Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting information

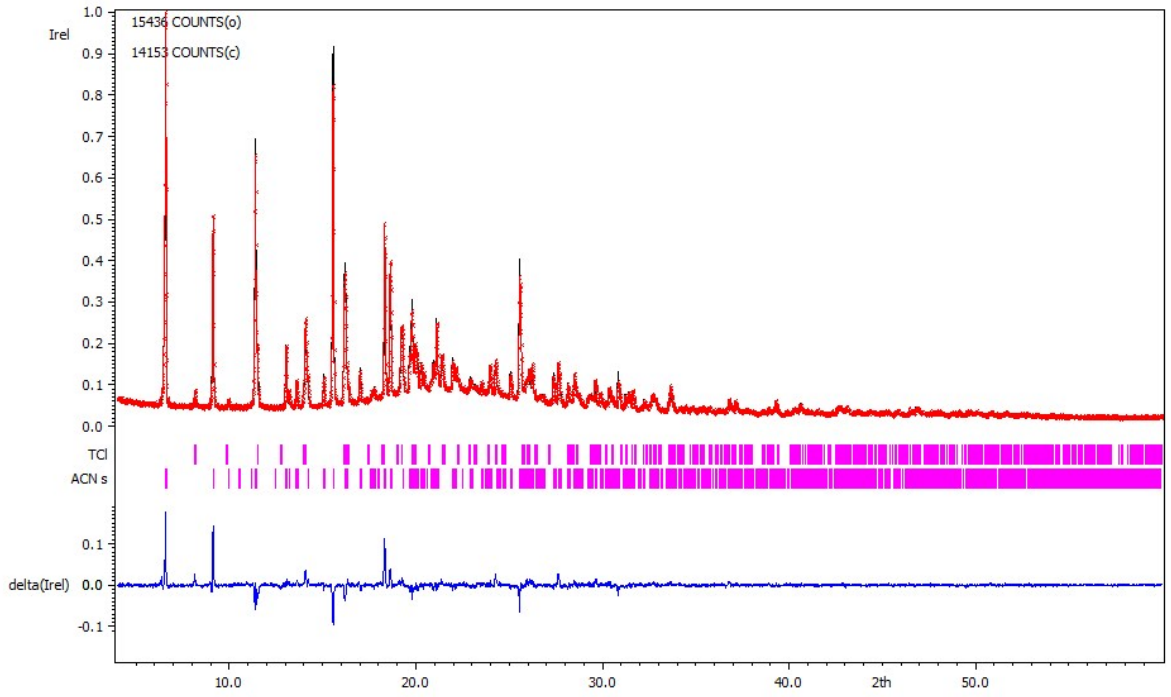


Figure 1 Final Rietveld plot of TCl ACN solvate showing the measured data (red line), calculated data (black line) and difference curve (blue line). Calculated Bragg positions are shown by vertical bars (top row: TCl, bottom row: TCl ACN).

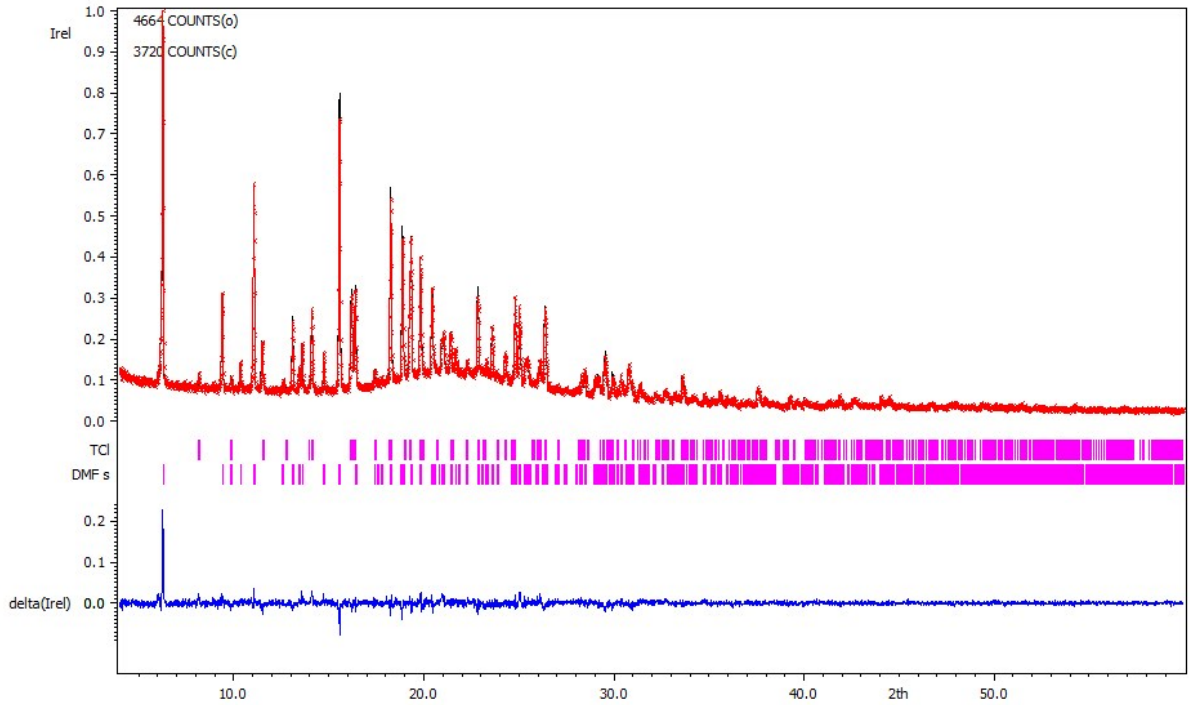


Figure 2 Final Rietveld plot of TCl DMF solvate showing the measured data (red line), calculated data (black line) and difference curve (blue line). Calculated Bragg positions are shown by vertical bars (top row: TCl, bottom row: TCl DMF).

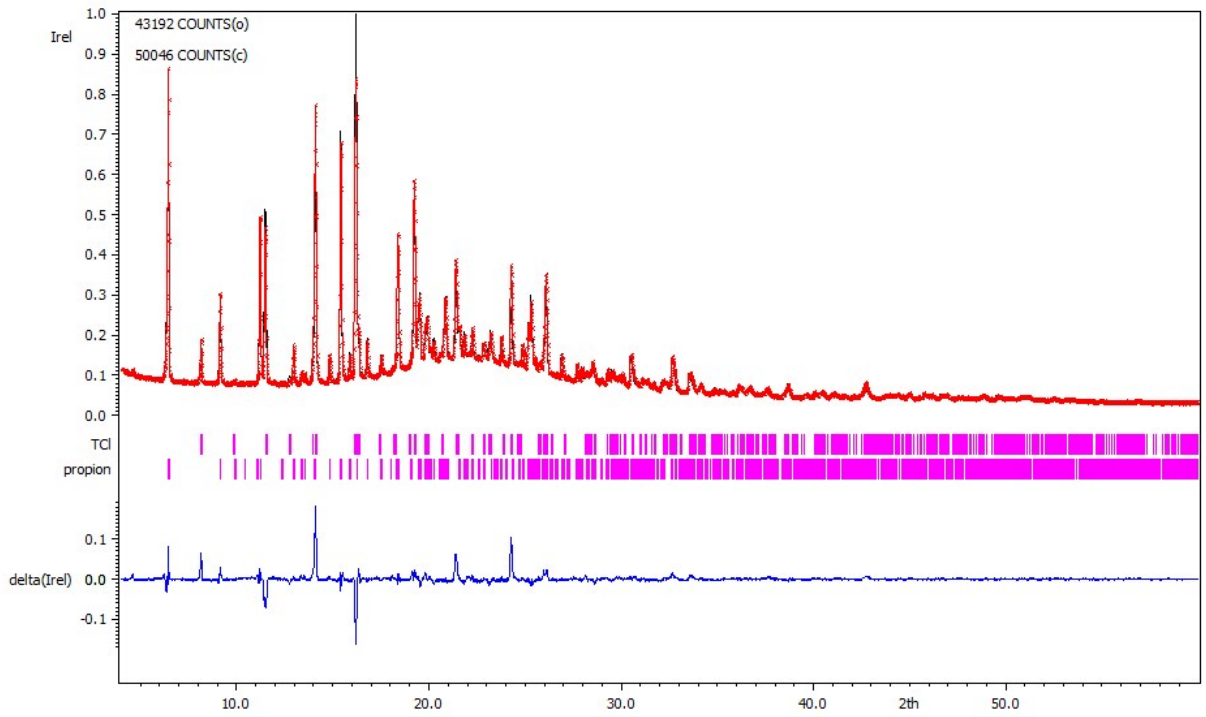


Figure 3 Final Rietveld plot of TCl propionitrile solvate showing the measured data (red line), calculated data (black line) and difference curve (blue line). Calculated Bragg positions are shown by vertical bars (top row: TCl, bottom row: TCl propionitrile).

