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Structure Determination from Powder Diffraction Data

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Revisiting the 1998 SDPD Round Robin

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INTRODUCTION

In the middle of 1998, the number of structure determinations by powder diffractometry (SDPD) was close to 300 of which 250 were published in the period 1992-1997 [1]. At that time, a huge number of methods and computer programs had already proven, at least once, their efficiency in succeeding in the various steps of the process of solving structures from powder diffraction data. The word "routine" was pronounced more and more frequently, so that it was considered timely to organize a Round Robin, in order to try to clarify the various claims about the ease or otherwise in performing SDPDs. Data and questionnaires were made available from a Web site starting from May 18, 1998 and the deadline was the last day of June. The competition was spammingly announced at many Newsgroups and Mailing lists related to crystallography and material science. Mails were sent also to some chemistry lists (Chemweb and CCL), trying to interest structure predictors to undertake first principles or semi-empirical calculations. Moreover, personal e-mails were sent to a number of well-known experts. As a consequence of this campaign, more than 800 visitors had a link to the homepage, which is still available [2]. 70 of the 800 visitors downloaded the data.

SELECTION OF SAMPLES FOR ANALYSIS

There is a clear distinction between compounds for which prior knowledge is available (molecular formula) or not. This difference may lead to one choosing quite different methods for solving the crystal structures. It was thus decided to propose two samples that fulfilled these conditions. We restricted the scope of this Round Robin to the structure solution part by providing the cell and space group information. The first sample was inorganic, a carbonatocobalt(III)pentamine nitrate hydrate; the second sample was organic, the pharmaceutical compound tetracycline hydrochloride. A medium resolution synchrotron pattern was provided for the latter, as well as a conventional X-ray powder pattern with similar resolution. The organic sample was especially selected for model location methods; the molecular shape, however, was not given. We considered that the shape could have been very easily obtained from various sources. During the Round Robin course, one of the participants gave a very accurate structure for tetracycline hydrochloride that even included hydrogen positions. Thus for validation purposes, it was found necessary to record a data set from a very small single crystal (40x30x20µ) selected in the powder, using the Daresbury 9.8 station equipped with the SMART Siemens system [3]. The subsequent structure was determined easily (*SHELXS*) and refined without any constraint, including the hydrogen atoms [4]. This raises the question of what constitutes a powder and what a single crystal sample. The inorganic structure is also published now proving that a solution was obtainable from powder data [5].

PARTICIPANTS

The 70 people who downloaded data may be considered to be subscribers to this Round Robin. The possibility was given for either anonymous download or filling a Web form asking for details about which methods and software will be used for 3 main steps : structure factors extraction, structure solution and structure completion and refinement. 31 subscribers filled in the Web form, more or less completely, indicating that they intended to use some of the best known programs such as *GSAS*, *FULLPROF*, *SHELX* and *SIRPOW*. 11 participants gave explicit answers to all the 3 main steps, simultaneously. One expert indicated after the deadline that he would have participated if the molecular shape had been given for sample 2.

RESULTS AND DISCUSSION

In the end, we received 5 full questionnaires from 4 final participants; one questionnaire for sample 1 and four for sample 2. Participant 1 made a very rapid reply but was unable to provide coordinates. By a search in the Cambridge Structural Database, he easily found the reference for the pharmaceutical compound as being the tetracycline (alias achromycin) hydrochloride. He then suggested that the coordinates should be found in this reference. Unfortunately, however, the coordinates were not available in this paper or in the Cambridge Structural Database. Only the molecular formula was available. Participant 2 was the only regular subscriber to have sent a successful questionnaire. He focused his attention exclusively on sample 2 and solved its structure, including the hydrogen atom positions by the global optimization method. A model for the molecule was taken from the tetracycline hydrate in the Cambridge Structural Database (TETCYH10 entry) and the water was removed. The tetracycline fragment and the Cl atom were positioned at random in the unit cell and an optimum position was searched (Fig. 1) by simulated annealing using the DRUID program against the 100 first structure factors extracted by the Pawley method from the synchrotron data. The final Rietveld refinement plot is shown on the Figure 2. There is something curious between the starting and final model. The main move is that O2 and N1 in the TETCYH10 model have rotated by 180° along the C2-C3 axis. The H

