 0.33, 0.78(2) and 0.38(2) determined experimentally by powder neutron diffraction [9].

This comparative analysis of the two forms of La$_2$Mo$_2$O$_9$ thus provides compelling evidence that the structure of the oxide ion conducting phase corresponds to a time-averaged version of the room temperature structure and that an order-disorder phase transition facilitated by the variable Mo coordination in the α-structure is responsible for the onset of high oxide-ion conductivity.

3. Structure Validation

The structure of α-La$_2$Mo$_2$O$_9$ is far from that of a "typical" inorganic oxide. The 312 atoms (48 La, 48 Mo, 216 O) in the asymmetric unit make it the second largest oxide structure solved by single crystal methods in the 2006 issue of ICSD (the first and the third containing 441 and 136 unique atoms, respectively); when deposited (2005) it was the sixth largest structure of any type in the ICSD. In many ways the structure complexity is closer to that of a small protein than a normal inorganic material and it is important to assess the quality and uniqueness of the solution in that light.

A first indication of the quality of the refinement is given by the range of the atomic displacement parameters, with min/max/average/esd of U_{equiv}/U_{iso} values for La, Mo and O sites of 0.009/0.067/.20/0.01, 0.010/0.045/0.017/0.007 and 0.009/0.11/0.04/0.02 Å^2, respectively. The values are

thus all within the range expected for materials of this type. Bond valence sums [10] have also been calculated to assess the quality of the refinement. It should, however, be noted that for a structure this complex, in which the scatter is dominated by La/Mo sites, the uncertainty on individual M-O bond lengths is relatively large. This in turn leads to an uncertainty in individual bond valence sums of up to half a unit. When bond length uncertainties are propagated into bond valence calculations as uncorrelated errors, the spread of bond valence sums is such that all observations are within 3 standard uncertainties from the expected values of 3 and 6 for La and Mo sites, respectively.
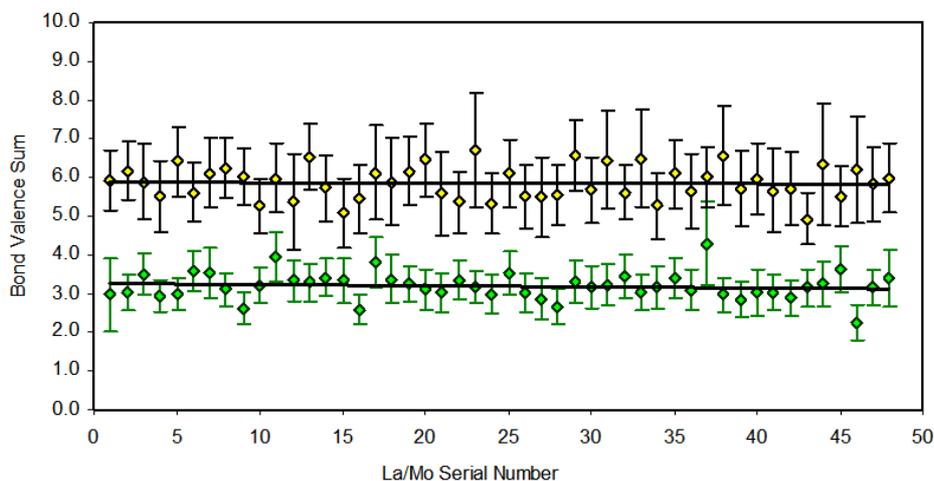
Figure 4: *Bond valence sums for the 96 cations in the freely refined structure (Mo in yellow, La in green). Error bars are plotted as ±1.5 esd's based on standard uncertainties in M-O bond lengths.*

To assess the sensitivity of the data to small variations in atomic arrangements, we have developed methods in Topas-Academic[11] for simultaneously refining against single crystal data and bond valence summation restraints and refined our model against both sets of observations. Restraints were weighed in such a way that individual La valence sums ranged from 2.94 to 3.17 and Mo from 5.99 to 6.05, i.e. a deliberately narrower range than one might expect to find in practice. The distribution of La, Mo and O bonds valence sums corresponding to the freely refined model and the refinement with bond valence restraints is shown in Figure 5.
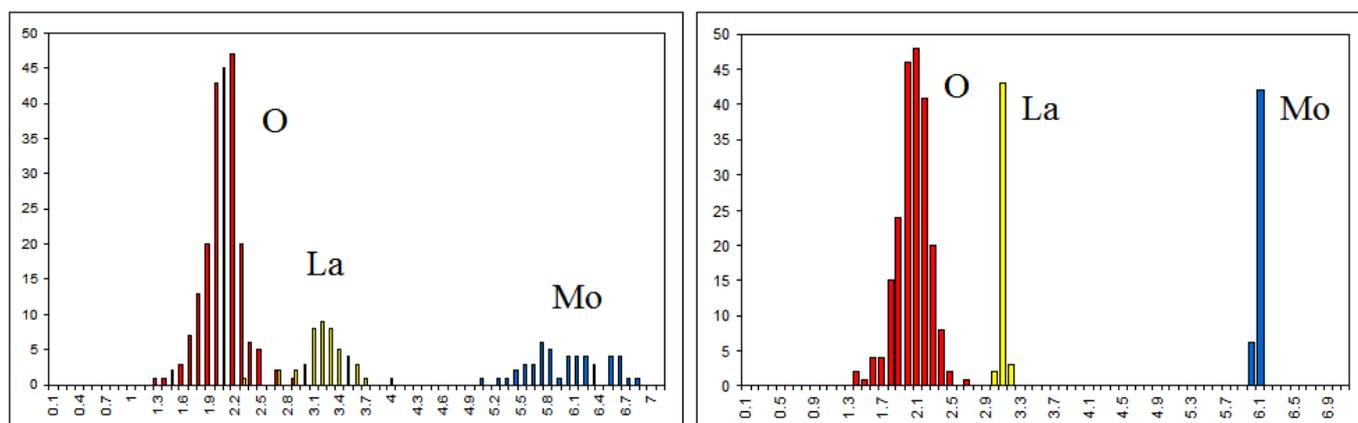
Figure 5: Histograms of bond valence sums for the 312 unique atoms in α-$La_2Mo_2O_9$. (a) in the freely refined structure, R=8.80%, (b) in the structure refined using cation bond valence restraints, R=9.25%.

The final agreement factor for the restrained refinement was 9.25%, slightly higher than 8.80% for the free refinement, but the key comparison is that between the two structural models obtained. In the restrained refinement model atomic coordinates differ by an average of 0.076 Å from those obtained by conventional unrestrained refinement, and the largest shift of any atom was 0.173 Å. We note that given the average standard uncertainties on the oxygen coordinates in the freely refined structure

(0.0027/0.0019/0.0016 for x/y/z coordinates), a shift of one esd in x/y/z would correspond to a distance of ~0.073 Å (essentially identical to the average shift of atoms between these models). We conclude that a restrained model with statistically insignificant shifts in coordinates from the freely refined one gives bond valence sums in excellent agreement with those expected.

Due to the complexity of the structure it is impossible to be as precise about individual oxygen atoms parameters as one could be for a simple material. There remains a possibility that a small number of the 216 oxygen sites are partially disordered over two or more positions. This can perhaps be inferred from the slightly higher atomic displacement parameters for certain O sites; 8 of the 216 oxygen sites have U_{iso} values in the range of 0.09-0.11 Å^2. However, the data quality is not sufficient to allow this possibility to be investigated further, but the magnitude of the atomic displacement parameters suggests that the extent of any possible disorder is relatively low. The structural model given for α-$La_2Mo_2O_9$ is consistent with powder neutron diffraction data, as shown by Rietveld fits, and the recently published results[12] of the neutron pair distribution function analysis carried out on the two forms of this material.

In conclusion, the use of bond valence sum restraints can be a powerful and useful method to validate complex inorganic oxide structures.

