The Crystal Structure of Tetrakis [trifluoroacetato-μ-(2-diethyl-aminoethanolato)copper(II)]

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The crystal structure of $Cu_4(Et_2NC_2H_4O)_4$-$(F_3CCOO)_4$, $C_{32}H_{56}Cu_4N_4O_{12}F_{12}$ is tetragonal with space group $I4_1/a$ and $a = 17.903(6)$ Å, $c = 14.543(4)$ Å. The structure was solved with direct and Fourier methods to $R = 0.051$ for 1451 reflections (3885 total).

The molecule has a cubane-type Cu_4O_4 core of boat conformation formed by bridging ethanolato oxygen atoms. The point group of the molecule is S_4. In the core there are four $Cu\cdots Cu$ distances of 3.206(1) Å and two of 3.714(1) Å.

The copper(II) ion has octahedral $(4+2)$ environment. In the basal plane there are two bridging oxygen atoms $Cu-O$ 1.933(4) and 1.947(4) Å a carboxylate oxygen atom $Cu-O2$ 1.949(4) Å and a nitrogen atom $Cu-N$ 2.100(5) Å.

In the fifth position is the ethanolato oxygen atom $Cu-O1$ 2.721(4) Å and in the sixth position the carboxylato oxygen atom $Cu-O3$ 2.756(5) Å. The angle $O3-Cu-O1$ is 143.1(1)°.

The trifluoroacetate is bridging asymmetrically in syn—syn configuration from an equatorial coordination site of one copper atom to an axial site of another.

The structures of many alkoxo-bridged copper-(II) complexes with N,N-dialkylaminoethanols $(R_2NCH_2CH_2OH = R_2LOH)$, as the second ligand have been reported. The structures have been shown to be dimeric,[1] trinuclear,[2] tetrameric[3-13] or hexanuclear.[14] Mergehem and Haase[3] have reported two different types of tetramers classified by the distortion of the idealized Cu_4O_4 cubane by stretching four edges. There are two extreme types, distinguished by the arrangement of the $Cu-Cu$ and $Cu-O$ distances. In the first type there are two short (~ 2.92 Å) and four long (~ 3.44 Å) and in the second type four short (~ 3.18 Å) and two long (~ 3.45 Å) intramolecular $Cu-Cu$ distances.

In the haloacetate complexes[7-13] have been found two long $Cu-Cu$ distances ranging from 3.609 to 4.024 Å and four short ones ranging from 3.094 to 3.372 Å, i.e. considerably longer than in the second type. The haloacetate complexes have the cubane tetramers in boat conformation. To have more information on the tetramers we have now prepared in the Et_2LOH series the first fluoroacetate complex of tetrakis[trifluoroacetato-μ-(2-diethylaminoetanolato)copper(II)].

EXPERIMENTAL

Copper(II) trifluoroacetate was prepared from basic copper(II) carbonate (Merck) and trifluoroacetic acid (Merck) by the method of Bateman and Conrad.[15] The salt was dissolved in methanol and an equimolar amount of 2-diethylaminoethanol (Fluka AG) was added. The solution was filtered and allowed to evaporate slowly at room temperature. After some weeks dark blue crystals were obtained. They were filtered off, washed and drained at ambient temperature.

Unit cell dimensions and the orientation matrix were determined by the least-squares method from 20 centered reflections measured at room temperature on a Syntex $P2_1$ four-circle diffractometer. The crystal used had approximate dimensions of $0.2 \times 0.2 \times 0.3$ mm.

Intensities were collected $(2° < 2\theta < 47°)$ with graphite monochromatized $MoK\alpha$-radiation. The ω-scan technique was employed with a scan range of 1.0° and the scan speed varied from 2.50 to 29.30° min^{-1}, depending on the number of counts accumulated in a preliminary scan. Background measurements were taken at both ends of the scan with a displacement of 1.0° from the $K\alpha$-peak. Each background was measured for half the scan time. The intensities of two standard reflections were

recorded after every 100 measurements and remained essentially constant. The intensities were corrected for Lorentz and polarization effects and for absorption from empirical ψ-scan data. Of the 3885 reflections collected, 1451 had $F_o > 4\sigma(F_o)$ and were used in subsequent calculations.