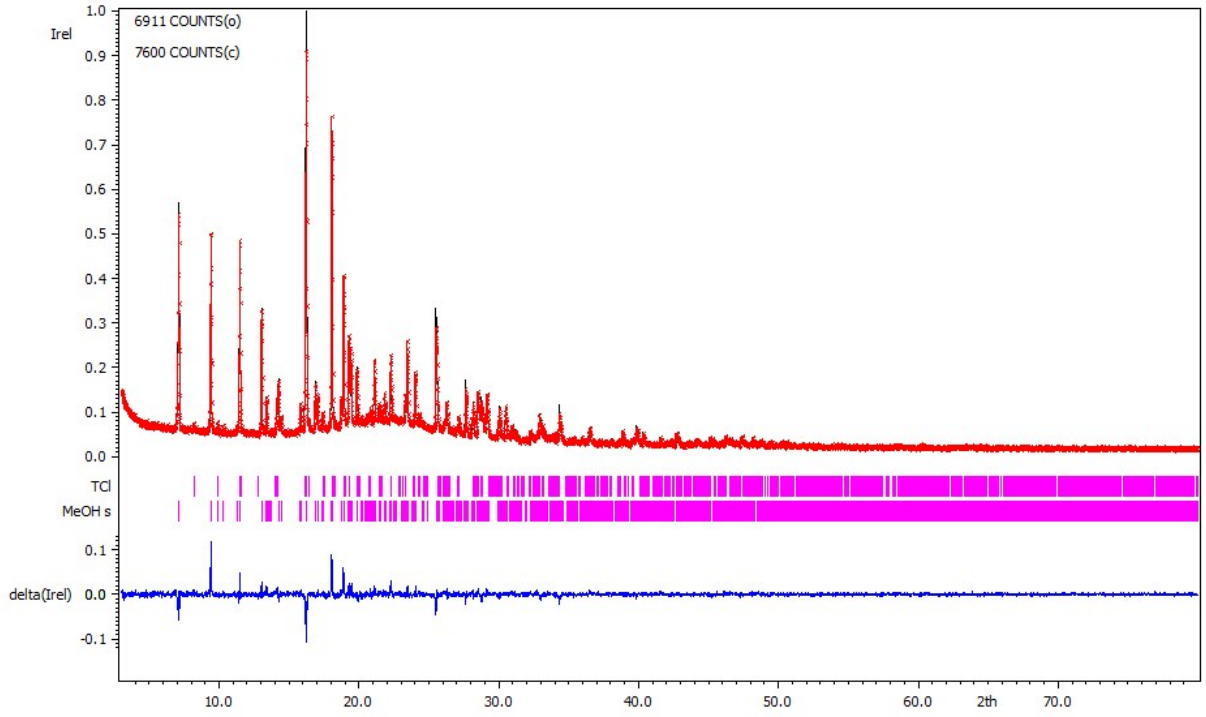


Figure 4 Final Rietveld plot of TCl MeOH solvate showing the measured data (red line), calculated data (black line) and difference curve (blue line). Calculated Bragg positions are shown by vertical bars (top row: TCl, bottom row: TCl MeOH).

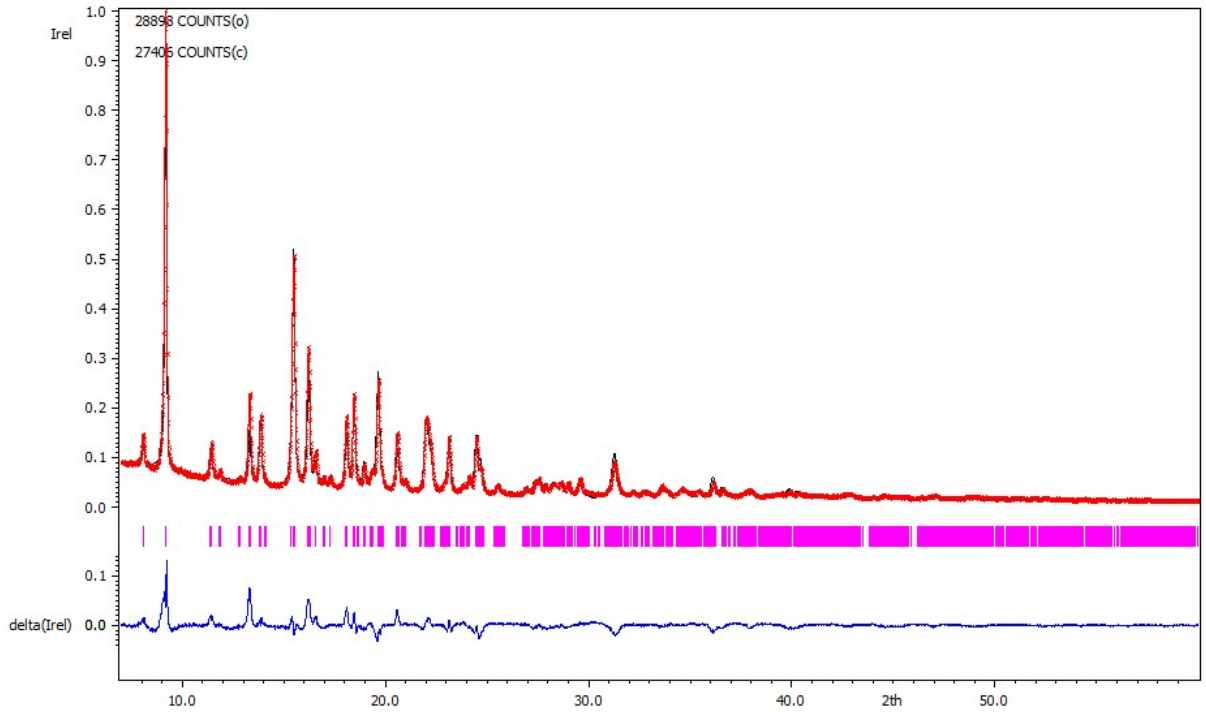


Figure 5 Final Rietveld plot of TCl dihydrate showing the measured data (red line), calculated data (black line) and difference curve (blue line). Calculated Bragg positions are shown by vertical bars.

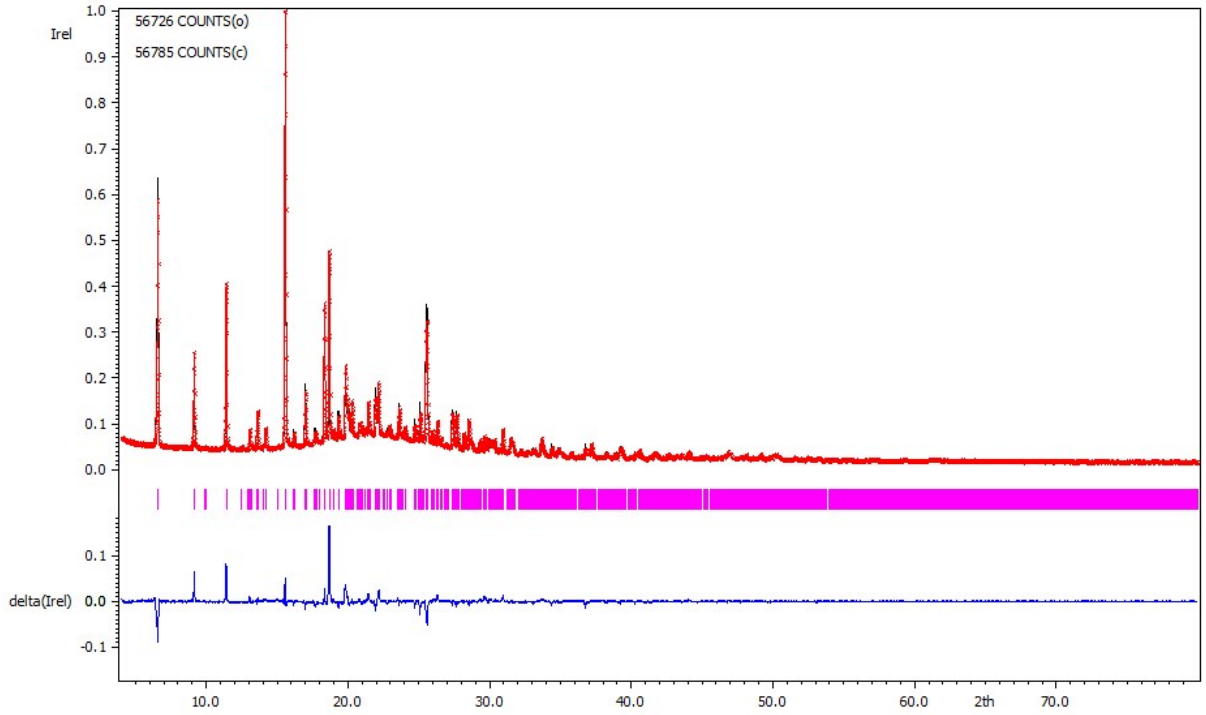


Figure 6. Final Rietveld plot of TCl nitromethane solvate showing the measured data (red line), calculated data (line) and difference curve (blue line). Calculated Bragg positions are shown by vertical bars.

Table 1. UV-Vis solubility measurement in detail. Solubility is expressed within relative deviation.

