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Neutron powder-profile study of chlorofluoromethane

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The crystal structure of chlorofluoromethane, CH_2ClF, has been determined at 100 and 30 K using indexing, packing considerations and Rietveld refinement of neutron powder profiles. There is only one phase, in monoclinic space group $P2_1$ and with two molecules in the unit cell occupying general positions. The structure has close packing in several directions and there are weak hydrogen bonds forming zigzag chains.

Comment

The study described here on chlorofluoromethane forms part of an extensive study of the structures, vibrational properties and intermolecular forces of crystals of the halogenated derivatives of methane (Schleuter *et al.*, 1994; Torrie *et al.*, 1999, and references therein). Chlorofluoromethane, CH_2ClF, also known as Freon 31, is a gas under normal atmospheric conditions, and its boiling and melting points are 264.1 and 140.2 K, respectively. The molecule is a strongly polar asymmetric top described by point group C_s and, in the solid, it is expected that there will be hydrogen bonding involving the F and H atoms of adjacent molecules. There is no report in the literature of the crystal structure of this compound. A recent Raman and IR study (Schleuter *et al.*, 1994) of the solid concluded that there is only one phase, with a space group that is likely to be non-centrosymmetric, based on the coincidence of Raman and IR peaks, and that there are at least two molecules, and more likely four, in the unit cell. The purpose of this paper is to report the crystal structure of CH_2ClF determined using neutron powder profiles and the Rietveld refinement procedure (Larson & Von Dreele, 1989).

Measured, calculated and difference profiles at 30 K are shown in Fig. 1, and the contents of the unit cell are shown in Fig. 2. The quality of the fit, as indicated by the *R* factors and the difference curve, is reasonably good, in view of the usual problems in obtaining good polycrystalline samples. The errors quoted are the errors produced by the fitting program and, as such, are likely to be underestimates of the true errors by a factor of three (Powell *et al.*, 1982).

Some short non-bonded distances are listed in Table 2. These distances are less than or close to the sum of the van der Waals radii. Only one H···F distance is significantly shorter than the sum of the van der Walls radii, indicating the formation of hydrogen-bonded chains. The same H atom is also in close contact with a second F atom. The second H atom is in close contact with two Cl atoms. Each Cl atom in the *ac* plane makes contact with two Cl atoms in two neighbouring molecules at approximately $y = \frac{1}{2}$. The internal structure of the molecule is only slightly distorted from its shape in the gas phase.

It is interesting to look at the sensitivity of the stretching-mode frequencies to the weak bonds formed in this crystal. The main peaks in the C—F stretch region of the Raman and IR spectra are ~4% lower than the gas-phase value. Similarly, the main peaks in the C—Cl stretch region are 2.8% lower than the gas-phase value (Krasnov *et al.*, 1970). Even though only one of the F···H distances and none of the Cl···H distances are significantly shorter than the sum of the van der Waals radii, there is still a pronounced effect on the stretching-mode frequencies for both types of interactions. Since there is

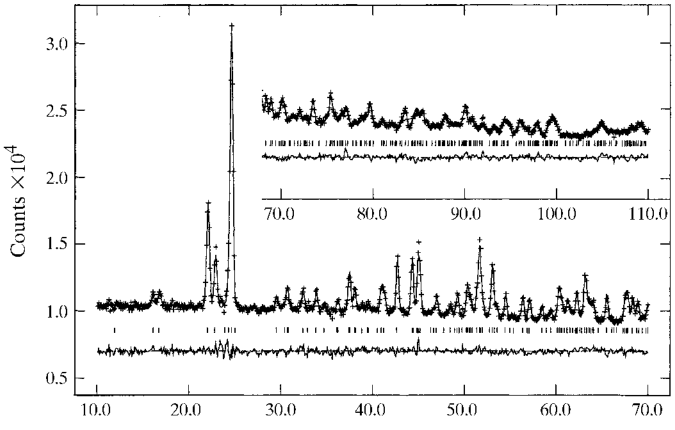

Figure 1
Observed, calculated and difference profiles for CH_2ClF at 30 K.

