Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

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Table 1. Determined equation of state for the TMA-I2 and TMA-ICl complexes. The compressibilities of each unit-cell axis are also shown.

Parameter	TMA-I_2	TMA-ICl
V_o (Å)	800.2(10)	1409(3)
B_0 (GPa)	5.83(15)	5.8(3)
B'	9.4(2)	10.1(4)
X_1 (TPa^{-1}) / *b*	26.9(2)	18.03(3)
X_2 (TPa^{-1}) / *a*	21.1(3)	15.2(2)
X_3 (TPa^{-1}) / *c*	10.7(1)	17.3(3)

Table 2. Correlation coefficients of TMA-ICl, including pressure, I-Cl distance, N-I distance and N-I-Cl angle

		Pressure	I-Cl	N-I	N-I-Cl
Pressure	Pearson Correlation	1	0.854**	-0.796*	-0.893**
	Sig. (2-tailed)		0.007	0.018	0.003
	N	8	8	8	8
ICl	Pearson Correlation	0.854**	1	-0.960**	-0.733*
	Sig. (2-tailed)	0.007		0.000	0.038
	N	8	8	8	8
NI	Pearson Correlation	-0.796*	-0.960**	1	0.583
	Sig. (2-tailed)	0.018	0.000		0.129
	N	8	8	8	8
NICL	Pearson Correlation	-0.893**	-0.733*	0.583	1
	Sig. (2-tailed)	0.003	0.038	0.129	
	N	8	8	8	8

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

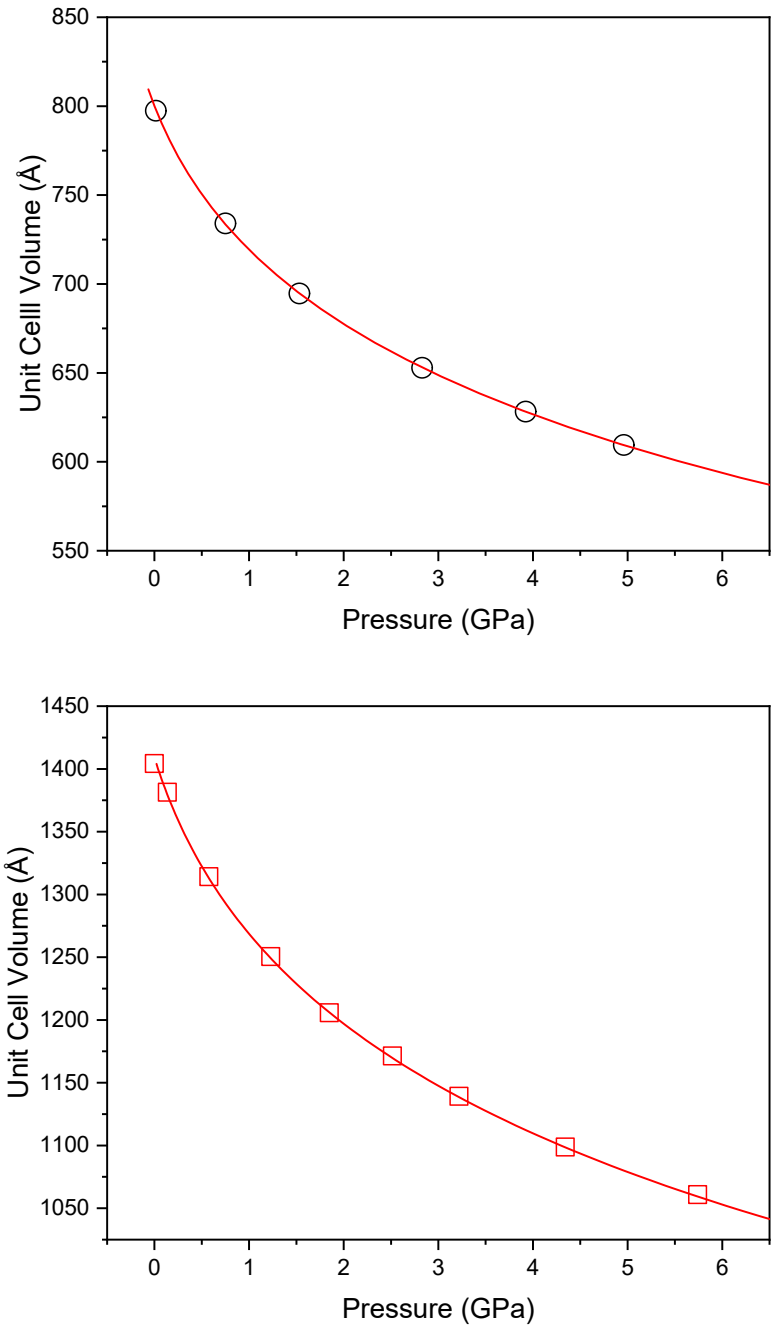
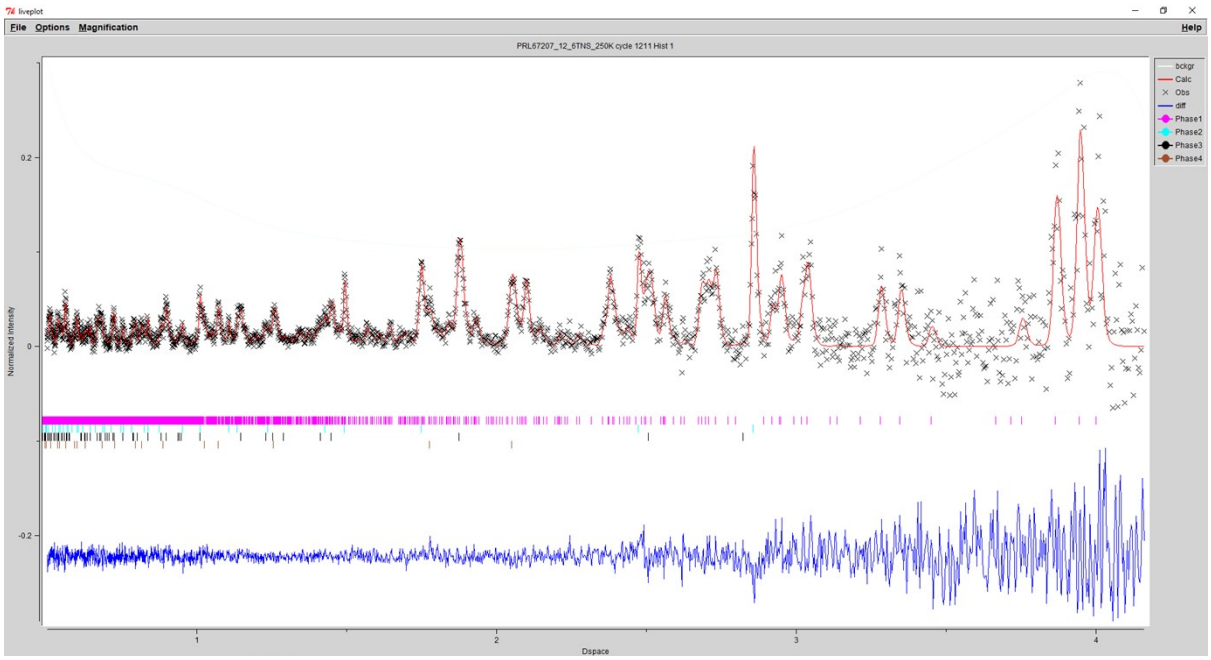


