

Guessing Unknown and Disordered Solvent Molecules with *SQUEEZE* in the Structure Validation Program *PLATON*

Seik Weng Ng

Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia.
Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah, Saudi Arabia.
seikweng@um.edu.my

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Summary: This report describes the assignment of the nature and number of solvent molecules in the refinement of several solvated crystal structures without a prior knowledge of the solvent system used for crystallization for the cases when the solvent molecule cannot be properly modeled. The solvent molecules can be assigned even for twinned crystal structures.

Keywords: *SQUEEZE*, Disordered solvent molecules, Crystallization.

Introduction

If a compound separates from solution with a solvent of crystallization, the solvent molecule can be identified in a difference Fourier map; the occupancy and/or atomic displacement parameters can be refined and the solvent molecule fitted to a restrained disorder model if the solvent molecule exists in a site that is of higher symmetry than the molecular symmetry. However, in some refinements, the difference Fourier map shows no distinct peaks. Crystallographers carrying out refinements on crystals provided by chemists are sometimes faced with having to decide on the nature of a solvent molecule for a variety of reasons. In the worst case scenario, the researcher's laboratory records are lost, so that the crystallographer has to make an educated guess and may even have to consider the possibility of a mixture of solvent molecules.

The *SQUEEZE* technique in the structure validation program, *PLATON* [1], is a method to take into account the contribution of disordered solvent molecules in the refinement of an otherwise ordered crystal structure [2] by extracting information on the electron density from a correctly-phased model of the ordered part. Implicit in the method is the requirement that the ordered part of the crystal structure has no excess electron density, so that all excess electron density then necessarily resides in the voids. A typical crystal structure has voids but some voids are large enough to accommodate small molecules; a *solvent accessible void* is defined as a spherical region of a 1.2 Å radius that does not intersect the van der Waals spheres of atoms [3]. According to *PLATON*, the volume of an isolated water molecule approximates 40 Å³, and that of a small solvent molecule ranges from 100 to 300 Å³. As voids in a crystal structure elicit an A-level alert

on the IUCr checklist, the alert is best dealt with in the early stages of the preparation of the manuscript.

Despite being a permitted procedure, it is not frequently mentioned even in crystallographic journals; obviously, the nature of the solvent cannot be unambiguously answered if other analyses have not carried out. Even then, analyses are performed on the bulk sample whereas the crystal in the study may not be representative of the bulk. A recent study used this procedure but admitted that the nature of the solvent was unknown [4]; the reported density must necessarily be incorrect as this was calculated from the molecular formula of the ordered structure only. In other reports of compounds having two independent solvent molecules, one crystal structure was treated on the assumption that the solvent molecule was the same as the ordered solvent molecule [5, 6]. Reports on the use of the procedure are scattered in the structural literature; clearly, whether a compound will crystallize with a disordered solvent or otherwise cannot be known beforehand. Presented in this report is a collection of crystal structures of organic compounds and coordination polymers whose solvent molecules are deduced by using *SQUEEZE*, aided by some chemical intuition. The diffraction measurements are of high quality as the crystals were measured at 100 K.

Example 1: Bis(2,2'-bipyridine)(3,5-dinitrobenzoato)copper(II) 3,5-dinitrobenzoate hemi(2,2'-bipyridine) 4.5hydrate: refinement of the occupancy of a water molecule lying on a general position

The occupancy of a molecular species on a general position is not usually refined but the case of

*To whom all correspondence should be addressed.

water itself represents an exception. The occupancy may be refined under special circumstances, as in this example. The ordered part of the crystal structure features four water molecules; the hydrogen atoms of the three ordered and one disordered water molecules could be refined. The fifth lies on a general position; however, the refinement of its oxygen atom led to a thermal ellipsoid that is much larger than those of the other water molecules. *SQUEEZE* estimated an electron count of 4, which corresponds to half a water molecule. As halving the occupancy led to a final difference Fourier map that was diffuse, the salt was consequently formulated as a 4.5 hydrate (Fig. 1). Another 2,2'-bipyridine coordinated copper salt of 3,5-dinitrobenzoic acid was formulated as a tetrahydrofuran solvate; the THF molecule was treated as a disordered entity [7] but the refinement would be equally robust if it was instead treated by *SQUEEZE*.