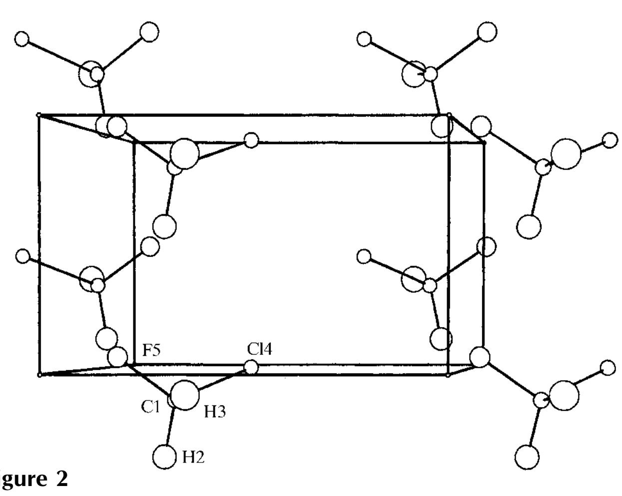

Figure 2
Unit-cell contents for CH_2ClF at 30 K. The spheres represent the thermal motion of the atoms (50% probability level).

close packing of the molecules as a whole, the distances between atoms will be determined by both the direct interactions between the atoms and the steric interference between other atoms in neighbouring molecules. In other words, the shifts in frequency should be a better measure of hydrogen bonding than the distances between the non-bonded halogen and H atoms. Note that, in the solid phase, the frequencies of stretching modes usually increase with decreasing temperature, so the fact that the frequencies decreased in the referenced measurements at 12 K has added significance.

Finally, a comment about the use of packing programs. We mentioned in an earlier paper (Torrie *et al.*, 1996) that, if the space group is known, the Williams packing program (Williams, 1981) with Buckingham potentials has been found to be very useful in finding the initial position of the molecule for insertion in the *GSAS* refinement program (Larson & Von Dreele, 1989). However, as in this case, when several space groups are initially indicated, the Williams packing program may still give a reasonable minimum energy position for a molecule without it being the correct one. In the current case, a triclinic cell, with a high figure of merit and the same volume as the correct cell, was tried in the packing program and the lattice energy was reasonable, but the refinement using *GSAS* diverged and the fitting was poor.

Experimental

Chlorofluoromethane was obtained from PCR (Gainesville, Florida, USA) and had a stated purity of better than 99%. It was used as supplied. Polycrystalline samples were obtained by condensing the gas into a thin-walled vanadium can, 5 mm in diameter by 5 cm in length, immersed in liquid nitrogen. At frequent intervals during the process, the resulting solid was ground with a sharp rod into a fine powder. The filled can was mounted in a top-loading helium cryostat and the sample was annealed at 120 K for about 1 h before starting measurements. Measurements were made at wavelengths of 1.32790 (4) and 2.3687 (1) Å. The profile collected with the longer wavelength was used for indexing purposes only and, in this case, the detector was shifted by 0.05° to give a total of 1600 data points recorded at 30 K and in the range 2θ = 26–106°. The data recorded at 100 and 30 K with the short wavelength were in the range 2θ = 5–117°, with a data-point separation of 0.10. Before the actual runs, the sample can was turned about the vertical axis through 70° in steps of 10°, and at each step a low-count diffraction pattern was taken. A comparison of the relative intensities of the peaks in these profiles showed that the preferred orientation about the cylinder axis was not a problem. Nevertheless, during the runs, the sample can was rotated continuously about a vertical axis to minimize any effects of preferred orientation about the cylinder axis.

Crystal data

CH_2ClF
$M_r = 68.48$
Monoclinic, $P2_1$
$a = 6.7676\ (6)$ Å
$b = 4.1477\ (3)$ Å
$c = 5.0206\ (5)$ Å
$\beta = 108.205\ (7)^\circ$
$V = 133.88\ (2)$ Å^3
$Z = 2$
$D_x = 1.699$ Mg m^{-3}

Neutron radiation
$\theta = 2.5$–58.5°
$T = 30$ K
Specimen shape: cylinder
50 × 5 × 5 mm
Specimen prepared at 77 K
Particle morphology: ground powder, white

Data collection

DUALSPEC diffractometer
NRU reactor, Chalk River
Specimen mounting: vanadium can

Specimen mounted in transmission mode
$2\theta_{\min} = 5.0$, $2\theta_{\max} = 117.0^\circ$
Increment in $2\theta = 0.1^\circ$

Refinement

$R_p = 0.013$
$R_{wp} = 0.017$
$R_{exp} = 0.010$
$S = 1.71$
$2\theta_{\min} = 10.1$, $2\theta_{\max} = 115.9^\circ$
Increment in $2\theta = 0.1^\circ$
Wavelength of incident radiation: 1.32790 (4) Å

Data reduction: two blocks of 800 (800) combined by *GENIE* (Rutherford Appleton Laboratory, 1986)
Profile function: Gaussian
344 reflections
35 parameters
H-atom parameters not refined
$(\Delta/\sigma)_{\max} = 0.03$

Table 1
Selected geometric parameters (Å, °).

