

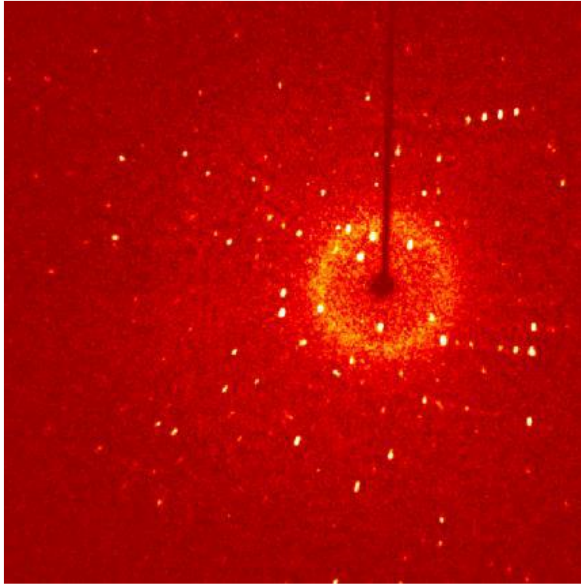
T1. Modeling disorder: Solvent masks

Slides and sample data from Dr. Brian Patrick, UBC

Edits and presentation by Dr. Louise Dawe, WLU

Based on: Spek, A.L. *Acta Cryst.* (2015). C**71**, 9–18.

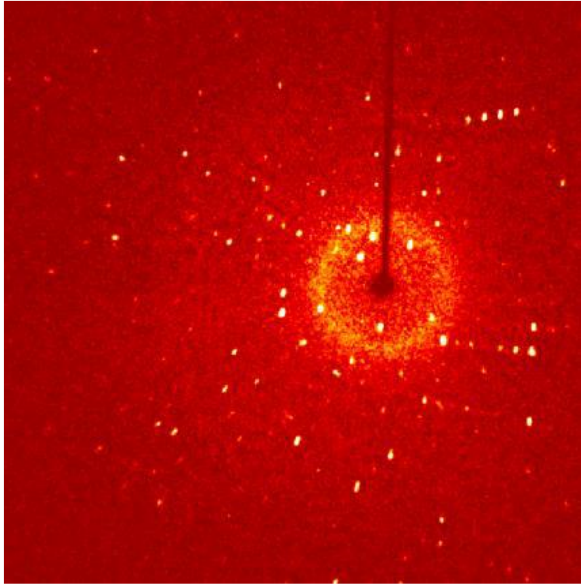
<https://journals.iucr.org/c/issues/2015/01/00/ln3172/ln3172.pdf>