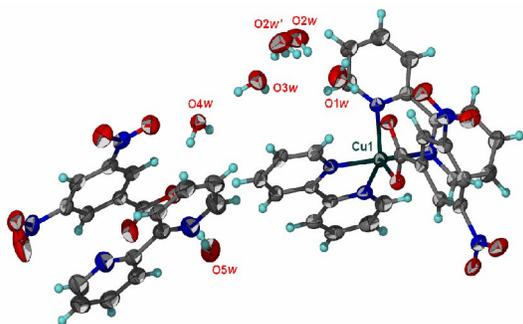


Fig. 1: Thermal ellipsoid plot of $[\text{Cu}(\text{C}_{10}\text{H}_8\text{N}_4)_2(\text{C}_7\text{H}_3\text{N}_2\text{O}_6)](\text{C}_7\text{H}_3\text{N}_2\text{O}_6) \cdot 4.5\text{H}_2\text{O} \cdot 0.5\text{C}_{10}\text{H}_8\text{N}_2$ at the 70% probability level; hydrogen atoms are drawn as spheres of arbitrary radius. The lattice 2,2'-bipyridine lies on a center-of-inversion; only the Cu atom and water molecules are labeled.

Crystal data: $\text{C}_{39}\text{H}_{35}\text{N}_9\text{O}_{16.5}\text{Cu}$, triclinic, $P-1$, $a = 11.4271(3)$, $b = 14.1455(6)$, $c = 14.2986(6)$ Å, $\alpha = 113.326(4)$, $\beta = 92.530(3)$, $\gamma = 100.108(3)$ °, $V = 2072.8(1)$ Å³ at 100 K; $R = 0.042$ for 7089 $I \geq 2\sigma(I)$ Cu- $K\alpha$ reflections. **CCDC 931457**.

Example 2. Dimethylwarifteine hemi-chloroform hemi-methanol: a compound with two different solvent molecules

Dimethylwarifteine is a bisbenzyl-isoquinoline alkaloid whose crystal structure has been previously described in its unsolvated form [8]. The example separated from an unknown solvent system with a solvent molecule that could be unambiguously identified as chloroform, which

should manifest itself through the heavy chlorine atoms. However, despite the heavy atoms, the refinement did not proceed to an R index less than 0.115% although the Flack parameter refined to 0.09(3). The application of *SQUEEZE* led to a lower R index and the solvent molecule was presumed to be a methanol molecule on the basis of the 113 Å³ void and the fact that methanol is commonly used as solvent for growing crystals of natural products (the procedure led to a somewhat worse value for the Flack parameter). The two independent molecules have similar geometrical features (Fig. 2).

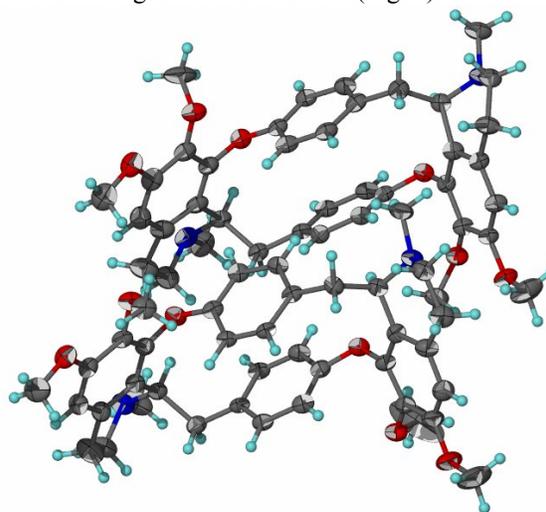


Fig. 2: Thermal ellipsoid plot of the two independent molecules of dimethylwarifteine at the 70% probability level; hydrogen atoms are drawn as spheres of arbitrary radius. The ordered chloroform molecule is not shown.

