461. The Crystal Structures of the Acid Salts of Some Monobasic Acids. Part X.[1] Potassium, Rubidium, and Cæsium Hydrogen Di-trifluoroacetates

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The acid salts of trifluoroacetic acid, $M\text{H}(\text{CF}_3\text{CO}_2)_2$, (where $M = \text{K}$, Rb, or Cs) have been studied by three-dimensional crystal-structure analysis. The potassium salt crystallises with four molecules in a cell, belonging to the space group $I2/a$, with $a = 8{\cdot}773$, $b = 10{\cdot}169$, $c = 9{\cdot}255$ Å, $\beta = 99°\ 51'$. Its structure is that of a type A acid salt, with the two equivalent trifluoroacetate residues joined by a short hydrogen bond ($\text{O} \cdots \text{O} = 2{\cdot}435$ Å) lying across a centre of inversion. Though not explicitly studied, the structure of the rubidium compound must be similar, since the crystal is isomorphous.

The cæsium salt has four molecules in a cell with $a = 13{\cdot}623$, $b = 5{\cdot}033$, $c = 14{\cdot}741$ Å, $\beta = 112°\ 46'$ and space group $A2/a$. Though the structure is different, it also belongs to type A; and the quasi-symmetrical hydrogen bond has $\text{O} \cdots \text{O} = 2{\cdot}38 \pm 0{\cdot}03_2$ Å.

TRIFLUOROACETIC acid (HT) forms acid salts, as was discovered by Hara and Cady,[2] who described compounds of formulæ NaH_2T_3 and $\text{KH}T_2$, and by Klemperer and Pimentel,[3] who studied the infrared spectrum of NaH_2T_3. We have prepared $\text{KH}T_2$, as well as the analogous salts $\text{RbH}T_2$ and $\text{CsH}T_2$, and we have determined their crystal structures, which prove to be [4] of type A with very short hydrogen bonds.

EXPERIMENTAL

Preparation.—The 1 : 1 acid salts were easily made by dissolving two equivalents of commercial trifluoroacetic acid and one of potassium hydroxide, or rubidium carbonate, or cæsium carbonate in a little hot water, and allowing the solution either to stand, or to evaporate in a desiccator. The crystals were prismatic, those of $\text{KH}T_2$ and $\text{RbH}T_2$ elongated in the c-direction, but those of $\text{CsH}T_2$ in the b-direction. All three compounds were hygroscopic and, for X-ray study, the crystals had to be sealed into glass capillary tubes. Their compositions were roughly checked by their equivalents, and confirmed by the subsequent crystal-structure analyses.

Crystal Data.—The crystal data in Table 1, were obtained from single crystal rotation, oscillation, Weissenberg and precession photographs, taken with CuK_α- and MoK_α-radiations. Accurate values for the cell dimensions, and their standard deviations, were derived from a least-squares (L.-S.) treatment of a number of high-order reflexions, whose values for sin θ were determined by comparison with superposed powder lines of aluminium, for which a was taken as 4·04907 Å, with λ for CuK_{α_1} radiation as 1·54051 Å.

We expected these three substances to be isomorphous and to be able to use their isomorphism to solve the phase problem. The first two were so, but the cæsium salt was not, though

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[1] Part IX, L. Golič and J. C. Speakman, preceding Paper.

[2] R. Hara and G. Cady, *J. Amer. Chem. Soc.*, 1954, **76**, 4285.

[3] W. Klemperer and G. C. Pimentel, *J. Chem. Phys.*, 1954, **22**, 1399.

[4] H. N. Shrivastava and J. C. Speakman (Part V), *J.*, 1961, 1151.

TABLE 1

Crystal values for some acid trifluoroacetates

Formula	$KH(CF_3CO_2)_2$	$RbH(CF_3CO_2)_2$	$CsH(CF_3CO_2)_2$
M	266·1	312·5	359·9
a (Å)	8·773 ± 0·005	18·813 ± 0·003	13·623 ± 0·003
b	10·169 0·006	10·550 0·004	5·033 0·002
c	9·255 0·006	9·546 0·006	14·741 0·004
β	99·85° ± 0·07	100·66° ± 0·06	112·76° ± 0·04
U (Å^3)	813·5	872·2	932·0
D_m	2·085	—	2·61
D_c	2·171	2·380	2·565
Z	4	4	4
μ (Cu$K\bar{\alpha}$)	68·5	97·2	321·4
F (000)	520	592	664
Space group	*I*2/*a*	*I*2/*a*	*A*2/*a*

all three crystallise in the same space group of the monoclinic system. In fact, we were able to determine the structure of the potassium compound without recourse to the isomorph with the heavier, Rb, atom; and we carried this analysis to an advanced stage of refinement. The structure of the rubidium salt was therefore also known by implication, though we did no further work on it. The different structure of the cæsium salt was determined also, and refinement was carried only as far as the less accurate intensity values warranted. For both analyses, the intensities were estimated visually from multiple-film photographs. The crystals used were cut to have an approximately square cross-section, and absorption corrections were applied as for a cylindrical specimen, with effective radii ~0·1 mm.

Potassium Hydrogen Di-trifluoroacetate.—Absent reflexions were those characteristic of the space groups *Ia* and *I*2/*a*. The $N(z)$-test indicated centrosymmetry and hence *I*2/*a* [No. 15—with point-positions 000, $\frac{1}{2}\frac{1}{2}\frac{1}{2} \pm (xyz;\ x, \bar{y}, \frac{1}{2} + z)$], and this was borne out by the subsequent analysis. This space group implies that the K$^+$ ion and the acidic hydrogen atom are in special positions, and that the two trifluoroacetate residues of the formula KHT_2 are equivalent. The situation is typical of class *A* acid salts, and the K$^+$ was assumed to occupy four-fold positions of type $0y\frac{1}{4}$. Details of the reflexions recorded are given in Table 2.

TABLE 2

Summary of terms used in the analysis of $KH(C_2F_3O_2)_2$

Reciprocal-lattice net	No. of obsvd. reflexions	Percentage of those accessible	R (%)
*hk*0	55	87·3	6·23
*hk*1	96	93·2	6·93
*hk*2	102	89·5	7·12
*hk*3	85	84·2	6·33
*hk*4	85	85·9	8·05
Other *hkl*	178	65·7	6·22
All	601	64·2	6·79

The value of y for the potassium ion was deduced from the sharpened *hk*0 Patterson projection. Otherwise, the three principal projections could not be deciphered at this stage. The sharpened three-dimensional Patterson function was therefore computed and the structure was solved by a careful study of this. The initial trial structure gave an R-value of 38%, which was reduced to 16% after two cycles of electron-density synthesis. Refinement was continued by three-dimensional L.–S. analysis, and the procedure was identical with that described in Part IX. Refinement was discontinued after 18 cycles, when the shifts were all less than one-tenth of the respective standard deviations, and the R-value for all observed reflexions had fallen to 6·79%. At a late stage the acidic hydrogen atom was included in structure-factor calculations, with $x = y = z = \frac{1}{4}$, and the isotropic Debye factor, $B = 3{\cdot}2$ Å^2. Observed structure amplitudes and calculated structure factors are listed in Table 3. Structure factors were also calculated for some 150 reflexions that lay within the region of reciprocal space covered but were too weak to have been observed. Of these terms, 54% had $|F_c|$ below the minimum observable, and only four terms had $|F_c|$ greater than three times the minimum. These were: 396(−4·72), 923(5·09), 378(−5·77), and $39\bar{8}$(5·99).

Final co-ordinates are given in Table 4, along with their standard deviations, and vibrational parameters are shown in Table 5 as tensor components for mean-square amplitudes. The

TABLE 3

Potassium hydrogen di-trifluoroacetate: observed structure amplitudes and calculated structure factors