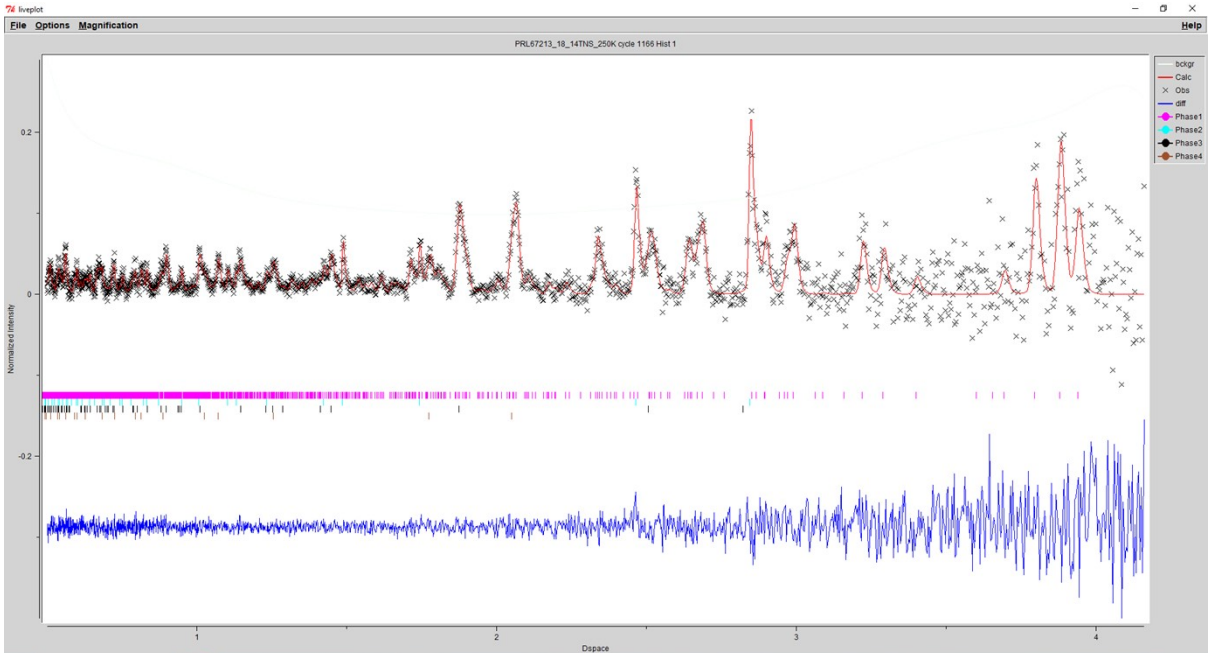
Figure 1. Third-order Birch-Murnaghan fits to unit cell volume data for TMA-I_2 (top) and TMA-ICl (bottom)

Figure 2. Rietveld refinements of TMA-ICl and TMA-I_2

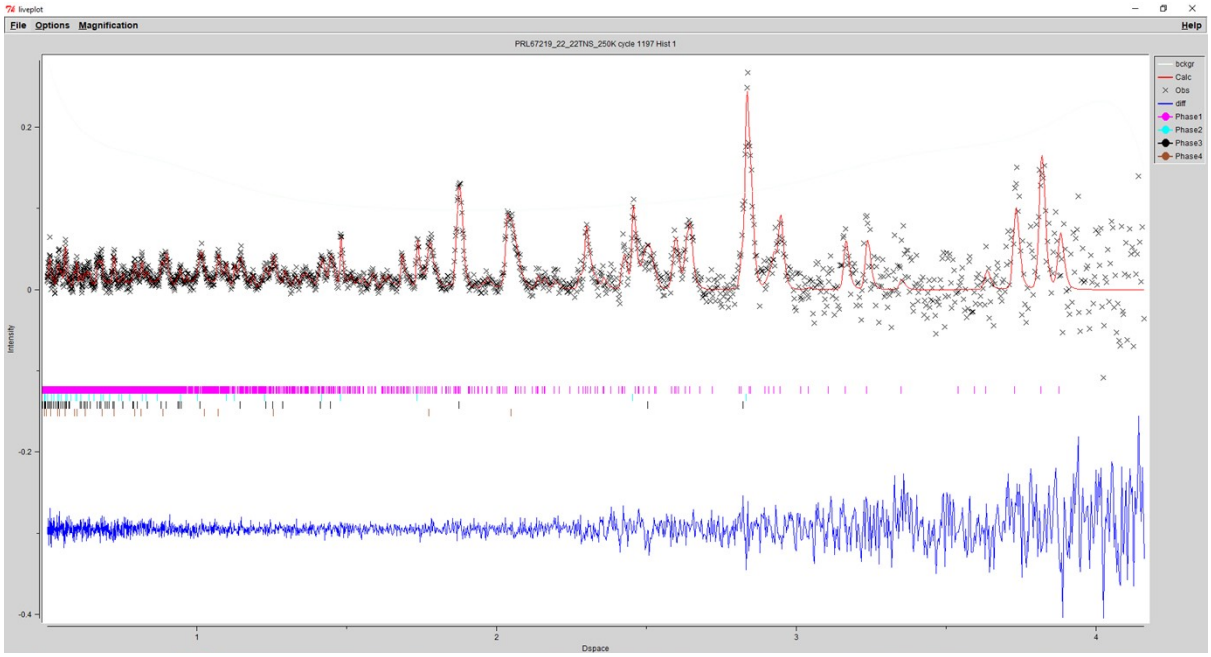
The raw data are shown by black crosses, the Rietveld fit by the red line, and the residual by the blue line. The vertical tickmarks show the refined peak positions of each phase included in the refinement; pink - TMA sample; light blue – lead (pressure marker); black – alumina (anvil); and brown – zirconia (anvil). All plots are shown with subtracted backgrounds, determined via fitting.