Crystal data: $\text{C}_{39}\text{H}_{42.5}\text{Cl}_{1.5}\text{N}_2\text{O}_{6.5}$, triclinic, $P-1$, $a = 10.2912(2)$, $b = 11.1721(3)$, $c = 15.5407(3)$ Å, $\alpha = 100.420(2)$, $\beta = 96.544(2)$, $\gamma = 90.022(2)$ °, $V = 1745.46(7)$ Å³ at 100 K; $R = 0.091$ for 12961 $I \geq 2\sigma(I)$ Cu- $K\alpha$ reflections. **CCDC 931458**.

Example 3. 2-[15-(2,3-Dihydro-1H-1,2,3-benzotriazol-2-yl)-5,17-bis(2,4,4-trimethylpentan-2-yl)-9,13-dioxatricyclo[12.4.0.0^{3,8}]octadeca-1(14),3(8),4,6,15,17-hexaen-7-yl]-2,3-dihydro-1H-1,2,3-benzotriazole toluene hemisolvate: a toluene on a center-of-inversion

A toluene lying on a center-of-inversion can be refined by fitting six carbon atoms to a hexagon and then restraining the methyl group by fixing the $\text{C}_{\text{phenyl}}-\text{C}_{\text{methyl}}$ distance. (A 'FRAG 17' refinement can be effected on an idealized toluene molecule but the procedure is somewhat complicated as the *.res output cannot be re-used in a subsequent refinement.)

The above compound shows a small amount of disorder in one of the *tert*-butyl groups (Fig 3a). The refinement converged at a preliminary *R* index of 0.099; *SQUEEZE* suggested a molecule having an electron count of 52 existing in a 199 Å³ void (Fig. 3b); the molecule is presumed to be toluene. A recent study used this procedure on a chlorobenzene molecule, whose disorder is unusual [9] as chlorine, which is expected to contribute significantly to the structure factors, should not be disordered.

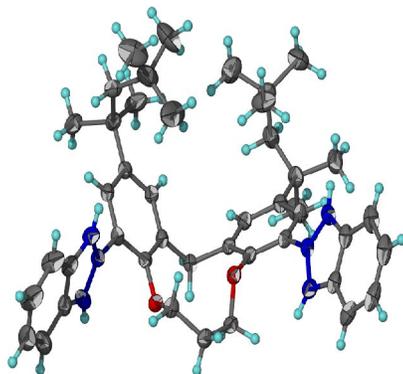


Fig. 3a: Thermal ellipsoid plot of C₄₄H₅₈N₆O₂·0.5C₇H₈ at the 70% probability level; hydrogen atoms are drawn as spheres of arbitrary radius. The disordered toluene molecule is not shown.

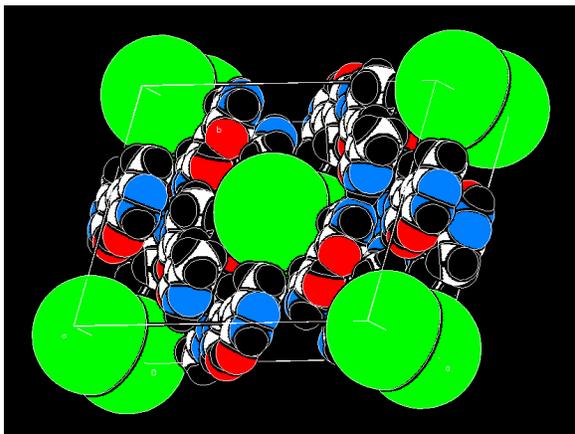
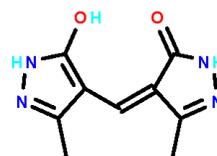


Fig. 3b: PLUTON plot of the packing illustrating the void (in green).

Crystal data: C_{47.5}H₆₂N₆O₂, triclinic, *P*-1, *a* = 11.1538(4), *b* = 13.7216(5), *c* = 14.7228(5) Å, α = 94.965(3), β = 98.265(3), γ = 106.196(3)°, *V* = 2122.3(1) Å³ at 100 K; *R* = 0.047 for 7336 *I* ≥ 2σ(*I*) Cu-*K*α reflections. **CCDC 931459**.

