

The Crystal Structure of Chlorotrifluoromethane, CF₃Cl; Neutron Powder Diffraction and Constrained Refinement

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Abstract

The structure of CF₃Cl has been investigated by neutron powder diffraction at three temperatures, 5, 57 and 81 K. There are no phase transitions; the space group is *Cmc*2₁ with *a*, *b*, *c* (Å), *V* (Å³): 7·1725 (7), 9·5689 (12), 4·6791 (6), 321·13 (5 K); 7·2295 (9), 9·5987 (10), 4·7101 (5), 326·85 (57 K); 7·2789 (37), 9·6156 (38), 4·7355 (21), 331·44 (81 K), respectively. The structure was solved by a simple packing procedure. Constrained refinement involved only four structural parameters, namely two bond lengths, a position along the *y* axis and a molecular rotation in the symmetry plane. The agreements with experiment are most satisfactory. Howard's [*J. Appl. Cryst.* (1982), **15**, 615–620] three-Gaussian peak-shape function was used giving a significant improvement over the one-Gaussian function, and its use as the standard peak-shape function is recommended.

Introduction

Many small rather globular molecules form solid phases with a phase transition from a plastic to a truly crystalline structure. The determination of such structures is made difficult because single crystals are hard to grow. An ideal technique for this work is that of neutron diffraction from powder samples. The technique is moreover suited to the study of any system which forms a solid only at low temperatures. The present work is part of a search of these small-molecule systems, using powder neutron diffraction as the sole means of structure solution.

Experimental

Solid CF₃Cl was formed by passing the gas into liquid nitrogen placed in a mortar surrounded by more liquid nitrogen. The solid formed very easily and when the nitrogen in the mortar had boiled off the solid was powdered with a pestle. The powder was then placed into a vanadium can (16 mm diameter) which was quickly transferred to a liquid-helium cryostat.

Diffraction scans were made with the diffractometer *D1A* at ILL, Grenoble, using neutrons of wavelength 2·98 Å at three temperatures, with an additional scan with 5·7 Å neutrons at 5 K. This extra scan was thought to be a useful precaution, yielding high-resolution results for the diffraction peaks of lowest order which are necessary for unit-cell determination. Data from the bank of ten counters were combined using the system developed by Hewat (1978).

Structure solution and refinement

The high-resolution scan of the low-order peaks led to the suggestion that none of the peaks essential for the unit-cell search were overlapping. Certain of the diffraction peaks were easily identified as from solid nitrogen, as expected after the method of preparation used. The scattering from nitrogen took the form of a cubic diffraction pattern at 5 K, hexagonal at 57 K and gas at 81 K. For the analysis of the scans at the lower two temperatures the regions occupied by the nitrogen peaks were discarded.

The pattern of peaks from the solid CF₃Cl was clearly the same at all three temperatures, except of course for thermal expansion. As expansion is expected to be anisotropic, having these scans is valuable as the thermal variation could well cause otherwise unidentified peak doubling to become apparent.

Peak positions for the twenty lowest orders were measured and input to the cell-analysis program of Visser (1969), which follows the procedure of de Wolff (1968). An orthorhombic unit cell was suggested for the data at 5 K, and this was substantiated by the 57 K results. From the systematic absences it was apparent that the cell was *C* face-centred. Division of the cell volume by the expected molecular volume (Immirzi & Perini, 1977) led to a cell with four molecules. As the cell was assumed to be *C*-centred it was deduced that half-molecules must correspond to the asymmetric unit for the Laue group *mm*2. All the possible space groups with these conditions are given in Table 1. As the molecules do not

Table 1. *The possible space groups and the reasons for choosing between them*

Number	Symbols	
35	<i>Cmm2</i> (2)	
36	<i>Cmc2₁</i>	<i>Ccm2₁</i> (2)
37	<i>Ccc2</i> (1)	
38	<i>C2mm</i> (3)	<i>Cm2m</i> (3)
39	<i>C2mb</i> (2)	<i>Cm2a</i> (3)
40	<i>C2cm</i>	<i>Cc2m</i> (4)
41	<i>C2cb</i> (1)	<i>Cc2a</i> (1)

Notes: (1) no mirror planes; (2) only mirror plane is the *xz* plane; (3) 001 not expected to be absent; (4) 201 and 401 not expected to be absent.

possess a twofold rotational symmetry element but do have a mirror plane *m*, it was concluded that each molecule must lie with this mirror plane in the plane of symmetry of the space group. This automatically rules out those space groups without a mirror plane, and these are indicated by (1) in Table 1.