h	*k*	*l*	|*F*o|	*F*c
0	0	2	12.6	-10.4
		4	11.6	-11.3
		6	91.8	-84.6
		8	21.3	20.8
		10	22.5	-21.2
0	1	3	40.1	41.6
		5	31.2	-31.7
		7	7.5	7.5
		9	5.4	-7.9
		11	15.1	16.3
0	2	0	40.5	43.0
		2	50.7	54.6
		4	64.0	-61.6
		6	36.5	37.6
		8	11.3	-11.3
0	3	1	104.8	95.7
		3	63.5	-62.9
		5	53.3	54.3
		7	15.2	-14.1
		9	22.7	23.2
0	4	0	5.8	-4.2
		2	7.2	-7.7
		4	12.3	-12.3
		8	8.2	8.8
		10	6.1	-5.1
0	5	1	50.5	-49.4
		3	35.6	34.6
		7	20.1	22.2
		9	11.0	-11.7
0	6	0	28.8	28.1
		2	43.3	44.2
		4	36.1	-38.2
		6	20.1	-20.5
		8	21.6	-19.7
		10	6.3	8.5
0	7	1	29.6	-29.5
		7	10.1	-10.6
		9	8.3	-10.0
0	8	0	4.7	5.2
		2	13.2	-13.4
		4	11.8	12.2
0	9	1	13.7	-14.1
		3	21.9	-23.4
		5	7.2	8.4
0	10	0	17.4	18.7
		2	7.6	-7.4
		4	9.4	10.1
0	11	1	3.9	-4.7
		3	4.5	5.3
0	12	0	5.8	6.3
		2	18.9	20.7
		4	6.5	-9.8
0	13	1	8.2	10.8
1	1	0	20.9	-18.9
		2	87.6	99.1
		4	65.5	71.3
		6	46.8	-48.1
		8	8.2	8.2
		-2	45.7	-44.2
		-4	26.3	25.0
		-6	6.0	8.1
		-8	38.0	-37.9
1	2	1	126.5	-139.6
		3	40.0	-40.7
		5	23.4	20.9
		7	12.3	12.3
		9	14.0	15.1
		-1	38.4	-38.6
		-3	30.1	-28.0
		-5	61.0	60.2
		-7	29.3	-27.2
		-9	18.9	19.5
1	3	0	16.3	16.2
		2	119.0	120.6
		4	8.8	-7.3
		8	22.6	-23.9
		10	7.2	8.9
		-2	4.5	-0.7
		-4	52.2	-49.8
		-6	34.4	-32.9
		-8	7.6	-9.7
		-10	17.3	16.5
1	4	1	95.5	91.9
		3	4.8	4.1
		5	10.4	8.0
		7	38.8	-38.6
		-1	52.1	-47.4
		-3	31.6	-29.6
		-5	39.0	-36.2
1	5	0	30.5	28.2
		2	17.5	-16.4
		4	22.9	20.6
		6	20.6	-18.4
		8	12.6	-13.7
		10	9.4	-10.5
		-2	43.8	-41.3
		-4	51.6	51.3
		-6	32.1	-29.0
		-8	30.9	29.8
		-10	8.4	-10.4
1	6	1	7.2	-5.0
		3	32.9	32.2
		5	39.2	-39.5
		7	26.3	24.3
		9	14.5	-15.3
		-1	28.7	26.9
		-3	35.9	-33.6
		-5	19.6	19.5
1	7	0	21.2	-19.3
		2	21.2	19.0
		4	34.5	-31.5
		8	14.8	-16.5
		-2	48.8	47.9
		-4	21.7	-20.8
		-6	15.4	15.2
		-8	12.5	-12.6
		-10	12.5	13.5
1	8	1	36.7	36.8
		3	25.3	-25.8
		5	7.5	7.2
		9	9.1	10.2
		-1	28.0	-29.6
		-3	17.3	17.4
		-7	38.9	36.1
		-9	17.5	-15.6
1	9	0	31.1	33.3
		2	6.3	-4.0
		4	27.6	26.1
		6	17.2	-17.1
		8	10.3	12.1
		-2	19.1	-18.3
		-4	5.7	-5.0
		-6	23.1	-22.9
1	10	1	13.0	12.4
		3	20.5	21.7
		5	15.3	-16.6
		-1	23.1	22.9
		-3	26.8	-28.9
		-5	17.7	17.0
1	11	0	9.8	-10.1
		2	22.1	22.2
		-2	6.7	6.8
		-4	9.2	-13.2
1	12	1	9.7	9.7
		3	8.6	-8.2
		-1	8.6	-9.7
		-3	4.5	4.1
1	13	0	7.0	10.3
2	0	0	22.7	-26.0
		2	93.9	-104.5
		4	7.5	6.6
		6	24.2	23.8
		8	14.8	14.2
		10	5.4	-4.4
		-2	41.2	43.6
		-4	39.6	-37.7
		-6	73.9	-70.8
		-8	31.9	31.5
		-12	11.0	11.9
2	1	1	54.6	-58.7
		3	92.2	97.6
		5	41.7	-42.0
		7	18.0	19.0
		9	19.7	-22.4
		-1	76.3	78.7
		-3	121.6	-143.8
		-5	16.3	15.7
		-7	17.1	-16.0
		-9	39.3	36.6
2	2	0	51.3	-53.5
		2	58.4	62.7
		4	13.4	12.5
		6	40.0	40.3
		8	31.4	-33.5
		-2	51.8	52.4
		-4	98.5	-101.0
		-8	11.0	-8.8
		-10	19.8	21.0
2	3	1	40.3	-39.4
		3	23.3	-22.8
		5	8.4	11.0
		7	10.9	-10.3
		-1	15.5	-13.2
		-3	26.3	24.4
		-5	7.5	-9.7
		-7	24.8	24.5
2	4	0	117.7	119.3
		2	24.8	-23.6
		4	66.1	61.9
		6	24.1	-25.0
		10	17.7	-18.1
		-2	59.5	-56.0
		-4	8.4	9.7
		-6	39.3	-37.2
		-8	22.5	21.4
2	5	1	59.8	-55.9
		3	12.2	-13.0
		5	9.8	-7.5
		-1	13.2	13.0
		-3	47.6	46.9
		-5	34.2	32.9
		-7	18.1	-16.2
2	6	0	26.0	25.3
		2	2.9	3.1
		4	18.4	-15.6
		-2	14.0	14.0
		-4	11.8	-13.0
		-6	12.8	14.2
2	7	1	31.0	29.1
		3	22.8	22.8
		5	26.6	26.1
		7	13.7	-13.4
		-1	44.7	-44.1
		-3	9.5	10.5
		-5	19.2	-19.0
2	8	0	5.3	-4.9
		2	32.7	30.7
		4	9.2	6.2
		-4	14.8	-17.5
		-6	7.5	7.1
2	9	1	5.9	-5.0
		3	20.7	22.0
		5	11.5	16.4
		-1	17.1	-18.5
		-3	12.7	11.6
2	10	2	5.8	4.7
		4	8.2	8.5
		-2	7.4	-7.5
		-4	8.0	-8.8
2	11	1	16.9	-18.4
		3	9.9	10.5
		-1	12.5	13.3
2	12	0	11.4	-14.0
		-4	5.9	-9.4
3	1	0	13.1	12.2
		2	40.3	42.4
		4	5.2	3.8
		6	7.0	8.4
		-2	136.0	-160.8
		-4	29.5	-28.7
		-6	15.9	14.3
		-8	44.1	43.5
3	2	1	17.9	17.1
		3	30.9	29.3
		5	23.4	-21.3
		7	12.5	12.5
		9	19.4	-18.0
		-1	24.4	22.8
		-3	21.2	21.5
		-5	6.0	7.4
		-7	10.7	9.9
		-9	14.1	-14.3
3	3	0	7.4	4.5
		2	30.2	29.7
		4	43.5	-41.5
		-2	47.4	45.0
		-4	22.0	-22.0
		-6	26.0	26.4
		-8	26.0	-28.1
3	4	1	60.3	55.4
		3	38.2	-38.2
		7	7.9	-6.5
		9	9.5	10.1
		-1	6.7	-6.0
		-3	17.4	16.4
		-5	23.3	-23.7
		-7	42.4	40.7
3	5	0	7.2	6.8
		2	31.1	29.5
		4	71.0	66.9
		6	10.9	-15.1
		8	10.7	12.2
		10	10.3	-10.0
		-2	74.6	-72.0
		-4	4.5	-2.3
3	6	1	40.2	-39.4
		3	7.6	6.0
		7	10.1	16.2
		-1	41.6	42.2

TABLE 3 (*Continued*)