Example 4. (4*Z*)-4-[*(*5-Hydroxy-3-methyl-1*H*-pyrazol-4-yl) methylidene]-3-methyl-4,5-dihydro-1*H*-pyrazol-5-one: a 'whole-molecule-disordered' molecule in a void

The compound, C₉H₁₀N₄O₂ (Scheme 1), belongs to the monoclinic *C2/c* space group. The initial model has a molecule lying on a general position and another on a two-fold rotation axis, i.e., the number of molecules in the unit cell is 12 for which the calculated density would be only 1.066 g cm⁻³.



Scheme-1: C₉H₁₀N₄O₂

Inclusion of solvent molecules would only marginally raise the density unless heavier molecules such as dichloromethane or chloroform were considered. On the other hand, the estimated electron count of 184 for the species in a 634 Å³ void is better regarded as another C₉H₁₀N₄O₂ molecule. This other molecule is 'whole-molecule-disordered' along two-fold rotation axis. The application of *SQUEEZE* lowered the *R* index from 0.141 to 0.045 (Fig. 4). The density, calculated on the basis of *Z* = 16, is a more acceptable value of 1.422 g cm⁻³. Other whole-molecule-disorder systems have been detailed but for these, the disorder could be resolved [10-12].

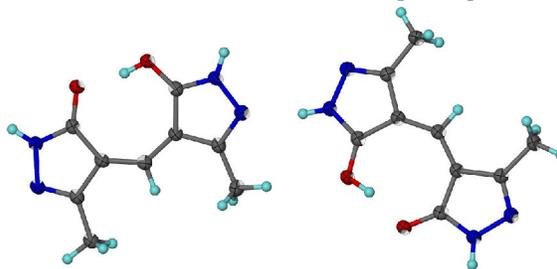


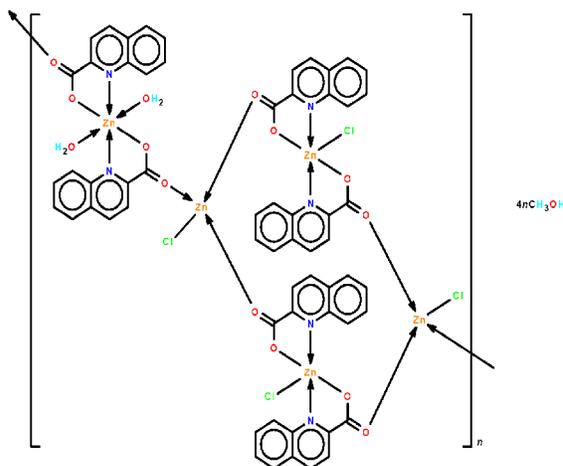
Fig. 4: Thermal ellipsoid plot of two C₉H₁₀N₄O₂ molecules (one on a general position and one on a special position) at the 70% probability level; hydrogen atoms are drawn as spheres of arbitrary radius. The 'whole-molecule-disordered' C₉H₁₀N₄O₂ molecule is not shown.

Crystal data: C₉H₁₀N₄O₂, monoclinic, *C2/c*, *a* = 29.9591(6), *b* = 18.4209(3), *c* = 7.0204(2) Å, β = 95.916(2)°, *V* = 3853.7(2) Å³ at 100 K; *R* = 0.045 for 3442 *I* ≥ 2σ(*I*) Cu-*K*α reflections. **CCDC 931460**.

Example 5. Diaquatetrachloridohexakis(quinolone-2-carboxylate)pentazinc methanol tetrasolvate: solvent molecules in a twinned crystal structure

The reaction of metal salts with organic linkers, some of which are commercially available, generates a wide range of coordination polymers, a class of chemicals that neatly fits in the fields of crystal engineering [13] and materials chemistry [14]. Polymeric $[Zn_5Cl_4(H_2O)_2(C_{10}H_6NO_2)_6]_\infty$ could be refined along with one ordered methanol molecule; however, the nature and number of other solvent molecules could not be known with certainty owing to complications arising from twinning. Whereas *PLATON* is implemented around the *SHELXL-97* [15] refinement program and is consequently unable to handle twinning, the updated *SHELXL-2012* version [16] outputs a detwinned *.*fcf* file (if a 'LIST 8' command is given) that can be used by *SQUEEZE*.