The packing density of molecules on the mirror plane would be too great for the *xz* plane as such a unit-cell section gives the minimum area. This rules out those space groups marked (2) in Table 1. To decide between the remaining five space groups the occurrence of particular absences was sought, absences which could not be obscured by overlapping and which persist as the unit cell changes due to expansion. *F*(001) was absent, an argument against those marked (3) in Table 1, for which this absence is not a condition. The absence of *F*(201) and *F*(401) argued against *Cc2m*, leaving only *Cmc2₁* or *C2cm* as the most likely space group. The former was found by trial to be the correct space group as follows.

A packing-analysis program was written to investigate *CF₃Cl* in *Cmc2₁*. Only two variables need investigation, namely the translation of the molecule along the *y* axis and the rotation of the molecule in the *yz* plane. A molecule with bonds of expected lengths directed tetrahedrally was used in the calculation, and for each pair of variables the closest approach r_{\min} between the neighbouring molecules was recorded. The maximum value of r_{\min} was then assumed to correspond to the crystal structure.

Before attempting a full refinement the unit cell was refined against the diffraction scan using the program *ALLHKL* (Pawley, 1981). This refinement was quick and stable, giving an accurate unit cell, scan zero, peak shape and background level. Full refinement was then started from these values with the proposed structure, thus introducing five more variables. Besides the two structural variables described above, the two bond lengths and overall temperature factor were refined. The molecule was constrained to have tetrahedrally oriented bonds, making use of the special features of the refinement program *EDINP* (see Pawley, 1980).

The course of the refinement of the four structural variables and $R = \sum_i |y_i^{\text{obs}} - y_i^{\text{calc}}| / \sum_i y_i^{\text{calc}}$, the *R* fac-

Table 2. *Course of refinement of the four constraint parameters; the two bond lengths (C-F and C-Cl)(Å), the position of the molecule centre along the *y* axis (Å), and angle of rotation of the molecule in the *xz* plane (°)*

C-F	C-Cl	Centre	Angle	<i>R</i> factor
1.3800	1.7600	0.2990	120.0	0.419
1.5149	1.7448	0.5647	129.0	0.295
1.1727	1.5670	0.5311	138.8	0.231
1.1284	1.6937	0.5469	139.8	0.174
1.1549	1.8510	0.6214	142.4	0.120
1.2017	1.8572	0.6437	140.9	0.092
1.2487	1.8226	0.6304	141.2	0.074
1.2719	1.7935	0.6217	140.5	0.061
1.2848	1.7789	0.6160	140.3	0.056
1.2905	1.7706	0.6130	140.1	0.054
1.2931	1.7669	0.6116	140.0	0.053
1.2943	1.7652	0.6109	140.0	0.053
1.2947	1.7645	0.6107	140.0	0.053

tor, is given in table 2 for the 5 K data. The index *i* runs over all the points in the scan except for the regions where the nitrogen peaks occur. Although the measured scan steps were 0.05° in 2θ, the data sets were reduced to a scan step of 0.1° without any apparent loss in resolution.*

The refinement was clearly stable and reached a conclusion in a single run sequence. The molecule centre moved by 0.3 Å during this sequence while the bond lengths initially moved to poorer values before returning to chemically reasonable values. Clearly the bond variables should have been constrained while the other two structural parameters were settling down, but the success of the actual refinement was more reassuring as the bond lengths returned unaided almost to their original values.

Results from the 5 K refinement were used, after small readjustments to the unit cell, to start the 57 and 81 K refinements. The full set of results is shown in Table 3. The errors presented with these results are based on the proposition (Pawley, 1980) that the effective number of observations to be used in the error analysis is roughly equal to the full scan width divided by the mean peak full-width at half height. Had the number of observations been taken as the number of points in the original scan the error estimates would have been smaller by a factor of 5.