CRYSTAL DATA

$Cu_4(C_6H_{14}NO)_4(F_3C_2O_2)_4$, $FW = 1171.08$
Crystal system: Tetragonal
Space group: $I\,4_1/a$ (No. 88)
$a = 17.903(6)$, $c = 14.543(4)$ Å
$V = 4661.2$ Å^3, $Z = 4$, $F(000) = 2384$
$\mu(MoK\alpha) = 19.8$ cm^{-1}, $\lambda(MoK\alpha) = 0.71069$ Å
$D_m = 1.67$ g cm^{-3} (flotation technique)
$D_x = 1.67$ g cm^{-3}

STRUCTURE DETERMINATION

The crystal structure was solved by direct methods which gave the positions of copper and oxygen atoms. The remaining nonhydrogen atoms were found from a Fourier synthesis. The structure was refined by the blocked-cascade full-matrix least-squares method[16] with anisotropic temperature factors for nonhydrogen atoms.

The hydrogen atoms were included at the calculated positions (C − H = 0.96 Å). In the final refinement the positions of the hydrogen atoms were refined. The isotropic thermal parameters for hydrogen atoms were set at 1.2 times the equivalent isotropic value for the corresponding carbon atom.

The final value of R was 0.051 and the weighted discrepancy factor R_w was 0.051. The weighting scheme was $w^{-1} = \sigma^2(F_o) + 0.0002F_o^2$ and the $R_w = \sum ||F_o| - |F_c|| \sqrt{w} / \sum |F_o| \sqrt{w}$.[16] The neutral atom scattering factors have been taken from *International Tables for X-Ray Crystallography*.[17]

The calculations were performed on a Nicolet R3m diffractometer system with SHELXTL[16] software for minicomputer (Nova 3).

Thermal parameters with their standard deviations for non-hydrogen atoms are given in Table 1 and the coordinates and isotropic thermal parameters of hydrogen atoms in Table 2. Bond distances and angles are given in Table 3.

DISCUSSION

The crystal structure of tetrakis[trifluoroacetato-μ-(2-diethylaminoethanolato)copper(II)] consists of four discrete tetrameric $[Cu(Et_2LO)(F_3Ac)]_4$ molecules per unit cell. The structure of the molecule is shown in Figs. 1 and 2.

Each molecule has an eight-membered Cu_4O_4 core formed by four copper and four ethanolato oxygen atoms with $Cu - Cu$ distances of 3.206(1) Å

Table 1. Fractional atomic coordinates ($\times 10^4$) and thermal parameters[a] ($\times 10^3$). Estimated standard deviations are in parentheses.

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu	−1006(1)	2248(1)	618(1)	43(1)	46(1)	51(1)	−11(1)	−8(1)	7(1)
F1	−3189(3)	3790(5)	915(6)	84(4)	302(10)	202(8)	133(8)	62(5)	78(5)
F2	−2705(4)	4584(3)	134(6)	124(5)	92(4)	272(8)	60(5)	−44(5)	22(3)
F3	−2963(4)	3583(4)	−406(7)	165(6)	177(7)	241(9)	−98(6)	−138(6)	103(5)
O1	−82(2)	1690(2)	631(3)	45(2)	41(2)	45(2)	−5(2)	−7(2)	5(2)
O2	−1878(2)	2888(2)	465(3)	58(3)	64(3)	84(4)	−27(3)	−24(3)	24(2)
O3	−1450(3)	4017(2)	966(3)	63(3)	60(3)	80(4)	−5(3)	2(3)	1(2)
N	−1185(3)	1770(3)	−682(3)	43(3)	49(3)	54(3)	−6(3)	−11(3)	2(2)
C1	−101(4)	1109(4)	−41(5)	56(4)	50(4)	58(4)	−9(3)	−1(4)	8(3)
C2	−453(3)	1426(4)	−899(4)	54(4)	63(4)	49(4)	−19(3)	1(3)	−6(3)
C3	−1379(4)	2358(4)	−1381(5)	66(5)	70(5)	57(5)	7(4)	−10(4)	−6(4)
C4	−1391(6)	2126(5)	−2384(6)	131(8)	109(7)	60(5)	20(5)	−2(5)	31(6)
C5	−1767(4)	1168(4)	−685(5)	55(4)	61(4)	58(4)	−5(4)	−11(3)	−5(3)
C6	−2534(4)	1411(4)	−440(5)	61(4)	79(5)	81(6)	−4(4)	7(4)	−1(4)
C7	−1931(4)	3585(3)	618(5)	58(4)	52(4)	58(4)	−6(3)	6(4)	13(3)
C8	−2689(4)	3888(4)	313(6)	71(5)	55(5)	88(6)	−3(4)	1(5)	18(4)

[a] The anisotropic thermal parameters are of the form $\exp|-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12} + ...)|$.

