The perils of large ‘small’ molecules – successful refinement of metallosupramolecular grid-like assemblies.

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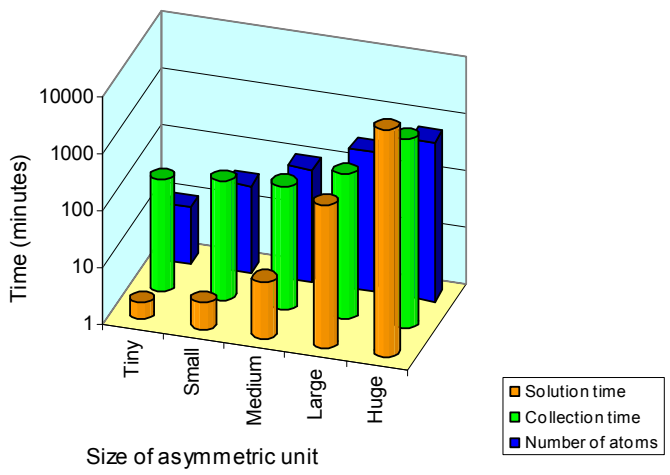
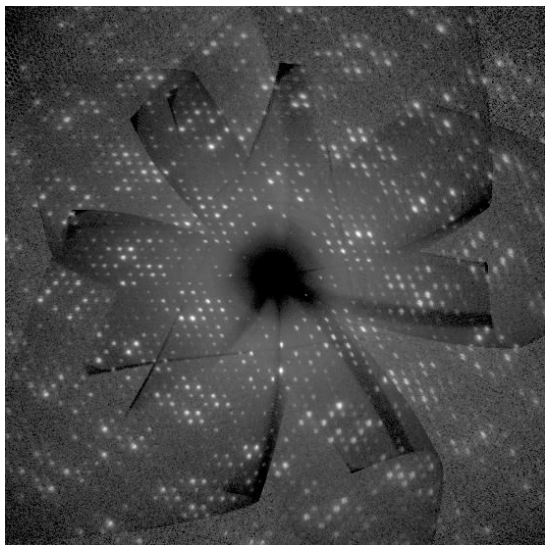
Introduction and Problem

With the advances in diffractometers and computers, the average routine data collection time of a normal small molecule is around two hours (longer for triclinic systems, shorter for high symmetry). Also the time taken to solve these structures to the chemist's satisfaction is generally in minutes.
However, chemists are now making larger molecules and they are expecting results from smaller and smaller crystals. These large molecules will almost always result in larger unit cells meaning there are fewer atoms contributing to each reflection resulting in longer collection times as more time is needed to obtain each image. This increase in time is nothing compared to that now required to solve the structure. Not only does each extra atom cause an increase in the time taken to run each refinement, but the many atoms create a much more complex energy profile which normally requires more iterations to obtain the best fit. It would be good if these structures could be solved in a timescale similar to the time taken to collect their data.

Collection and Solution Times



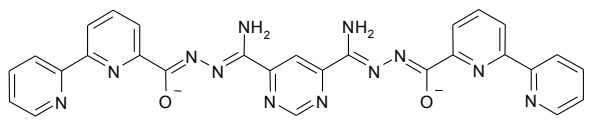


0KL Precession Image

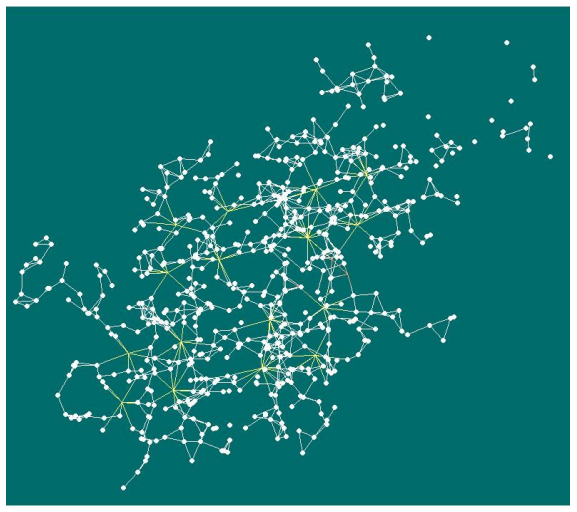
The example is of a lead supramolecular grid.
(A large structure)

$Pb_{16}L_8(F_3CSO_3)_{16}.xH_2O$ (L = $C_{28}H_{20}N_{12}O_2$)

The ligand is known to have the following structure:



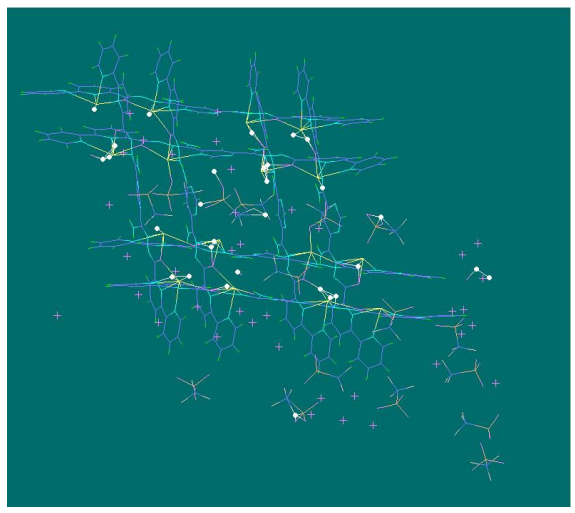
The crystals were small orange blocks and took 12 hours to collect the data.



Initial Solution

Possible solutions?

There are a variety of programs available to solve and refine these large structures, but most were not specifically designed for that purpose. This results in some problems, of which the most common is the program crashing (generally believed to be mathematical errors). With some tweaking it was at least possible to run most solving programs but the results were generally poor. In fact the more ‘advanced’ and ‘predictable’ the program was, the worse the results.
The example structure is shown using what appears to be the best program for these larger structures, SHELXS-97. Although basic, with few confirmed atom positions, the Q peaks appear to at least give a hint to the latter overall structure.
Of the others, most predicted the lead atom locations, but were unreliable elsewhere and with the need to re-label the given atoms the use of these programs was discontinued.
For the actual refinement, SHELXH-97 was used with the work shared over a variety of different PCs.



Final Solution

Crystal Data

Unit cell dimensions	a = 15.689(3) Å b = 31.782(6) Å c = 37.709(8) Å α = 112.14(3)° β = 93.11(3)° γ = 98.53(3)°
Volume	17100(6) Å^3
$F(000)$	10405
Index ranges	$-19 \le h \le 19$, $-39 \le k \le 39$, $-47 \le l \le 47$
Reflections collected	133702
Data / Restraints	57118 / 3853
Parameters	2167
Goodness-of-fit on F^2	1.068
Final R indices [$F^2 > 2\sigma(F^2)$]	$R1$ = 0.1256, $wR2$ = 0.2826
R indices (all data)	$R1$ = 0.2378, $wR2$ = 0.3519

Refining

Initial refinements just involved locating all the non-hydrogen atoms, with much time spent (re)labelling the atoms into a rational order. Each ligand was numbered systematically to allow comparisons to be much more easily made. Once the ligand and anion atoms were determined a few were not as stable in position as hoped for and thus some general (but weak) SAME restraints were included. With 8 ligands and 16 solvent anions these quickly result in the thousands of restraints present. The solvent water was a problem - Most were disordered in the cavities between grids, but some were bonding to the lead ions. SQUEEZE could have been used on the disordered water, but was deemed inappropriate as they were heavily mixed with the triflate anions and their rough positions were known. The final few full least squares refinements were taking about one hour per iteration, with a resulting time close to one day of refinements to obtain the final result.

To the Future

Although this is a large structure, much larger structures (with 6 or 7 thousand parameters) have been solved. With each iteration taking 3+ hours, these refinements can take several days to run. Ideally to run the service most efficiently the solution times should be less than the collection times.

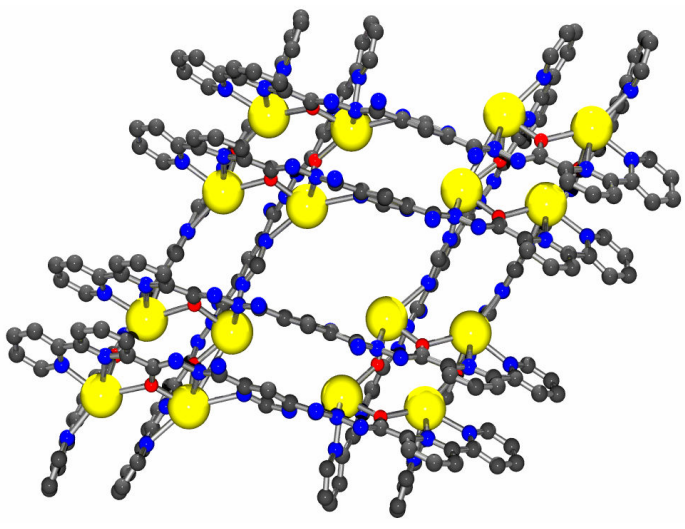


Diagram of the supramolecular grid

References

Self-assembly of a unique hexadecanuclear [4 ´ (2 ´ 2)]-Pb16 "grid of grids" type structure – S. T. Onions, A. M. Frankin, P. N. Horton, M. B. Hursthouse, C. J. Matthews, Chem Comm, 2003, 23, 2864-2865.

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