References

(1)   Evans, J. S. O.; Evans, I. R., *Chemical Society Reviews.* **2004,** 33, 8, 539.

(2)   Stinton, G. W.; Hampson, M. R.; Evans, J. S. O., *Inorganic Chemistry.* **2006,** 45, 11, 4352.

(3)   Lister, S. E.; Evans, I. R.; Howard, J. A. K.; Coelho, A.; Evans, J. S. O., *Chemical Communications.* **2004,** 22, 2540.

(4)   Fournier, J. P., Fournier, J., Kohlmuller, R., *Bull. Chim. Soc. Fr.* **1970**, 4277.

(5)   Lacorre, P.; Goutenoire, F.; Bohnke, O.; Retoux, R.; Laligant, Y., *Nature.* **2000,** 404, 6780, 856.

(6)   Evans, I. R.; Howard, J. A. K.; Evans, J. S. O., *Chemistry of Materials.* **2005,** 17, 16, 4074.

(7)   Altomare, A. C., G.; Giacovazzo, C.; Guagliardi, A.; Burla, M.C.; Polidori, G.; Camalli, M, *Journal of Applied Crystallography.* **1994,** 27, 437.

(8)   Betteridge, P. W., Carruthers, J.R.,   Cooper, R.I.,   Prout, K.,   Watkin, D.J, *Journal of Applied Crystallography.* **2003,** 36, 1487.

(9)   Georges, S.; Goutenoire, F.; Altorfer, F.; Sheptyakov, D.; Fauth, F.; Suard, E.; Lacorre, P., *Solid State Ionics.* **2003,** 161, 3-4, 231.

(10)   Brown, I. D.; Altermatt, D., *Acta Crystallographica Section B-Structural Science.* **1985,** 41, AUG, 244.

(11)   Coelho, A. A. *TOPAS Academic*, 2005.

(12)   Malavasi, L.; Kim, H.; Billinge, S. J. L.; Proffen, T.; Tealdi, C.; Flor, G., *Journal of the American Chemical Society.* **2007,** 129, 21, 6903.

Teaching of Molecular Symmetry to Pakistani Students

Zia Khan
Professor of Physical Chemistry, Department of Chemistry, The Islamia University of Bahawalpur, Pakistan. E-mail: zfk2000@mul.paknet.com.pk

Although Pakistan had to face many problems after independence in 1947, the education sector was already established and working satisfactorily. School education was stable and there were number of quite famous high schools in almost all parts of country. Another reason was, foreign teachers, especially from western countries were teaching in some institutions. Also there were colleges of good reputation in Lahore, Rawalpindi, Bahawalpur, Multan, Peshawar and Hyderabad.

In early 1950's only one university, the University of Punjab was working, which was founded in 1882. Most of the colleges were affiliated with Punjab University and some were more than 100 years old. Most of the high schools, all over the country were well established and major science subjects, like physics, chemistry, mathematics, biology etc, were being taught along with necessary lab work. However the science education at B.Sc. level was slightly lagging behind the rest of the world, due to lack of funds, skilled teacher, shortage of labs etc. At the B.Sc level in the early 50', chemistry, physics, maths and biology used to be taught, but the courses were old, lacking in atomic and molecular theories, quantum mechanics, spectroscopy, etc. In some colleges, the standard of teaching chemistry was appreciable. Especially the standard of organic chemistry. Though some could lack chemical bonding and other modern structural chemistry knowledge. Some chapter like "stereo chemistry", just gave some introduction about "symmetry", since the topics like optical activity were already present even in old books.

Some more new universities were established between 1955 to 1960, e.g. the university of Karachi, Sind, Baluchistan and Peshawer. Some post graduate colleges were also established, like F.C College (Lahore), Govt. College (Lahore), and Islamia College (Peshawar). After 1960, Islamabad University was established, which enjoyed the benefit of being in the capital, and more funds. However the educational system was still under experiments. Many systems were running at the same time such as:

i.   Two years B.Sc.
ii.   Three years B.Sc. (Hons)
iii.   Semester system at M.Sc. level

Such difference created distance from "real" science courses. Although chemistry and physics were progressing steadily, important topics like spectroscopy, crystallography, atomic and molecular theories and molecular symmetry were still far from the students and teachers. At that time, there was a great need of specialist teachers in all major science subjects. The government realized this and started sending the teachers abroad for PhD, mostly to Europe, USA and Canadian universities. Unfortunately most of the teachers started their PhD in relatively easy and less important fields, which were not of any use for the real development of science education. Symmetry, crystallography, spectroscopy, structural science were left ignored. After returning back to Pakistan, there was still no satisfaction, and teachers (PhD) were still lacking in Molecular symmetry knowledge. Spectroscopy was another important field in Chemistry, Physics and other Natural science. There are some important branches like UV/VIS, IR, NMR, ESR etc. and spectroscopy can never be understood completely without the knowledge of symmetry, especially symmetry of atomic and molecular orbitals, symmetry of various energy levels (ground state and excited), symmetry in NMR and ESR allowed and forbidden transitions, symmetry in selections rules of spectroscopy. Furthermore the perturbation theory is also involved in spectroscopy, and so the symmetry. Reaction mechanism also need the understanding of symmetry of the reactants and products.

Around 1970, there was much revolution in the courses of all the universities and their affiliated colleges. Punjab University was controlling most of the colleges, who were offering B.Sc classes (two years). Following subjects were of major interest.

i.   Physics + Chemistry + Mathematics (All majors)
ii.   Physics + Math A + Math B (All majors)
iii.   Statistics + Physics + Mathematics (All majors)
iv.   Statistics + Math A + Math B (All majors)
v.   Chemistry + Zoology + Botany (All majors)

While English was compulsory in all combinations, each student had to opt for one of the above combinations. Unfortunately there were two major groups of students all the time

a.   Students with no or very little mathematical background.
b.   Students will enough mathematical background.

Also, there were three main parties all the time; teachers, students and their parents, and 90% of the parents knew nothing about graduate level subjects. Mainly they were interested to force their children into "money making" or "well paid" jobs. That is why students in their high school time, used to think of going to medical colleges and other similar fields, where no math was required.

Students whose interest was only in physics, rushed to (physics + math A+ Math B) group. Student interested in chemistry, with enough math background selected, (physics + chemistry + math) group. While another option was (zoology + botany + chemistry). At that stage there were also two main groups of science teachers. One with strong math back ground and other with no or weak back ground. Ideally, the best combination for B.Sc was the (Physics + Chemistry +Math) group, since in this group students had enough back ground of all the there subjects. At B.Sc level, courses were strong and following topics were taught in two years program.

i.   **Physics: -**   the main topics were classical Mechanics, Modern physics, wave mechanics, solid state, thermodynamics, electronics etc.
ii.   **Chemistry: -** Physical chemistry, Inorganic chemistry and organic chemistry
iii.   **Mathematics: -**   Algebra, calculus, vectors, analytical geometry, classical mechanics, wave mechanics etc.

There was a great need for a general collaboration among some of the above subjects, namely Physics, Chemistry and Mathematics. Unfortunately, each subject was taught in such a way, that even if molecular symmetry and group theory had to be present in all these subjects, the students would have interpreted them differently. There was a one chapter "Group Theory" in the mathematics syllabus in detail, but it was more mathematical and most of the Math teachers used to teach some theorems, and tedious exercises. There were no examples, or links to any atomic or molecular structure and also, no correlation of "Group Theory" with any practical examples.

Similarly if a student of B.Sc is attending the Physics class, the student was only following, long mathematical steps, almost in each chapter, with no understanding of symmetry at all. There were some topics in Physics, like polarization of light, solid state Physics, spectroscopy etc. which directly or indirectly involved symmetry.