Solvent	Dilution of saturated solution	Lambda max (nm)	%RSD ($q_{0.95}$)	Solubility (mg/mL)
ACN	1.667x	257.6	3.70	0.94
DMF	2.5x	264.2	3.10	1.85
PRN	312.5x	221.0	n.a.	0.17
WA	1000x	257.2	0.75	606

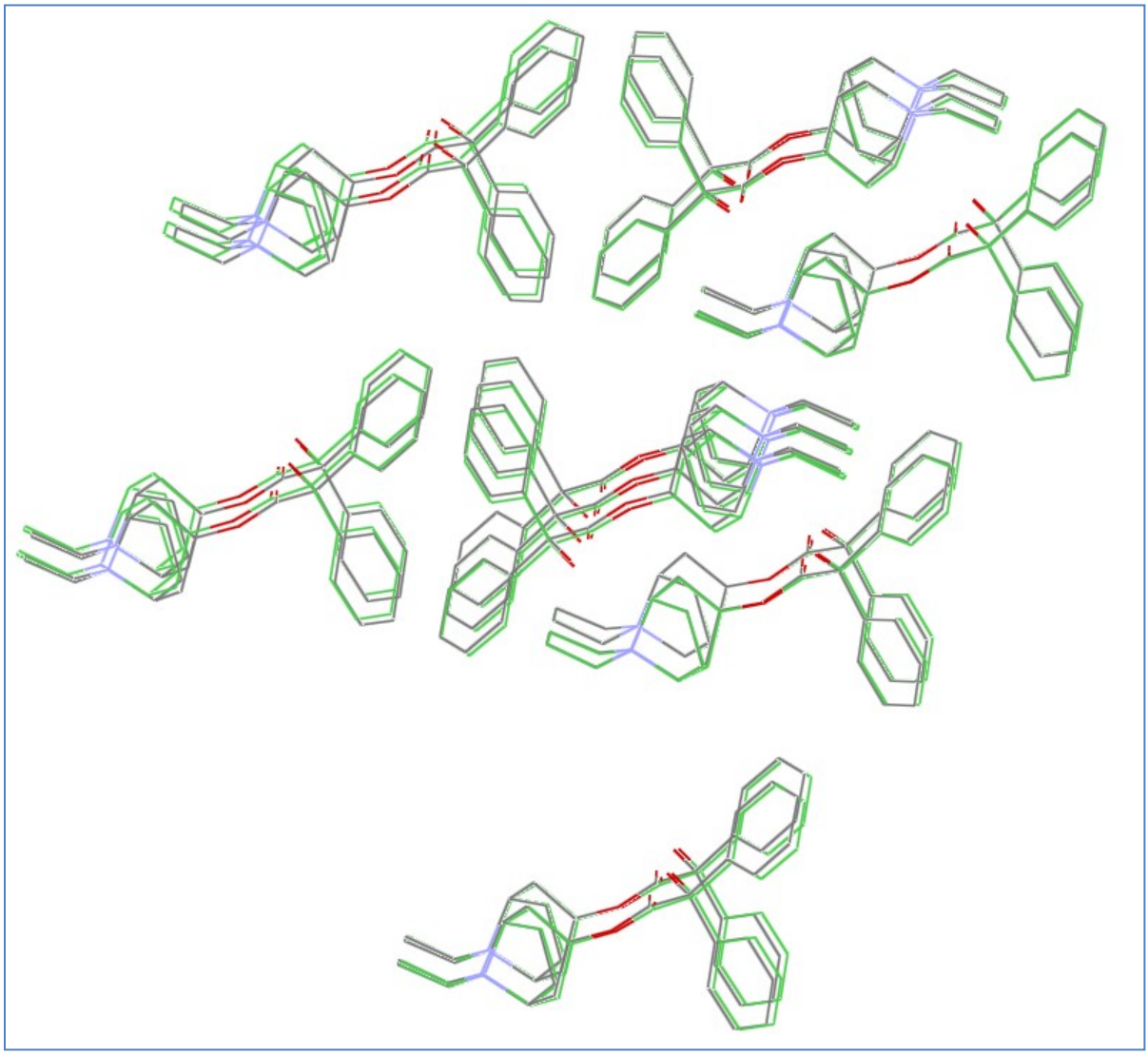


Figure 7. Example from crystal packing similarity calculation for the construction of a tree diagram. For TCl DMF (gray) and ACN (green) solvates, all 15 molecules of trospium in the clusters fit to each other.

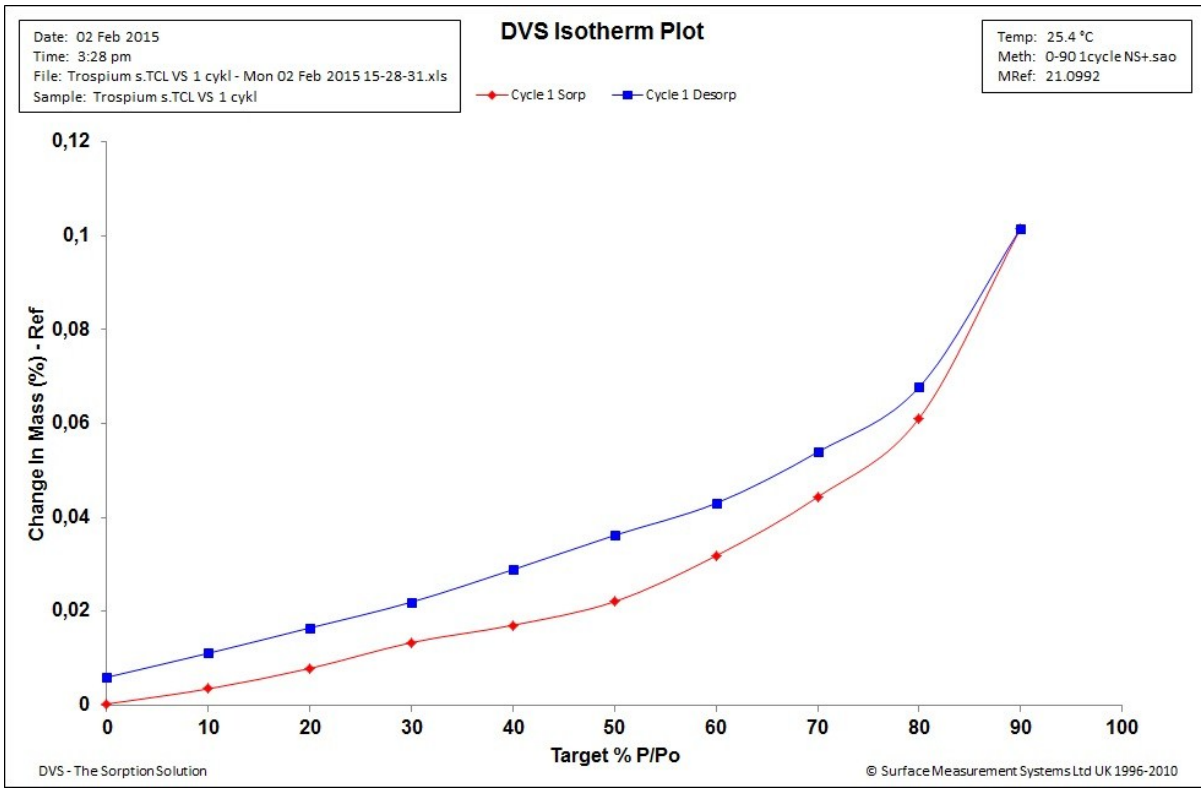


Figure 8. The dynamic vapor sorption curves of trospium chloride polymorf I. The bulk was not hygroscopic and increased its weight up till 0.1 wt. %.

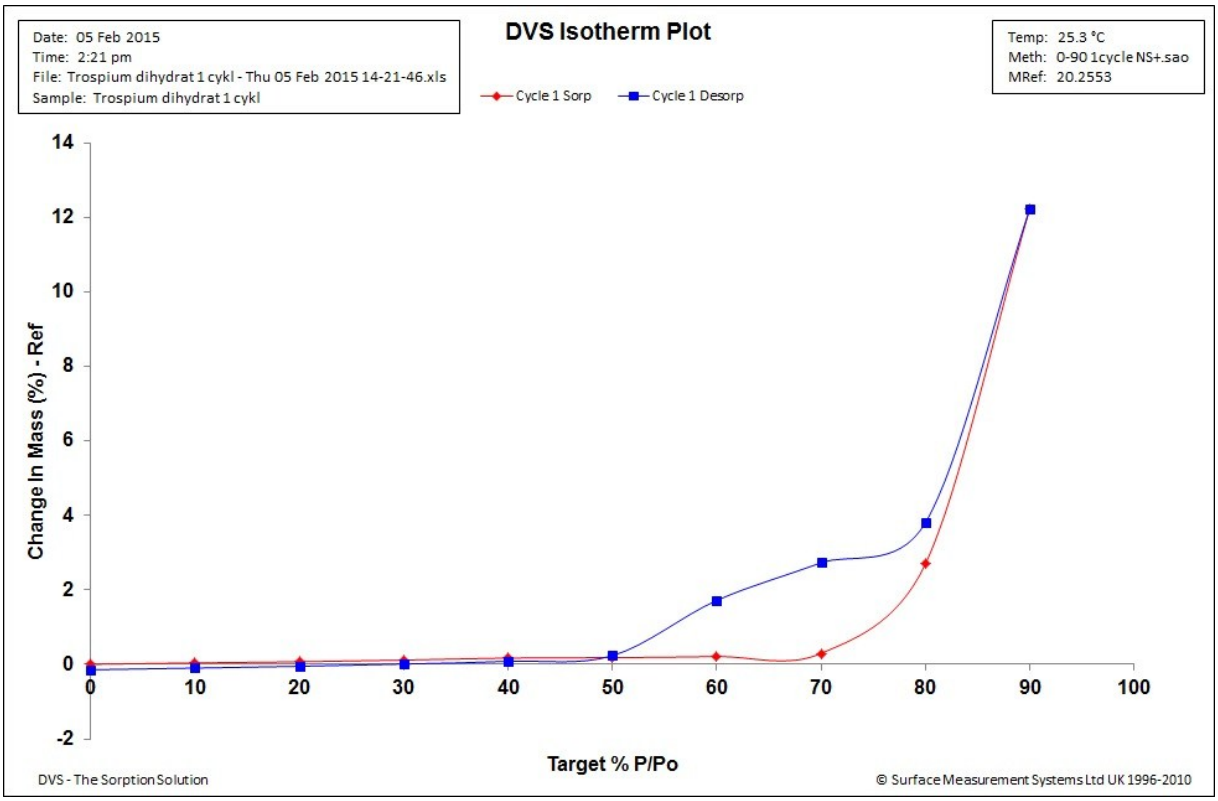


Figure 9. The dynamic vapor sorption curves of trospium chloride dihydrate (8). The bulk was hygroscopic above 70 % of RH and increased its weight up till 13 wt. %, the crystalline material partly dissolved.