(4×) and 3.714(1) Å (2×), the O−O distances are 2.736(6) Å (4×) and 2.914(7) Å (2×). The arrangement of the oxygen atoms in the Cu_4O_4 core is nearly tetrahedral, Fig. 1.

The clusters are of the cubane type and have boat conformation with S_4 point group molecular symmetry as in $[Cu(Et_2LO)(ClAc)]_4$[7] and in $[Cu(Me_2LO)(ClAc)]_4$.[10] The molecular symmetry in $[Cu(Me_2LO)(F_3Ac)]_4$[12] is close to S_4. $[Cu(Et_2LO)(NCO)]_4$,[4] $[Cu(Et_2LO)Br]_4 \cdot 4CCl_4$[5] and $[Cu(Et_2LO)Cl]_4 \cdot 4CCl_4$[5] also have S_4 symmetry but not the boat conformation. Other nearly similar but distorted boat conformations have been reported. The molecular symmetries of $[Cu(Me_2LO)(Cl_2Ac)]_4$,[11] $[Cu(Et_2LO)(Cl_2Ac)]_4$,[8] $[Cu(Et_2LO)(Cl_3Ac)]_4$,[9] $[Cu(Bu_2LO)(Cl_2Ac)]_4$[13] are C_2, close to C_2, C_1 and C_1, respectively.

This lowering in the symmetry of the tetramers follows the differences between the longest and shortest intramolecular Cu−Cu and axial Cu−O distances. The differences increase with increasing

Table 2. Fractional atomic coordinates ($\times 10^3$) and isotropic thermal parameters[a] ($\times 10^2$) for hydrogen atoms.

Atom	X	Y	Z	U
H1(C1)	38(3)	97(3)	−8(4)	6
H2(C1)	−40(3)	69(3)	19(4)	6
H1(C2)	−53(3)	101(3)	−139(4)	7
H2(C2)	−9(3)	183(3)	−116(4)	7
H1(C3)	−181(4)	253(4)	−124(5)	8
H2(C3)	−101(3)	274(3)	−128(4)	8
H1(C4)	−148(5)	262(5)	−274(5)	12
H2(C4)	−179(5)	181(4)	−253(6)	12
H3(C4)	−91(5)	197(5)	−255(6)	12
H1(C5)	−162(3)	81(3)	−20(4)	7
H2(C5)	−176(3)	99(3)	−128(4)	7
H1(C6)	−289(4)	99(4)	−49(5)	9
H2(C6)	−273(3)	182(4)	−86(5)	9
H3(C6)	−253(4)	165(4)	16(5)	9

[a] The isotropic thermal parameters are set at 1.2 times the equivalent isotropic value for the corresponding carbon atom.

Table 3. Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses.[a]

The copper(II) environment

Cu−O1	1.933(4)	O1−Cu−N	86.0(2)	$O1^{ii}-Cu-O1^i$	69.5(1)
Cu−O2	1.949(4)	$O1-Cu-O1^i$	89.7(2)	$O3^{iii}-Cu-O1$	82.0(1)
Cu−N	2.100(5)	N−Cu−O2	90.8(2)	$O3^{iii}-Cu-N$	93.1(2)
$Cu-O1^i$	1.947(4)	$O2-Cu-O1^i$	94.0(2)	$O3^{iii}-Cu-O2$	105.3(1)
$Cu-O1^{ii}$	2.721(4)	O1−Cu−O2	172.1(2)	$O3^{iii}-Cu-O1^i$	81.7(1)
$Cu-O3^{iii}$	2.756(5)	$N-Cu-O1^i$	173.7(2)	$O3^{iii}-Cu-O1^{ii}$	143.1(1)
$Cu...Cu^i$	3.206(1)	$O1^{ii}-Cu-O1$	75.4(1)		
$Cu...Cu^{ii}$	3.714(1)	$O1^{ii}-Cu-N$	113.6(2)		
$Cu...Cu^{iii}$	3.206(1)	$O1^{ii}-Cu-O2$	99.4(1)		