On the other hand in chemistry, where several topics need the understanding of symmetry. More or less following chemistry topics like;

i.   Atomic spectroscopy
ii.   Molecular spectroscopy
iii.   Solid state chemistry

iv.   Atomic and molecular orbitals
v.   Stereo chemistry
vi.   Statistical thermodynamics
vii.   Photo chemistry
viii.   Structural chemistry

Despite a poor background in Molecular symmetry, students used to "memorize" many topics. It was expected from a B.Sc student to obtain a sound knowledge of all those topics, which required enough knowledge of symmetry, but all was not right. A professor of organic chemistry at a Pakistani University was teaching "conformational Analysis" around 1980. He realized that it is very tedious job to make the students fully understand, how rotation around a single bond happened. He was feeling difficulty to illustrate various atoms or groups to rotate on the board. He even tried good ball and stick models, but students were never satisfied. He took the help of a mathematics professor to teach "group theory" to his students. The mathematician spent two weeks, but he failed. The only reason was that he was explaining all, without any illustrations, on direct examples of organic compounds.

At the same time, a chemistry teacher decided to deliver "chemical applications of group theory" lecturers. He too could not satisfy the students. He then asked all the students to make models of various symmetric molecules, and then to show, various symmetry elements, like axis of rotation, planes of symmetry etc. Surprisingly 90% of the students were able to explain the symmetry of C2v, C3v, Td and Oh points groups in few days.

However at the National level, there was need for full collaboration among various universities to make symmetry, an interesting topic and not a mystery.

Several chemists, biologists and physicists tried in various meetings to find some best solution, but students could not follow beyond the "point group". Some followed till "Multiplication tables" of simple molecule, H_2O, NH_3 etc. After 1980 there were new attempts to upgrade the courses at B.Sc, M.Sc, M.Phil and higher level. Following topics were added to master level.

- basic concepts
- symmetry operation
- point groups (C2v, C3v, Td, Oh)
- multiplication tables applications of symmetry to spectroscopy,
- crystallography etc.

Some courses in 1980s concerning crystallography (as a part of solid state) were also redesigned, with the following topics.

- symmetry in crystals
- symmetry in unit cells
- transformation matrices'
- space groups.

However "space groups" need more discussion at master or higher level due to lack of explaining techniques and illustration. In fact, it can be confusing to explain symmetry on the class board alone. One also needs various excellent Molecular models, audio visual methods etc. There is also the need of encouraging the students to deliver lectures themselves, some nice assignments, some discussion groups and 3-D structure building in the lab.

Here is the syllabus which was presented in 1980's to be part of M.Phil in Math and Physics.

- Linear vector spaces.
- Groups.
- Representations of groups.
- Characters.
- Schur's Lemmas.
- Lie groups.
- Representation of lie groups.
- Rotation group and SU(3).
- Clebsch-Gordon coefficients.
- Rotation matrices.
- Wigner-Eckart theorem.
- Kronecker product of irreducible representations.
- Spinor representations of Lorentz group.
- Elementary theory of Wigner's unitary representations of Poincare group.

After 1990, the introduction of PCs and Internet has brought a major change in molecular symmetry teaching. Some easy to follow software has solved the problem of understanding crystal symmetry, point groups, 3-D illustrations of symmetry operations, multiplication tables even for large molecules, character of a matrix, Transformation matrices, space groups etc. Moreover, many Internet resources contained freely downloadable software for symmetry and even all branches of spectroscopy. There are quite a few software packages for the following spectroscopy fields:

- IR
- UV/VIS
- General and High Resolution NMR
- ESR
- Rotation-vibration spectroscopy
- Statistical mechanics software

The CCP14 also offered its wonderful crystallographic software CD ROM, which are free for academic users and of great help in teaching and research.

Coming back to important topic of spectroscopy, where it is impossible to interpret any spectrum in detail without the knowledge of molecular symmetry. In Pakistan, spectroscopy is generally used in all major fields of physical and biological sciences. In Karachi there is a centre of excellence in natural products which use to work on isolation and characterization of natural products. They often need work on various spectroscopic techniques such as UV-visible, IR, NMR etc. But strangely there is no regular courses which can provide enough background of symmetry to their research students up to PhD level. There is another centre of excellence of analytical chemistry in Hyderabad which offers many post graduate courses to PhD, and also use spectroscopic technique like UV-visible, IR, NMR, mass spectroscopy. They offer courses to their students but symmetry is still mystery there.

Peshawar University is also having centre of excellence in physical chemistry but they deal with Polymer chemistry and surface chemistry mostly. Even then at some stages they must need crystal structure and knowledge of molecular structure, point group and space group etc. Another centre of excellence in geology is also working in Peshawar, but symmetry knowledge is missing, either in courses or research.

In Punjab University's Centre of Excellence in Solid State Physics, courses in crystallography at postgraduate level are offered. Even in the recent survey, they are far away from essence of symmetry and its applications in crystallography.

Quaid-e-Azam university Islamabad has well funded departments, such as physics, chemistry, geology, where is no shortage of good instruments. However they offer solid state and crystal knowledge as an optional paper. In their short semester courses in M.Phil and PhD level ignore symmetry of crystals, space groups etc.

Chemistry department, at Bahawalpur is offering symmetry courses to Ph.D., M.Phil., and MSc. Students and mainly following topics are being taught;

- introduction
- symmetry operations
- point groups
- examples
- multiplication tables
- C2v, C3v, D6d, Td, Oh point groups
- transformation matrices
- reducible and irreducible representations
- symmetry of orbitals
- symmetry and spectroscopy
- space group and its applications.

Symmetry is of a much consideration and important for new generation of biological sciences. There is centre of excellence in molecular biology in Faisalabad which is offering a two week workshop for all Pakistan university teachers and research scholars recently. Unfortunately they use older method of spectroscopy, UV-visible, IR, NMR, involving no knowledge of symmetry.

There is a great need of national organization which should review the courses of all university from time to time from B.Sc. to Ph.D level. Pakistan universities cannot get away with simple and old courses. In the present age of international competition, and the courses of Pakistan universities must be made in comparable with other world leading institutions.

Teaching of Crystallography to Chemistry and Physics students in Pakistan

Zia Khan
Professor of Physical Chemistry, Department of Chemistry, The Islamia University of Bahawalpur, Pakistan. E-mail: zfk2000@mul.paknet.com.pk

Pakistan came into being into 1947. Right from the beginning, Pakistan has to face many educational problems, although there was no shortage of good high schools and colleges throughout the country. However at that time only one university, the University of Punjab was present. There were few affiliated colleges enrolling the students for a bachelor degree and in some disciples for master degree. The minimum requirements for bachelor degree was two years of registration follow the higher secondary school certificate, while at master level two years of registration following the successful completion of the bachelor degree programme. The University of Punjab had a very strict policy of admission purely based on merit and there were a limited number of seats available in every discipline that the university offered. The University of Punjab was founded in 1882 with very rich tradition of scholarly learning in many disciplines of moral philosophy and natural philosophy, including chemistry, physics and life sciences. Due to the political disturbance soon after World War II and after 1945, the highly qualified foreign staff had left the Punjab University. The country also needed more colleges and universities since the students in Pakistan no longer had to access to the institute of higher learning in other parts of united India. The government of Pakistan instituted a few new universities around 1955, such as university of Karachi, university of Sindh, university of Peshawar and university of Balochistan. All universities were having affiliated and constituent colleges. The majority of colleges offering B.Sc in chemistry, physics, mathematics and biological sciences. Crystallography was included in the required course contents of the subject of chemistry and a part of it was also added in the subject of physics. Therefore a student opting chemistry, physics and mathematics had both theoretical perspective and analytical ability to learn the fundaments of the subjects such as crystal systems, Weiss indices, Miller indices, Bragg's law, X-ray diffraction, powder method, single crystal method, general indexing and many other theories and laws.