h	k	l	$\lvert F_o \rvert$	F_c
		-3	42.7	-43.0
		-5	28.5	28.5
		-7	16.4	-17.4
		-9	20.0	18.4
3	7	0	41.0	-39.5
		2	49.5	46.2
		4	12.4	12.4
		6	23.7	24.1
		-2	6.0	-4.9
		-4	23.5	-25.1
		-6	14.3	15.4
		-8	11.7	-12.4
		-10	14.1	12.7
3	8	1	16.2	15.7
		3	26.9	-26.1
		5	29.1	28.6
		-1	7.4	-6.7
		-3	9.0	8.3
		-5	36.8	-34.4
3	9	0	22.6	23.2
		2	22.1	-21.4
		4	5.0	3.8
		-2	13.3	-14.5
		-4	24.6	26.0
		-6	19.5	-20.6
3	10	1	16.5	-17.2
		3	4.7	4.2
		-1	14.8	15.1
		-3	18.2	-19.2
3	11	0	15.1	-16.0
		2	6.7	6.6
		4	8.2	-9.1
		-4	12.0	-16.2
3	12	1	5.3	5.9
		-1	8.0	-10.3
		-3	6.7	9.3
4	0	0	47.7	49.8
		2	58.4	-60.8
		4	65.9	72.4
		6	34.9	-35.3
		8	9.1	9.3
		10	14.5	-13.7
		-2	46.8	-43.9
		-4	94.1	93.6
		-6	51.1	-45.3
		-8	11.8	10.0
		-10	6.3	-3.4
4	1	1	20.9	19.6
		3	13.1	12.3
		5	31.8	-31.5
		-1	73.6	74.9
		-3	4.9	2.5
		-5	13.3	14.4
		-7	43.9	-40.4
		-9	10.4	11.8
		-11	13.4	-13.4
4	2	0	89.3	-93.1
		2	33.7	33.0
		4	12.0	10.7
		6	14.5	15.1
		8	16.3	-15.3
		-2	6.7	6.4
		-4	13.2	-14.1
		-6	41.9	41.0
		-10	19.9	20.3
4	3	1	62.1	57.9
		3	11.4	-8.9
		-1	72.1	-69.2
		-3	66.2	64.8
4	4	0	53.3	-50.3
		2	23.8	-21.9
		4	26.9	25.7
		-2	23.2	-20.7
		-4	8.3	7.8
4	5	1	38.3	-36.2
		3	46.4	45.6
		-1	24.9	-23.3
		-3	30.4	-29.1
4	6	0	24.0	-21.5
		-2	27.9	26.1
		-4	29.5	-30.6
4	7	1	7.0	6.4
		-1	8.3	6.7
		-3	8.1	-6.4
4	8	2	8.9	-7.1
		4	14.1	12.6
		-2	19.3	-18.4
		-4	7.9	-6.7
4	9	3	7.6	-8.0
		-1	17.1	-18.6
4	10	2	11.5	-11.4
		-2	12.0	-12.1
		-4	11.5	13.5
4	11	1	7.0	-7.6
		-1	6.4	-7.7
		-3	6.5	-7.1
4	12	-2	6.0	8.3
5	1	0	20.3	19.5
		2	7.4	-6.0
		4	11.0	10.4
		-2	18.0	17.3
		-4	18.5	-16.5
		-6	17.7	16.6
		-8	7.0	5.9
5	2	1	64.1	-62.4
		3	5.6	-4.7
		5	19.1	19.2
		7	15.1	17.0
		-1	8.5	9.5
		-3	26.8	-25.6
		-5	33.4	33.5
		-7	13.1	-13.1
		-9	12.5	12.9
		-11	19.0	-17.9
5	3	0	39.5	-37.9
		2	22.9	-21.4
		4	15.6	-13.6
		-2	8.4	-8.6
		-4	11.4	-9.4
5	4	1	23.6	23.0
		3	23.5	-23.0
		-1	21.0	19.7
		-3	16.9	16.1
5	5	0	33.0	30.9
		2	22.4	-20.2
		4	6.4	-5.0
		-2	63.5	-62.4
		-4	17.1	13.2
5	6	1	28.5	-28.3
		3	19.5	18.0
		-1	17.0	16.2
		-3	5.4	-3.2
5	7	0	25.2	-25.6
		2	13.0	11.2
		4	27.1	-24.3
		-2	8.1	7.9
		-4	20.9	-21.1
5	8	1	4.6	-6.0
		3	22.8	-20.9
		-1	23.8	-25.0
		-3	40.1	41.5
5	9	2	19.7	-18.0
		4	17.0	15.9
		-2	16.7	-16.7
		-4	12.8	13.8
5	10	1	12.1	-11.6
		3	7.6	8.3
		-1	18.4	21.7
		-3	8.0	-8.3
5	11	0	8.1	-9.7
		2	11.7	12.6
		-2	9.0	11.1
6	0	0	31.8	-31.6
		2	43.0	-41.1
		6	11.3	12.9
		8	21.7	22.2
		-2	17.7	-16.8
		-4	61.7	64.8
		-8	8.7	10.2
		-10	32.4	-31.2
6	1	1	41.0	-38.6
		3	16.9	15.4
		5	26.5	-26.9
		7	20.3	21.4
		-1	33.2	33.4
		-3	47.1	-48.6
		-5	20.2	20.4
		-7	20.6	-18.4
		-9	16.3	16.6
6	2	0	33.9	-33.7
		2	38.7	36.8
		4	8.3	-13.1
		6	11.8	11.7
		-2	11.0	10.4
		-4	21.9	-22.8
		-6	22.6	23.9
		-8	17.3	-17.4
		-10	9.7	9.1
6	3	1	14.8	14.9
		3	14.2	-11.7
		-1	30.9	-30.2
		-3	14.5	-14.5
6	4	0	10.0	8.0
		2	20.5	-16.8
		4	27.8	26.0
		-2	39.7	-36.2
		-4	37.6	39.3
6	5	1	7.0	2.2
		-1	7.6	8.6
		-3	19.9	-17.9
6	6	0	39.5	-37.4
		2	22.9	-22.4
		4	11.1	-8.9
		-2	17.1	16.6
		-4	35.1	37.1
6	7	1	15.6	13.9
		3	17.9	-15.9
		-3	7.3	6.8
6	8	0	7.3	-7.1
		2	2.9	3.3
		-2	3.7	4.8
6	9	1	6.8	7.3
6	10	-2	3.1	-3.7
6	11	-1	7.1	10.1
7	1	0	4.5	-2.6
		2	23.7	-22.6
		-2	15.9	-13.8
		-4	11.0	9.8
		-6	10.5	-10.6
		-8	9.4	11.0
7	2	1	7.8	-6.0
		3	22.7	23.5
		-1	21.0	-20.8
		-3	4.6	-1.7
		-9	8.7	7.2
7	3	0	17.8	-15.8
		2	13.7	-11.9
		-2	50.6	49.3
		-4	5.7	3.9
7	4	1	9.1	-8.3
		3	24.7	-23.5
		-1	14.7	-15.0
		-3	49.7	48.7
7	5	0	25.2	24.3
		2	23.9	-21.8
		-2	15.9	14.4
		-4	8.3	8.6
7	6	1	19.2	-17.6
		3	17.0	15.5
		-1	13.8	14.6
		-3	16.1	-16.4
7	7	0	10.5	-11.4
		2	6.3	5.3
		-2	21.5	20.3
		-4	11.1	-10.8
7	8	1	17.7	16.0
		-1	13.8	-14.7
		-3	4.8	6.1
7	9	0	12.2	13.6
		2	13.7	-14.6
		-2	9.0	-8.8
		-4	17.1	20.5
7	10	-1	8.9	12.7
8	0	0	12.3	12.7
		2	23.3	-25.6
		4	14.6	17.9
		6	14.0	-13.9
		-2	29.6	-29.6
		-4	31.5	31.6
		-6	8.7	-9.2
		-8	10.7	10.5
8	1	1	6.8	-8.8
		5	9.4	-9.4
		-1	39.4	40.8
		-5	11.7	14.0
		-7	24.7	-23.5
		-9	9.1	10.1
8	2	0	7.6	-6.1
		4	22.0	-24.8
		-2	26.9	25.7
		-4	9.8	-7.8
		-6	18.0	19.5
		-8	17.2	-17.0
8	3	1	25.5	23.8
		3	22.2	-21.9
		-1	3.2	4.7
		-3	23.5	23.3
8	4	0	17.2	17.5
		-2	7.2	-6.8
		-4	16.3	15.9
8	5	1	13.2	-12.4
		3	5.8	5.7
		-1	10.5	10.5
		-3	15.7	-15.1
8	6	0	3.2	-1.9
		2	17.1	15.2
8	7	-1	8.0	8.5
		-3	5.3	5.2
8	8	0	7.8	7.9

TABLE 3 (*Continued*)

h	k	l	$\lvert F_o \rvert$	F_c	h	k	l	$\lvert F_o \rvert$	F_c	h	k	l	$\lvert F_o \rvert$	F_c
		-2	3.5	4.6			-2	5.3	-5.4			-5	13.4	16.1
8	9	-3	3.1	-4.3			-4	14.9	15.1			-7	11.7	-12.0
9	1	0	17.1	15.9	9	6	-1	6.4	7.6	10	2	2	10.5	13.5
		-2	23.5	24.2			-3	10.9	-12.6			-2	15.3	16.1
		-6	6.7	-8.2	9	7	0	5.6	-6.3			-4	17.6	-18.5
9	2	-1	8.7	10.4			-2	12.4	14.2	10	3	-1	10.6	-12.0
		-3	16.0	-15.8			-4	8.9	-13.7			-3	10.7	10.2
		-5	18.0	16.7	9	8	-1	6.1	-13.4	10	4	0	14.4	15.9
9	3	0	19.1	-19.6	10	0	0	16.7	19.7			-2	7.3	-8.1
		-2	5.6	5.4			-2	10.1	-8.6	10	5	-1	5.8	7.1
		-4	4.5	3.9			-4	17.0	14.6			-3	5.1	-6.2
9	4	-1	8.1	-9.4			-6	6.7	-8.4	10	6	-2	4.0	4.8
		-3	6.4	5.2	10	1	1	18.8	-23.5	11	1	-2	3.7	-5.6
9	5	0	12.3	12.5			-1	4.4	4.2	11	2	-3	9.6	-12.2
							-3	7.8	-8.7					

TABLE 4

Potassium hydrogen di-trifluoroacetate: fractional (x, y, z, $\times 10^5$) and orthogonal (X', Y, Z', Å, $\times 10^4$) co-ordinates. (The quantities in parentheses are the estimated standard deviations; X' and Y are, respectively, parallel to x and y, whilst Z' is perpendicular to both. For the numbering of atoms see Figure 1.)