'Twinning' reflections should, on the other hand, preferably be collected for twinned crystals; in this example, as the two overlapping sets had a high R_{int} , the refinement was carried out on only one set of reflections only. The *TwinRotMat* routine in *PLATON* was then used to establish a twin component of 0.226(3). The R index at this stage was 0.115. Removing the electron density in the voids allowed the R index to drop slightly, to 0.105; included in the formula unit are the three additional methanol molecules (Scheme 2). There are, however, not enough examples to substantiate the validity of the *SQUEEZE* for twinned crystal structures; it should be pointed out that the percentage of twinning is a variable factor, and crystals may have more than two components.

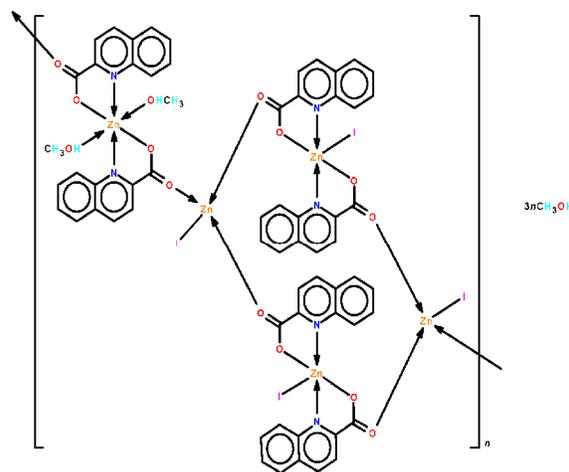


Scheme-2: Polymeric $Zn_5Cl_4(H_2O)_2(C_{10}H_6NO_2)_6 \cdot 4CH_3OH$.

Crystal data: $C_{64}H_{56}N_6O_{18}Cl_4Zn_4$, triclinic, *P*-1, $a = 13.6328(6)$, $b = 15.9912(9)$, $c = 17.1859(9)$ Å, $\alpha = 102.373(5)$, $\beta = 93.050(4)$, $\gamma = 106.168(4)$ °, $V = 3489.3(3)$ Å³ at 100 K; $R = 0.105$ for 12310 $I \geq 2\sigma(I)$ Mo- $K\alpha$ reflections. **CCDC 931461**.

Example 6. Di(methanol) tetraiodidohexakis(quinolone-2-carboxylate)pentazinc methanol trisolvate: solvent molecules in a large structure (ca. 14,000 Å³)

The structure differs from the preceding structure in having the coordinated water replaced by methanol (Scheme 3), but the unit cell is now much larger. One lattice methanol molecule could be refined; *SQUEEZE* suggested eight symmetry-related voids of 144 each that could accommodate two methanol molecules (Scheme 3). When the electron density was removed, the R index dropped from 0.067 to 0.054, which is significant because of the size of the unit cell.



Scheme-2: Polymeric $Zn_5I_4(CH_3OH)_2(C_{10}H_6NO_2)_6 \cdot 3CH_3OH$

Crystal data: $C_{65}H_{56}N_6O_{17}I_4Zn_4$, orthorhombic, *Pbca*, $a = 13.6183(2)$, $b = 30.4811(6)$, $c = 33.9210(6)$ Å, $V = 14080.6(4)$ Å³ at 100 K; $R = 0.054$ for 12946 $I \geq 2\sigma(I)$ Mo- $K\alpha$ reflections. **CCDC 931462**.