Around 1960s, Punjab University and other new universities were well established according to Pakistan needs. The standard of BSc education, especially in physics and chemistry was appreciable. Some of the colleges, affiliated with Punjab University were offering the chemistry and physics combination at 2 years BSc level. However at some places due to the laboratory problems standards were not up to mark. There were also BSc (Hons) were offered at university of Pufnjab in the chemistry department. The only problem at that stage was the deficiency in specialist teachers, so the government of Pakistan arranged to send university teachers abroad, to Europe, USA and Canada for Ph.D degree in all major science fields. Meanwhile a new university in Islamabad was established, was fully funded more than any other university in Pakistan.

The course work of various universities was revised and crystallography got the boost not only at BSc level but also at master level of physics and chemistry. The syllabus of crystallography in physics was as follow; basic concepts, crystal system, Miller indices, Brag's Law, single crystal and powder method of X-ray diffraction (mainly inorganic crystals). While in chemistry all the above topic plus application to organic compounds was preferred. However due to deficiency of specialist teachers, students used to "memorize" rather than understanding the crystallography in detail. Furthermore the concepts of unit cell and crystal planes in 3-D were never cleared to both physics and chemistry students, due to the lack of knowledge of geometry and trigonometry. Even in the solved problems and exercises, there was not enough guidance to the students who already were in the habit of memorizing. There were also some more difficulties for the students in getting a clear picture of various lattice types, such as FCC, BCC, ICC etc. Even for a NaCl crystal it was a great confusion among the students, how positive and negative ions are surrounded in a unit cell. Furthermore the organic crystals were more difficult, due to having different types of bonds. On the other hand, mathematicians in various universities could not help in

crystallographic teaching, even to explain the Fourier-synthesis and the structure factor mathematical steps.

At the B.Sc level, courses were strong and following topics were taught in two years program.

i. **Physics:-** the main topics were classical Mechanics, Modern physics, wave mechanics, solid state, thermodynamics, electronics etc.
ii. **Chemistry:-** Physical chemistry, Inorganic chemistry and organic chemistry
iii. **Mathematics:-** Algebra, calculus, vectors, analytical geometry, classical mechanics, wave mechanics etc.

In physics, crystallography was the part of the solid state, and following articles were included.

- basic concepts
- crystalline systems
- Weiss and Miller indices
- Bragg's Law with examples.

While in chemistry, crystallography was included in physical chemistry course, where the following topics were taught.

- introduction
- crystalline systems
- examples of organic and inorganic crystals
- Bragg's Law
- interference and diffraction and effects on Bragg's law
- Weiss and Miller indices
- some basic symmetry of crystals.

Mathematics consisted of classical Mechanics and major topic of "Groups Theory". Although "Group Theory" was much help, especially for crystallography, unfortunately it was written in more mathematical way and applied examples were limited only to numbers. Most of the students used to leave this "Group Theory" topic; and leave at an even higher rate if the maths teacher did not guide properly.

Further more, the experimental techniques like single crystal and powder methods were taught to both physics and chemistry students. However, there was no real interpretation both for physics and chemistry students. There were experiments, separately about interference, diffraction and polarization of light experiments to physics and chemistry students. But these experiments were always lacking in true applications to crystallography. In brief, despite balanced courses, supporting books and some very good teachers, crystallography at B.Sc. level was never well described.

Soon after 1970 master courses in physics and chemistry were also re-designed. In physics following topics were included in the first year of the two years M.Sc program.

i. Classical Mechanics
ii. Solid state physics
iii. Electronics
iv. Modern physics
v. Quantum Mechanics
vi. Statistical mechanics

In the 2nd year, students used to opt for some specialization, such as one or two of the above along with some short research project. However limited numbers of students opted for crystallography.

The following topics were included in crystallography.

- basic concepts
- crystalline systems
- unit cell
- Weiss and Miller indices
- single crystal and powder method
- Bragg's law and its application to calculates inter planer distance and Bragg's angle
- Fourier synthesis, etc.

However physics students obtained little knowledge about nature of the crystals, which was limited to mainly simple cubic crystal systems (like NaCl etc). And also to calculate unit cell dimensions, a, b, c, α, β, γ (mainly cubic) etc. Due to lack of knowledge in organic structures, it was not possible for them to carry out work on organic crystals (which are more complicated due to them often being monoclinic and triclinic).

Chemistry students had to study the following courses in their 1st part of M.Sc (two year)

i.   Physical chemistry
ii.   Inorganic Chemistry
iii.   Organic Chemistry
iv.   Basic Math

While in 2nd year one of the following fields, along with a research project had to be chosen.

i. Physical Chemistry   (Quantum chemistry, Photochemistry), Statistical mechanics, solid state surface chemistry, spectroscopy, molecular symmetry and group theory)

ii. Organic Chemistry   Synthesis, Basic spectroscopy, various reactions mechanism etc.

iii. Inorganic chemistry   Inorganic theories, basic spectroscopy, P, D & F block chemistry, chromatography etc.

iv. Analytical chemistry   Mostly qualitative and quantitative analysis etc

Ideally students who opt for physical chemistry in a better position to understand crystallography, since they will have studied the following:

i.   various crystal systems
ii.   Bragg's law and applications
iii.   Weiss and Miller indices, along with its role in inorganic and organic crystals
iv.   Single crystal and powder methods, with applications to both inorganic and organic compounds.
v.   Fourier synthesis
vi.   Structure factor
vii.   Impetration of single and powder diffraction pattern
viii.   3-D structure determination etc.

This B.Sc and M.Sc system was successful not only in Punjab university from 1970-1980, but also in other new universities, like Multan, Karachi, Bahawalpur, Peshawar etc.

However, after 1980, the system of education was changed due to different teaching styles, due to many of the Pakistani teachers returning home after completing their Ph.Ds in Western countries. New discussions started to adopt the following systems:

i.   Already existing two year B.Sc and two years M.Sc programs.
ii.   Four year B.Sc (Hon) (term system)
iii.   M.Sc (semester) two years
iv.   M.Phil (two years)
v.   Ph.D (pure research)
vi.   Ph.D (by course + research)

Furthermore, most of teachers were not specialized in crystallography at all. Since all universities were independent in deciding their courses, so new courses covered crystallography only in few universities (Punjab, Bahawalpur, Multan, Karachi, Peshawar) while other universities were attracted to non-mathematical topics. Even in semester settings, teachers designed those topics, which were easy for them to teach. There was only one institution to advise the universities, the University Grants Commission (UGC) at Islamabad, but uniform courses could never been finalized

Some universities even purchased X-ray diffractometers (powder method) like centre of excellence in solid state physics (Punjab university) Multan, Karachi, Islamabad etc, which were useful for both physics and chemistry students who used to work on inorganic and organic crystals.

In the 1990s the introduction of PC's and the Internet totally changed the situation for crystallographers. Many confusing points were clarified by using software from the Internet (especially freely available), and later by the CCP14.

Although powder method instruments were available along with some good software, there were some problems, both for physics and chemistry students. Students were lacking in the space group knowledge. Even very good physics students could not follow additional lectures about crystal symmetry, due to lack of molecular knowledge, especially of organic compounds.

On the other hand, a chemistry student, even having enough molecular knowledge could not follow beyond simple crystals (cubic), and unfortunately most of the organic crystals belong to other systems (monoclinic, triclinic etc). This was because of "memorizing" the lecture notes and the shortage of specialist teachers in universities. There were never a shortage of excellent looks in Pakistani librararies, but both physics and chemistry students need professional, practical help in interpreting the X-ray diffractograms. Most of the students could not operate personal computers and hence they also needed practical help to install and run crystallographic software properly.

After 2000, there was a new trend among physical sciences students. With the development in computers, most of the parents "advised" their children to "more money making" subjects in B.Sc and master levels. Most of the physics students, rushed into B.Sc (computer science), a four years course. While some joined many professional business oriented programs, even at private colleges. Furthermore, many private universities opened, offering computer sciences, I.T, and business oriented degrees.

Finally it can be said with great regret, that crystallography standard in Pakistan universities has never been satisfactory. During a recent survey of various Pakistani universities, following useful results have been obtained.