Atom	x	y	z	X'	Y	Z'
K	50,000	21,876	25,000	39,907	28,599(16)	22,796
F(1)	6204	32,461	59,619	−3997(31)	33,008(34)	54,365(33)
F(2)	23,590	38,638	77,440	8435(34)	39,291(34)	70,614(29)
F(3)	10,544	53,053	63,729	−841(33)	53,951(32)	58,114(36)
O(1)	27,638	33,947	43,080	17,425(33)	34,520(36)	39,281(33)
O(2)	39,977	49,506	57,579	25,956(36)	50,342(37)	52,504(37)
C(1)	17,507	41,230	63,804	5256(48)	41,925(54)	58,182(51)
C(2)	29,307	41,198	53,617	17,224(46)	41,894(48)	48,891(50)
H	50,000	50,000	50,000	—	—	—

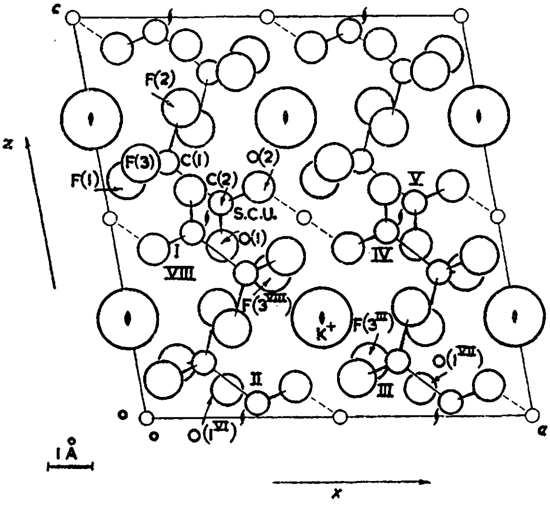

FIGURE 1. Potassium hydrogen di-trifluoroacetate: view of the unit cell in its b-axial projection. (S.C.U. indicates the standard chemical unit, the co-ordinates of whose atoms appear in Table 4; other symmetry-related units are denoted by Roman numerals as is explained in the text)

numbering of atoms is explained in Figure 1. The group of atoms covered in the Table constitutes the standard chemical unit (S.C.U). Other symmetry related units are as follows:

		S.C.U.			x	y	z
I	$\frac{1}{2} - x$	$\frac{1}{2} + y$	$1 - z$	V	$\frac{1}{2} + x$	$\frac{1}{2} - y$	z
II	x	$1 - y$	$-\frac{1}{2} + z$	VI	$\frac{1}{2} - x$	$\frac{1}{2} - y$	$\frac{1}{2} - z$
III	$\frac{1}{2} + x$	$-\frac{1}{2} + y$	$-\frac{1}{2} + z$	VII	$1 - x$	y	$\frac{1}{2} - z$
IV	$1 - x$	$1 - y$	$1 - z$	VIII	$\frac{1}{2} - x$	$-\frac{1}{2} + y$	$1 - z$

These results will be discussed later along with those for the cæsium salt.

Cæsium Hydrogen Di-trifluoroacetate.—Absorption with these crystals was high, μR (for CuK_α-radiation) being 3·2 for a typical crystal mounted to rotate about its *b*-axis. Though formally corrected for absorption, the intensity values are therefore less accurate, and notably so for the 85 reflexions measured for a crystal set to rotate about its *c*-axis. The terms used in the analysis are summarised in Table 6.

TABLE 5

Potassium hydrogen di-trifluoroacetate: vibrational parameters (Å², × 10⁴)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{31}	Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{33}	U_{31}
K	377	316	379	—	—	151	O(1)	389	373	397	−23	−76	57
F(1)	443	644	598	−196	−51	93	O(2)	422	519	478	−162	−154	127
F(2)	659	585	343	8	50	77	C(1)	382	395	317	59	−53	12
F(3)	564	528	641	210	−85	133	C(2)	316	305	376	−8	16	36

TABLE 6

Summary of terms used in analysis of $CsH(C_2F_3O_2)_2$

Reciprocal-lattice net	No. of obsvd. reflexions	Percentage of those accessible	*R*(%)
*h*0*l*	121	93·8	7·23
*h*1*l*	170	73·0	8·16
*h*2*l*	205	94·6	9·33
*h*3*l*	186	98·4	15·03
All about *b*-axis	682	63·6	9·51
hkl (about *c*-axis)	85	90·4	23·16
All	767	71·5	10·28

Though the structure is different from that of the potassium salt, the space group is the same, as are its structural implications. In fact, we have used the space group in a different orientation, $A2/a$ [with equipoints 000, $0\frac{1}{2}\frac{1}{2}$ $\pm$ $(x, y, z;\ \frac{1}{2} + x, \bar{y}, z)$]. Since the *b*-axis is short and the cæsium atom heavy, the projected structure was immediately obvious in the *h*0*l* Patterson projection, and there was no difficulty in assigning *y*-co-ordinates by trial. Refinement proceeded as before. The atomic scattering function for Cs⁺ was taken from Sagel,[5] and corrected

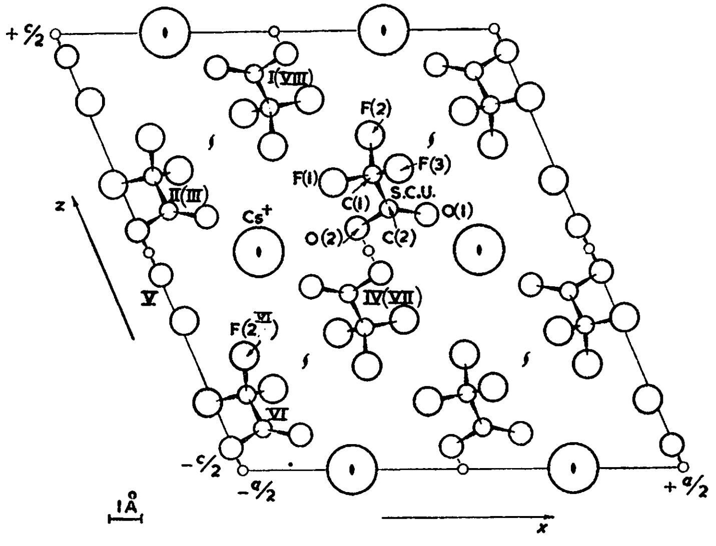

FIGURE 2. Cæsium hydrogen di-trifluoroacetate: view of the unit cell in its *b*-axial projection. (S.C.U. indicates the standard chemical unit, the co-ordinates of whose atoms appear in Table 8; other symmetry-related units are denoted by Roman numerals as is explained in the text)

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[5] K. Sagel, " Tabellun zur Röntgenstrukturanalyse," Berlin, 1958.

TABLE 7

Cæsium hydrogen di-trifluoroacetate: observed structure amplitudes and calculated structure factors