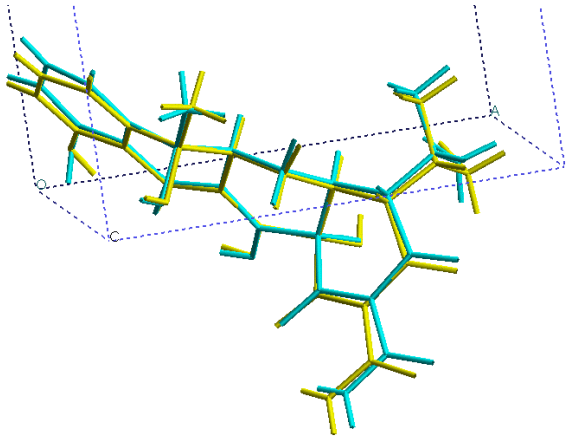

Fig. 1 Comparison of the molecular structures of tetracycline hydrochloride obtained from global optimization and from the final Rietveld refinement (Participant 2)

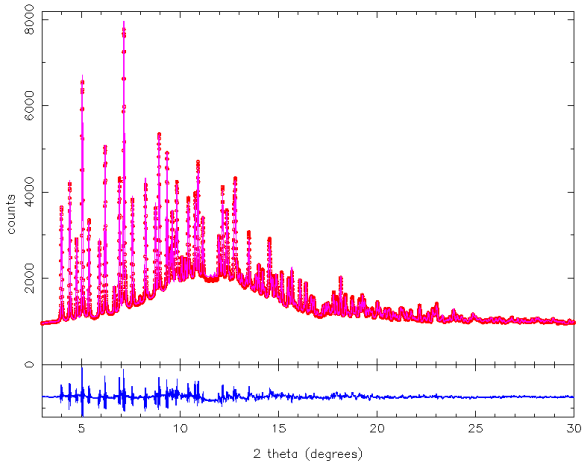

Fig. 2 Final synchrotron X-ray diffraction Rietveld plot for tetracycline hydrochloride.

atoms did not moved much between the initial and final model. An additional hydrogen atom should have been found for building the complete sample 2 structure, O2 in the hydrate becoming an OH. This hydrogen was not included by participant 2. Interviewed on this question, participant 2 commented that the exclusion of the hydrogen atom was an oversight caused by no sleep on the previous night. The diffraction pattern had been downloaded and the structure solved the day after a trans-Atlantic flight. The total time for solution was two hours.

Participant 3 did not have easy Web access and obtained the data by e-mail. He thought that sample 2 would be unsolvable without the molecule connectivity and asked for it. We had anticipated that we would reply positively to such a request, as the connectivity could normally be independently determined by a chemist using other methods such as magnetic resonance. Participant 3 sent filled questionnaires for samples 1 and 2, estimating finally that both of them were unsolvable. We are forced to conclude that the remaining participants found the structures either non-routine, non-solvable or too uninteresting.

Participant 4 downloaded the data anonymously and solved the sample 2 structure from the conventional X-ray data by using the CSD package. 158 structure factors were extracted by using the CSD-PROFAN program. Using the CSD-MAIN program, the chlorine atom was located by Patterson methods. The first Fourier map produced the coordinates of ten of the other atoms. Several cycles of Rietveld and Fourier syntheses were required to complete the structure (Figs. 3 and 4). According to participant 4, the full time needed for solution and refinement was only 3 hours, 2 cups of coffee and 5 cigarettes by using a low-end Intel PC. Participant 4 wrote also that "the structure of the inorganic complex is very simple and that is why it is not interesting."