1)   Crystallography is mostly being taught at masters, M.Phil and PhD level in very few universities.
2)   Crystal growing techniques are very limited and most of the chemists are lucky if they can grow any crystals.
3)   Very few universities have purchased a powder diffractometer.

4)   There is no real collaboration among universities to give access to other universities students who have not any diffractrometer.

5)   Most of the staff of various universities, both in physics and chemistry departments, are unaware of crystallographic software.

6)   Theoretical knowledge about crystallography is limited and basic. Teaching on advance topics like Fourier synthesis, space group calculation and structure elucidation is far from satisfactory, if taught at all.

There is a need for collaboration among the various universities. Regular workshops, lectures, discussions are required with physics and chemistry departments. The idea of a national crystallography curriculum is required, which should be funded by government.

Maximum Entropy Method - A Tool for Complete Structural Characterization of Crystalline Compounds

Roxana Flacau

Steacie Institute for Molecular Sciences, National Research Council, Ottawa, Canada; E-mail: Roxana.Flacau@nrc-cnrc.gc.ca

A detailed structural characterization of crystalline phases should not be limited to finding the system symmetry and accurate atom positions in the unit cell, but should also extend to the determination of all the other topological properties of the associated electronic charge-density distribution. Among other methods to calculate charge density distributions from diffraction data (i.e. multipole refinement), the Maximum Entropy Method (MEM) is unique due to the fact that it is a model-free method. The first successful MEM analysis of X-ray diffraction data, carried out for the purpose of deriving accurate electron density distributions, was reported for the case of silicon by Sakata and Sato in 1990 [1]. Since then, numerous MEM studies of X-ray and neutron diffraction data have been successfully carried out, revealing in-depth insights regarding the structural properties of various compounds [2-9].

The purpose of this paper is to introduce the steps required to calculate the most probable charge density distribution from powder X-ray diffraction data using MEM, as implemented in the package of analysis software RIETAN-2000/PRIMA [10, 11] and demonstrate the effectiveness of the combined Rietveld/MEM using some of our results.

MEM as Applied to Charge Density Distributions Calculations

As the information of electron distribution in the unit cell is contained in the structure factors, analysis of the experimental data needs to be initiated by Rietveld refinements. Once the observed structure factors are estimated from the X-ray diffraction data, they are used as constraints in the MEM analysis. The values of the observed structure factors can, obviously, be extracted by any of the available Rietveld software, but this author finds RIETAN-2000 more practical to use since it outputs the these values in a file format recognizable by the MEM software, PRIMA.

The procedure used by PRIMA for the purpose of calculating the most probable charge density distribution consistent with the observed structure factors will be briefly summarized, as the method is described in detail in the literature [10, 14]. First, the unit cell is divided in N pixels of equal sizes and then, the normalized, discrete charge density of electrons at each pixel, ρ_i, is considered as a probability distribution of independent events. Following these considerations, the entropy of the system takes the following form:

$$S = -\sum_{i=1}^{N} \rho_i \ln\left(\frac{\rho_i}{\tau_i}\right), \qquad (1)$$

where τ_i is the normalized density at i^{th} pixel derived from prior information (usually initially set to a uniform distribution at the beginning of analysis). S is then maximized subject to the following three constraints:

$$\rho_i > 0 \qquad (2)$$

$$\sum_{j=1}^{N_F} \frac{\left|F_c(K_j) - F_o(K_j)\right|^2}{\sigma_j^2} = N_F \qquad (3)$$

$$\sum_{i=1}^{N} \rho_i = 1, \qquad (4)$$

where N_F is the number of resolved reflections observed,

$F_c(K_j)$ and $F_o(K_j)$ are the calculated and the observed structure factors

for reflection K_j, respectively,

σ_j is the estimated standard deviation of the observed structure factor.

A problem that arises in using "observed" structure factors estimated by Rietveld method is that these factors are biased towards the structural model used as both phases and calculated profiles used for the intensity partitioning are derived from the model. This approximate nature of the procedure for extracting the structure factors lowers the accuracy of the electron densities determined by combining Rietveld and MEM for analysis. To minimize the bias due to the structural model, the MEM/Rietveld analysis is followed by iterations that utilize another analysis method, **M**EM-based **P**attern **F**itting (MPF) [13]. The MPF is implemented in the same software as the Rietveld analysis, RIETAN-2000. The MEM software evaluates calculated structure factors, F_c(MEM), by Fourier transform of the electron densities.
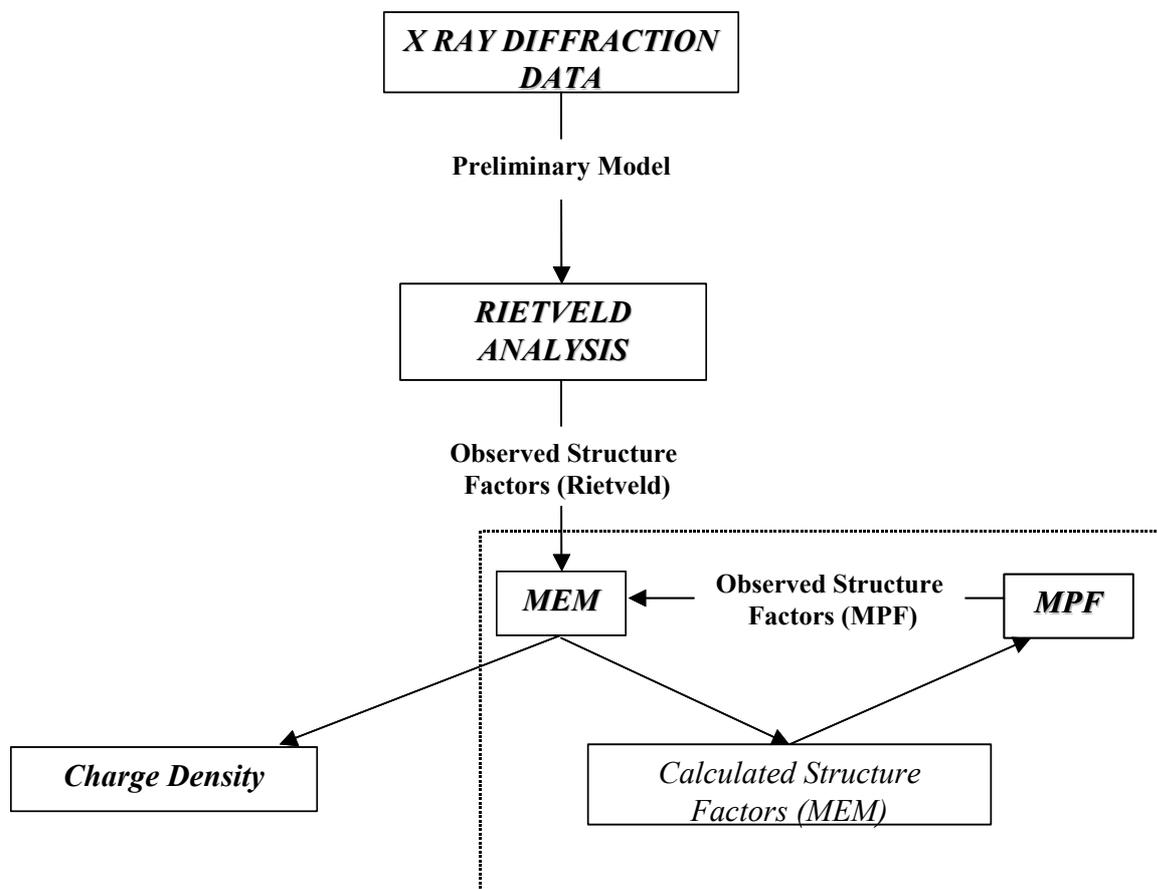
Fig. 1: *Rietveld/MEM/MPF analysis. The lower frame comprises the MEM/MPF iterative process*