Integrate reflections



$$F_o = \sqrt{I / Lp}$$



Integrate reflections



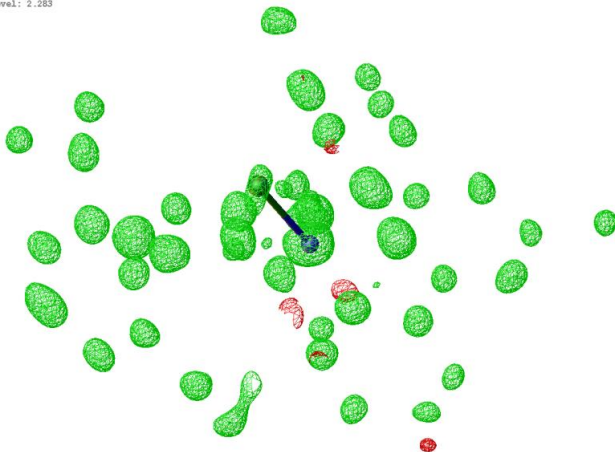
$$F_o = \sqrt{I / Lp}$$



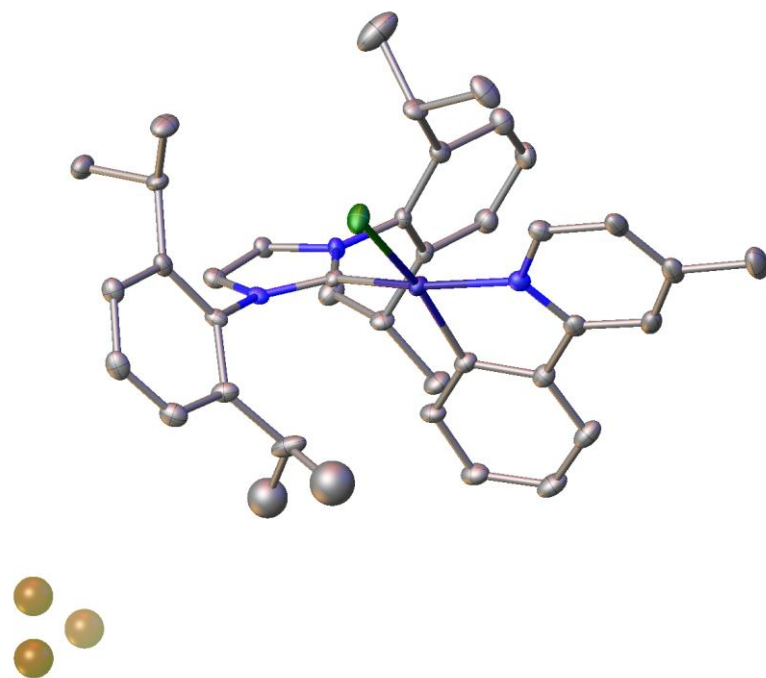
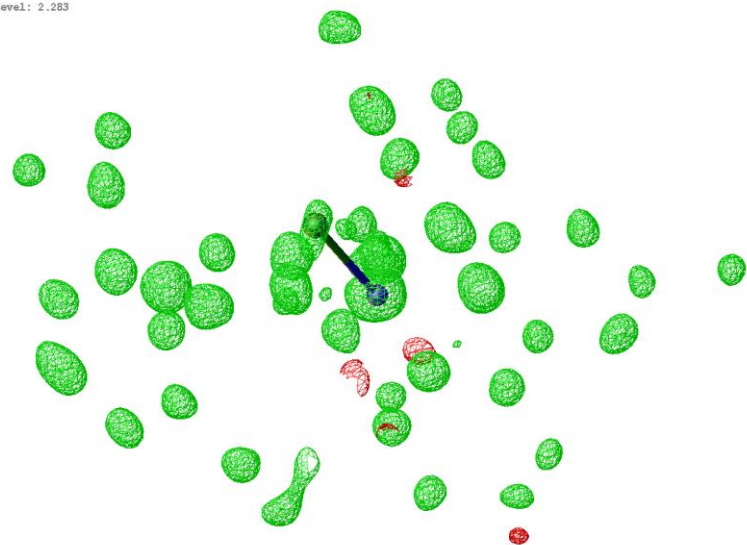
$$\rho(xyz) = \frac{1}{V} \sum_{hkl} \bar{F}_{hkl} \cos 2\pi(hx + ky + lz)$$