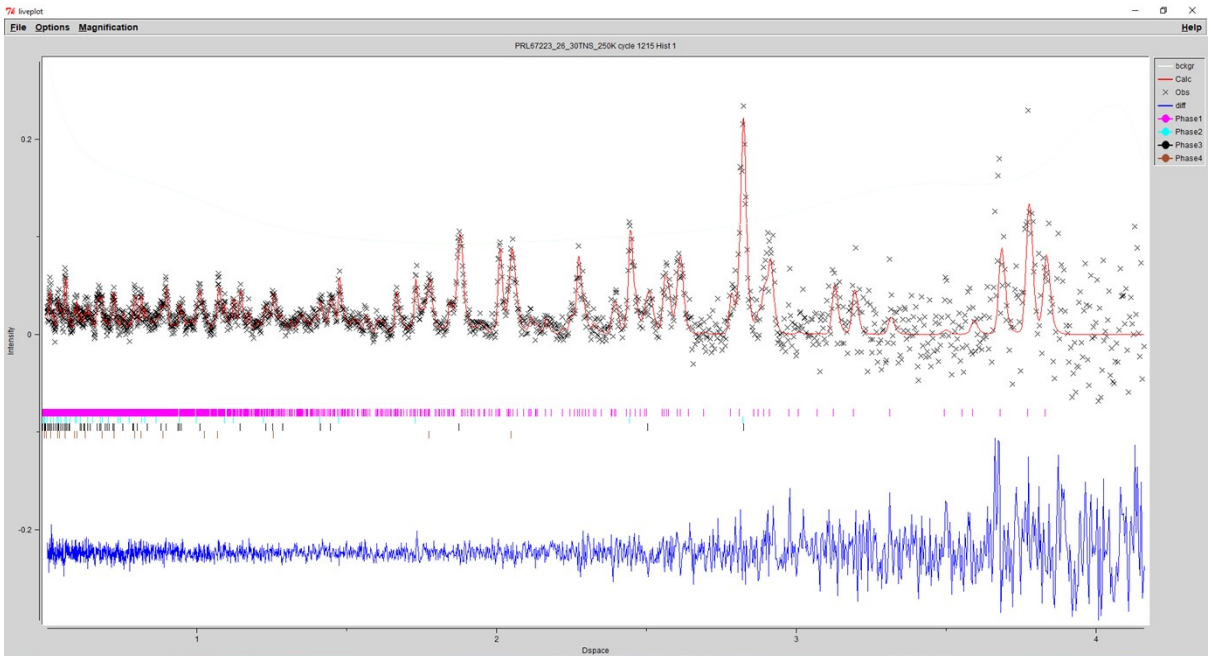
TMA-ICl. Pressure: 0.136 GPa



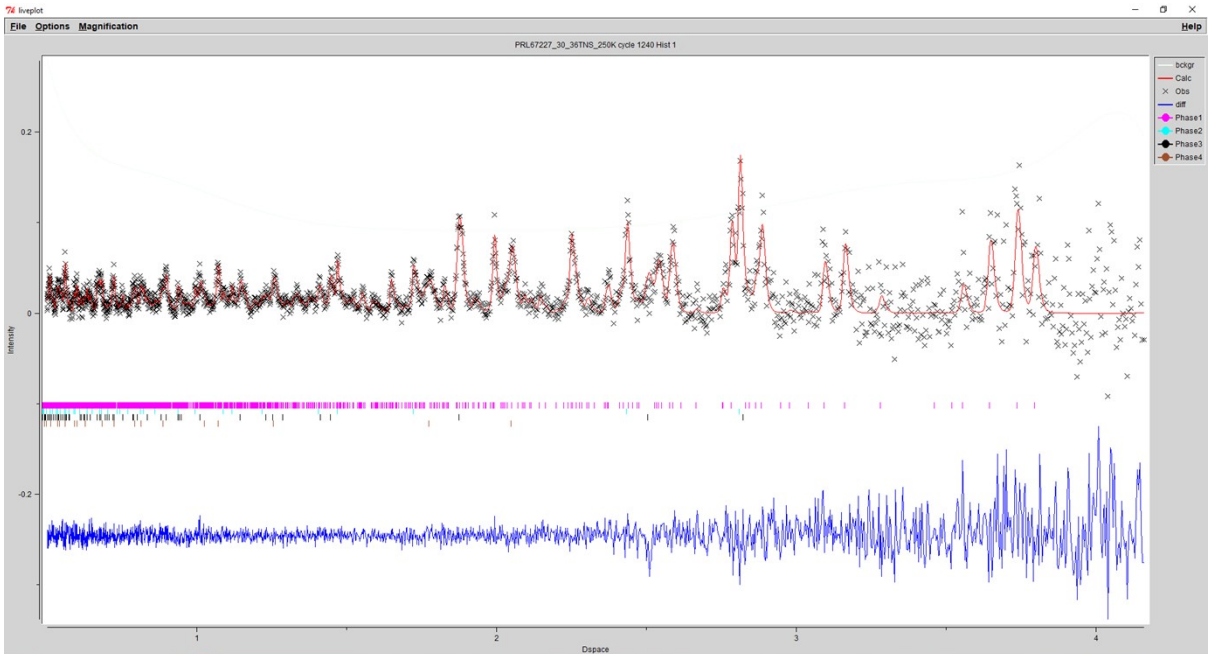
TMA-ICl. Pressure: 0.575 GPa



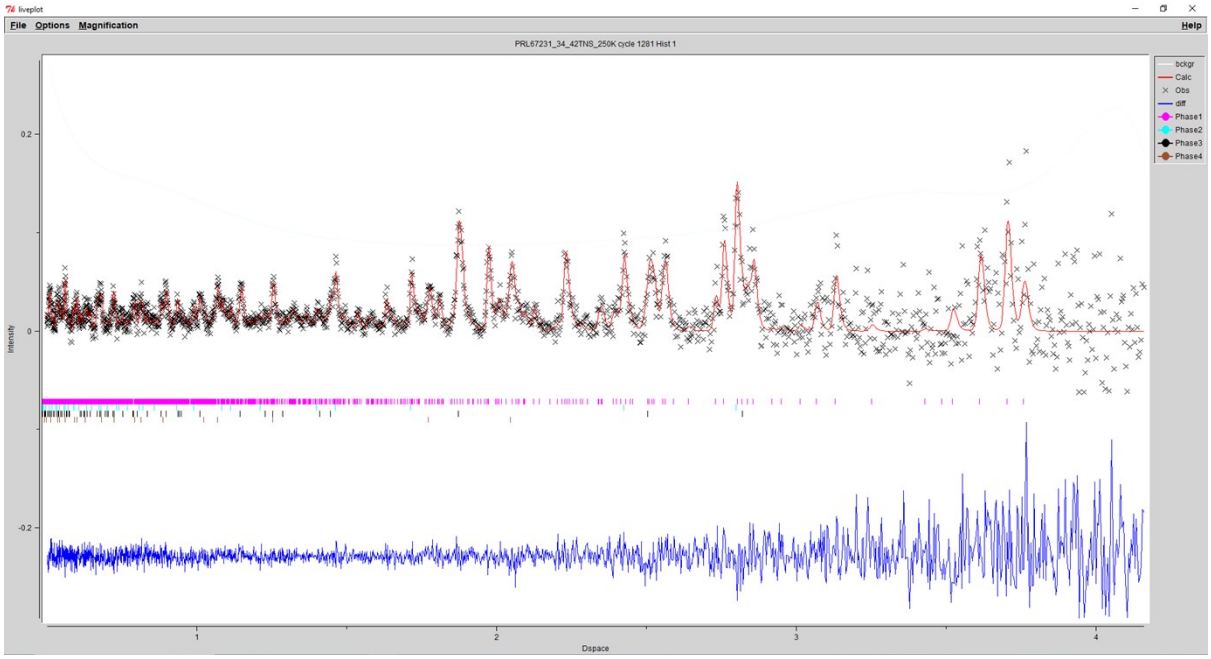
TMA-ICl. Pressure: 1.23 GPa