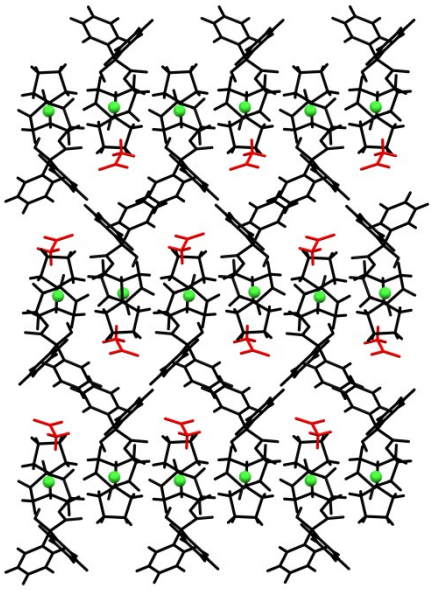
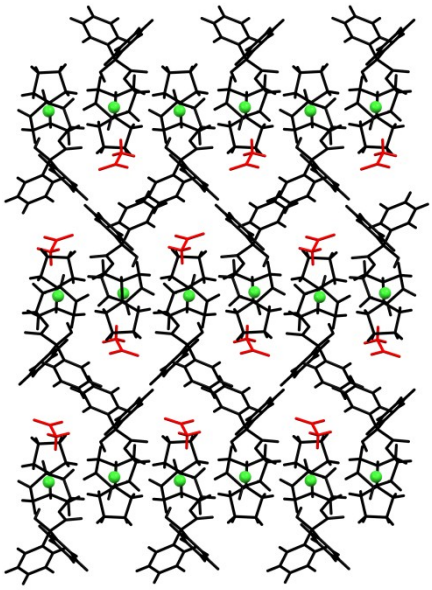
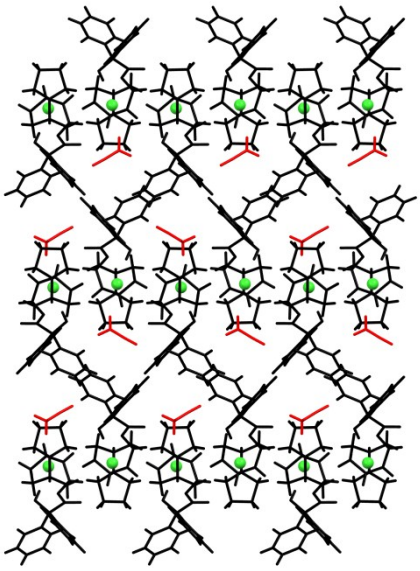
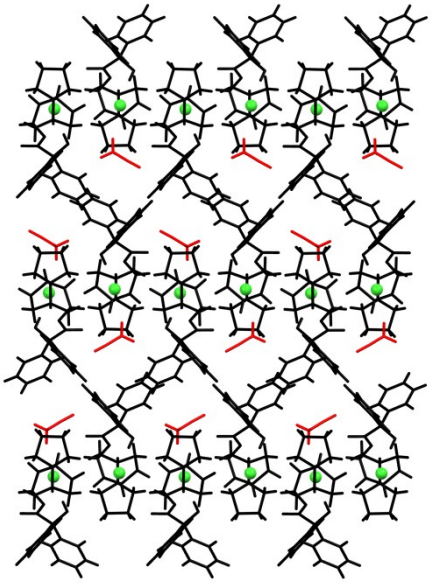
	Layer 1	Layer 2
TCl $MeNO_2$		
TCl ACN		

Figure 10. Layers in red branch protic x aprotic demonstrated on TCl ACN and TCl $MeNO_2$.

The C(ar)–H···X interaction is aprotic part of red branch.