Then, the calculated pattern is fitted to the observed one by fixing structure factors at values of F_c(MEM) obtained from the previous MEM analysis and refining only parameters irrelevant to the crystal structure (background, peak profile…). Calculated structure factors estimated by the MPF method as described before, F_o(MPF), are analyzed again by MEM. A schematic of the complete data analysis process is shown in Figure 1. This iterative procedure is repeated until the goodness-of-fit parameters (especially R_I and R_F) of the pattern fitting procedure no longer decreases.
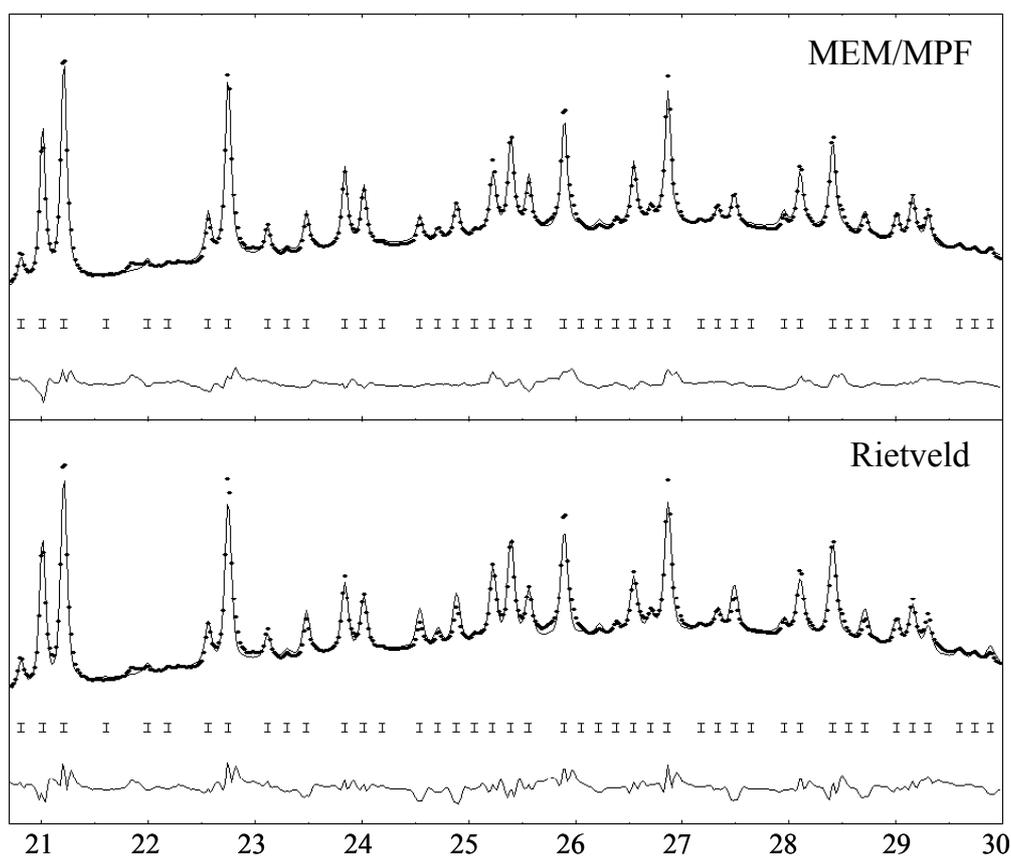
Fig. 2: *Observed and calculated X-ray diffraction patterns of Ba_8Si_{46}, in the high angle region. The goodness-of-fit parameters were R_{wp} =1.32%, R_I =5.80% for the Rietveld analysis and R_{wp} =1.05%, R_I =2.86% after 4 MEM/MPF cycles. The dot symbols denote the experimental data; the solid line, the calculated pattern; tick marks the calculated peak positions; the bottom curve represents the difference between observed and calculated patterns.*

Repetition of the MPF reduces the influence of the structural model on F_o (MPF). Once calculated, the charge density distribution can be visualized and examined using a computer program named VESTA [15].

The decrease of goodness-of-fit parameters during the MPF/MEM procedure shows that this iterative method is not only weakening the influence of the model initially used in the Rietveld analysis, but at the same time providing a more accurate system model to describe the experimental measurements. As an example, Figure 2 illustrates the improvement of the fit between the observed and calculated patterns after 4 MEM/MPF iterations as opposed to conventional Rietveld refinement for the case of Ba_8Si_{46} clathrate.

On the Accuracy of Charge Density Distributions as Constructed by MEM

The analysis of errors that affect the charge density distributions derived by MEM from XRD data is a complex problem, as different sources of uncertainties reflect into the accuracy of these distributions: experimental errors, errors related to the ability of Rietveld and MPF methods to extract the "observed" structure factors from the diffraction data, errors in the MEM calculation method (primarily influenced by the completeness of the observed structure factors set). Even though the estimation of uncertainties is a very important aspect for a full understanding and correct interpretation of the MEM charge densities, only a few studies of this problem have been reported so far in the literature [16-18], and charge density maps obtained by MEM are usually presented without discussion of errors. It should be first emphasized

that, since MEM is a model free method, the quality of X-ray diffraction data to be analyzed is critical. MEM is not reconstructing accurately the charge density distribution if the calculations are initiated from a diffraction pattern affected by systematic errors. Other intrinsic problems of MEM have also been emphasized lately in the literature. It has been shown that the incompleteness in the dataset of structure factors in the low angle region leads to non-physical features in the charge density distribution [16]. In very extreme cases, it would be even impossible to correctly assess atom positions. Also, if an insufficiently high number of structure factors is included in the MEM analysis, the fine details of the charge density distribution may be distorted [16, 18]. Merli and Pavese [18] argued that one should consider diffraction data up to at least $\sin(\theta)/\lambda \approx 1.5$ Å^{-1} to obtain accurate charge density distributions. From our experience, reliable charge density distributions can be produced even when only X-ray diffraction data in the $\sin(\theta)/\lambda < 1$ Å^{-1} range are available, if a large number of reflections compensate this relatively short range in $\sin(\theta)/\lambda$. The accuracy of the MEM-calculated charge density distribution of a polipeptide (trialanine) was very recently discussed by comparing MEM results with the results from the multipole refinement [19]. The two results were found to be in good agreement.

In the next section, some of our results that indicate the degree of complexity of problems that can be approached using MEM will be presented. We believe the study presented here is a clear example of MEM being able to access information beyond the reach of the classical Rietveld analysis.

Example of Questions Answered by MEM

We successfully applied the combined Rietveld/MEM/MPF method to explore the changes in the electronic density distribution induced in Ba_8Si_{46} clathrate by the application of high pressure [9]. Ba_8Si_{46} is a cage-like material, with silicon atoms forming the framework of the cages. Its cubic unit cell is formed by 6 large cages (on the faces) and 2 small cages (at the corners and in the center). At full occupancy, each cage contains one barium atom. One unit cell, delimited by the dotted black lines, is represented in Figure 3a.