h	*k*	*l*	|*F*o|	*F*c
0	0	2	112.5	136.6
		4	149.5	141.4
		6	130.3	120.5
		8	74.4	62.2
		10	55.1	50.7
		12	84.6	77.5
		14	24.4	21.2
		16	18.5	21.1
0	1	3	130.1	126.8
		5	22.9	18.9
		7	10.1	-7.7
		9	52.5	43.5
		11	15.0	-12.1
		13	16.0	10.8
0	2	0	179.4	-187.2
		2	114.6	-162.0
		4	96.8	-102.0
		6	59.1	-54.4
		8	64.6	-56.3
		10	65.2	-58.5
		12	37.4	-34.0
		14	23.0	-23.8
		16	11.4	-15.1
0	3	1	64.0	-50.0
		3	49.9	-59.8
		5	45.7	-56.4
		7	34.4	-39.1
		9	21.4	-17.0
		11	11.1	-12.5
		13	12.5	-14.6
		15	5.0	-6.0
1	1	1	124.3	-127.4
		3	73.3	-67.2
		5	109.2	-100.4
		7	166.1	-137.8
		9	87.0	-69.5
		11	55.6	-49.8
		13	31.0	-30.3
		15	22.2	-22.9
		-1	129.9	-162.4
		-3	157.2	-187.9
		-5	301.6	-309.7
		-7	102.5	-83.5
		-9	98.1	-83.0
		-13	31.8	-38.3
		-15	25.3	-22.1
		-11	54.7	-49.0
		-17	18.1	-19.7
1	2	0	76.5	-86.5
		2	13.5	-12.2
		4	67.0	-77.5
		6	9.8	9.0
		8	31.0	-27.0
		10	13.1	-11.0
		12	38.5	-31.9
		16	6.5	-8.3
		-2	75.7	-93.7
		-4	28.0	-28.7
		-6	32.1	-33.3
		-8	76.7	-63.6
		-10	22.2	-17.7
		-12	11.4	-11.2
		-14	12.3	-11.5
1	3	1	73.9	60.7
		3	29.2	39.2
		5	66.7	79.0
		7	46.2	53.7
		9	26.1	29.9
		11	22.9	28.4
		13	10.8	14.1
		15	6.6	10.4
		-1	99.9	75.5
		-3	62.3	90.5
		-5	49.8	63.7
		-7	60.5	70.6
		-9	29.8	32.7
		-11	29.8	29.9
		-13	15.5	17.3
		-15	14.8	17.2
2	0	0	70.2	-67.5
		2	261.4	-282.5
		4	151.1	-167.1
		6	107.4	-95.5
		8	96.8	-92.8
		10	47.0	-46.5
		12	60.0	-60.6
		14	32.9	-28.8
		16	17.0	-20.0
		-2	77.2	-53.3
		-4	195.7	-197.3
		-6	109.0	-105.4
		-8	135.8	-120.5
		-10	182.5	-165.4
		-12	36.0	-24.9
		-14	42.6	-46.2
		-16	24.4	-24.7
		-18	9.2	-13.3
2	1	1	41.4	37.2
		5	18.7	-14.2
		7	60.1	-49.2
		11	25.3	-21.4
		-1	129.7	-128.1
		-3	57.2	61.3
		-5	69.4	-63.0
		-7	56.1	-52.0
		-11	11.1	-12.1
2	2	0	127.5	145.5
		2	121.4	132.0
		4	89.6	95.7
		6	98.6	97.6
		8	45.4	40.9
		10	42.0	40.7
		12	38.1	38.4
		14	20.0	21.6
		-2	45.9	53.2
		-4	73.0	82.4
		-6	90.9	109.4
		-8	90.5	87.5
		-10	76.5	65.7
		-12	54.4	50.4
		-14	21.8	24.9
		-16	14.5	15.6
2	3	1	18.5	16.6
		3	38.8	44.1
		5	15.2	18.6
		7	43.4	51.1
		9	33.8	36.8
		11	16.1	16.7
		13	8.0	11.7
		-1	63.1	60.0
		-3	51.0	53.8
		-5	43.4	55.9
		-7	34.3	36.5
		-9	32.5	37.1
		-11	21.4	23.0
		-13	18.2	19.1
		-15	10.5	11.0
3	1	1	158.8	161.1
		3	124.4	133.3
		5	80.2	80.3
		7	121.1	123.1
		9	63.9	59.0
		11	58.9	57.5
		13	22.2	22.4
		15	8.3	11.9
		-1	177.5	196.0
		-3	166.1	183.2
		-5	91.1	99.8
		-7	68.6	68.1
		-9	111.6	99.1
		-11	72.7	59.4
		-13	52.2	50.4
		-15	43.5	41.1
		-17	16.4	16.2
3	2	0	14.5	9.9
		2	96.7	96.9
		4	54.0	58.2
		6	43.8	41.6
		8	30.2	29.0
		10	16.1	14.4
		14	8.7	8.8
		-2	32.6	32.2
		-6	72.3	72.6
		-8	11.7	-4.7
		-10	51.2	46.1
		-12	23.8	19.9
		-14	17.8	15.8
		-16	6.5	8.4
3	3	1	85.6	-91.2
		3	48.0	-54.0
		5	34.3	-35.1
		7	37.0	-44.3
		9	36.5	-44.5
		11	13.3	-18.0
		13	12.2	-17.6
		-1	57.4	-50.7
		-3	91.0	-91.9
		-5	63.8	-77.6
		-7	26.0	-30.3
		-9	34.2	-40.7
		-11	31.7	-35.4
		-13	18.5	-22.5
		-15	13.0	-15.3
4	0	0	126.0	121.5
		2	218.3	246.6
		4	97.3	104.0
		6	131.7	137.0
		8	63.6	62.1
		10	41.5	35.2
		12	12.6	13.2
		14	22.6	25.3
		-2	212.2	232.2
		-4	131.2	125.3
		-6	169.3	170.9
		-8	100.8	107.7
		-10	66.1	61.3
		-12	51.9	53.8
		-14	61.2	55.5
		-16	19.1	18.6
		-18	16.0	20.4
4	1	1	54.1	48.7
		3	43.7	44.4
		5	18.1	15.5
		11	15.3	14.2
		-1	44.2	39.1
		-3	73.7	71.4
		-5	18.1	15.4
		-11	29.9	30.2
		-13	25.3	-11.8
		-15	21.4	17.2
4	2	0	83.4	-82.9
		2	123.0	-130.2
		4	82.1	-95.1
		6	64.1	-74.4
		8	61.0	-55.5
		10	20.5	-20.5
		12	15.4	-19.2
		14	12.5	-14.3
		-2	104.2	-104.1
		-4	124.1	-134.3
		-6	69.0	-76.1
		-8	76.7	-80.1
		-10	62.4	-66.1
		-12	31.4	-30.8
		-14	36.7	-30.0
		-16	23.0	-22.6
4	3	1	64.5	-51.9
		3	48.9	-50.0
		5	30.9	-35.2
		9	16.5	-20.7
		11	14.2	-16.5
		13	4.5	-5.7
		-1	90.5	-77.8
		-3	62.4	-54.2
		-5	33.0	-33.6
		-7	30.2	-37.9
		-9	14.7	-19.8
		-11	24.0	-23.3
		-13	13.7	-13.9
		-15	11.6	-13.2
5	1	1	154.5	-159.3
		3	108.1	-117.7
		5	46.1	-48.9
		7	43.3	-41.1
		9	53.3	-50.4
		11	30.5	-30.3
		-1	122.2	-123.1
		-3	218.4	-230.4
		-5	114.7	-117.8
		-7	127.7	-129.6
		-9	68.6	-76.4
		-11	68.7	-70.0
		-13	41.4	-41.8
		-15	35.4	-34.0
		-17	21.5	-19.8
5	2	0	58.2	-53.2
		2	12.5	-9.1
		4	19.4	-17.9
		6	41.2	-41.0
		10	25.5	-22.5
		-2	80.5	-77.8
		-4	36.7	-35.4
		-6	57.3	-58.3
		-8	42.2	-47.3
		-10	18.1	-19.7
		-12	17.6	-15.8
		-14	12.0	-11.0
		-16	7.5	-9.5
5	3	1	53.5	48.8
		3	59.7	58.9
		5	37.1	39.5
		7	18.4	26.7
		9	16.2	21.0
		11	13.3	17.3
		-1	111.9	94.7
		-3	75.7	64.0
		-5	51.3	49.8
		-7	52.0	55.6
		-9	43.3	52.8

TABLE 7 (*Continued*)

h	k	l	$\|F_o\|$	F_c
		-11	20.3	22.3
		-13	29.7	31.8
		-15	16.2	17.8
6	0	0	76.3	-64.5
		2	72.8	-65.6
		4	110.6	-111.9
		6	66.3	-72.1
		8	57.1	-59.8
		10	54.4	-56.4
		12	21.0	-26.0
		-2	132.3	-150.5
		-4	143.3	-143.0
		-6	117.7	-115.3
		-8	169.9	-177.4
		-10	82.4	-81.5
		-12	81.2	-75.6
		-14	28.1	-28.3
		-16	33.9	-34.0
		-18	18.5	-16.9
6	1	1	51.8	-49.1
		5	23.9	-21.9
		7	13.5	-12.4
		9	16.1	-17.3
		-1	13.8	10.3
		-3	25.9	-25.0
		-5	32.8	-30.7
		-7	40.0	-36.8
		-11	20.4	-17.9
6	2	0	65.0	58.9
		2	68.2	71.3
		4	65.8	68.4
		6	39.3	43.8
		8	48.6	52.6
		10	31.8	31.5
		12	14.2	16.3
		-2	106.7	101.2
		-4	89.1	91.5
		-6	92.9	97.9
		-8	97.1	95.9
		-10	56.4	60.7
		-12	42.0	44.2
		-14	35.3	34.4
		-16	15.6	17.7
6	3	1	54.8	45.8
		3	18.4	13.8
		5	40.8	39.6
		7	20.4	21.2
		9	11.4	13.1
		11	9.3	13.4
		-1	43.7	35.9
		-3	32.1	32.3
		-5	59.8	50.7
		-7	47.6	44.4
		-9	23.5	25.2
		-11	27.1	32.0
		-13	19.2	18.8
		-15	13.9	13.4
7	1	1	100.0	98.4
		3	91.3	94.2
		5	82.9	94.7
		7	44.5	48.5
		9	39.0	41.1
		11	19.5	19.2
		-1	143.7	142.2
		-3	94.1	92.5
		-5	57.4	53.8
		-7	104.2	102.2
		-9	78.3	77.4
		-11	63.4	69.4
		-13	44.2	70.3
		-15	37.5	35.7
		-17	23.2	23.3
7	2	0	48.1	41.2
		2	45.3	41.0
		4	35.2	35.2
		6	18.9	19.4
		8	22.6	20.4
		10	11.1	10.4
		-2	18.8	-7.3
		-4	65.0	63.6
		-6	19.8	16.6
		-8	34.2	31.9
		-10	29.1	30.8
		-12	25.0	25.6
		-14	6.9	7.5
		-16	16.1	14.4
7	3	1	58.3	-49.8
		3	52.5	-51.9
		5	31.4	-31.4
		7	18.7	-25.6
		9	14.9	-19.9
		11	6.3	-13.6
		-1	74.2	-55.1
		-3	65.6	-54.6
		-5	55.4	-51.3
		-7	40.5	-40.9
		-9	33.5	-36.9
		-11	32.9	-42.2
		-13	24.6	-24.4
		-15	19.6	-18.1
8	0	0	147.4	148.6
		2	91.6	87.8
		4	79.5	83.9
		6	44.2	49.8
		8	43.4	46.2
		10	16.8	15.1
		12	11.5	18.8
		-2	103.9	96.7
		-4	134.2	145.7
		-6	135.0	140.7
		-8	70.8	70.3
		-10	47.7	46.4
		-12	57.0	59.6
		-14	41.2	39.5
		-16	40.1	37.3
		-18	24.2	25.8
8	1	1	15.0	11.9
		3	24.2	23.0
		5	25.7	20.7
		-1	55.5	47.9
		-3	31.9	29.8
		-9	32.1	30.4
8	2	0	84.5	-79.6
		2	49.1	-49.2
		4	62.4	-65.8
		6	38.2	-42.5
		8	21.3	-21.1
		10	19.1	-22.7
		-2	112.0	-99.3
		-4	76.3	-74.5
		-6	100.9	-92.2
		-8	71.0	-66.6
		-10	31.0	-33.6
		-12	36.3	-40.6
		-14	31.4	-30.4
		-16	23.7	-23.9
8	3	1	58.9	-47.1
		3	37.1	-31.4
		5	19.6	-15.5
		7	13.9	-19.1
		9	7.2	-9.1
		-1	47.3	-36.2
		-3	63.2	-44.7
		-5	39.5	-33.3
		-7	12.1	-9.9
		-9	35.4	-34.9
		-11	23.2	-23.1
		-13	18.4	-16.6
		-15	16.4	-14.4
9	1	1	85.5	-86.7
		3	64.1	-70.6
		5	32.1	-40.6
		7	27.2	-29.1
		9	20.9	-23.8
		11	11.6	-19.9
		-1	106.6	-105.3
		-3	80.3	-74.9
		-5	109.6	-113.8
		-7	87.6	-84.9
		-9	89.8	-89.5
		-11	66.3	-72.9
		-13	29.2	-40.0
		-15	24.4	-21.4
		-17	24.2	-23.5
9	2	0	33.1	-31.8
		2	12.5	-11.7
		4	12.3	-14.7
		6	18.6	-14.6
		8	9.8	-10.6
		-2	51.5	-43.7
		-4	50.1	-43.0
		-6	46.5	-42.4
		-8	39.0	-33.4
		-12	9.8	-8.2
		-14	21.0	-19.9
		-16	9.1	-6.9
9	3	1	59.7	47.6
		3	27.4	27.7
		5	27.7	31.2
		7	12.8	17.0
		-1	66.7	48.8
		-3	48.3	36.8
		-5	48.9	39.5
		-7	59.7	55.3
		-9	38.8	38.5
		-11	33.1	34.3
		-13	21.3	24.1
		-15	12.9	15.5
10	0	0	70.7	-63.0
		2	38.8	-37.8
		4	45.5	-49.2
		6	37.2	-40.9
		8	29.2	-32.2
		10	19.9	-26.7
		-2	129.4	-121.1
		-4	103.0	-98.2
		-6	92.9	-92.6
		-8	70.1	-74.8
		-10	72.9	-78.3
		-12	49.4	-49.8
		-14	61.7	-56.7
		-16	30.7	-29.0
		-18	15.8	-17.3
10	1	1	25.9	-21.2
		3	10.1	-10.9
		7	15.3	-15.2
		-5	38.8	-36.6
		-7	19.8	-17.9
		-9	18.9	-15.5
10	2	0	62.9	63.6
		2	39.4	39.5
		4	24.1	23.7
		6	33.2	34.0
		8	20.5	23.7
		-2	64.1	57.6
		-4	97.1	83.4
		-6	77.9	70.1
		-8	42.3	38.3
		-10	61.1	54.1
		-12	39.2	47.1
		-14	31.5	29.5
		-16	29.4	26.4
10	3	1	20.4	19.1
		3	30.0	26.0
		5	14.0	13.3
		7	8.4	11.0
		-1	27.0	22.7
		-3	33.3	23.0
		-5	29.5	24.3
		-7	17.0	41.0
		-9	38.1	36.0
		-11	18.4	18.8
		-13	16.7	19.6
		-15	7.9	8.6
11	1	1	57.8	57.7
		3	50.4	55.0
		5	44.5	49.5
		7	25.7	32.5
		-1	46.2	48.3
		-3	50.4	47.3
		-5	79.5	76.5
		-7	89.1	85.2
		-9	71.3	71.0
		-11	48.6	52.9
		-13	43.0	37.2
		-15	34.8	35.2
		-17	23.4	22.8
11	2	0	18.4	13.7
		2	26.9	26.0
		4	10.1	12.6
		6	8.3	11.3
		8	6.9	11.3
		-2	35.4	31.0
		-4	24.6	23.2
		-6	17.2	14.1
		-8	15.4	11.7
		-10	32.5	28.2
		-12	22.1	20.5
		-14	17.2	15.7
		-16	9.4	10.2
11	3	1	29.3	-29.6
		3	28.6	-27.9
		5	11.8	-20.6
		-1	23.0	-21.8
		-3	44.2	-36.7
		-5	53.7	-43.4
		-7	40.9	-33.8
		-9	42.9	-38.5
		-11	27.4	-26.7
		-13	14.5	-17.0
		-15	15.8	-15.9
12	0	0	95.2	88.3
		2	67.7	68.1
		4	27.9	27.9
		6	22.1	27.2
		-2	72.5	69.7
		-4	74.1	64.5
		-6	60.6	59.2
		-8	42.4	39.4