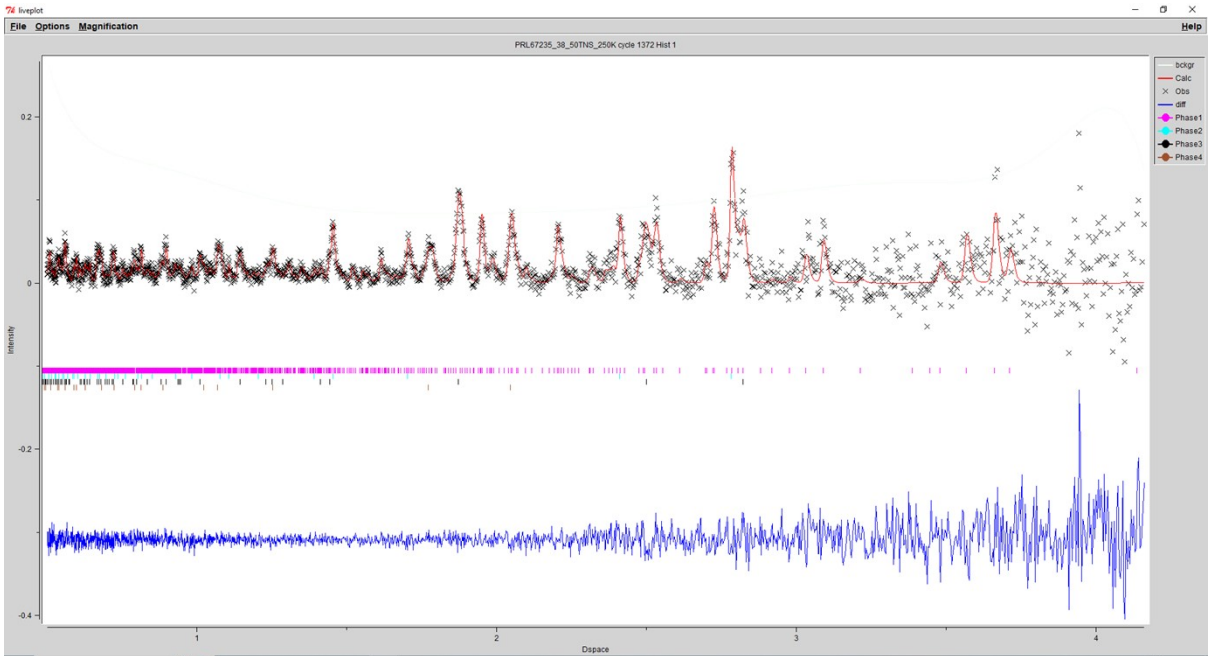
TMA-ICl. Pressure: 1.849 GPa



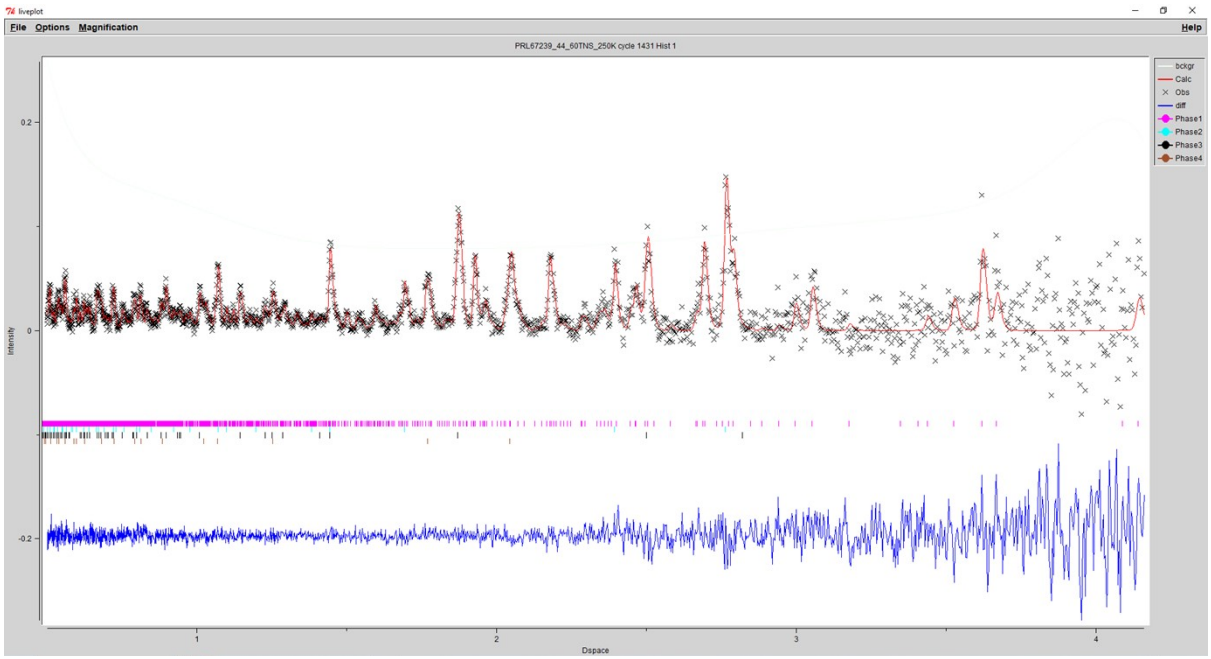
TMA-ICl. Pressure: 2.515 GPa



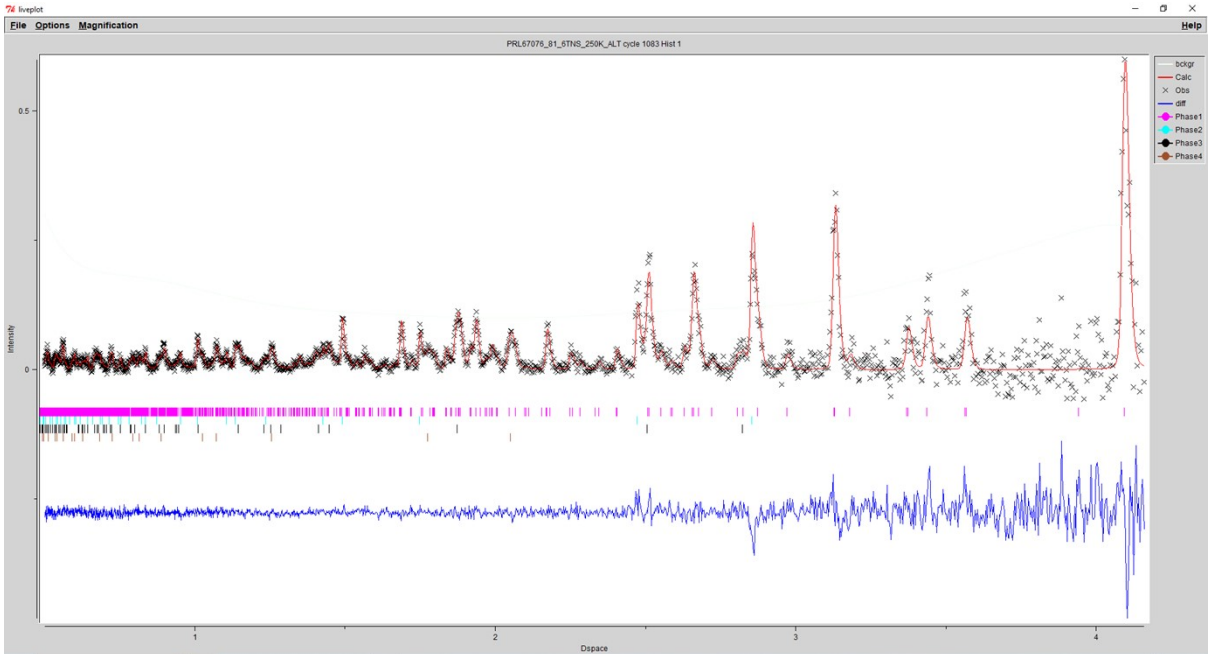
TMA-ICl. Pressure: 3.219 GPa