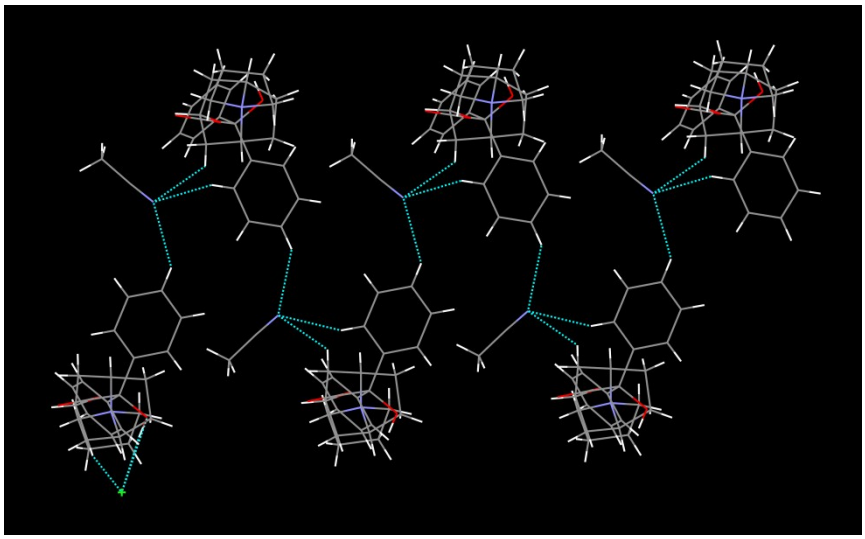


Figure 11. TCl ACN

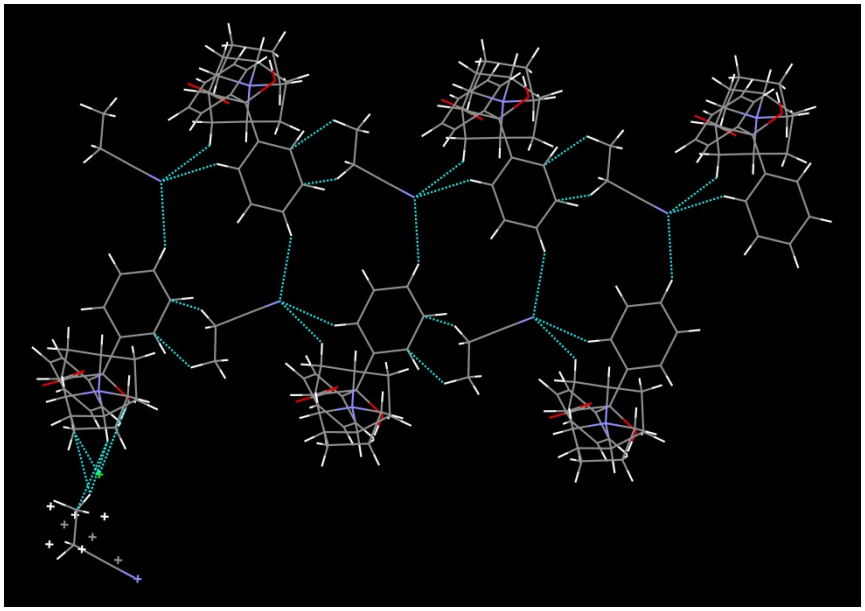


Figure 12. TCl PRN

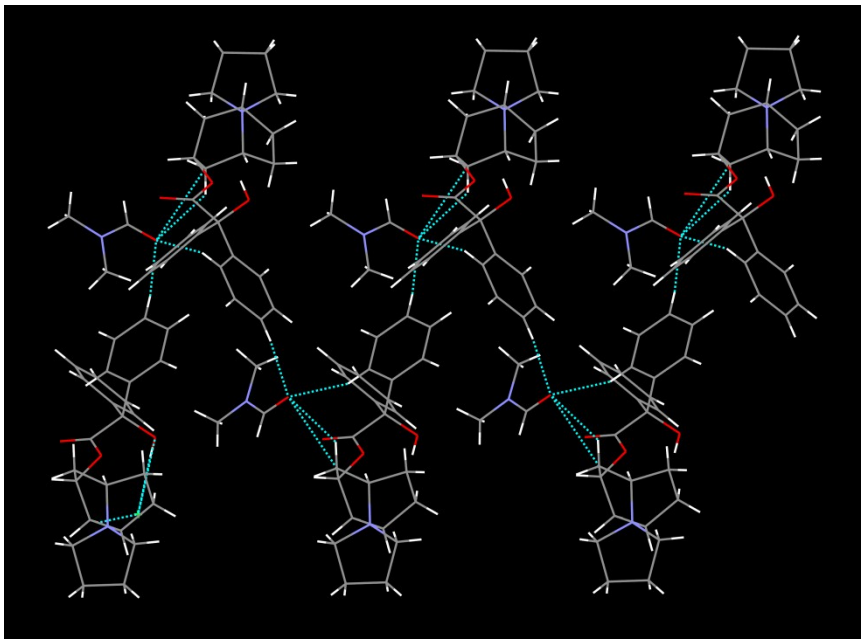


Figure 13. TCl DMF

Table 2. Table of hydrogen bonds of solvates with ACN, DMF and *i*PrOH

solvate	D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
ACN	O3–H1o3···Cl1	0.820 (16)	2.242 (14)	3.0579 (14)	173.6 (19)
	C10–H1c10···N1s^{i}	0.96	2.84	3.739 (4)	157
	C12–H1c12···N1s	0.96	2.71	3.502 (3)	140
	C16–H1c16···O3^{ii}	0.96	2.66	3.618 (2)	173
	C17–H1c17···O2^{iii}	0.96	2.49	3.259 (2)	138
	C18–H1c18···Cl1^{iii}	0.96	2.81	3.6532 (18)	147
	C20–H1c20···Cl1^{iv}	0.96	2.99	3.7742 (16)	140
	C21–H1c21···N1s^{i}	0.96	2.71	3.454 (4)	134
	C21–H2c21···Cl1^{ii}	0.96	2.94	3.7157 (19)	139
	C22–H1c22···Cl1^{iv}	0.96	2.95	3.7827 (17)	146
	C22–H2c22···Cl1^{ii}	0.96	2.93	3.7612 (19)	146
	C25–H2c25···Cl1^{iv}	0.96	2.86	3.7031 (19)	148
DMF	O3–H1o3···Cl1	0.820 (10)	2.285 (11)	3.1009 (12)	173.1 (18)
	C4–H1c4···O1s^{i}	0.96	2.53	3.417 (2)	154
	C6–H1c6···O1s^{ii}	0.96	2.42	3.371 (3)	173
	C16–H1c16···O1s^{i}	0.96	2.43	3.162 (2)	133
	C17–H1c17···Cl1^{iii}	0.96	2.94	3.7485 (12)	143
	C19–H2c19···Cl1^{iv}	0.96	2.94	3.8048 (12)	150
	C20–H1c20···O2^{iv}	0.96	2.48	3.2629 (18)	138
	C21–H1c21···Cl1	0.96	2.86	3.7918 (11)	164
	C22–H1c22···Cl1^{iii}	0.96	3.03	3.8574 (13)	146
	C25–H2c25···Cl1^{iii}	0.96	2.88	3.7426 (15)	150
*i*PrOH	O3–H1o3···Cl1^{i}	0.820 (19)	2.264 (18)	3.0768 (14)	170.8 (18)
	O1sa–H1o1sa···Cl1^{ii}	0.89 (3)	2.28 (3)	3.127 (2)	161 (3)
	O1sb–H1o1sb···Cl1^{ii}	0.89 (4)	2.38 (4)	3.20 (2)	154 (5)
	C17–H1c17···Cl1	0.96	2.92	3.7839 (17)	151
	C19–H2c19···Cl1^{iii}	0.96	2.84	3.764 (2)	163

	C20–H1c20···O2	0.96	2.45	3.307 (2)	148
	C21–H1c21···Cl1^{i}	0.96	2.89	3.8363 (17)	169
	C22–H1c22···Cl1^{ii}	0.96	2.82	3.6870 (19)	151
	C24–H1c24···O1sa^{iii}	0.96	2.62	3.212 (3)	120
	C24–H1c24···O1sb^{iii}	0.96	2.49	3.20 (2)	130
	C24–H2c24···O2^{iv}	0.96	2.50	3.379 (3)	153
	C25–H1c25···Cl1	0.96	2.96	3.854 (2)	156
	C25–H2c25···Cl1^{iii}	0.96	2.97	3.914 (2)	168

Symmetry codes: ACN: (i) –*x*+3/2, *y*-1/2, -*z*+1/2 (ii) –*x*+1/2,*y*-1/2,-*z*+1/2 (iii) –*x*+1/2,*y*+1/2,-*z*+1/2 (iv) *x*+1/2,-*y*+1/2,*z*+1/2 DMF: (i) –*x*+1,*y*-1/2,-*z*+1/2 (ii) *x*,-*y*+3/2,*z*+1/2 (iii) –*x*+2,*y*+1/2,-*z*+1/2 iPrOH: (i) *x*-1,*y*,*z* (ii) –*x*+3/2,*y*+1/2,-*z*+1/2 (iii) –*x*+3/2,*y*-1/2,-*z*+1/2 (iv) –*x*+1/2,*y*-1/2,-*z*+1/2

Table 3. Table of hydrogen bonds of solvates with MeOH, $MeNO_2$ and PRN

solvate	D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
MeOH	O3–H1o3···Cl1	0.820 (15)	2.297 (15)	3.1136 (16)	174 (2)
	O1s–H1o1s···Cl1	0.820 (14)	2.405 (16)	3.131 (4)	148.0 (12)
	O1s'–H1o1s···Cl1	0.82 (2)	2.405 (16)	3.087 (14)	141.1 (15)
	C5–H1c5···O2^{i}	0.96	2.68	3.630 (3)	169
	C8–H1c8···Cl1	0.96	2.74	3.648 (2)	158
	C12–H1c12···O1s^{ii}	0.96	2.70	3.405 (4)	130
	C16–H1c16···Cl1	0.96	2.91	3.8442 (18)	166
	C17–H1c17···O2^{iii}	0.96	2.62	3.334 (2)	131
	C18–H1c18···O2^{iii}	0.96	2.71	3.373 (3)	127
	C20–H1c20···Cl1^{iv}	0.96	2.95	3.7705 (19)	144
	C22–H1c22···Cl1^{iv}	0.96	3.04	3.883 (2)	147
	C22–H2c22···Cl1^{v}	0.96	2.93	3.763 (2)	146
	C25–H2c25···Cl1^{iv}	0.96	2.96	3.813 (2)	148
$MeNO_2$	O3–H1o3···Cl1^{i}	0.820 (17)	2.246 (16)	3.0642 (14)	175.7 (18)
	C16–H1c16···Cl1^{i}	0.96	2.95	3.8941 (19)	168
	C17–H1c17···O2^{ii}	0.96	2.43	3.228 (2)	140
	C18–H1c18···Cl1^{iii}	0.96	2.77	3.6424 (18)	152
	C20–H1c20···Cl1	0.96	3.02	3.8109 (19)	141
	C21–H1c21···Cl1^{iv}	0.96	2.94	3.7107 (19)	138
	C22–H2c22···Cl1^{iv}	0.96	2.93	3.7844 (19)	149
	C23–H1c23···O2s^{iii}	0.96	2.63	3.463 (4)	145
	C25–H2c25···Cl1	0.96	2.74	3.631 (2)	155
	C1s–H1c1s···O2	0.96	2.66	3.511 (3)	148
	C1s–H3c1s···Cl1^{vi}	0.96	2.75	3.678 (3)	164
PRN	O3–H1o3···Cl1	0.820 (10)	2.249 (11)	3.0614 (12)	171.0 (19)
	C6–H1c6···N1sa^{i}	0.96	2.59	3.420 (5)	145
	C6–H1c6···N1sb^{i}	0.96	2.57	3.408 (14)	146
	C16–H2c16···N1sa^{ii}	0.96	2.63	3.411 (7)	138
	C16–H2c16···N1sb^{ii}	0.96	2.62	3.418 (18)	141
	C17–H1c17···Cl1^{iii}	0.96	2.94	3.7438 (14)	141
	C19–H2c19···Cl1^{iv}	0.96	2.88	3.7319 (15)	149
	C20–H1c20···O2^{iv}	0.96	2.51	3.266 (2)	135
	C22–H1c22···Cl1^{ii}	0.96	2.90	3.7526 (15)	148
	C22–H2c22···Cl1^{iii}	0.96	2.94	3.7805 (15)	147
	C25–H1c25···Cl1^{iii}	0.96	2.89	3.7351 (16)	148

Symmetry codes: MeOH: (i) –*x*+2,-*y*+1,-*z* (ii) *x*+1,*y*,*z* (iii) –*x*+3/2,*y*+1/2,-*z*+1/2 (iv) *x*+1/2,-*y*+3/2,*z*+1/2 (v) -*x*+3/2,*y*-1/2,-*z*+1/2 $MeNO_2$: (i) *x*-1,*y*,*z* (ii) –*x*+1/2,*y*+1/2,-*z*+1/2 (iii) –*x*+3/2,*y*+1/2,-*z*+1/2 (iv) -*x*+3/2,*y*-1/2,-*z*+1/2 PRN: (i) *x*+1,*y*,*z* (ii) –*x*+3/2,*y*+1/2,-*z*+1/2 (iii) *x*+1/2,-*y*+1/2,*z*+1/2 (iv) -*x*+3/2,*y*-1/2,-*z*+1/2