TABLE 7 (*Continued*)

h	*k*	*l*	|*F*o|	*F*c
		-10	65.7	62.2
		-12	57.1	60.2
		-14	36.4	35.6
		-16	29.5	27.4
12	1	3	13.0	15.2
		-3	30.5	26.0
		-7	22.9	17.4
		-9	18.9	14.7
		-13	14.2	5.4
		-15	11.1	12.9
12	2	0	51.5	-51.1
		2	39.8	-44.3
		4	21.5	-26.5
		6	9.8	-15.6
		-2	61.4	-56.8
		-4	55.1	-47.2
		-6	35.9	-31.7
		-8	51.1	-45.5
		-10	48.7	-44.9
		-12	31.6	-33.0
		-14	31.9	-32.6
		-16	18.6	-18.7
12	3	1	19.7	-16.9
		3	17.3	-17.3
		-1	22.7	-20.3
		-3	30.9	-24.2
		-5	32.0	-26.4
		-7	31.2	-25.9
		-9	19.3	-15.2
		-11	15.4	-16.5
		-13	10.7	-11.4
		-15	8.9	-11.4
13	1	1	34.9	-35.2
		3	24.2	-27.0
		5	19.3	-24.0
		-1	45.0	-43.7
		-3	77.7	-77.7
		-5	80.3	-75.5
		-7	56.1	-58.6
		-9	46.8	-47.6
		-11	37.0	-37.1
		-13	27.4	-29.3
		-15	29.6	-29.8
		-17	13.5	-21.6
13	2	0	21.2	-22.9
		2	12.5	-13.2
		-2	21.2	-22.5
		-4	16.5	-13.7
		-6	25.9	-22.8
		-8	30.4	-23.3
		-10	15.2	-11.7
		-12	16.3	-15.8
		-14	9.8	-9.6
13	3	1	15.0	18.1
		-1	27.5	26.9
		-3	33.1	30.4
		-5	39.6	34.4
		-7	36.9	33.1
		-9	25.0	23.7
		-11	18.5	18.1
		-13	18.1	20.6
14	0	0	32.9	-34.8
		2	33.7	-37.3
		4	23.9	-29.4
		-2	41.4	-39.2
		-4	55.7	-47.8
		-6	51.1	-47.8
		-8	80.3	-73.1
		-10	60.9	-57.7
		-12	39.6	-38.1
		-14	31.4	-31.6
		-16	21.9	-23.3
14	1	-5	14.6	-15.4
		-7	18.1	-13.8
14	2	0	25.2	28.4
		2	22.7	27.3
		-2	26.4	29.4
		-4	34.5	31.8
		-6	42.7	40.4
		-8	49.0	44.4
		-10	39.6	39.3
		-12	29.6	32.4
		-14	20.3	21.3
14	3	-1	14.2	14.7
		-3	21.2	19.7
		-5	27.4	22.2
		-7	22.2	19.6
		-9	17.8	16.5
		-11	17.6	15.8
15	1	1	24.3	28.6
		-1	34.6	39.1
		-3	37.3	40.7
		-5	37.7	36.9
		-7	39.9	38.8
		-9	34.0	36.7
		-11	35.7	34.7
		-13	35.6	37.2
		-15	20.6	26.5
15	2	0	5.9	8.6
		-2	7.4	7.1
		-4	15.6	13.1
		-6	15.8	12.0
		-8	16.5	14.5
		-10	17.8	17.7
15	3	-3	20.4	-24.6
		-5	19.1	-21.2
		-7	19.4	-18.5
		-9	19.1	-19.6
16	0	0	22.1	27.6
		-2	32.4	32.2
		-4	38.8	37.5
		-6	41.9	41.0
		-8	40.3	38.5
		-10	33.6	33.2
		-12	31.3	31.8
		-14	16.5	24.9
16	2	-2	15.7	-22.7
		-4	25.1	-26.3
		-6	29.7	-30.7
		-8	28.3	-29.7
		-10	21.5	-25.0
17	1	-5	24.6	-31.0
		-7	26.2	-29.0
		-9	25.3	-28.8
0	4	0	44.0	42.2
		2	48.3	44.3
0	5	1	23.9	24.4
0	6	2	17.8	-5.3
1	4	0	41.7	45.2
		2	45.0	56.5
		-2	24.7	43.2
1	5	1	19.4	-18.3
		3	29.2	-15.1
		-1	19.0	-13.4
		-3	29.7	-16.0
1	6	0	20.7	-16.9
		-2	8.8	-16.1
2	4	0	40.9	-44.9
		2	54.4	-50.1
		-2	33.3	-26.8
2	5	1	14.8	-18.6
		3	16.0	-20.4
		-1	37.5	-30.8
		-3	17.7	-32.7
2	6	0	10.3	6.0
		2	15.9	4.6
		-2	15.2	7.7
3	4	0	34.9	-38.5
		2	49.3	-33.1
		-2	36.1	-37.5
3	5	1	13.1	13.8
		3	18.0	12.3
		-1	20.9	17.3
		-3	17.7	19.0
3	6	0	15.8	14.9
4	4	0	23.5	25.7
		2	26.1	28.6
		-2	37.6	36.2
4	5	1	40.2	32.8
		3	13.0	18.7
		-1	38.3	31.4
		-3	16.4	20.5
4	6	2	7.5	-5.1
		-2	15.8	-2.1
5	4	0	36.8	37.8
		2	23.6	27.7
		-2	30.9	35.3
5	5	1	16.2	-13.4
		3	16.9	-13.9
		-1	20.5	-16.9
		-3	23.9	-14.2
5	6	0	14.3	-14.2
		2	6.5	-11.8
		-2	5.8	-13.6
6	4	0	34.2	-35.2
		2	20.3	-22.2
		-2	25.1	-30.9
6	5	1	18.4	-18.6
		3	11.8	-21.1
		-1	18.8	-21.3
		-3	12.0	-26.3
7	4	0	31.1	-32.3
		2	16.1	-27.9
		-2	29.9	-25.8
7	5	1	14.5	12.8
		3	10.9	9.2
		-1	17.9	14.6
		-3	19.2	11.3
8	4	0	18.5	20.4
		2	22.7	22.7
		-2	37.0	30.0
8	5	1	23.4	21.5
		-3	11.9	19.3
9	4	0	19.7	19.0
		2	16.0	21.9
		-2	30.2	30.8
9	5	1	9.4	-10.3
		3	3.9	-8.7
		-3	13.0	-10.6
10	4	0	23.4	-23.4
		2	10.1	-16.6
		-2	33.1	-23.5
10	5	1	6.0	-14.6
11	4	0	21.7	-21.7
		2	5.9	-14.8
		-2	26.2	-25.0
12	4	0	13.0	17.0
		2	3.2	12.9
		-2	21.9	17.7