The 2-diethylaminoethanolato ligand

O−C1	1.428(7)	Cu−N−C2	103.0(3)	N−C3−C4	117.6(6)
C1−C2	1.507(9)	Cu−N−C3	111.0(4)	N−C5−C6	115.5(5)
N−C2	1.483(8)	Cu−N−C5	113.7(4)	O−C1−C2	107.7(5)
N−C3	1.503(9)	C2−N−C3	110.6(5)	C1−O−Cu	110.4(3)
N−C5	1.499(8)	C2−N−C5	108.3(5)	$C1-O-Cu^{iii}$	121.1(3)
C3−C4	1.516(11)	C3−N−C5	110.0(5)	$Cu-O-Cu^{iii}$	111.4(2)
C5−C6	1.482(10)	N−C2−C1	110.5(5)		

The trifluoroacetate ligand

O2−C7	1.271(7)	O2−C7−O3	131.0(6)	F1−C8−F2	105.2(8)
O3−C7	1.204(8)	O2−C7−C8	111.4(6)	F1−C8−F3	103.6(7)
C7−C8	1.527(10)	O3−C7−C8	117.7(6)	F2−C8−F3	104.0(8)
C8−F1	1.264(11)	C7−C8−F1	112.2(7)		
C8−F2	1.273(10)	C7−C8−F2	115.3(7)		
C8−F3	1.278(12)	C7−C8−F3	115.3(7)		

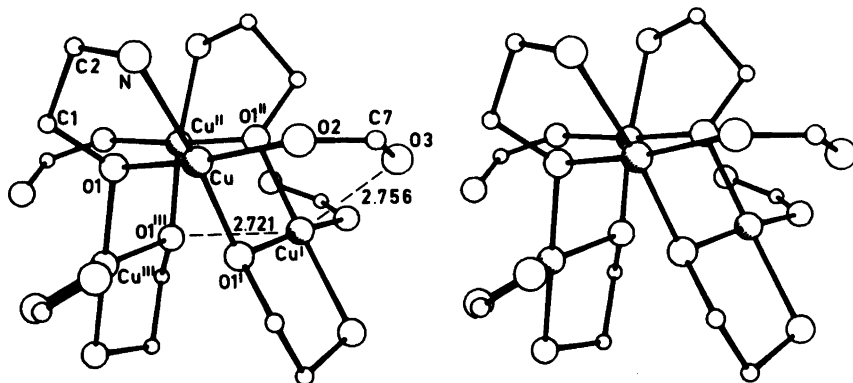[a] i: $-1/4+y$, $1/4-x$, $1/4-z$; ii: $-x$, $1/2-y$, z; iii: $1/4-y$, $1/4+x$, $1/4-z$.

Fig. 1. Stereoview of the $Cu_4(NCCO)_4(COO)_4$ fragment.

number of chloro substituents. In the ethyl series they are 0.546 and 0.057 Å in $[Cu(Et_2LO)(ClAc)]_4$,[7] 0.848 and 0.67 Å in $[Cu(Et_2LO)(Cl_2Ac)]_4$.[8] In $[Cu(Et_2LO)(Cl_3Ac)]_4$[9] where the number of chloro substituents is three the Cu – Cu difference is 0.902 Å and one Cu – O (carboxylate) bond is presented by an ethyl group of the 2-diethylaminoethanolato ligand.

The situation is similar in the methyl series where the differences are 0.584 and 0.025 Å in $[Cu(Me_2LO)$-$(ClAc)]_4$[10] and 0.811 and 0.546 Å in $[Cu(Me_2LO)$-$(ClAc)]_4$.[11]

In the $[Cu(Bu_2LO)(Cl_2Ac)]_4$[13] complex the Cu – Cu difference is 0.686 Å and also here one Cu – O (carboxylate) bond is blocked by a butyl group.

In the $[Cu(Et_2LO)(F_3LO)]_4$ cluster the distances, the angles and the differences 0.508 and 0.035 Å are nearly similar to the ethyl[7] and methyl[10] monochloroacetate complexes.