The figures show the structure as projected down the *x* and *z* axes. The closest interatomic vectors between neighbours are 3.12 (F-F), 3.42 (F-Cl) and 4.81 Å (Cl-Cl), showing that the Cl atoms take up positions as distant from each other as possible. Fig. 1 shows a space-filling projection down the shortest axis, the *z* axis, with radii for F and Cl of 1.5 and 1.8 Å respectively. In this diagram the shaded

* Lists of the observed and calculated scan data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39812 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Final values of the refined parameters

	5 K	57 K	81 K
Overall scale factor	2.62 (3)	2.49 (4)	2.38 (11)
Flat background	454 (7)	518 (7)	670 (17)
Scan zero angle	0.005 (15)	0.035 (13)	0.019 (52)
Peak-shape parameters (°)			
<u>u</u>	0.22 (2)	0.15 (2)	0.20 (5)
<u>v</u>	-0.43 (4)	-0.35 (5)	-0.47 (10)
<u>w</u>	0.39 (2)	0.33 (3)	0.38 (5)
Asymmetry <i>P</i> parameter	0.19 (4)	0.28 (3)	0.03 (11)
Unit-cell parameters (Å)			
<u>a</u>	7.1725 (7)	7.2295 (9)	7.2789 (37)
<u>b</u>	9.5689 (12)	9.5987 (10)	9.6156 (38)
<u>c</u>	4.6791 (6)	4.7101 (5)	4.7355 (21)
Overall temperature factor (Å ²)	1.2 (1)	2.1 (2)	4.0 (6)
<i>y</i> translation (Å)	0.611 (6)	0.605 (6)	0.608 (17)
Rotation in <i>xz</i> plane (rad)	2.443 (6)	2.439 (6)	2.445 (16)
C-F bond length (Å)	1.495 (12)	1.519 (12)	1.519 (40)
C-Cl bond length (Å)	2.037 (8)	2.014 (9)	2.022 (25)
<i>R</i> factor	0.053	0.061	0.136

Table 4. Atom positions and scattering lengths (fm) from the final refinement of the 5 K data of CF₃Cl

	<i>b</i>	<i>x</i>	<i>y</i>	<i>z</i>
C	6.65	0.0	0.6105	0.0
F	5.5	0.0	0.7180	1.2905
F	5.5	1.0573	1.1831	-0.4808
F	5.5	-1.0573	1.1831	-0.4808
Cl	9.6	0.0	-1.0958	-0.4480

molecules are nearer the viewer by $\frac{1}{2}c$. In Fig. 2, the projection down the *x* axis, the bold molecules are at $\frac{1}{2}a$. The coordinates used for these figures are given in Table 4.

The goodness-of-fit values between observations and calculations are shown in Fig. 3 in the usual manner.

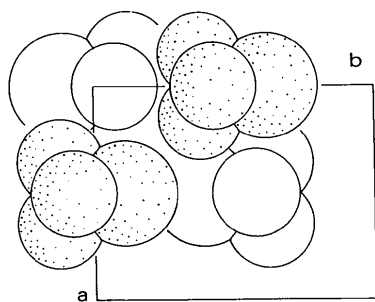


Fig. 1. Projection of the 5 K structure of CF₃Cl down the *z* axis. The stippled molecules are centred at $\frac{1}{2}c$; the F and Cl radii are 1.5 and 1.8 Å respectively.

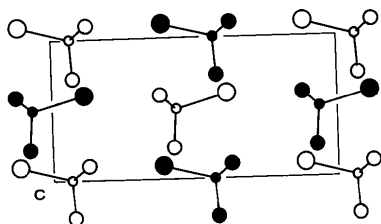


Fig. 2. Projection of the 5 K structure of CF₃Cl down the *x* axis. The bold molecules are centred at $\frac{1}{2}a$.

The peak-shape function

The results presented herein have been obtained using Howard's (1982) three-Gaussian peak-shape function. The asymmetry parameter *P* in Table 3 is as defined by Howard, and gives a result which is a significant improvement over the one-Gaussian function. The improvement may not seem much, but it must be realized that the result achieved is very close