*Example 7. catena-[Bis- μ_4 -terephthalato)(μ_2 -2,2'-dimethyl-4,4'-bipyridine)dizinc *N,N*-dimethylformamide]: correction of the formulation of an incorrectly squeezed published structure*

The coordination polymer, $[Zn_2(C_{12}H_{12}N_2)(C_8H_4O_4)_2]_\infty$ is reported to crystallize with a DMF molecule along with two water molecules; the dihydrate formulation was assumed

from a *SQUEEZE* run [17]. The room-temperature diffraction measurements were of a marginal quality only as noted from the reported *R* index of 0.076. In contrast, the present low-temperature measurements unambiguously proved the formulation to be $[\text{Zn}_2(\text{C}_{12}\text{H}_{12}\text{N}_2)(\text{C}_8\text{H}_4\text{O}_4)_2\text{DMF}]_\infty$; the re-determination established the non-merohedrally twinned nature, which is the probable cause of the incorrect assignment in the reported structure. ‘Twinned’ data, i.e., two overlapping sets of reflections, were collected; the R_{int} values for the two individual sets were 0.034 and 0.040 but the combined set was lower, at 0.026. The refinement yielded a twin fraction of 0.447(1). The two independent DMF molecules were located and refined; these lie near a center-of-inversion (Fig. 5). When both DMF molecules were excluded from the refinements, *SQUEEZE* suggested one DMF per formula unit, i.e., the *SQUEEZE* refinement is the same as the regular refinement.

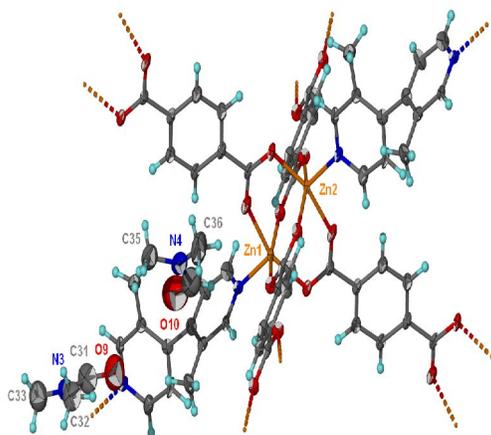


Fig. 5: Thermal ellipsoid plot of a portion of the 0.45:0.55 twinned $[\text{Zn}_2(\text{C}_{12}\text{H}_{12}\text{N}_2)(\text{C}_8\text{H}_4\text{O}_4)_2\text{DMF}]_\infty$, at the 70% probability level; hydrogen atoms are drawn as spheres of arbitrary radius.

Crystal data: $\text{C}_{61}\text{H}_{27}\text{N}_3\text{O}_9\text{Zn}_2$, triclinic, *P*-1, $a = 10.8818(5)$, $b = 10.9054(5)$, $c = 13.8889(5)$ Å, $\alpha = 95.342(3)$, $\beta = 99.931(3)$, $\gamma = 100.703(4)$ °, $V = 1581.9(1)$ Å³ at 100 K; $R = 0.062$ for 10283 $I \geq 2\sigma(I)$ Mo- $K\alpha$ reflections. **CCDC 931463**.

Example 8. Tris[1,2-(4-pyridyl)ethane]bis(2,5-thiophenedicarboxylato)cadmium pentahydrate: solvent molecules between layers

The dicarboxylate anion and the *N*-heterocycle in this compound connect the metal

atoms into a sandwich motif. The initial refinement could go no lower than an *R* factor of 0.067, and the difference Fourier map had peaks as well as holes. Additionally, one pyridine ring of the *N*-heterocycle that lies on a general position adopts several orientations as this part of the ligand does not engage in coordination. The formula unit is best assumed to possess 2.5 water molecules, as suggested by *SQUEEZE*. These are clustered at $(\frac{1}{2} \frac{3}{4} 0)$. The water molecules occupy the spaces in the *OLEX*-style [18] sandwich (Fig. 6).