It should be stated that participant 2 had provided the most accurate results with mean displacements relative to the single crystal data lower by a factor 2 than those from participant 4 and from the organisers [2]. Even the hydrogen atom positions were well located with a mean error of 0.2 angstroms.

COMMENTS

If the structure was in fact quite simple to solve using Patterson - doesn't it say something t hat there was not a

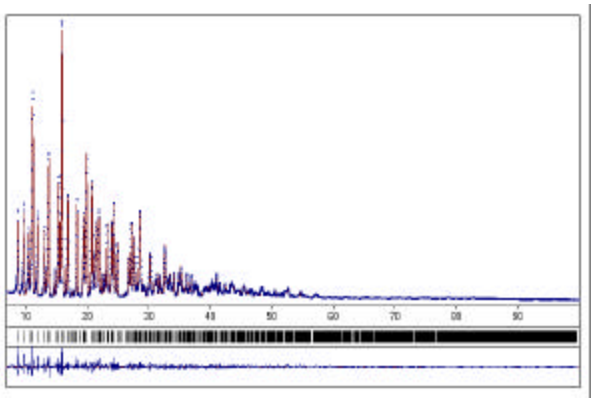

Fig. 3 Final conventional X-ray diffraction Rietveld plot for tetracycline hydrochloride.

flood of results? The solving of sample 2 structure from Patterson is not really the way that most crystallographers would have expected. Preconceived ideas would have prevailed that the unique Cl atom would not have been so heavy that a Patterson would have easily disclosed it.

Participant 4 obtained R_F=0.57 with the Cl atom. Remember that putting anything at any place gives you already R_F=0.5 or 0.6. In fact, the structure solution as described by participant 4 appears disarmingly simple, but it is not that straightforward. Here is why. Let us examine the Fourier difference as Participant 4 provided it. The 2 main first peaks are not atoms, neither is the fourth, the seventh nor the ninth. Many standard crystallographers would have given up at this stage, but not Participant 4. He was able to recognize a connected chain of 6 atoms. Here is the importance of skill, and experience. Most people would have stopped, rejecting this Fourier synthesis because of the two first intense peaks do not correspond to anything, or perhaps would have attempted a refinement of the coordinates, which would have failed. Many would not even have believed that a Fourier synthesis with only the Cl atom would have a chance to be successful. The organizers did not try the Patterson method because they had the preconceived idea that it was impossible (in fact we continue to think that way). Because the SDPDRR is mainly a YES/NO Round Robin (i.e. you win or not), we should take all those lacking questionnaires for 68x2 as a failure to solve. Perhaps, we should not count the 70 data downloaded but only the 31 regular subscribers. Anonymous downloaders never formally declared their intention to solve the problems. However, it should be noted that if single crystal data had have been provided, structure solving would have been “routine” using all freely and commonly available single crystal structure

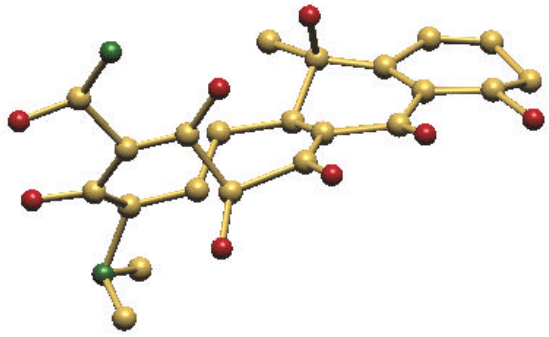

Fig. 4 Tetracycline hydrochloride model built from Patterson and Fourier recycling (Participant 4).

solution packages; e.g.; *SHELXS*, *SIR*, *DIRDIF*, *CRUNCH*.