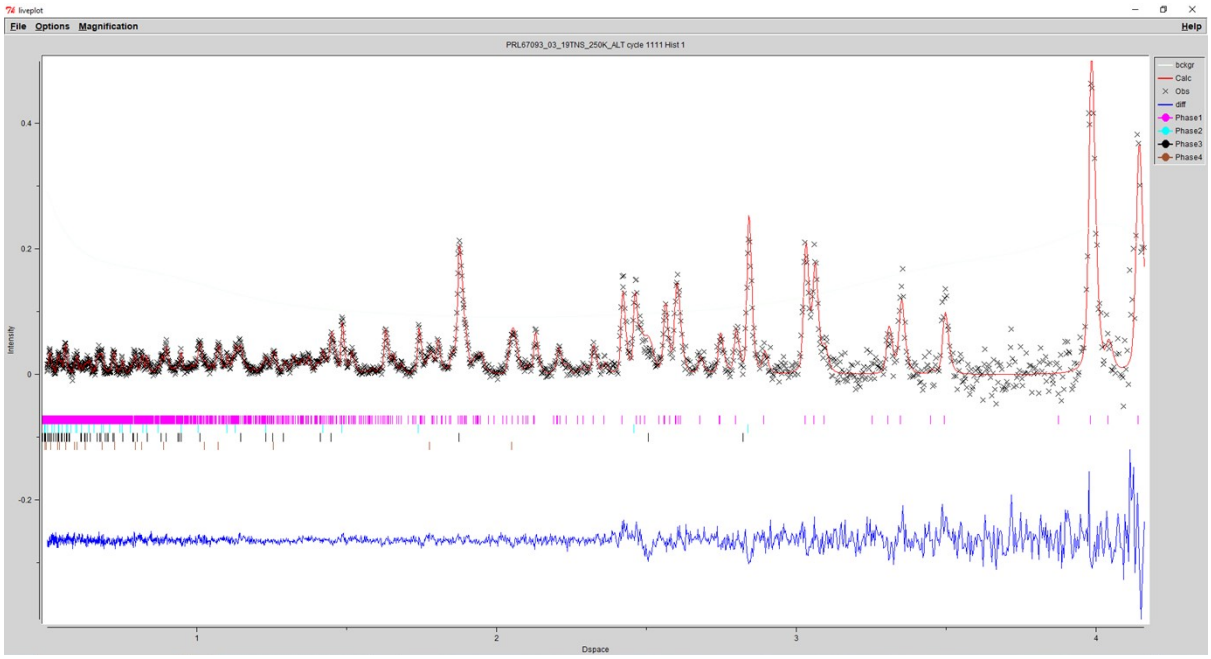
TMA-ICl. Pressure: 4.342 GPa



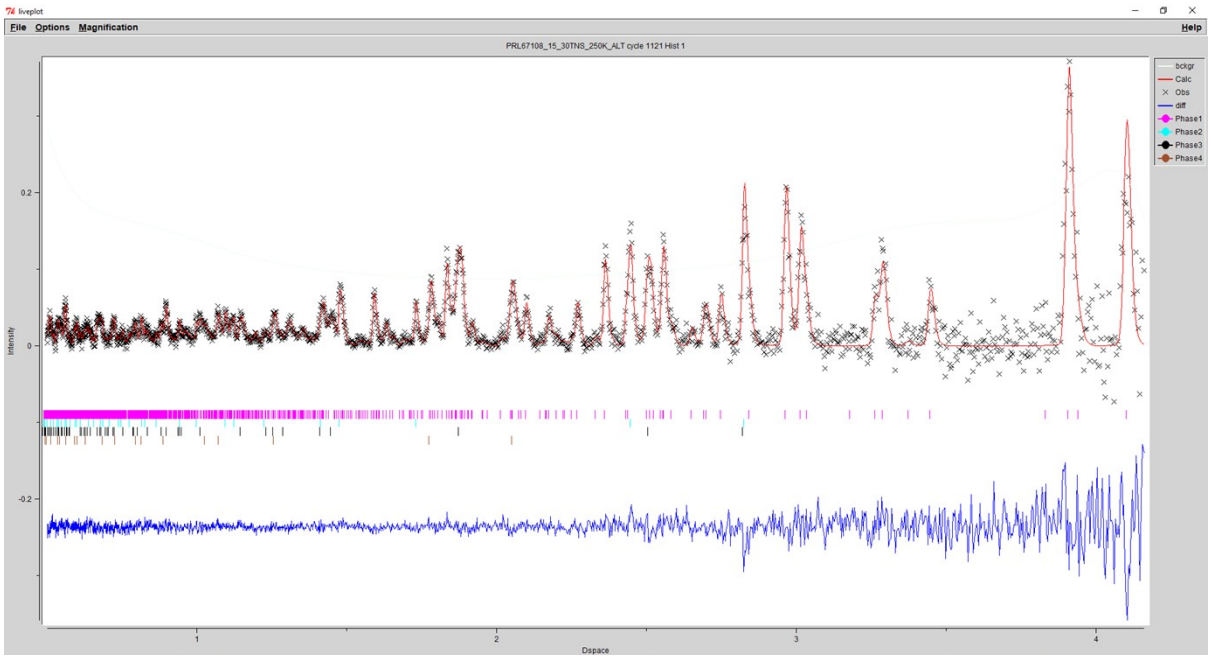
TMA-ICl. Pressure: 5.742 GPa



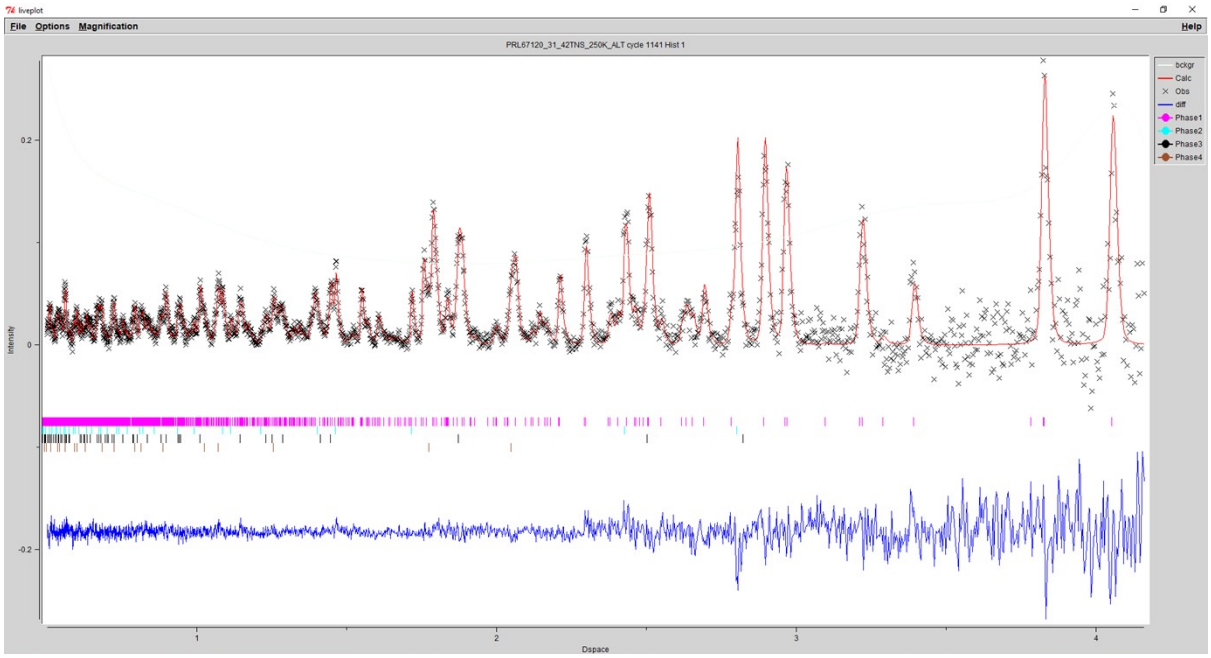