The analysis was initiated from high quality high pressure angle dispersive X-ray powder diffraction of Ba_8Si_{46} clathrate measured as the pressure was increasing from 0 to 31 GPa. The total number of reflections, overlapping and nonoverlapping, considered in this study varied from 129 (at 0.3 GPa) and 95 (at 25.8 GPa). An example of the 3D charge density distribution in one unit cell calculated using MEM is shown in Figure 3b.
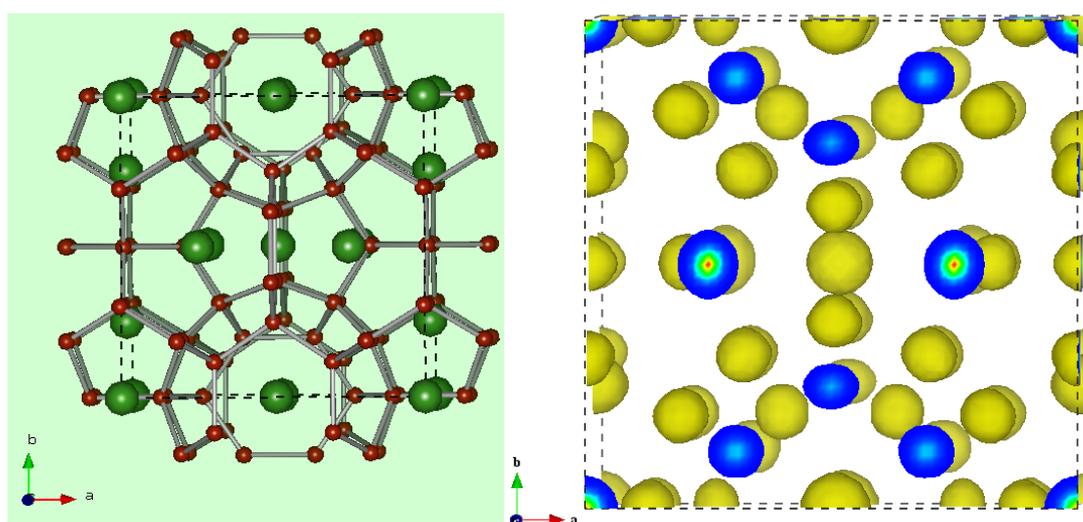
Fig. 3: *(a) The cubic unit cell of Ba_8Si_{46} clathrate with guest (Ba) full occupancy. The gray sticks represent the Si bonds forming the cage framework. The small and large spheres show the position of Si and Ba atoms, respectively. The dotted line marks the limits of the unit cell; (b) 3D equal charge density surface in Ba_8Si_{46} unit cell at 0.3 GPa obtained from the MEM analysis. The isosurface level is 2 e/ Å^3.*

Previous X-ray diffraction studies [20, 21] revealed that a homothetic phase transition takes place at around 16 GPa. The examination of the MEM calculated electron density distributions in our study explains the mechanisms of this unusual pressure induced transition. In Figure 4, 2D charge density distributions at selected pressures in the (110) plane, cutting through the middle of the Si-Si bond forming the cage framework, are presented.

A strong σ-covalent Si-Si bond can be observed at low pressure (1 GPa). As the pressure is increased the electron density between the two Si atoms becomes more diffused and delocalized. π-bonding like interactions are present above 16 GPa. The weakening of the Si-Si bonds results in the volume contraction assessed from Rietveld refinements.

1 GPa　　　　**9 GPa**

16 GPa　　　　**22 GPa**
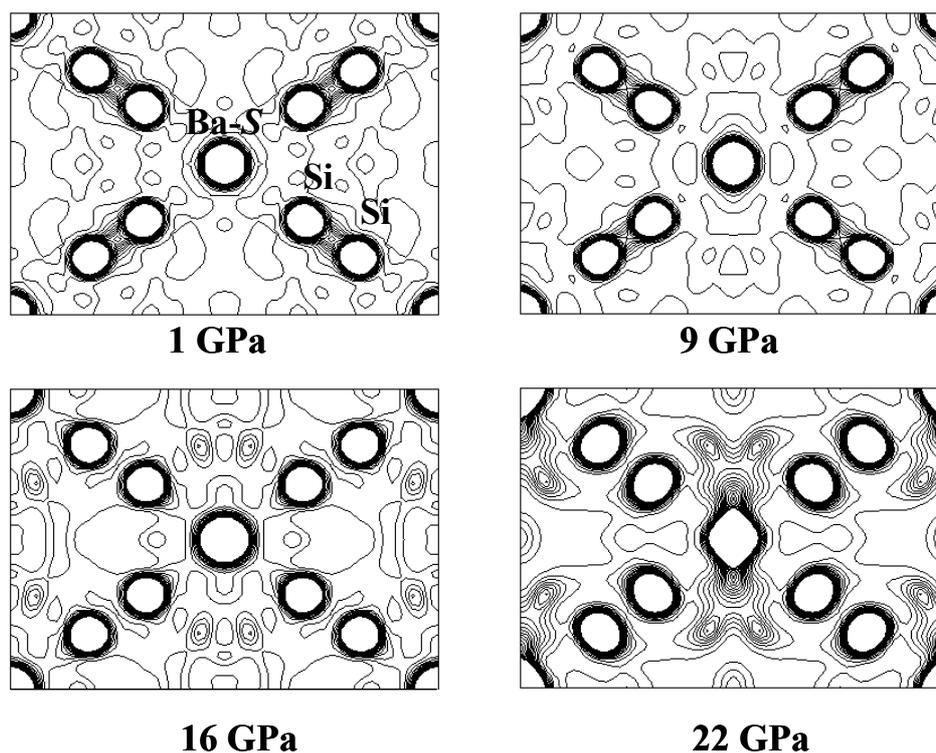
Fig. 4: *Contour plots of the electron density in the (110) plane at selected pressures, highlighting the Si-Si bond. Contour lines are drawn from 0.06 to 2.00 e/ $Å^3$ at intervals of 0.10 e/ $Å^3$.*

Another open question regarding the results of Rietveld refinements was the significant and unexpected increase of the isotropic thermal parameters of both Ba and Si atoms with the increase of pressure [21]. Again, the combined Rietveld/MEM/MPF method was very useful for understanding the nature of the disorder implied by this anomalous behavior of the thermal parameters. The (100) and (200) crystallographic planes were plotted as they highlight the barium atoms in the large (Ba-*L*) and small (Ba-*S*) cages, respectively.
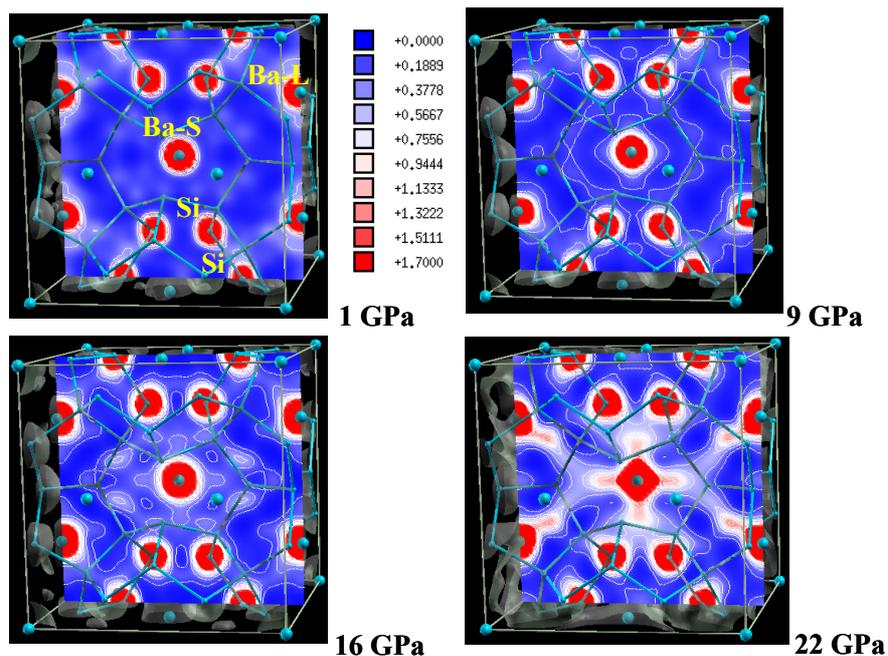
(100)
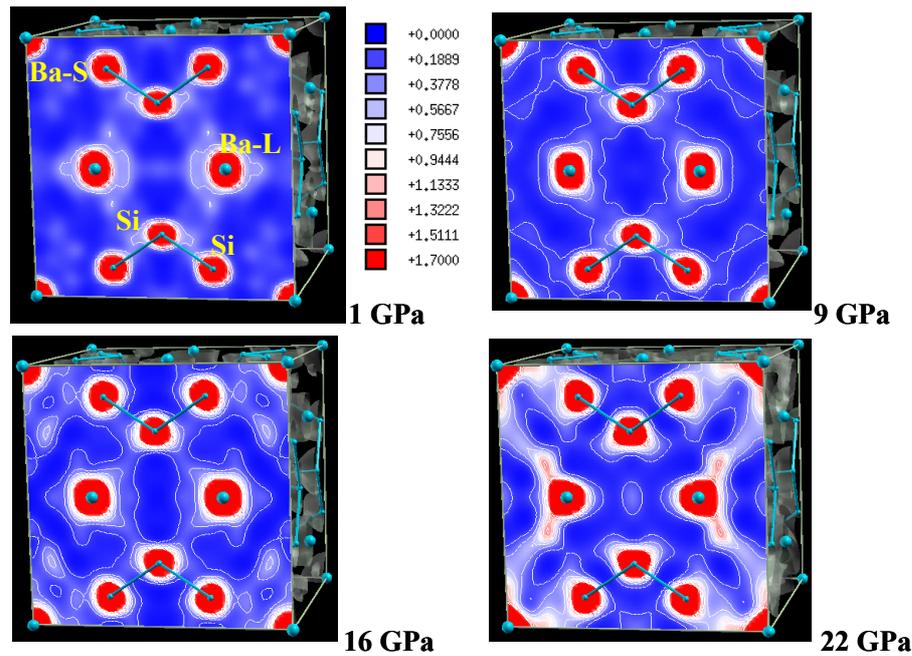
Fig. 5: *Contour plots of the charge density in the (100) plane, at selected pressures, highlighting the Ba atom in the large cage. Contour lines are drawn from 0 to 1.7 e/ Å³ at intervals of 0.10 e/ Å³.*