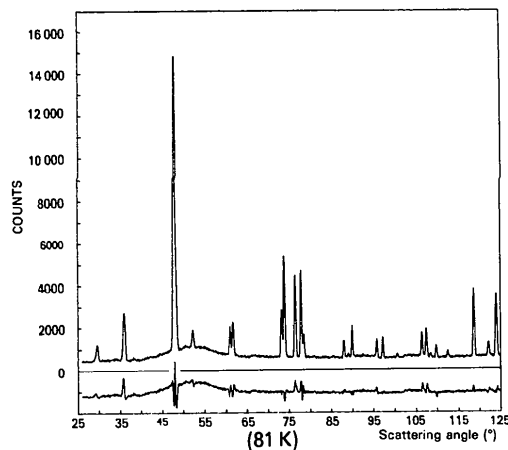
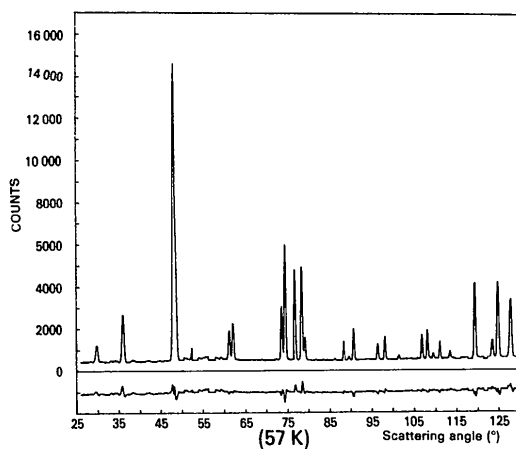
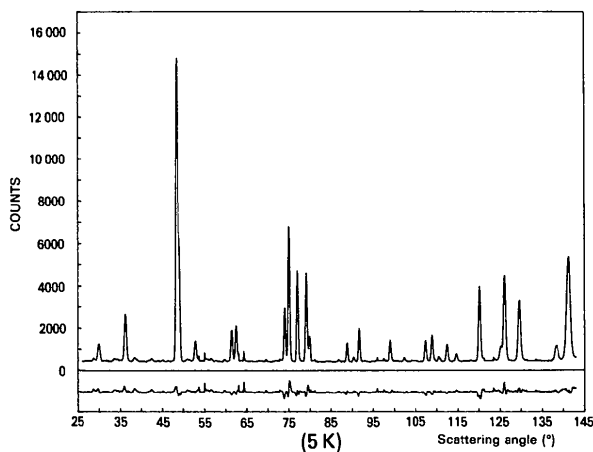


Fig. 3. The diffraction scans at 5, 57 and 81 K. The difference (observed - calculated) is plotted below each scan.

Table 5. Comparison of results with 5 K data for the one-Gaussian and Howard's (1982) three-Gaussian peak-shape functions

The errors in the lattice constants do not include the absolute error in the neutron wavelength.

	One-Gaussian	Three-Gaussian
R factor	0.057	0.053
Scan zero	0.082 (4)	0.005 (15)
Unit-cell parameters (Å)		
<i>a</i>	7.1689 (3)	7.1725 (7)
<i>b</i>	9.5631 (5)	9.5689 (12)
<i>c</i>	4.6766 (3)	4.6791 (6)

to the statistical limit for these data. The difference between the refined scan origins for the two peak-shape functions is very considerable, being about 6 standard deviations, and the unit-cell volume changes systematically for the 5 and 57 K data by about 0.22% (see Table 5). This shows that the new function should be taken as a standard in powder refinements, especially as there is no noticeable slowing down of the program. Users of *EDINP* are invited to request an update description from the first author to incorporate the new function.

The error estimates for those parameters affected by the asymmetry function (for the 5 and 57 K data) increase when the better function is used. This appears to be quite a usual result in least-squares refinements when an improved function is used.

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Structure of a Serine Protease from Rat Mast Cells Determined from Twinned Crystals by Isomorphous and Molecular Replacement

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Abstract

The structure of rat mast cell protease II, a serine protease from the mucosal mast cells of rat small intestine, has been determined by a combination of

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Concluding remarks

The structure of solid CF_3Cl between 5 and 81 K is found to be orthorhombic $Cmc2_1$. A phase transition below 5 K is most unlikely, leaving only 81 K to the melting point at 92 K as a possible range in which a plastic phase might exist. The mean thermal linear expansivities along *x*, *y* and *z* in the ranges 5–57 and 57–81 K are 0.0011, 0.0006, 0.0006 and 0.0021, 0.0007, 0.0011 K^{-1} respectively, showing no anomaly in the upper range.

Structure solution has been achieved solely with the use of neutron powder diffraction data. The unit cell was solved by using diffraction peak positions estimated without correction for peak shift due to finite-size counter apertures, whereas the refinement has shown this shift to be significant. Future unit-cell analyses should certainly take this shift into account, and it is suggested that Howard's (1982) three-Gaussian function should be used throughout the profile refinement.

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single isomorphous replacement and molecular replacement. The crystals, space group $P3_1$, have two molecules per asymmetric unit, related by a local twofold axis of symmetry approximately parallel to *a*, resulting in pseudo space-group symmetry $P3_121$. The crystals are invariably twinned in such a way that the *hkl* and *kh \bar{l}* reflections superimpose. Methods used to 'detwin' the data are described. An initial electron density map phased on a single heavy-atom derivative could not be interpreted, but provided the basis for the eventual determination of the structure. An automatic procedure was used to determine the approximate molecular boundaries. A search within