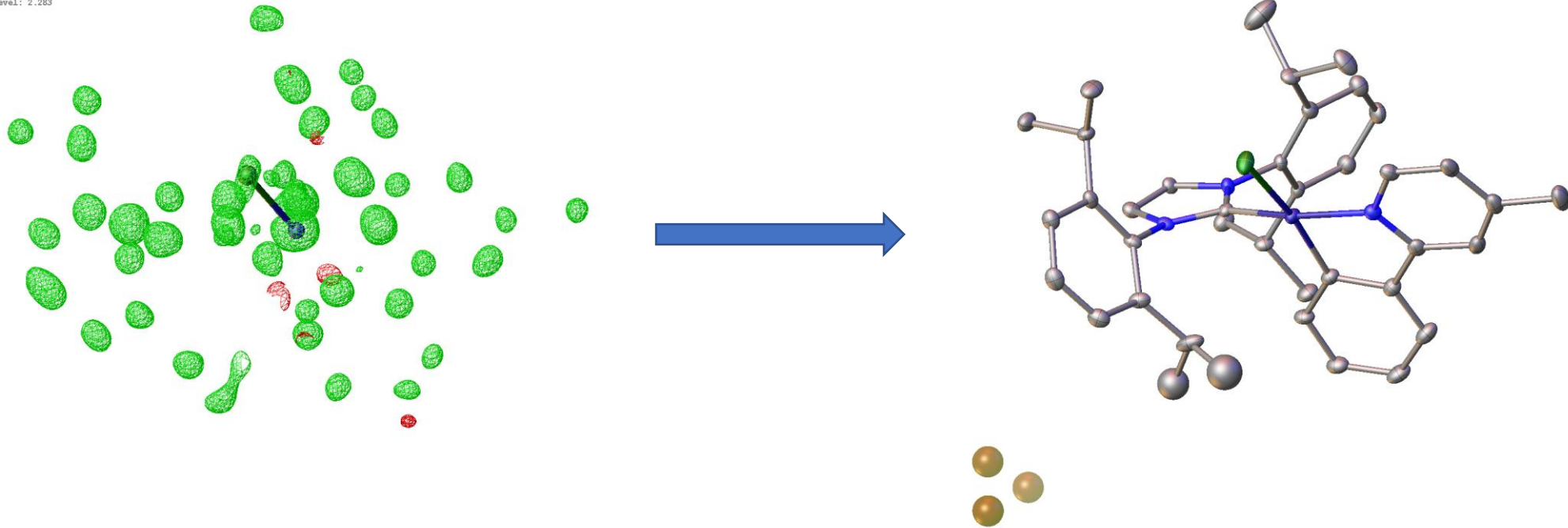
Current level: 2.283



Current level: 2.283



Current level: 2.283



Use scattering factors and coordinates (x, y, z) for each atom (j) in the unit cell to calculate structure factors (F) for each reflection.

$$\vec{F}(hkl) = \sum f_j \exp[2\pi i(hx_j + ky_j + lz_j)]$$

Least-squares refinement tries to minimize

$$\sum_{hkl} w' (F_o^2 - F_c^2)^2$$




Your measured intensities

The diagram consists of a central mathematical equation at the top. Two blue arrows originate from the equation. One arrow points from the summation index hkl down to the text 'Your measured intensities'. The other arrow points from the calculated structure factor term F_c^2 down to the text 'Calculated from your model'.

Calculated from your model

Each atom in your model contributes to the calculated structure factor.

Least-squares refinement tries to minimize

$$\sum_{hkl} w' (F_o^2 - F_c^2)^2$$


Your measured intensities

Calculated from your model

The closer your model approximates the electron density in your unit cell, the smaller the difference.