In the chloro substituent series of the ethyl complexes the maximum distortion and lowest molecular symmetry is in the trichloroacetate complex. The difference between the trichloroacetate and trifluoroacetate complexes is considerable. When the chlorine atoms are replaced by fluorine atoms there is a change in the molecular symmetry from the lowest C_1 to the maximum S_4. This is apparently due to more favourable packing effects as the covalent radius decreases. When the ethyl groups replace the methyl groups the sym-
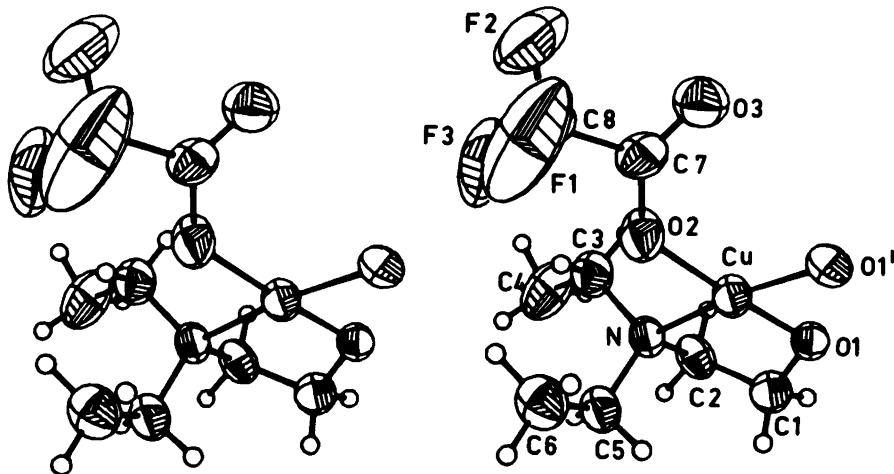

Fig. 2. Stereoview of the $Cu(Et_2NC_2H_4O)(F_3CCOO)O^i$ fragment with thermal ellipsoids at the 50 % probability level, hydrogen atom radii are set at 0.1 Å.
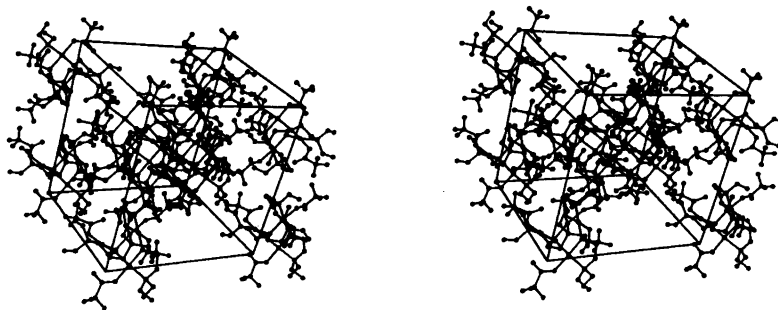
Fig. 3. Stereoview of the packing.

metry gets lower though it is still close to S_4. Here steric hindrance and packing effects may also have influence.

The copper(II) ion has a distorted octahedral (4+2) environment. In the basal plane there is an amino nitrogen atom, two bridging ethanolato oxygen atoms and a carboxylate oxygen atom at quite normal distances for coordination bonds.[1-14]

The O1 and O2 atoms lie 0.102 and 0.093 Å below and N and O1[i] ($-1/4+y$, $1/4-x$, $1/4-z$) 0.096 and 0.098 Å above the least-squares plane of atoms O1,O2,N,O1[i]. The copper(II) ion is practically in the plane, only 0.02 Å above. There is some tetrahedral distortion which can also be seen from the dihedral angle of 8.3° between the Cu,O1,N and Cu,O1[i],O2 planes.

In fifth position there is an ethanolato oxygen atom O1[ii] ($-x$, $\frac{1}{2}-y$, z) and in sixth position a carboxylate oxygen atom O3[iii] ($1/4-y$, $1/4+x$, $1/4-z$). The Cu−O distances are nearly equal but the copper ethanolato oxygen length is slighty shorter (0.035 Å). In the other complexes with S_4 molecular symmetry the copper carboxylate distance is shorter than the copper ethanolato distance as in $|Cu(Me_2LO)(ClAc)|_4$[10] (2.712 and 2.737 Å) and in $|Cu(Et_2LO)(ClAc)|_4$[7] (2.663 and 2.720 Å). In $|Cu(Me_2LO)(F_3Ac)|_4$[12] where the symmetry is close to S_4 the copper ethanolato distances varied from 2.717 to 2.819 Å and the copper carboxylate distances from 2.663 to 2.847 Å.