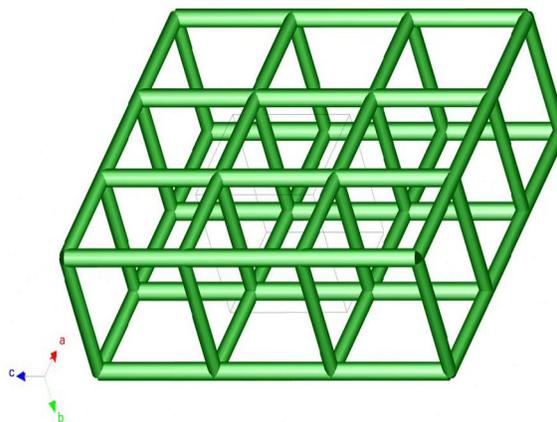
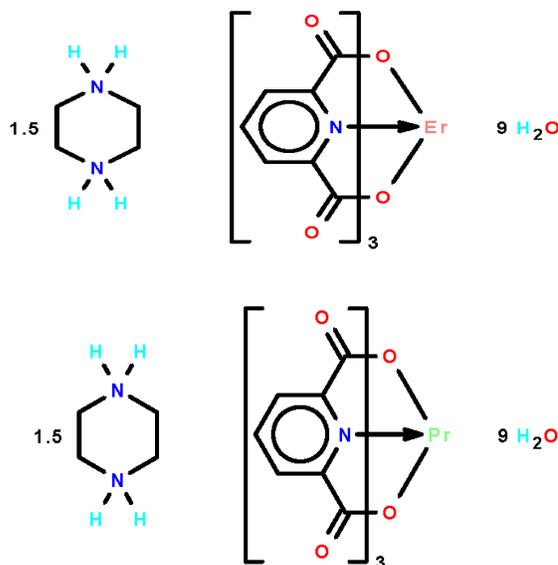


Fig. 6: *OLEX* representation of the sandwich motif.

Crystal data: $\text{C}_{48}\text{H}_{50}\text{N}_6\text{O}_{13}\text{S}_2\text{Cd}_2$, triclinic, *P*-1, $a = 10.3739(5)$, $b = 10.7239(5)$, $c = 13.8490(7)$ Å, $\alpha = 106.347(4)$, $\beta = 100.967(4)$, $\gamma = 107.292(4)$ °, $V = 1347.0(1)$ Å³ at 100 K; $R = 0.049$ for 5056 $I \geq 2\sigma(I)$ Mo- $K\alpha$ reflections. **CCDC 931464**.

Examples 9 and 10: Sesqui(piperazinium) tris(pyridine-2,6-dicarboxylato)erbate nonahydrate and sesqui(piperazinium) tris(pyridine-2,6-dicarboxylato)praseodymate nonahydrate: two isostructural salts

The two piperazinium salts both belong to the trigonal *P*-3 space group and both salts (Scheme 3) are isostructural but the atomic coordinates different in their Wyckoff sites. Two water molecules could be located; one lies on a general position. The other lies on a three-fold rotation axis, and was allowed to refine off this symmetry element. The refinement hovered around 7 to 8%; *SQUEEZE* suggested ten water molecules in the unit cell. When this procedure was applied, the *R* index dropped to 0.030 for the erbium salt and to 0.036 for the praseodymium salt.



Scheme-3: $1.5(\text{C}_4\text{H}_{12}\text{N}_2) \text{Er}(\text{C}_7\text{H}_3\text{NO}_4)_3 \cdot 9\text{H}_2\text{O}$ and $1.5(\text{C}_4\text{H}_{12}\text{N}_2) \text{Pr}(\text{C}_7\text{H}_3\text{NO}_4)_3 \cdot 9\text{H}_2\text{O}$.

Crystal data: $\text{C}_{27}\text{H}_{45}\text{N}_6\text{O}_{21}\text{Er}$, trigonal, $P\bar{3}$, $a = 14.5639(3)$, $c = 10.1793(2)$ Å, $V = 1869.84(5)$ Å³ at 100 K; $R = 0.030$ for 2483 $I \geq 2\sigma(I)$ Mo- $K\alpha$ reflections. **CCDC 931465**.

Crystal data: $\text{C}_{27}\text{H}_{45}\text{N}_6\text{O}_{21}\text{Pr}$, trigonal, $P\bar{3}$, $a = 14.7590(3)$, $c = 10.0789(2)$ Å, $V = 1901.33(5)$ Å³ at 100 K; $R = 0.036$ for 2541 $I \geq 2\sigma(I)$ Mo- $K\alpha$ reflections. **CCDC 931466**.