Table 4. Table of hydrogen bonds of TCl sesquihydrate and TCl dihydrate

solvate	D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
sesHyd	O3a–H1o3a···Cl1a	0.820 (8)	2.255 (7)	3.0706 (11)	172.7 (19)
	O3b–H1o3b···Cl1b^{i}	0.820 (9)	2.217 (8)	3.0323 (11)	172 (2)
	O1w–H1o1w···Cl1b	0.820 (18)	2.299 (18)	3.1129 (14)	172 (2)
	O1w–H2o1w···O2b	0.820 (19)	2.118 (19)	2.9317 (19)	171 (2)
	O2w–H1o2w···Cl1a	0.82 (2)	2.34 (2)	3.1502 (15)	172 (2)
	O2w–H2o2w···O2a	0.820 (18)	2.134 (19)	2.9420 (18)	168 (2)
	O3w–H1o3w···O1w	0.820 (16)	2.152 (16)	2.939 (2)	161 (3)
	O3w–H2o3w···Cl1a	1.04 (4)	2.22 (4)	3.214 (2)	160 (2)
	C18a–H2c18a···O2a^{ii}	0.96	2.63	3.5525 (18)	162
	C19a–H1c19a···O2w^{iii}	0.96	2.65	3.473 (2)	144
	C20a–H1c20a···O3w	0.96	2.49	3.190 (2)	130
	C22a–H1c22a···O2w^{ii}	0.96	2.55	3.371 (2)	143
	C25a–H1c25a···O2w	0.96	2.57	3.464 (2)	154
	C25a–H2c25a···Cl1a	0.96	2.81	3.5919 (15)	139
	C15b–H1c15b···Cl1b	0.96	2.86	3.5768 (15)	133
	C16b–H1c16b···Cl1b^{i}	0.96	2.91	3.7641 (14)	149
	C18b–H2c18b···O1w^{iii}	0.96	2.65	3.501 (2)	149
	C19b–H1c19b···O2b^{iii}	0.96	2.60	3.5413 (19)	168
	C22b–H2c22b···O1w^{ii}	0.96	2.52	3.391 (2)	150
	C25b–H1c25b···Cl1b^{ii}	0.96	2.85	3.6412 (15)	141
	C25b–H2c25b···O1w^{iii}	0.96	2.67	3.576 (2)	158
diHyd	O3–H1o3···O2w	0.860 (15)	1.816 (15)	2.668 (2)	170.8 (17)
	O1w–H1o1w···Cl1	0.860 (10)	2.315 (12)	3.1645 (12)	169.7 (17)
	O1w–H2o1w···Cl1^{i}	0.860 (19)	2.326 (19)	3.1842 (13)	175.8 (16)
	O2w–H1o2w···Cl1^{i}	0.860 (17)	2.255 (17)	3.1134 (14)	176 (2)
	O2w–H2o2w···Cl1	0.86 (2)	2.35 (2)	3.2030 (17)	172 (2)
	C7–H1c7···O3^{ii}	0.96	2.58	3.475 (2)	156
	C15–H1c15···O1w^{iii}	0.96	2.54	3.1822 (19)	124
	C17–H1c17···O2^{iv}	0.96	2.38	3.2161 (18)	145
	C20–H1c20···Cl1^{ii}	0.96	2.75	3.6590 (16)	158
	C21–H1c21···Cl1	0.96	2.82	3.6778 (15)	149
	C22–H1c22···O3^{v}	0.96	2.64	3.3752 (19)	134
	C22–H2c22···O2^{v}	0.96	2.51	3.1208 (18)	121
	C25–H1c25···O1w^{iii}	0.96	2.46	3.3428 (19)	152
	C25–H2c25···O1w^{vi}	0.96	2.67	3.433 (2)	137

Symmetry codes: sesHyd: (i) *x*,*y*+1,*z* (ii) *x*,-*y*+1/2,*z*+1/2 (iii) *x*,-*y*+3/2,*z*+1/2 diHyd: (i) *x*,-*y*-1/2,*z*+1/2 (ii) *x*,-*y*-1/2,*z*-1/2 (iii) –*x*+2,*y*+1/2,-*z*+3/2 (iv) *x*,-*y*+1/2,*z*-1/2 (v) *x*,*y*,*z*-1 (vi) –*x*+2,-*y*,*z*+1

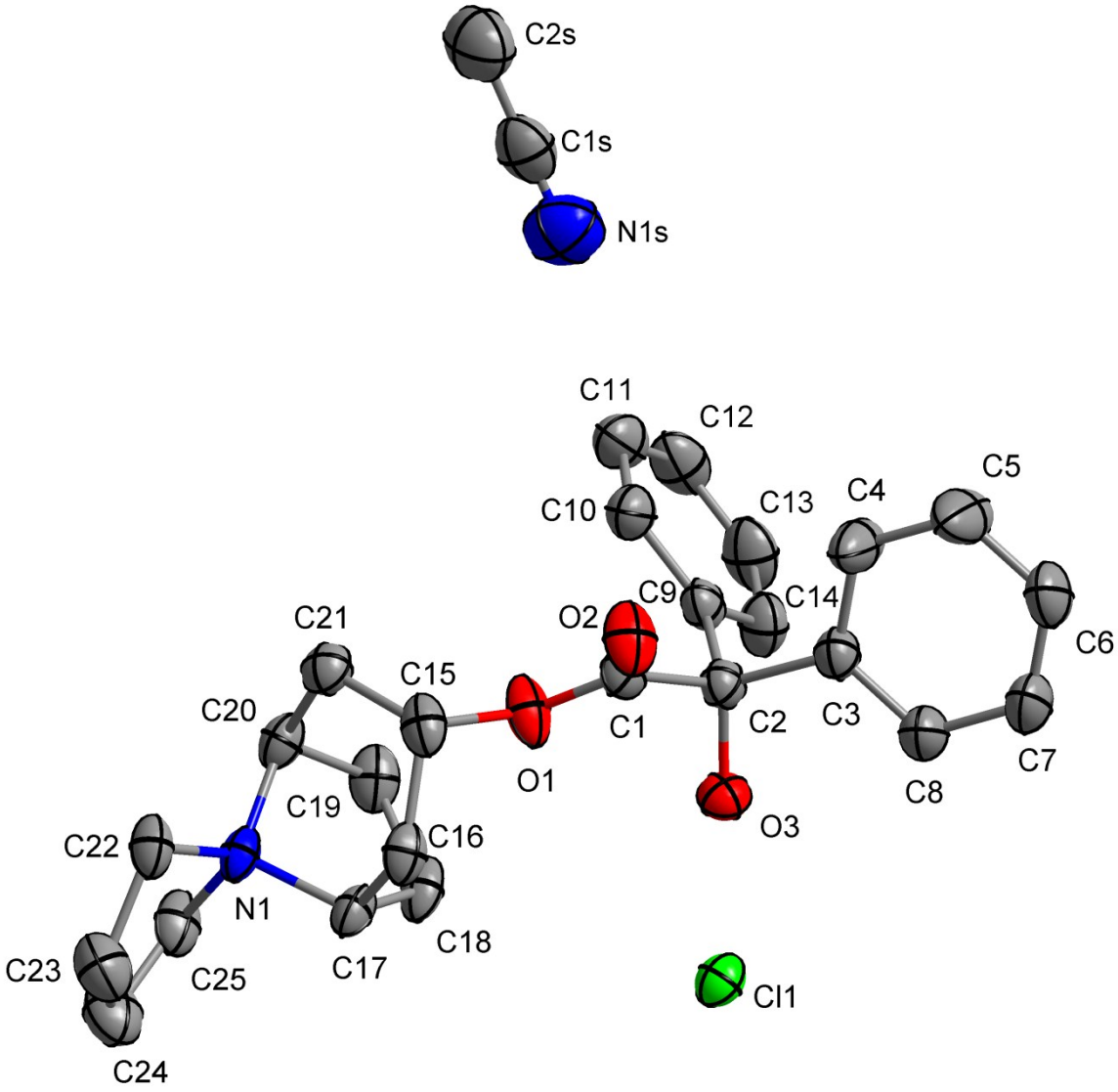


Figure 14. ORTEP of TCl ACN solvate (**1**).