Solvent Masking via PLATON's SQUEEZE

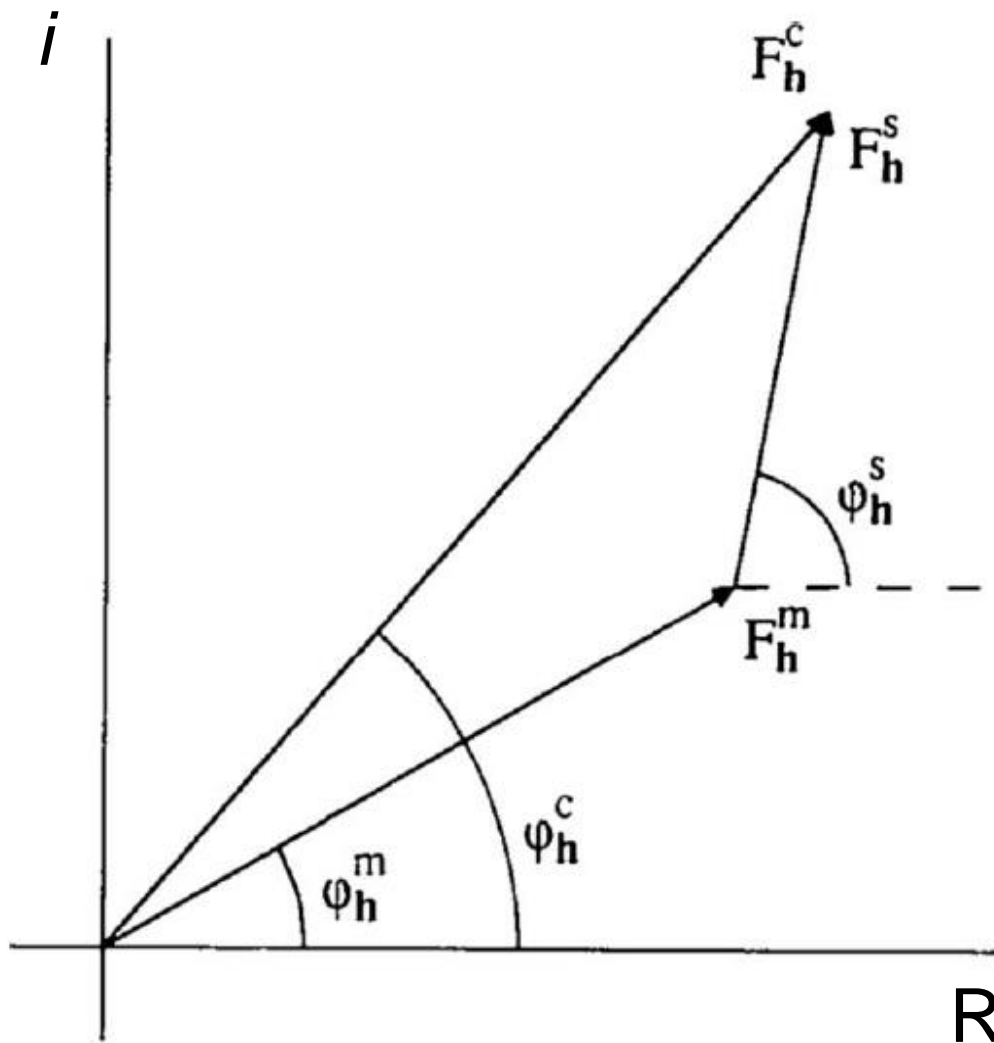
Identifies solvent accessible regions in the unit cell.

Calculates unresolved (unmodeled) electron density in that region.

SQUEEZE calculates the solvent contribution to the structure factors by back-Fourier transformation of the electron density found in the solvent-accessible region

$$F_{calc} = F_{Main} + F_{Solvent}$$

Solvent Masking via PLATON's SQUEEZE

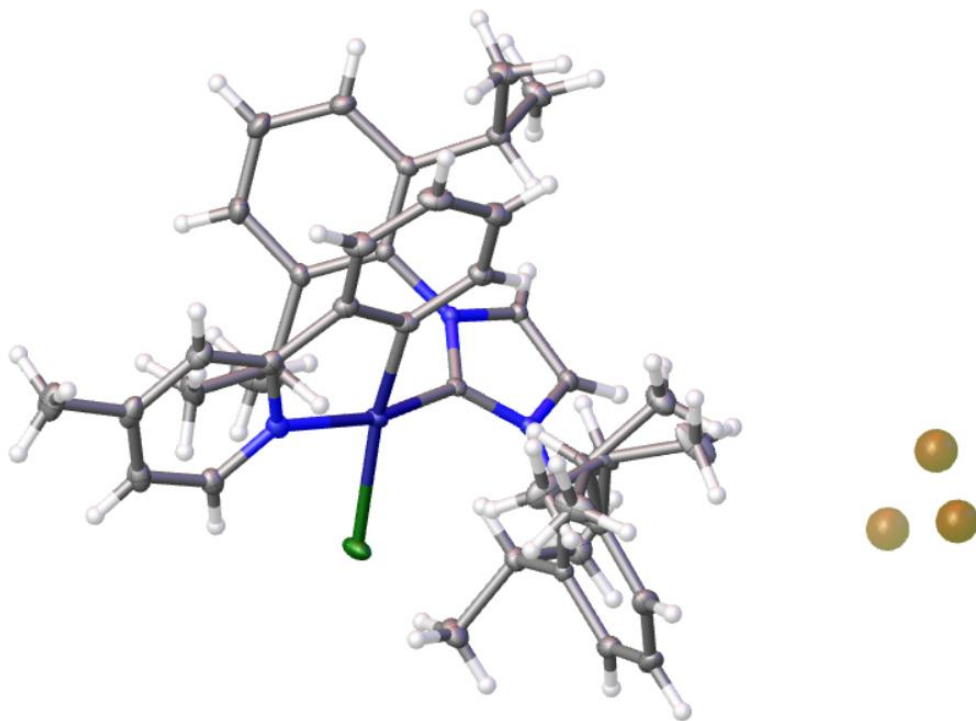
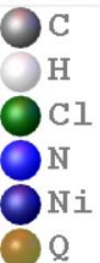