CONCLUDING REMARKS AND RECOMMENDATIONS

The conclusion from this 1998 Round Robin is that solving structures "on demand" from powder diffraction is non-routine and non-trivial, requiring much skill and tenacity on the part of practitioners (though this should be tempered by the fact that no molecule location program was easily available for free from any website in 1998). Publications stating that structure solution using powder diffraction data is now "routine" (especially from the perspective of single crystal practitioners attempting powder diffraction based structure solution) could be considered misleading. Providing inaccurate, rosy reviews can be counter productive with respect to bringing the field into disrepute as being one populated by the crystallographic equivalent of snake-oil salesmen. The crystallographic definition of "routine" structure solution is presently based on the single crystal experience, of one where structures literally solve to near completion at the click of a button. At present much work can be done to enhance powder diffraction based software to give them single crystal quality automation and robustness to help make structure solution from powder diffraction more an attractive method than it is at present.

TODAY

A report on the SDPD Round Robin delivered at the ECM-18 congress is still available [6], as well as one written by a scientific journalist, David Bradley [7]. The number of determined structures using powder diffraction data is now approaching 500, and the proportion of organic compounds slightly increases, but remains lower than 20%. New programs for molecule location have been made available [8]: *POWDERSOLVE* (having proposed a post-deadline contribution [9]), *PSSP*, *ENDEAVOUR*, *TOPAS*, *ESPOIR*, etc, or new options of old programs (the upcoming version of *EXPO2000* and the renamed *DASH*, which was formally *DRUID*. Alas a good number of these programs are commercial. Moreover, the use of the Internet has grown since 1998 so that if the Round Robin had been proposed in 2001, more participants would have had a chance to succeed with both samples. Nevertheless, confirming this hypothesis needs a new Round Robin to be organized. Perhaps now is a good time.

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A 117-Atom Structure from Powder Diffraction Data

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INTRODUCTION

This is the story of how the structure of the very complex zeolite UTD-1F, with 117 atoms in the asymmetric unit, could be solved from powder diffraction data[1]. The structure solution was the culmination of a long period of method development that required not only new data analysis software, but also a new way of collecting data [2]. But let us begin at the beginning.

Our research group has a long-standing interest in zeolite structure analysis, and, because zeolites are rarely available in the form of single crystals, this has always included development of powder diffraction methodology. In our search for more powerful approaches to zeolite structure solution, model calculations reported by Hedel et al.[3] prompted us to consider the possibility of exploiting texture (preferred orientation of the crystallites). Usually, powder diffractionists go to great lengths to avoid any preferred orientation in their samples, because it can severely distort the intensities in the measured diffraction pattern. However, if the data are collected appropriately, this distortion, which is a function function of the orientation of the crystallites in the sample and of the sample in the X-ray beam, can provide additional information about the relative intensities of reflections that overlap in 2θ.

CONCEPT

Consider the three types of samples (single crystal, "ideal" powder and textured powder) sketched in two dimensions in Fig. 1a-c. The textured sample is intuitively intermediate between a perfectly oriented single crystal, and a powder with crystallites oriented in all directions, and the corresponding two-dimensional diffraction patterns support this view. The three reflections highlighted in (a),

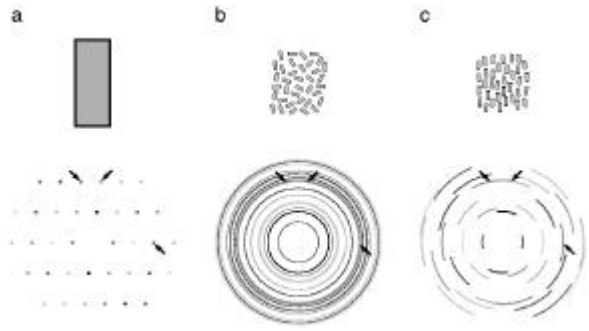

Fig 1 Two-dimensional schematic drawings of a specimen and its diffraction pattern for (a) a single crystal, (b) a powder with randomly oriented crystallites, and (c) a textured powder. The arrows highlight three reflections with similar diffraction angles that are separated in the single-crystal pattern, but overlap in the normal powder pattern. The diffraction angle 2θ increases radially from the center of each diffraction pattern.