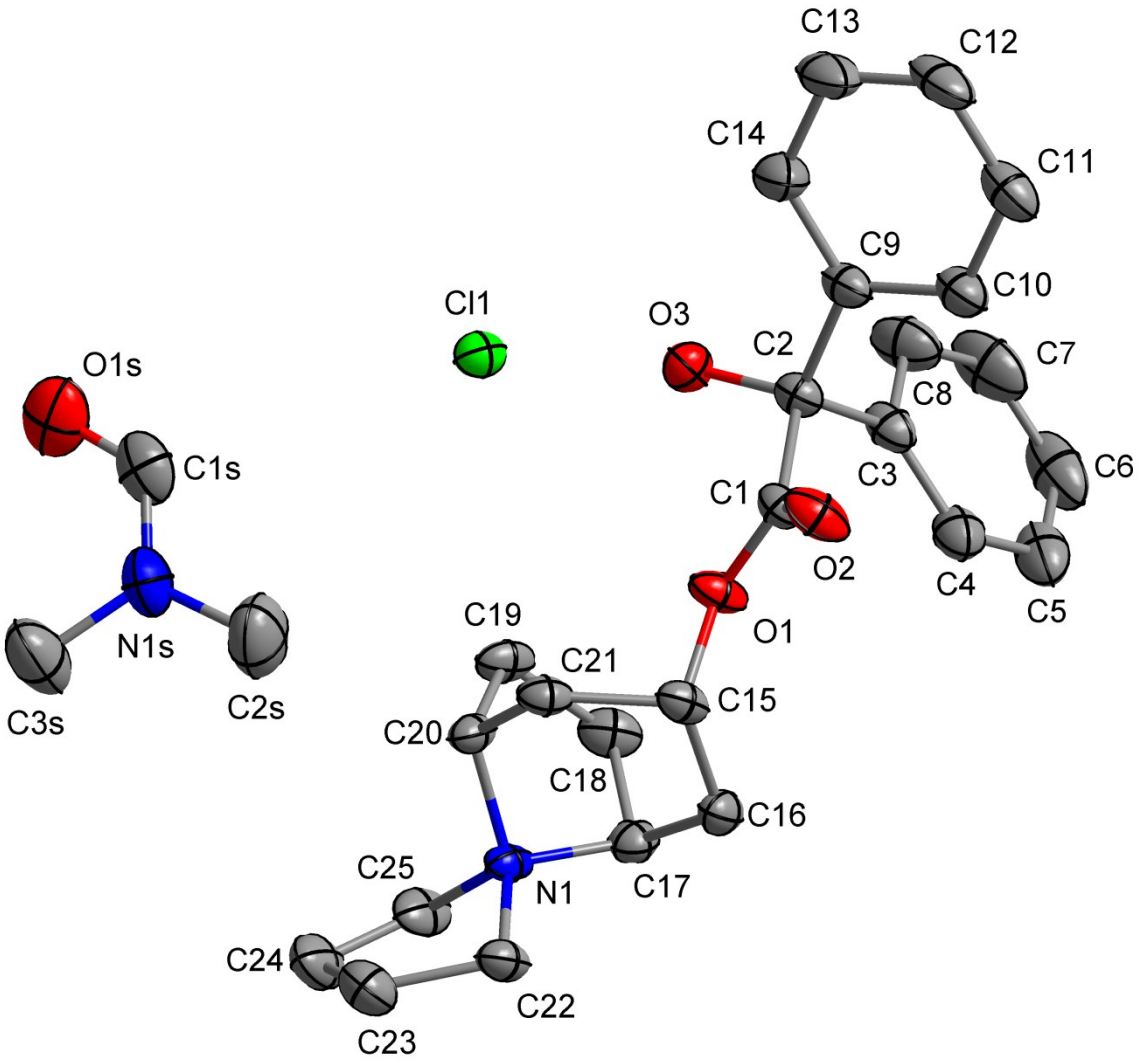


Figure 15. ORTEP of TCl DMF solvate (**2**).

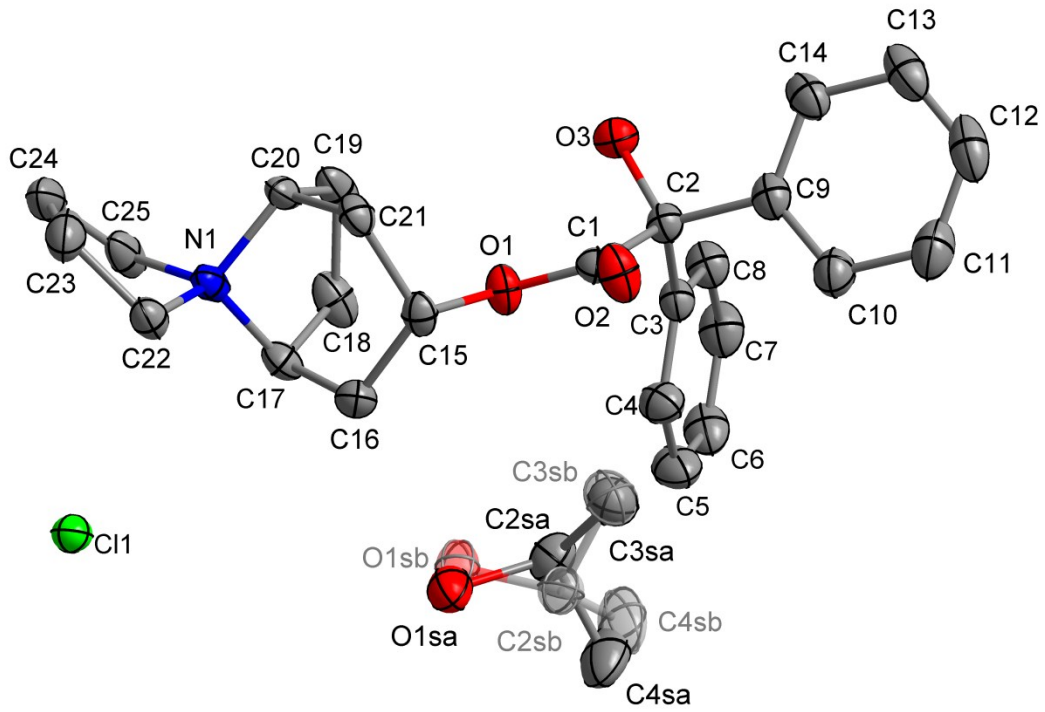


Figure 16. ORTEP of TCl *i*PrOH solvate (**3**).

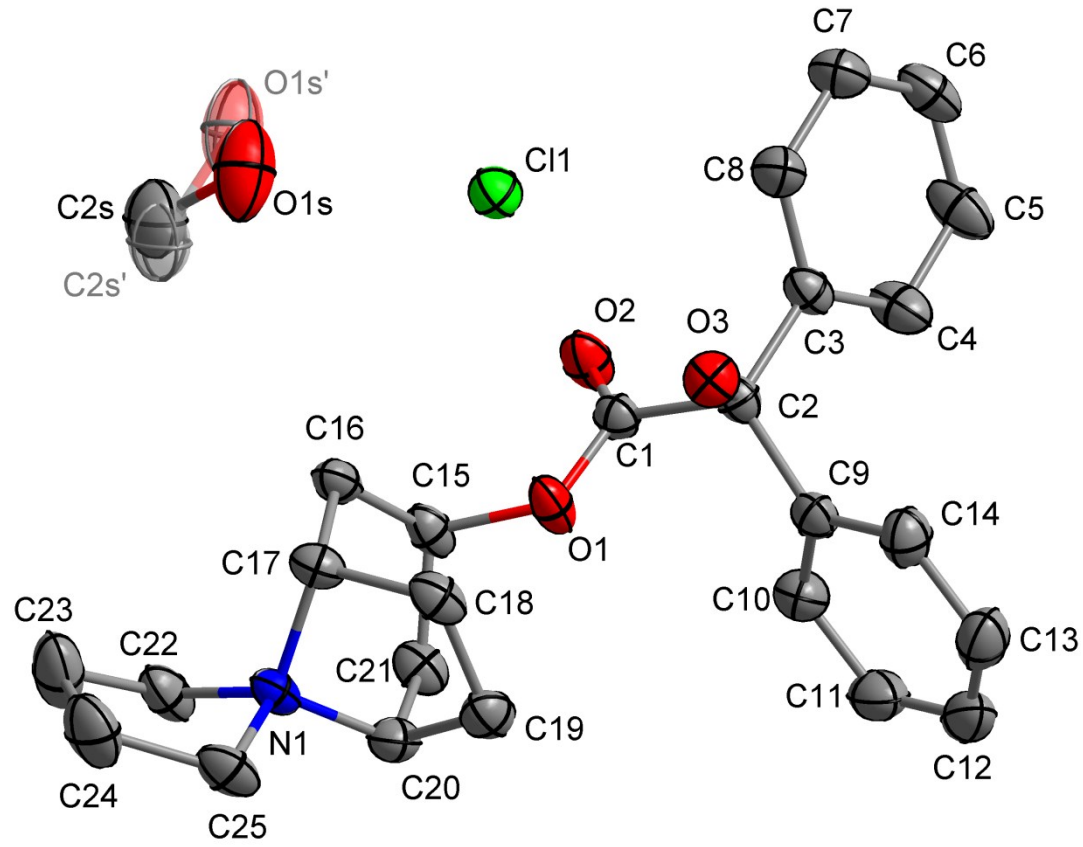


Figure 17. ORTEP of TCl MeOH solvate (**4**).

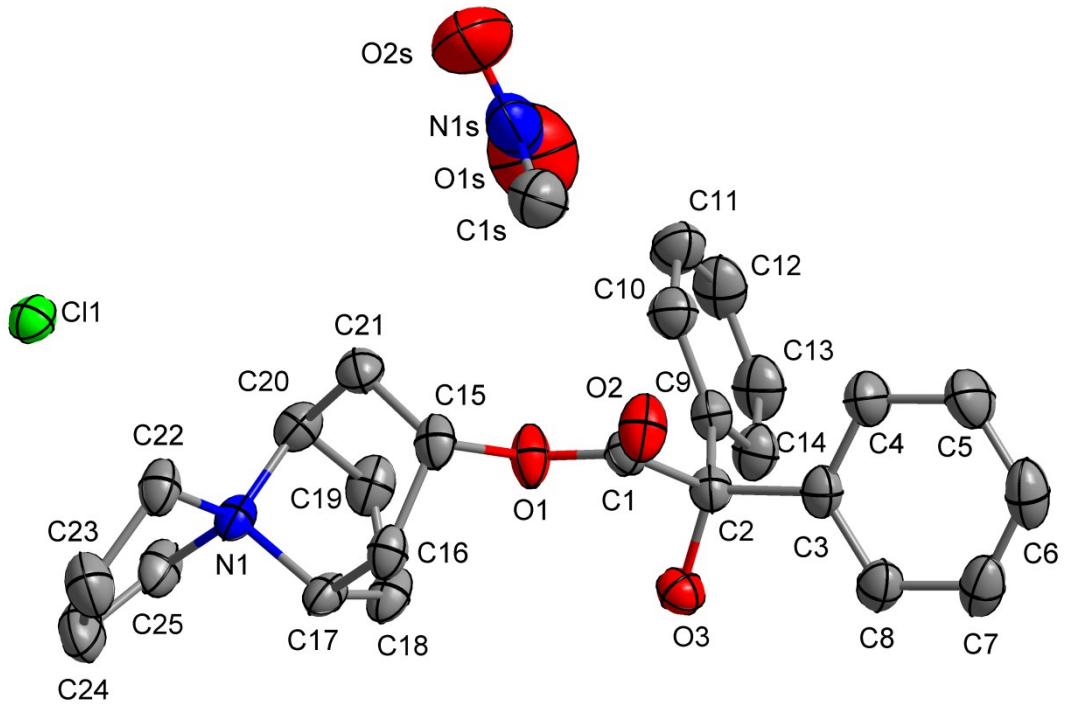


Figure 18. ORTEP of TCl $MeNO_2$ solvate (**5**).