$$F_{calc} = F_{Main} + F_{Solvent}$$

- Refine everything in the main structure, including non-solvent disorder and hydrogen atoms.
- Refinement must include the ACTA and LIST 4 command in the .ins file. This will create the .cif and .fcf in a format that can be used by PLATON SQUEEZE.
- Twinned data with HKLF5 or TWIN/BASF data requires LIST 8 (not 4).

- Initiate PLATON/SQUEEZE. It will:
 - Search for solvent accessible voids
 - Calculate the electron density in each void
 - Calculate the correction (.fab file) required to each reflection to remove that electron density from the void.

- Initiate PLATON/SQUEEZE. It will:
 - Creates new .ins file (name_sq.ins) containing the ABIN instruction
 - Creates new .hkl file (name_sq.hkl), identical to original .hkl file
 - Creates new .fab file (name_sq.fab), includes the solvent contribution to the calculated structure factors



solvent P6₅

C:\Users\ldawe\OneDrive - Wilfrid Laurier

C₃₉H₄₆ClN₃Ni

a = 23.7330(14) α = 90° Z = 6
 b = 23.7330(14) β = 90° Z' = 1
 c = 10.7187(9) γ = 120° V = 5228.5(6)

R₁ **3.41** %
 wR₂ **10.85** %

d min (Mo) **0.71** | I/σ(I) **53.1** | Rint **4.12** % | Full 50.5° **100**
 2θ = 60.1° | m = 12.65

Shift **-0.009** | Max Peak **1.9** | Min Peak **-0.3** | Goof **1.165** | Hoof **.002(2)**

Refinement Finished

Home **Work** **View** **Tools** **Info**

Solve **Refine** **Draw** **Report**

Program **ShelXL** | L.S. | Cycles **5** | Peaks **25**
 hkl file **solvent.hkl** | Fri Jun 2 21:43:01 2023
 Weight ☒ **.065 | .067** | **2.24 | 2.15** | EXTI ☐ SWAT ☐ **ACTA**
☐ Use Solvent Mask This is the Olex2 implementation of BYPASS (a.k.a. SQUEEZE)
 Refinement Settings Extra

Toolbox Work

Labels | ☐ Label H ☐ No symm **Hide**

C H Cl N Ni | ☐ **Add H**

Q to H | **H to Q** | **Q to H** | **H to Q** | **Q to H** | **H to Q** | **Q to H** | **H to Q** | Z' = **1**

MAP **Diff** | **Show Map** | **Map Settings**

Disorder Tools
 Peak & Uiso Sliders
 Growing
 Finishing

History

As a first step, you can explore the disordered solvent. Some suggestions:

CTRL + Q to connect the three largest peaks

GROW

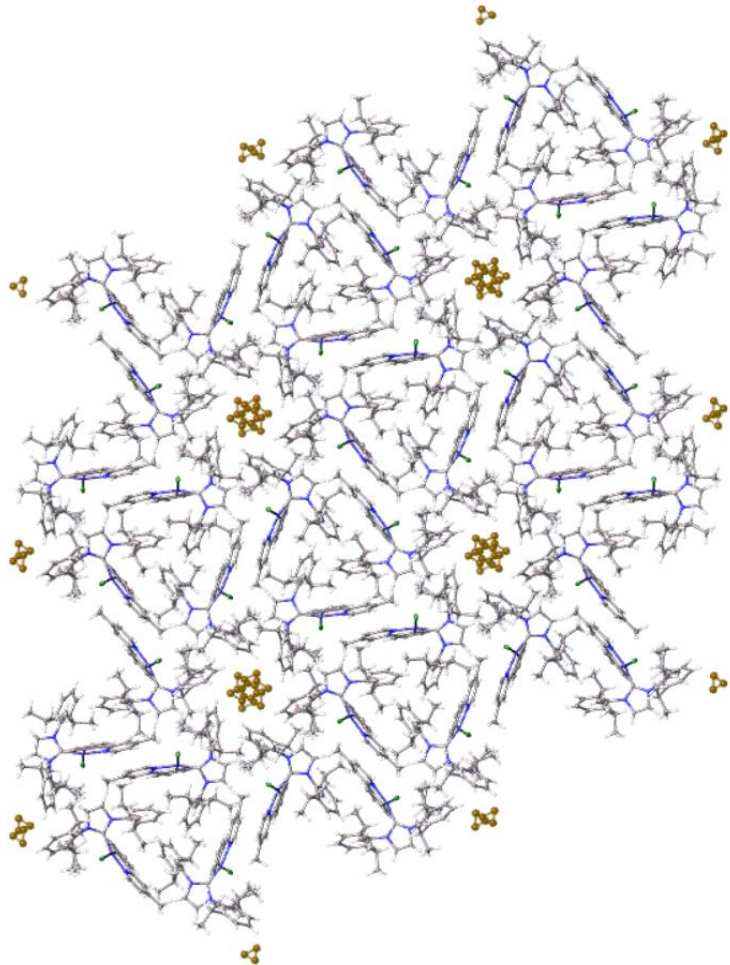
PACK

MATR 3

Olex2

File Edit View Structure Mode Tools Model Select Help

C
H
Cl
N
Ni
Q



solvent *P6₅*
C:\Users\ldawe\OneDrive - Wilfrid Laurier
C39H46ClN3Ni

$a = 23.7330(14)$ $\alpha = 90^\circ$ $Z = 6$
 $b = 23.7330(14)$ $\beta = 90^\circ$ $Z' = 1$
 $c = 10.7187(9)$ $\gamma = 120^\circ$ $V = 5228.5(6)$

$R_1 = 3.41\%$
 $wR_2 = 10.85\%$

$d \text{ min (Mo)} = 0.71$ $|I/\sigma(I)| = 53.1$ $R_{\text{int}} = 4.12\%$ $\text{Full } 50.5^\circ = 100\%$
 $2\theta = 60.1^\circ$ $\text{Shift} = -0.009$ $\text{Max Peak} = 1.9$ $\text{Min Peak} = -0.3$ $\text{GooF} = 1.165$ $\text{Hooft} = .002(2)$

Refinement Finished

Home Work View Tools Info

Recent Files

Electron Density Peaks

Peaks Select Delete

Transparency

Label	Value
Q1	1.890
Q2	1.530
Q3	1.010
Q4	0.830
Q5	0.390
Q6	0.390
Q7	0.360
Q8	0.350
Q9	0.340
Q25	0.280

Refinement Indicators

Bad Reflections

Reflection Statistics

Reflection Statistics Summary

As a first step, you can explore the disordered solvent. Some suggestions:
Navigate to INFO → Electron Density Peaks

FUSE

Launch PLATON (if you do not have the PTON button, you can launch from the folder that hosts pwt.exe).

PLATON

A Multipurpose Crystallographic Tool

(C) 1980-2022 A.L.Spek - Version: 51222 [WEB: May 23, 2023]