The examination of the charge density distribution plotted at selected pressures in the (100) plane (Figure 5) reveals that, while at low pressures the electron density is concentrated close to the center of the Ba-*L* atom, as the pressure is increasing the density distribution becomes more diffused. Above 16 GPa a dramatic distortion from the atom-characteristic spherical distribution takes place. The same picture emerges from the investigation of the charge density distributions plotted in the (200) plane (Figure 6) for the case of Ba-*S* and silicon atoms.

(200)

Fig. 6: *Contour plots of the charge density in the (200) plane, at selected pressures, highlighting the Ba atom in the small cage. Contour lines are drawn from 0 to 1.7 e/ Å³ at intervals of 0.10 e/ Å³.*

Moreover, a significant overlap of the valence electrons from the Si and Ba-*S* atoms can be clearly observed above 16 GPa. This leads us to the conclusion that the large thermal parameters determined from Rietveld refinements are indicating a dramatic change in hybridization of the electronic structure of the atoms.

Conclusion

Our Ba_8Si_{46} study, along with many others [2-9], demonstrates the ability of MEM analysis to detect and characterize subtle details in electron density distributions. Moreover, is has been shown that MEM can often locate unknown and disordered sites more precisely than the conventional Fourier analysis [22-24]. These accomplishments recommend the combined Rietveld/MEM/MPF method as an important tool for analysis of diffraction data (both neutron and X-ray), leading to a complete structural characterization of crystalline compounds.

Acknowledgements

References

1. M. Sakata and M. Sato, *Acta Cryst.* **46**, 66 (1990).
2. H. Shimotani, T. Ito, Y. Iwasa, A. Taninaka, H. Shinohara, E. Nishibori, M. Takata, and M. Sakata, *J. Am. Chem. Soc.* **126**, 364 (2004).
3. E. Nishibori, I. Terauchi, M. Sakata, M. Takata, Y. Ito, T. Sugai, and H. Shinohara, *J. Phys. Chem.* **110**, 19215 (2006).
4. M. Takata, E. Nishibori, B. Umeda, M. Sakata, E. Yamamoto, and H. Shinohara, *Phys. Rev. Lett.* **78**, 3330 (1997).
5. A. Hoshikewa, N. Igawa, H. Yamauchi, and Y. Ishii, *J. Chem. Phys.* **125**, 034505 (2006).
6. K. Kato, M. Sakata, E. Nishibori, M. Takata, N. Hamada, and Y. Moritomo, *J. Phys. Soc. Jpn.* **74**, 2137 (2005).
7. B. B. Iversen, F. K. Larsen, M. Souhassou, and M. Takata, *Acta. Cryst. B* **51**, 580 (1995).
8. J. Baumert, C. Gutt, M. R. Johnson, J. S. Tse, D. D. Klug, and W. Press, *J. Chem. Phys.* **120**, 10163 (2004).
9. J. S. Tse, R. Flacau, S. Desgreniers, T. Iitaka, and J. Z. Jiang, *Phys. Rev. B* **76**, 1 (2007).
10. F. Izumi and T. Ikeda, *Mater. Sci. Forum*, **321-324,** 198 (2000); also see http://homepage.mac.com/fujioizumi/rietan/angle_dispersive/angle_dispersive.html
11. F. Izumi and R. A. Dilanian, *Recent Research Developments in Physics* **3**, Transworld Research Network, Trivandrum, 699 (2002); also see http://homepage.mac.com/fujioizumi/visualization/VENUS.html
12. M. Takata, E. Nishibori, and M. Sakata, *Z. Kristallogr* **261**, 71 (2001).
13. F. Izumi and T. Ikeda, *IUCr Newsletter* **26**, 7 (2001).
14. F. Izumi, *Rigaku J.* **17**, 34 (2000).
15. see http://www.geocities.jp/kmo_mma/crystal/en/vesta.html
16. M. Takata and M. Sakata, *Acta Cryst.* A **52**, 287 (1996).
17. L. Dobrzynski and J. Waliszewski, *J. Phys. Soc. Japan* **72**, 2203 (2003).
18. M. Merli and A. Pavese, *Z. Kristallogr.* **221**, 613 (2006).
19. A. Hofmann, J. Netzel, and S. van Smaalen, *Acta Cryst. B* **63**, 285 (2007).
20. A. San Miguel, A. Merlen, P. Toulemonde, T. Kume, S. Le Floch, A. Aouizerat, S. Paskarelli, G. Aquilanti, O. Mathon, T. Le Bihan, J.P. Itié, S. Yamanaka, *Europhys. Lett.* **69**, 556 (2005).
21. L. Yang, Y. M. Ma, T. Iitaka, J. S. Tse, K. Stahl, Y. Ohishi, Y. Wang, R. W. Zhang, J.F. Liu, H.-K. Mao and J. Z. Jiang, *Phys. Rev. B* **74**, 245209 (2006).
22. T. Ikeda, A. Akiyama, F. Izumi, Y. Kiyozumi, F. Mizukami, and T. Kodaira, *Chem. Mater.* **13**, 1286 (2001).
23. T. Ikeda, F. Izumi, T. Kodaira, and T. Kamiyama, *Chem. Mater.* **10**, 3996 (1998).
24. R. J. Papoular and D. E. Cox, *Europhys. Lett.* **32**, 337 (1995).

Call for Contributions to the Next Teaching Commission Newsletter

Providing there is enough interest, the 3rd issue of the Teaching Commission Newsletter is expected to appear around June of 2009 (2008 is an IUCr Congress year) with the primary theme to be determined. If no-one is else is co-opted, the newsletter will be edited by Lachlan Cranswick.

Contributions would be also greatly appreciated on matters of general interest to the crystallographic teaching community.

Please send articles and suggestions directly to the editor.

Lachlan M. D. Cranswick
National Research Council,
Building 459, Station 18,
Chalk River Laboratories,
Chalk River, Ontario,
Canada, K0J 1J0
E-mail: lachlan.cranswick@nrc.gc.ca
WWW: http://neutron.nrc.gc.ca/peep.html#cranswick