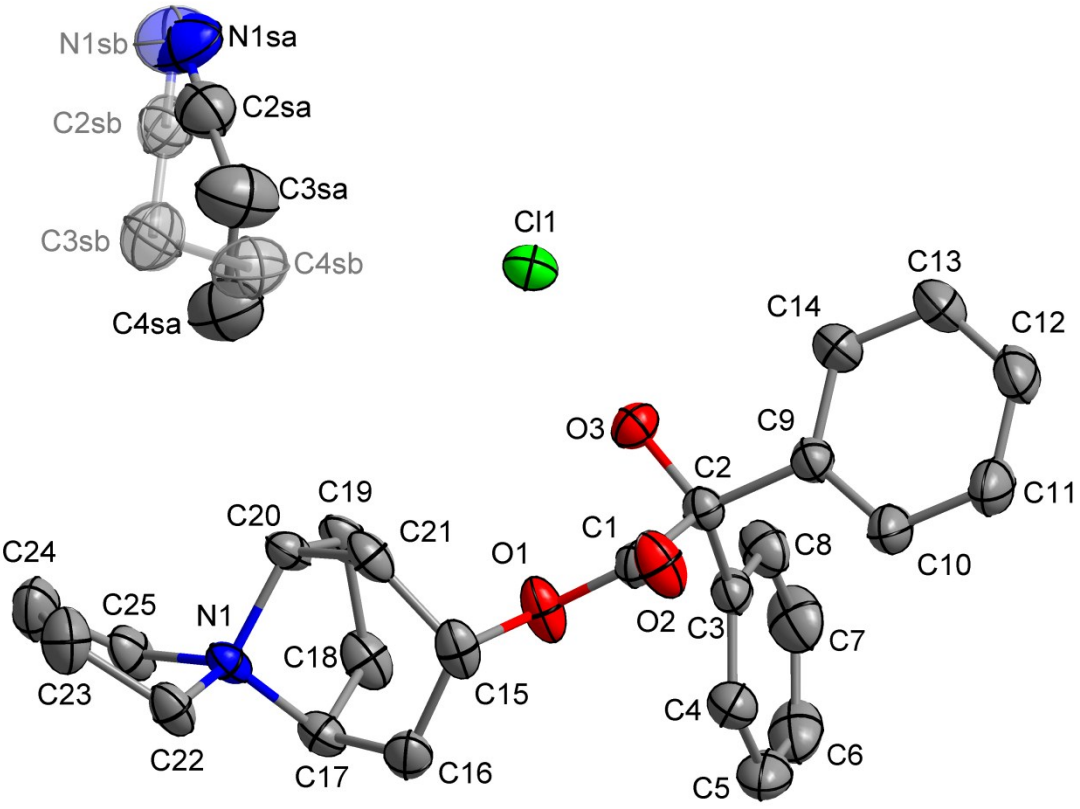


Figure 19. ORTEP of TCl PRN solvate (**6**).

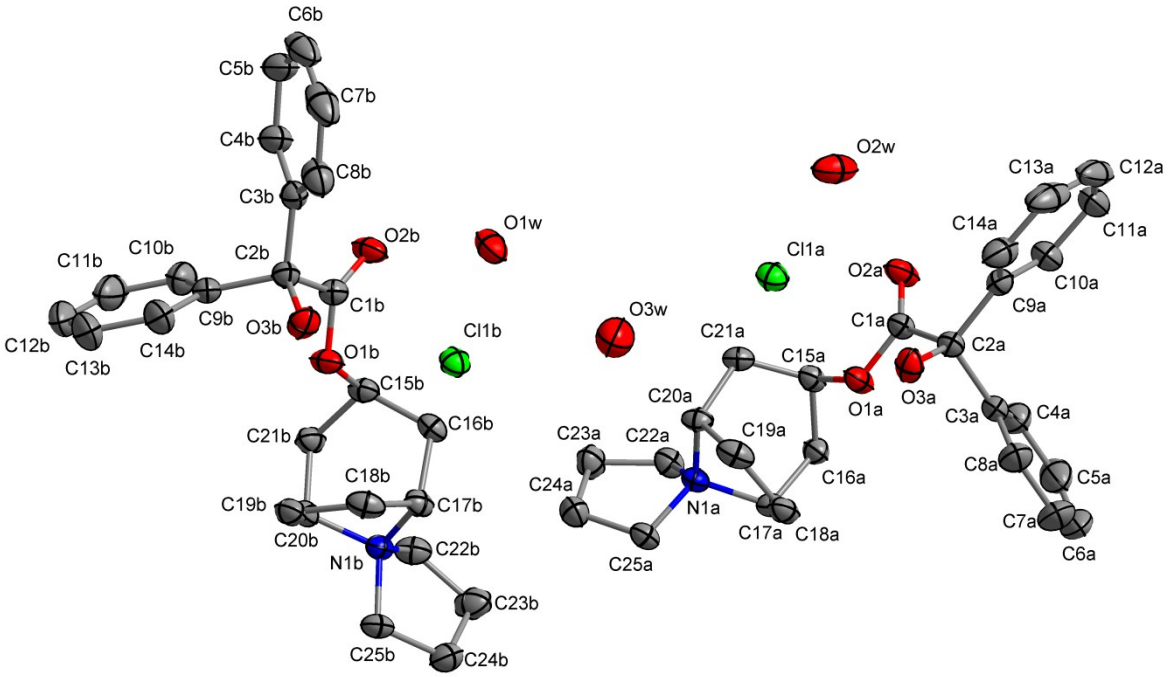


Figure 20. ORTEP of TCl sesquihydrate (**7**).

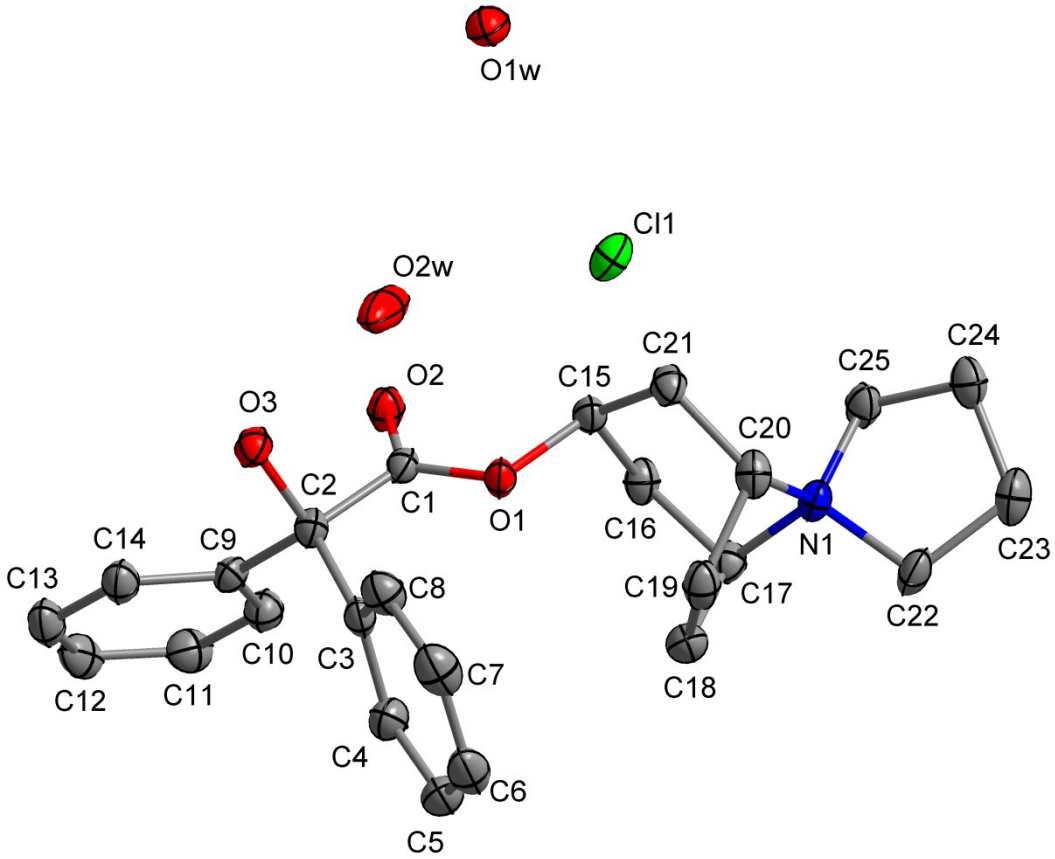


Figure 21. ORTEP of TCl dihydrate (**8**).