GRAPHICS	GEOM-CALC	VOIDS FLIP	SYMMETRY	ABSORPTION	REPORT	MISC-TOOLS
PlutonAuto	Calc All	Calc Solv	Addsym	MULscanABS	Validation	System-S
Ortep-Plot	Calc Intra	Calc K.P.I	Addsym-EQL	ABSPstScan	Asym-Vlew	fcf2hkl
NewmanPlot	Calc Inter	Squeeze	Addsym-EXT	ABSTompa	FCF-Valid	Expand2P1
Ring-Plots	Calc Coord	Hybrid	Addsym-PLT	ABSGauss	DifFourier	FCF-Gener
Plane-Plot	Calc Metal	CalcFCFsqr	Addsym-SHX	ABSxtal	ANALofVAR	HKLF-Gener
PolyPlot	Calc Geom	ContourSol	Newsym	ABSSphere	ByvoetPair	HKL-Transf
ContourDif	Calc Hbond	Solv F3D	Nonsym	ShxAbs	AsymExpect	Exar-Res
Contour-Fo	Calc TMA	Solv Plot	LePage	AnomDisVal	Asym-Valid	Ants-Res
AutoMolFit	L.S.-Plane	CavityPlot	Delhed	AnomDisPlt	SupplMater	Rename-Res
hkl2Powder	DihedAngle	Calc SASA	Molsym	MuPlat	Expect-hkl	Auto-Renum
SimPowderP	AngleLines	Flip Menu	SPGRfromEX		CSD-Cell	Create-spf
RadDistFun	AngLsplLin	Flip Show	Asym		CSD-Quest	Create-res
Patterson	CremerPopl	Flip Patt	ASYMaverFR		StructTidy	Create-clf
ShelxtPlot	BondValenc	Flipper 25	LePageTwln	XtLPLanAgl	StralnAnal	Create-pdb
	Volcal	Structure?		Xtal Habit		HFIX-Res
WLLsonPlot	R/S-CIP					clf2fcf
PLutoNatlv	Mol Volume		TwlnRotMat			clf2shelxl

Xtal Data (CIF) solvent.clf- Set 2(): solvent

Refl Data (LIST4) solvent.fcf [FCF] (): solvent

Browser - HELP

<http://www.platonsoft.nl/PLATON-MANUAL.pdf> http://www.platonsoft.nl/PLATON_HOW_TO.pdf

INPUT INSTRUCTIONS via KEYBOARD or LEFT-MOUSE-CLICKS (HELP with RIGHT CLICKS)

PLATON 10

OptionMenus

NoMove

Join-Expand

Organic

Round

Parentheses

Label-Alias

R/S-Determ

Norm-H-bond

NoSymm

NoDisorder

LstARU RCel

LstCellSymm

ListAtoms

ListBonds

List Uij

Exclude H

MinQPeakHgt

MinQPeakDis

Q-Peak-Incl

KeyInstruct

Prev Next

SAVE-InstrS

ENTRY-LIST

Reset End

Exit

MenuActive

2. Apply a solvent mask.

1. Visualize the solvent accessible region.

Values below for gridpoints and volumes in []
refer to areas where atom centers may reside.

Area	#GridPoint	VolPerc.	Vol(A ³)	X(av)	Y(av)	Z(av)	Eigenvector(frac)	Sig(Ang)
1	34650[9462]	5	262[71.6]	0.000	0.000	-0.023	1 -0.058 0.055 1.000	3.16
							2 0.979 1.000 0.000	1.53
							3 -1.000 0.937 -0.803	1.40

	x	y	z	Shortest Contacts within 4.5 Ang. (Excl. H)
1	0.000	0.000	-0.023	C20 3.47; C21 3.94; C19 4.16;

:: Note: use CALC VOID (not CALC SOLU) for Packing Index.

Report the Distance from VOID-CG to Boundary in EU-Directions

Nr	MinEU1	MaxEU1	MinEU2	MaxEU2	MinEU3	MaxEU3	MaxDist (Ang)
1	-6.78	6.38	-3.87	1.87	-2.85	2.86	6.78

:: ADP <C24A 0.005 0.020 0.072 - RATIO(MAX/MIN) = 15.1 prolate

:: TRMX = (1.00 0.00 0.00/ 0.00 1.00 0.00/ 0.00 0.00 1.00)
:: CELL = 23.733 23.733 10.719 90.000 90.000 120.000

:: Reflection Data are READ from File : solvent.fcf - (OBS-Data)
W: No Reflections Supplied !

:: END Statement Executed for this Entry
:: *** FILES for Final Refinement with SHELXL201n ***

:: SQUEEZE ins on :solvent_sq.ins
:: SQUEEZE hkl on :solvent_sq.hkl
:: SQUEEZE fab on :solvent_sq.fab
:: SQUEEZE cif on :solvent_sq.sqf
:: SQUEEZE xyz on :solvent_sq.sqz

1. Return to OLEX2.
2. Open solvent_sq.ins.
3. Change your hkl file to solvent_sq.hkl.
4. Refine.
5. Examine the result (including the CIF).