In $|Cu(Me_2LO)(ClAc)|_4$[11] where the symmetry is C_2 one copper ethanolato distance is 2.633 Å

Tables 4. The shortest and longest interatomic Cu−Cu and axial Cu−O distances (Å), the differences (Å) between the longest and shortest distances and the point group molecular symmetry in cubane type molecules of haloacetate complexes.

Compound	Cu−Cu Long	Short	Δ	Cu−O LO	Ac	Δ	Symmetry	Ref.
$[Cu(Me_2LO)(ClAc)]_4$	3.766	3.182	0.584	2.737	2.712	0.025	S_4	10
$[Cu(Me_2LO)(Cl_2Ac)]_4$	3.609	3.124	0.811	2.633	2.517	0.546	C_2	11
	3.935	3.256		2.858	3.063			
$[Cu(Me_2LO)(F_3Ac)]_4$	3.713	3.154	0.659	2.717	2.663	0.184	close to S_4	12
	3.813	3.231		2.819	2.847			
$[Cu(Et_2LO)(ClAc)]_4$	3.746	3.200	0.546	2.720	2.663	0.057	S_4	7
$[Cu(Et_2LO)(Cl_2Ac)]_4$	3.658	3.176	0.848	2.71	2.59	0.67	close to C_2	8
	4.024	3.290		2.95	3.26			
$[Cu(Et_2LO)(Cl_3Ac)]_4$	3.672	3.094	0.902	2.52	2.44	a	C_1	9
	3.996	3.372		3.01	2.60			
$[Cu(Et_2LO)(F_3Ac)]_4$	3.714	3.206	0.508	2.721	2.756	0.035	S_4	This work
$[Cu(Bu_2LO)(Cl_2Ac)]_4$	3.619	3.134	0.686	2.60	2.43	a	C_1	13
	3.824	3.313		2.97	2.74			

^{a} Ethyl or butyl group is blocking the carboxylate oxygen place of one copper(II).

and the other is elongated to 2.858 Å. Corresponding to this the copper carboxylate distances are 3.063 to 2.517 Å, respectively. In $|Cu(Et_2LO)(Cl_2LO)|_4$[8] where the symmetry is pseudo C_2 there are two copper ethanolato distances ~ 2.93 Å and two ~ 2.72 Å while two copper carboxylate distances are ~ 2.62 Å and one 2.90 Å. The fourth copper carboxylate distance is elongated to 3.26 Å.

In C_1 complexes $|Cu(Et_2LO)(Cl_3Ac)|_4$[9] and $|Cu(Bu_2LO)(Cl_2Ac)|_4$[13] the ethanolato Cu – O distances vary from 2.52 to 3.01 Å and the carboxylate distances from 2.43 to 2.74 Å. In both clusters one of the four copper atoms has square-pyramidal environment where the apical position is occupied by an ethanolato oxygen atom (2.52 – 2.60 Å). The sixth position is blocked by an ethyl or butyl substituent of the aminoethanolato ligand.

The bond lengths and angles of the 2-diethylaminoethanolato ligand are as expected. The mean value of the angles around the ethanolato oxygen atoms is 109.0° which indicates sp^3 hybridization. It is quite distorted, however because the angles vary from 85.0 to 121.4°. In the five-membered ethanolato ring the dihedral angle O,C1,C2,N is 53.5°.

The trifluoroacetate group is bridging two copper atoms asymmetrically in syn – syn configuration. One oxygen is coordinated equatorially and the other is in the axial coordination position of a copper atom. The C – O bond lengths are different, corresponding to the short and long Cu – O distances. The acetate group is planar with the largest deviation from the least-square plane defined by O2,C7,-C8,O3 on the carbon atom C7 (0.008 Å). The mean value of the C – F bond lengths is 1.272 Å. These lengths and angles agree well with data from trifluoroacetate groups.[18–20]

The CF_3 group displays a relatively high degree of anisotropic thermal motion. This has also been observed in other structures containing CF_3 groups[19–21] and may be due to torsional motion and rotational disorder.

The molecules are held together by van der Waals forces. The shortest intermolecular distances are F2···C6^v 3.314 Å and F2···C5^v 3.383 Å $(x, \frac{1}{2}+y, -z)$.

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