TMA-I_2. Pressure: 0.0160 GPa



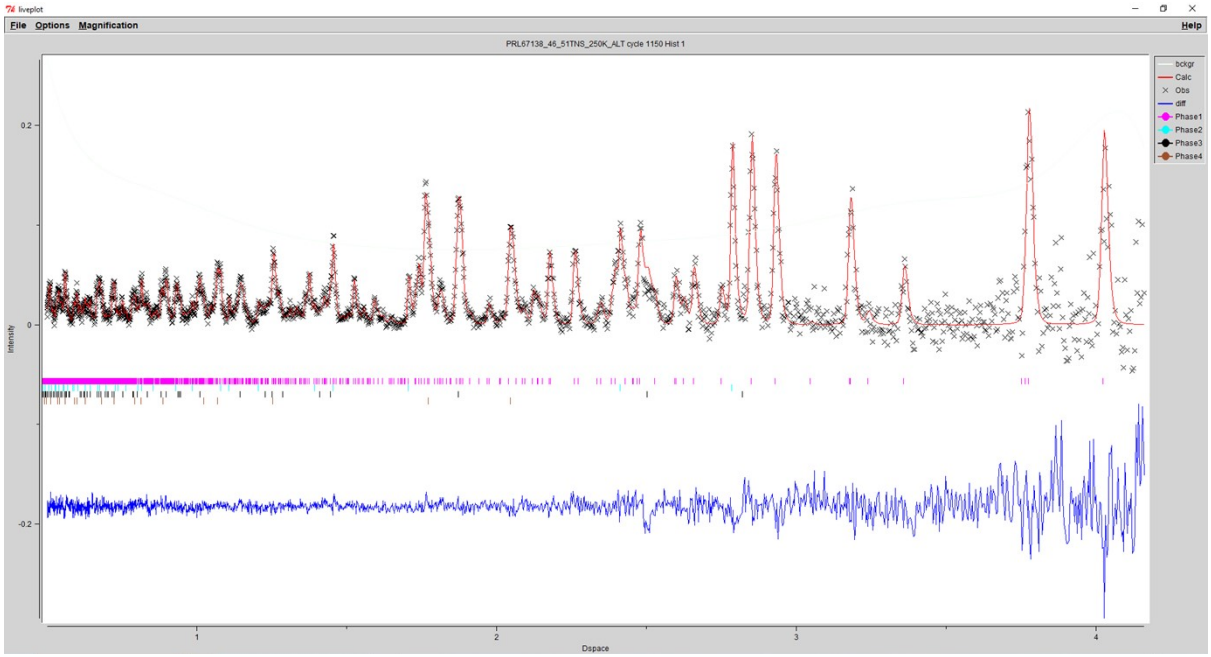
TMA-I_2. Pressure: 0.751 GPa



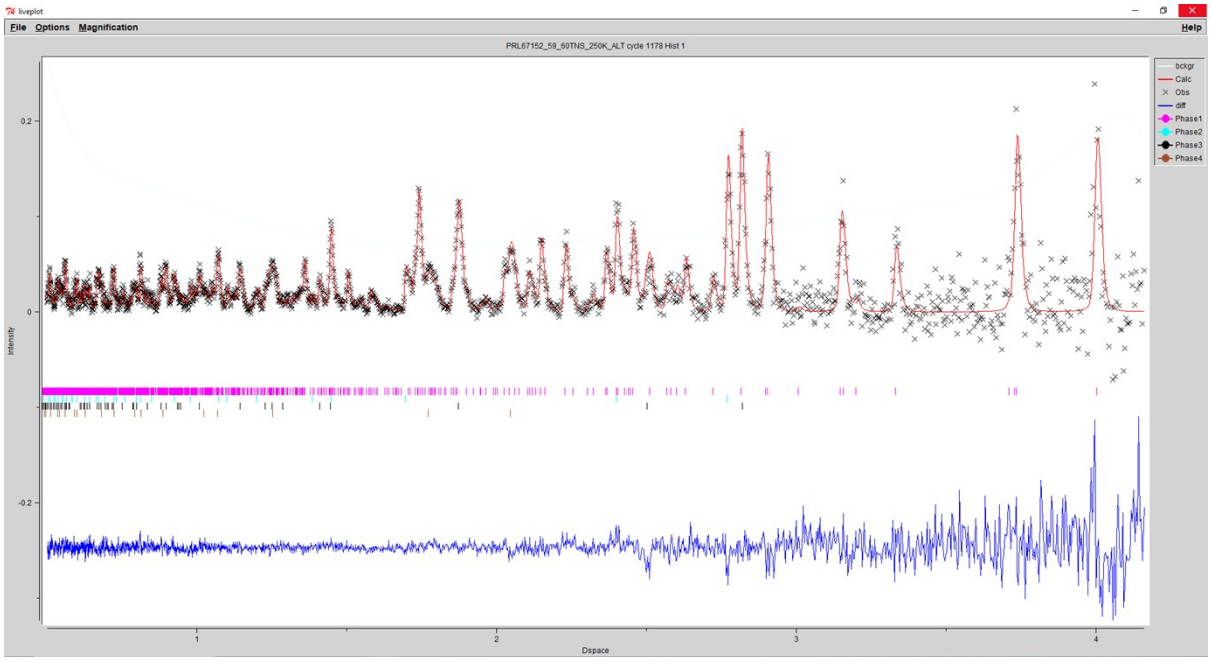
TMA-I_2. Pressure: 1.533 GPa



TMA-I_2. Pressure: 2.829 GPa



TMA-I_2. Pressure: 3.924 GPa



TMA-I_2. Pressure: 4.960 GPa

Table 3. Rietveld refinement statistics for TMA-I_2

Pressure (GPa)	***a*-axis (Å)**	***b*-axis (Å)**	***c*-axis (Å)**	**Unit cell volume (Å^3)**	**χ^2**	***wRp***