Conclusion

The SHELX website [19] cautions the use of *SQUEEZE* because as the complex scattering factors are estimated values that are then included in the structure factor calculations, compelling reasons should be given on its use. The cif may not pass the IUCr checks, so that a crystal structure having a large number of solvent-accessible voids should, at least, provide a satisfactory account of the procedure if the solvent molecule could not be modeled even with a number of restraints. In some instances, the solvent molecules stack over each other in an aperiodic manner; in fact, it is this aperiodicity [3] that cannot be modeled in a regular refinement, so that the contribution must be estimated. Not being able to model a solvent molecule owing to aperiodicity is different from not being able to refine the solvent molecule because of severe disorder, but the difference is subtle. For the examples described in this report, because the formulations were not independently corroborated by other analyses, the refinements on which *SQUEEZE* was applied are

regarded as a last resort to a cosmetically lower R index. Voids in crystal structures are presumed to be as spherical cavities according to *PLATON*; the solvent molecule that occupies the cavity is also implied to adopt a spherical conformation. Voids may be connected to each other; if the voids are connected in one-, two- and three-dimensions to lead to the formation of channels, a more realistic approach computes the surface areas in addition to volumes of voids [20,21], and characterizes all empty space [22]. The crystal structure of $\text{C}_9\text{H}_{10}\text{N}_4\text{O}_2$ (Scheme 1) features voids in which the *SQUEEZED* $\text{C}_9\text{H}_{10}\text{N}_4\text{O}_2$ molecules reside; the voids are not isolated voids but are connected into channels (Fig. 7). Finally, as the crystal structures in this study are not discussed, the owners of the crystals should be free to publish them elsewhere if and when they can confirm the formulation.

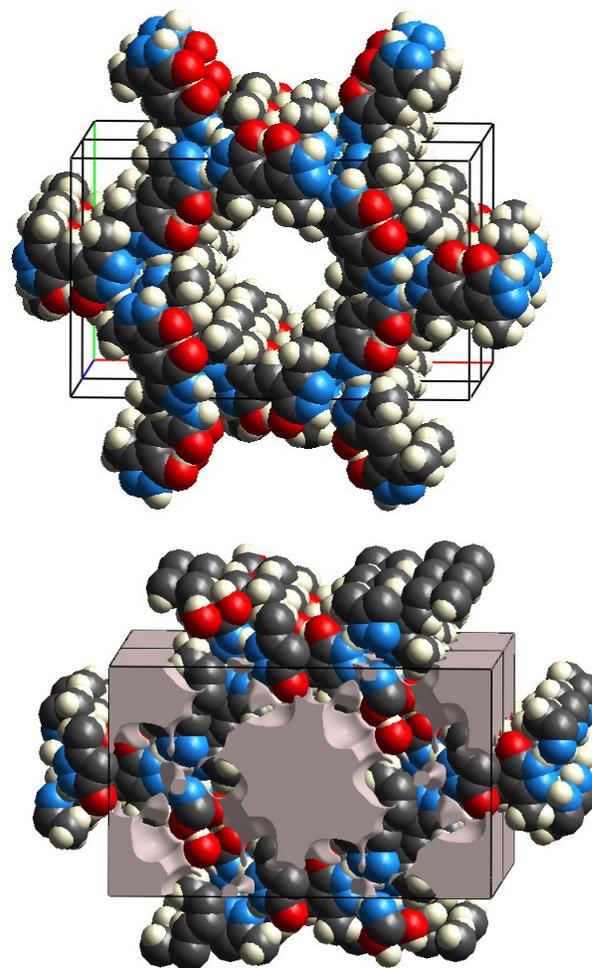


Fig. 7: Space-filling plot of $\text{C}_9\text{H}_{10}\text{N}_4\text{O}_2$ showing voids (a); packing illustrating voids as channels (in brown) (b).

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