for anomalous dispersion. Though the overall *R*-value of 10·3% after ten cycles of L.–S. refinement was reasonably good, the values for some groups of reflexions were rather high. After the eighth cycle a three-dimensional difference-synthesis was calculated; the map was remarkably featureless, except for a complex region of positive and negative density round the site of the cæsium atom. Taken at its face value, this indicated a vibration too complicated to be represented by a centrosymmetric ellipsoid. We think a more realistic explanation is that our intensity values had errors, probably due to inadequate allowance for absorption.

The single hydrogen atom was included in structure-factor calculations, with $x = y = z = 0$, and $B = 3{\cdot}8$ Å.[2] Table 7 includes observed structure amplitudes and calculated structure-factors for the terms used in the analysis. The final parameters are included in Tables 8 and 9.

TABLE 8

Cæsium hydrogen di-trifluoroacetate: fractional (x, y, z, $\times 10^5$) and orthogonal (X', Y, Z', Å, $\times 10^3$) co-ordinates. (The quantities in parentheses are the estimated standard deviations; Y and Z' are, respectively, parallel to y and z, whilst X' is perpendicular to both. For the numbering of atoms see Figure 2.)

Atom	x	y	z	X'	Y	Z'
Cs	−25,000	21,704	00,000	−3140	1092(1)	−1318
F(1)	−01,397	59,125	15,638	−176(11)	2976(17)	2379(11)
F(2)	11,625	38,021	26,241	1460(16)	1914(20)	3255(11)
F(3)	14,726	70,498	18,430	1850(21)	3548(17)	1940(18)
O(1)	16,498	28,404	8000	2073(15)	1430(14)	309(18)
O(2)	−479	17,766	5131	−60(14)	894(19)	782(15)
C(1)	8426	50,222	17,385	1059(20)	2528(21)	2118(15)
C(2)	8574	30,548	9601	1077(21)	1537(22)	963(20)
H	00,000	00,000	00,000	—	—	—

TABLE 9

Cæsium hydrogen di-trifluoroacetate: vibrational parameters (Å², $\times 10^4$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{31}	Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{31}
Cs	433	623	671			254	O(1)	476	877	925	51	−37	302
F(1)	854	999	878	122	−150	382	O(2)	481	1114	752	−66	−221	165
F(2)	1204	1244	503	−5	138	182	C(1)	819	752	451	−54	56	166
F(3)	1162	1167	995	−402	−368	371	C(2)	569	794	639	−36	41	50

The numbering of atoms is explained in Figure 2. Apart from the S.C.U., other units are denoted as follows:

S.C.U.	x	y	z
I	$-x$	$\frac{1}{2} - y$	$\frac{1}{2} - z$
II	$-\frac{1}{2} + x$	$1 - y$	z
III	$-\frac{1}{2} + x$	$-y$	z
IV	$-x$	$-y$	$-z$
V	$\frac{1}{2} - x$	y	$-z$
VI	$-\frac{1}{2} + x$	$\frac{1}{2} - y$	$-\frac{1}{2} + z$
VII	$-x$	$1 - y$	$-z$
VIII	$-x$	$1\frac{1}{2} - y$	$\frac{1}{2} - z$

RESULTS AND DISCUSSION

The more important interatomic distances and angles are given in Tables 10 and 11. For the potassium salt averaged standard deviations are as follows: C–C 0·007, C–O 0·006, C–F 0·006, K · · · O/F 0·004, O · · · H · · · O 0·007 Å; angles ~0·4°. For the cæsium salt they are: C–C 0·028, C–O 0·026, C–F 0·025. Cs · · · O 0·016, O · · · H · · · O 0·032 Å; angles ~1·8°.

Though different, the structures of the potassium (or rubidium) and cæsium salts both belong to type *A*: the two acid residues of the formulæ are crystallographically equivalent,

TABLE 10

Potassium hydrogen di-trifluoroacetate: interatomic distances (Å) and bond-angles

C(2)–O(1)	1·212	O(2) · · O(2$^{\text{IV}}$)	2·435
C(2)–O(2)	1·268		
C(1)–C(2)	1·515	K$^+$ · · · O(2$^{\text{II}}$)/O(2$^{\text{IV}}$)	2·840
C(1)–F(1)	1·341	K$^+$ · · · O(1)/O(1$^{\text{VII}}$)	2·850
C(1)–F(2)	1·310	K$^+$ · · · F(3$^{\text{III}}$)/F(3$^{\text{VIII}}$)	2·962
C(1)–F(3)	1·348	K$^+$ · · · O1($^{\text{VI}}$)/O(1$^{\text{V}}$)	2·966
O(1)–C(2)–O(2)	128·4°	C(2)–O(2) · · · H · · · O(2$^{\text{IV}}$)	115·6°
O(1)–C(2)–C(1)	120·1		
O(2)–C(2)–C(1)	111·6	F(3$^{\text{III}}$) · · · K$^+$ · · · F(3$^{\text{VIII}}$)	61·2
F(1)–C(1)–C(2)	111·7	O(1$^{\text{VI}}$) · · · K$^+$ · · · O(1$^{\text{V}}$)	131·1
F(2)–C(1)–C(2)	113·0	O(1) · · · · K$^+$ · · · O(1$^{\text{VII}}$)	156·0
F(3)–C(1)–C(2)	110·9	O(2$^{\text{II}}$) · · · K$^+$ · · · O(2$^{\text{IV}}$)	73·5
F(1)–C(1)–F(2)	107·7		
F(2)–C(1)–F(3)	107·1		
F(1)–C(1)–F(3)	106·3		

TABLE 11

Cæsium hydrogen di-trifluoroacetate: interatomic distances (Å) and bond-angles

C(2)–C(1)	1·52	O(2) ·· O(2^{IV})	2·38
C(2)–O(1)	1·20		
C(2)–O(2)	1·32	Cs^+ ··· O(2)/O(2^{V})	3·13
C(1)–F(1)	1·34	Cs^+ ··· O(1^{II})/O(1^{VII})	3·18
C(1)–F(2)	1·35	Cs^+ ··· O(1^{III})/O(1^{IV})	3·19
C(1)–F(3)	1·30		
O(1)–C(2)–O(2)	127°	F(1)–C(1)–F(2)	105°
C(1)–C(2)–O(1)	119	F(2)–C(1)–F(3)	107
C(1)–C(2)–O(2)	114	F(3)–C(1)–F(1)	109
C(2)–C(1)–F(1)	112	C(2)–O(2) ··· O(2^{IV})	114·5
C(2)–C(1)–F(2)	110	O(1^{II}) ··· Cs^+ ··· O(1^{III})	105
C(2)–C(1)–F(3)	113·5	O(1^{III}) ·· Cs^+ ··· O(1^{IV})	75

and joined by a short hydrogen bond lying across a centre of inversion. The cæsium salt has exactly the structural scheme found in most of the acid salts of the aromatic acids so far studied [6]—a scheme symbolised in Figure 3(a). It can be likened to a sandwich: layers of cations (M^+) or acidic hydrogen atoms, lying in the (002)-planes in this example, have a layer of carboxylate residues ($RCO_2^{-\frac{1}{2}}$) on either side. The carboxyl groups are directed inwards, so that their oxygen atoms are either co-ordinated to the metal ions or linked by the hydrogens. The *R*-groups face outwards and make only van der Waals contacts with the next sandwich. There is, to be sure, one noteworthy approach between a cæsium ion ion and a fluorine atom belonging to the next sandwich; but, as will be described later, this is longer than any of the six Cs^+ ··· O contacts that appear to constitute the significant environment of the ion. This cæsium salt has a short *b*-axis of about 5 Å, and the cationic (002) planes are about 7 Å apart.