0.016(9)	11.296(2)	8.3957(15)	8.4088(17)	797.472(3)	1.3	3.5
0.75(1)	10.9778(17)	8.0780(9)	8.2783(11)	734.109(2)	1.5	3.0
1.53(1)	10.7590(17)	7.8757(9)	8.1976(11)	694.621(2)	1.4	3.2
2.83(1)	10.5269(18)	7.6535(9)	8.1036(11)	652.888(2)	1.3	3.2
3.92(1)	10.3764(16)	7.5241(8)	8.0464(10)	628.207(2)	1.3	3.2
4.96(2)	10.2662(16)	7.4188(8)	8.0017(10)	609.433(2)	1.3	3.4

Table 4. Rietveld refinement statistics for TMA-ICl

Pressure (GPa)	***a*-axis (Å)**	***b*-axis (Å)**	***c*-axis (Å)**	**Unit cell volume (Å^3)**	**χ^2**	***wRp***
0	11.6168(4)	11.1573(4)	10.8342(3)	1404.2437(6)	1.2	3.1
0.14(11)	11.560(4)	11.081(3)	10.784(4)	1381.391(6)	1.1	3.2
0.58(11)	11.403(4)	10.893(3)	10.580(4)	1314.172(6)	1.1	3.9
1.23(12)	11.249(3)	10.710(3)	10.388(3)	1251.513(5)	1.1	3.9
1.85(14)	11.125(3)	10.561(3)	10.262(3)	1205.694(5)	1.2	4.1
2.52(14)	11.021(3)	10.461(3)	10.159(3)	1171.238(5)	1.1	4.1
3.22(17)	10.916(3)	10.360(3)	10.073(3)	1139.153(5)	1.1	4.2
4.34(15)	10.799(3)	10.219(3)	9.956(3)	1098.694(5)	1.1	4.3
5.74(14)	10.672(3)	10.095(3)	9.846(3)	1060.747(5)	1.4	3.7

Experiment procedure

The complexes of trimethylamine with diiodide and iodine monochloride were made by condensing perdeuterated trimethylamine (acetone/carbon dioxide bath) and adding a

stoichiometric quantity of either iodine monochloride or iodine solution. The resulting precipitate was extracted via filtration.

High-pressure time-of-flight neutron powder diffraction data were collected using the PEARL diffractometer at the ISIS Neutron and Muon Facility, Rutherford Appleton Laboratory, UK[1] which optimised to collect powder data from a Paris–Edinburgh (P-E) press[2]. In sequential preparations of the press, the TMA-ICl and TMA-I_2 samples were gently ground and placed in the P-E press with a small lead pellet which acted as a pressure calibrant (via Rietveld fitting and using its known equation of state). Hydrostatic conditions were maintained using a 1:1 (v/v) mixture of perdeuterated pentane and methylbutane[3]. The loaded gasket was then sealed within the P-E press with an applied load of 6 tonnes. In the case of TMA-I_2 diffraction data were collected up to a maximum applied load of 71 tonnes. For TMA-ICl, diffraction patterns were collected up to 60 tonnes. Rietveld refinement was performed using the GSAS suite of programmes[4]. The equation of state and compressibilities were determined using the PASCal programme[5].

References

1. C. L. Bull, N. P. Funnell, M. G. Tucker, S. Hull, D. J. Francis and W. G. Marshall, *High Pressure Res.*, (2016), **36**, 493–511.
2. J. M. Besson, R. J. Nelmes, G. Hamel, J. S. Loveday, G. Weill and S. Hull, *Physica B*, (1992), **180**, 907–910
3. S. Klotz, J. C. Chervin, P. Munsch and G. L. Marchand, *J. Phys. D: Appl. Phys.*, (2009), **42**, 075413.
4. B. H. Toby, *J. Appl. Crystallogr.*, (2001), **34**, 210–213.
5. M. J. Cliffe and A. L. Goodwin, *J. Appl. Crystallogr.*, (2012), **45**, 1321–1329

Calculation of partial charges

Calculation of partial charges on the N, I, and X (X=Cl/I) atoms, as well as the partial charges were calculated using population analysis in Gaussian03. In all cases, the molecular geometry was held fixed to the refined crystallographic coordinates. A representative input file is shown below – coordinates (obtained from the relevant Crystallographic Information File) are supplied in .xyz format.

```
%chk=checkpoint.chk
# lsda/lanl2dz pop=nbo rsvwn

6tons DFT

0 1
N             1.87036655    0.02024686   -0.02227997
C             2.33906326   -0.56414506    1.25047288
C             2.39697932    1.40033137   -0.16063485
C             2.35528255   -0.87517619   -1.08995752
H             2.05839676    0.10673344    2.03048411
H             1.96065169   -1.47561969    1.42886803
H             3.46413059   -0.61888759    1.29252002
H             2.10069556    1.99364253    0.59043835
H             2.01174196    1.81243111   -1.14892335
H             3.52690936    1.28514969   -0.16402408
H             3.36554014   -0.89059030   -1.08062123
H             2.00292092   -1.87845999   -0.90998786
H             2.01280766   -0.48883058   -2.03723266
I            -0.49562623    0.00610909    0.00501825
Cl           -3.05153655   -0.00453759   -0.00651834
```