C1—H2	1.095 (13)	C1—F5	1.371 (10)
C1—H3	1.078 (19)	C14—C14^{i}	3.526 (8)
C1—Cl4	1.787 (9)	Cl4—Cl4^{ii}	3.526 (8)
H2—C1—H3	113.5 (12)	H3—C1—F5	109.6 (5)
H2—C1—Cl4	108.1 (10)	Cl4—C1—F5	108.5 (5)
H2—C1—F5	108.3 (11)	C1—Cl4—Cl4^{i}	125.9 (3)
H3—C1—Cl4	108.6 (9)	C1—Cl4—Cl4^{ii}	161.7 (3)

Symmetry codes: (i) $1 - x, y - \frac{1}{2}, -z$; (ii) $1 - x, \frac{1}{2} + y, -z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C1—H2$\cdots$F5^{i}	1.095 (13)	2.512 (14)	3.579 (10)	164.5 (13)
C1—H2$\cdots$F5^{ii}	1.095 (13)	2.67 (2)	3.237 (11)	111.5 (10)
C1—H3$\cdots$Cl4^{iii}	1.078 (19)	2.891 (16)	3.948 (9)	167.5 (5)
C1—H3$\cdots$Cl4^{iv}	1.078 (19)	2.940 (14)	3.544 (9)	115.8 (9)
C1—H2$\cdots$Cl4^{i}	1.095 (13)	3.094 (12)	3.975 (7)	137.9 (12)

Symmetry codes: (i) $x, y - 1, z$; (ii) $-x, y - \frac{1}{2}, -z$; (iii) $x, y, 1 + z$; (iv) $1 - x, y - \frac{1}{2}, 1 - z$.

Some 20 low-angle lines from the long-wavelength profile were used in the indexing programs contained in the *CRYSFIRE* system for automatic powder indexing (Shirley, 1999). The indexing was initially complicated by the presence of two weak lines in the long-wavelength profile. One of these was absent in the short-wavelength profile, suggesting that it was probably an instrumental artifact. The other showed up as a weak peak at the foot of a strong line and is believed to be an impurity. Several unit cells were suggested, but three of them, all monoclinic, had high figures of merit and were multiples of each other in volume. The smallest cell, large enough to contain two molecules, was considered likely, but the number of lines recorded was not sufficient to indicate the space group clearly. $P2$, $P2_1$, $P2/m$ and $P2_1/m$ were possibilities, but only $P2_1$ allowed an arrangement of molecules consistent with hydrogen-bonded chains. Packing considerations also showed that the unit cell was of reasonable dimensions. Lattice parameters at 30 K are given above. At 100 K, the lattice parameters were a = 6.8123 (8) Å, b = 4.1963 (4) Å, c = 5.0524 (5) Å, β = 108.106 (8)° and V = 137.27 (2) Å^3. The initial positions and orientations of the molecules in the unit cell were found using the Williams packing program (Williams, 1981), with Buckingham potentials as given by Gavezzotti (1983). The base molecule was given arbitrary orientations and, from these starting

Acta Cryst. (2002). C**58**, o672–o674 Omar S. Binbrek *et al.* • CH_2ClF **o673**

positions, it was shifted through the asymmetric unit until the energy was minimized with respect to position and orientation. Care was taken to avoid false minima with unphysical bond lengths. The final solution was tried in the profile-fitting program *GSAS* (Larson & Von Dreele, 1989) and it refined to give structural parameters as listed. Initially, the background, histogram scale factor, diffractometer zero position and lattice parameters were varied. Refinements of the molecular translations and rotations were added later. Refinements of the isotropic displacement parameters, preferred orientation parameter and peak-shape parameter, *viz.* U, V and W, followed. The peak-shape functions were assumed to be Gaussian. In the final stages, the rigid-body constraints were completely removed, allowing the individual atoms to vary independently of each other, and isotropic displacement parameters were introduced.

Data collection: local program; cell refinement: *CRYSFIRE* (Shirley, 1999); data reduction: *GENIE* (Rutherford Appleton Laboratory, 1986); program(s) used to solve structure: packing program (Williams, 1981); program(s) used to refine structure: *GSAS* (Larson & Von Dreele, 1989); molecular graphics: *GSAS*; software used to prepare material for publication: *GSAS*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1582). Services for accessing these data are described at the back of the journal.

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o674 Omar S. Binbrek *et al.* • CH_2ClF *Acta Cryst.* (2002). C**58**, o672–o674