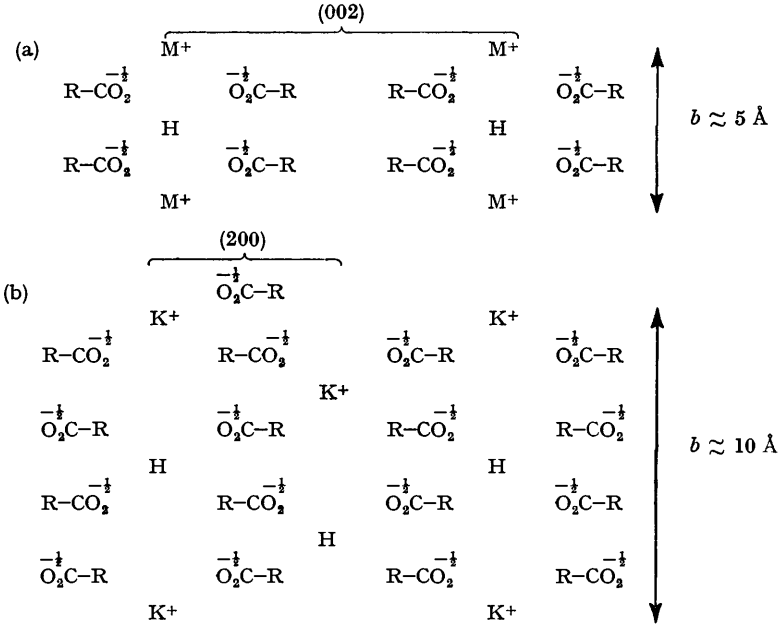

FIGURE 3. Schematic diagram illustrating the layer structures of (a) several acid salts of aromatic acids, and (b) acid potassium trifluoroacetate

In the potassium salt the *b*-axis is about twice as long, but the cationic planes, (200) in this case, only about 4 Å apart. This changed situation is formally represented in

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[6] *E.g.*, J. M. Skinner, G. M. D. Stewart, and J. C. Speakman, *J.*, 1954, 180.

Figure 3(b), and it can be related to a close contact between the potassium ion and a fluorine atom of the neighbouring sandwich, with $K^+ \cdots F(3^{VIII}) = 2{\cdot}962$ Å. We may surmise that the intenser field of this smaller cation attracts the fluorine, and that the consequent mutual inter-penetration forces the RCO_2-groups of any one sandwich further apart.

We have made no corrections for the effects of torsional vibration of the trifluoroacetate groups. With the cæsium salt, the thermal parameters were quite large, but the limited accuracy of our analysis made it unlikely that any such corrections would be significant. In any case, the application of vibrational corrections is difficult with molecules that are clamped by relatively stronger forces at one end. The analysis of the potassium salt was more highly refined, but the same difficulty obtains. Moreover, the anisotropic vibrational parameters of the three fluorine atoms, given in Table 5, suggest the presence of intramolecular libration of the trifluoroacetate group about the C–C bond; the vibrational ellipsoids of these atoms have their greatest diameters roughly tangential to the circle passing through the fluorine atoms.

We are indebted to Professor D. W. J. Cruickshank for the following discussion of the torsional vibration within the trifluoroacetate residue. Loos [7] has measured the torsional frequency of the CF_3COF molecule—presumably in the gaseous state—and found it to be 50 cm.$^{-1}$. The $CF_3CO_2^-$ ion is ioselectronic. If it has the same frequency when isolated, this can be shown to correspond to a root-mean-square amplitude of about 6° for the CF_3-group against one, with opposite phase, of about 16° for the CO_2-group, at room temperature. However, the ion is not isolated; in the crystal, its oxygen atoms are bonded to their environment. If the carboxyl group is assumed to be rigidly clamped by that bonding, the torsional frequency of the CF_3-group is diminished, and its root-mean-square amplitude increased, by a factor of about 3. An amplitude of some 16° is thus estimated for the CF_3-group, and this corresponds to a contribution or about 0·16 Å to the mean-square U_{ij}. The experimentally determined values of U_{ij} are all much below 0·16 Å^2 in fact. If then we guess the torsional contribution to be roughly 0·016 Å^2, corresponding to a 6° intramolecular libration, the C–F distances reported in Table 10 would need increasing by 0·006 Å.

The hydrogen bonds in both acid salts are formally symmetrical and very short. The $C(2)–O(2) \cdots O(2)$ angle in each compound is about 115°, and favourable for strong bonding. Lying in crystallographically special environments, these hydrogen bonds have the standard deviations of their lengths enhanced. So the $O \cdots O = 2{\cdot}38$ Å in the cæsium salt has to be qualified by $\pm 0{\cdot}032$; but the $2{\cdot}435 \pm 0{\cdot}007$ Å in the potassium salt ranks with $2{\cdot}437 \pm 0{\cdot}004$ Å in potassium hydrogen maleate [8] and with $2{\cdot}433 \pm 0{\cdot}010$ Å in sodium hydrogen diacetate [9] (after correction [10]) as amongst the shortest hydrogen bonds, between carboxylic oxygen atoms, to have been measured with any accuracy. [According to a personal communication from Dr. Levy, he finds $O \cdots O = 2{\cdot}41$ Å within the chloromaleate anion, with an uncertainty of 0·01 Å. This ion lacks the crystallographic M-symmetry of the maleate anion.] A hydrogen bond between two phosphate groups has been found [11] to have $O \cdots O = 2{\cdot}398$ Å, but the standard deviation is $\pm 0{\cdot}018$.

The carboxyl groups in type *A* acid salts are intermediate in character between carboxylate anion and neutral carboxyl. The difference of 0·06 Å between the C–O distances in potassium hydrogen di-trifluoroacetate is in line with differences of 0·05 Å in sodium hydrogen diacetate and in potassium hydrogen maleate. The difference found in the cæsium salt is 0·12 Å, but this may not be significantly higher.

In both acid trifluoroacetates one C–F distance is shorter than the other two; whilst

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[7] K. R. Loos, S.M. Thesis, 1963 (M.I.T., Research in Materials, AnnualReport, 1963—1964).

[8] S. F. Darlow and W. Cochran, *Acta Cryst.*, 1961, **14**, 1250.

[9] J. C. Speakman and H. H. Mills, *J.*, 1961, 1164.

[10] H. H. Mills and J. C. Speakman, *J.*, 1963, footnote on p. 4360.

[11] M. Calleri and J. C. Speakman, *Acta Cryst.*, 1964, **17**, 1097.

the effect is not significant in the cæsium salt, the differences of 0·038 and 0·031, each ±0·0085 Å, in the potassium salt are significant at the 0·01% level or less. The fluorine atom concerned is F(2), which makes a van der Waals contact of 2·828 Å across a centre of inversion with another F(2) atom. The C–C–F angle to F(2) is greater than those to the other two fluorines. These other C–F distances agree well with the mean value of 1·346 ±0·005 Å found in ammonium trifluoroacetate.[12] In this neutral salt, as well as in the two acid salts here studied, the C–C–F angles average 112°, against 107° for the F–C–F angles.

The five atoms O(1), O(2), C(1), C(2), and F(1) of the acid residue in the potassium salt are coplanar: only one of them, C(2), lies as much as 0·006 Å from the mean plane, $0{\cdot}4405X' - 0{\cdot}7028Y + 0{\cdot}5585Z' = 0{\cdot}5386$ (Å). This planarity seems to be without structural significance, since it does not occur in the cæsium salt, nor in ammonium trifluoroacetate.

The environment of the cæsium ion, which lies on a two-fold axis, is similar to that found in many type *A* acid salts. There are six oxygen atoms of different acid residues, all at distances in the range 3·13—3·19 Å. Two pairs of O(1) atoms, related by the *b*-translation, form a 4 × 5 Å^2 rectangle with the Cs$^+$ very near its centre. Two O(2) atoms then complete a very skew octahedron. This skew arrangement is perhaps ameliorated by the presence of two fluorine atoms, F(2$^{\mathrm{I}}$) and F(2$^{\mathrm{VI}}$), at a distance of 3·30 Å. The environment of the potassium ion is more complicated, though it also lies on a digonal axis; it is shown in Figure 4. Moving in the *b*-direction we first find a pair of F(3) atoms at a *y*-level 2·55 Å below K$^+$; next, 1·23 Å below K$^+$, we come to a pair of O(1) atoms, in a line roughly at right-angles to the F · · · F line; 0·59 Å above the ion is another pair of O(1) atoms, roughly parallel to F · · · F; finally, 2·27 Å above the ion is a pair of O(2) atoms, roughly at right-angles to F · · · F. These eight atoms belong to eight different acid groups.

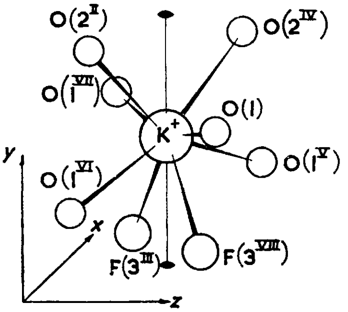

FIGURE 4. The environment of the potassium ion in the acid trifluoroacetate

The shortest non-bonded contact in the potassium salt is the F(2$^{\mathrm{I}}$) · · · F(2$^{\mathrm{VI}}$) already mentioned. In the cæsium salt, F(1) lies 3·08 Å from F(1$^{\mathrm{VIII}}$), related to it by the centre of inversion at $0\frac{3}{4}\frac{1}{4}$ and 3·21 Å from F(2$^{\mathrm{I}}$). These distances are distinctly greater than double the conventional van der Waals radius of fluorine (1·35 Å); the structure is surprisingly open in this region.

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[12] D. W. J. Cruickshank, D. W. Jones, and G. Walker, *J.*, 1964, 1303.