attributed to a strong *trans* effect, which has already been observed in this type of compound (Rieskamp & Mattes, 1976).

Ammonium ions bind the anionic chains together with the contact distances given in Table 2. Each ammonium ion is coordinated by eight F and two O atoms.

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Structure of and Hydrogen Bonding in Dicaesium Aquapentachloroferrate(III)

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Abstract. $Cs_2[FeCl_5(H_2O)]$, orthorhombic, *Cmcm*, $a = 7.426$ (4), $b = 17.306$ (7), $c = 8.064$ (2) Å, $Z = 4$, $D_x = 3.301$ Mg m^{-3}. 539 observed reflections at $T = 243$ K using Mo $K\alpha$ radiation were used to refine the structure to $R_w = 0.027$. H atoms were located and their positions refined. The compound is isostructural with $Cs_2[RuCl_5(H_2O)]$.

Introduction. During attempts to prepare crystals of $Cs_2Na[FeCl_6]$ by slow evaporation of a $2M$ HCl solution of NaCl, CsCl, and $FeCl_3.6H_2O$ in appropriate amounts (Morss, Siegal, Stenger & Edelstein, 1970), we noted the presence of three crystalline phases: colourless cubes of NaCl, small (~1 mm) orange octahedra of $Cs_2Na[FeCl_6]$, and large (several mm) red-orange acicular crystals of a hitherto unknown composition. These acicular crystals were found to contain Cs, Cl and Fe but no Na by emission spectrographic analysis. Subsequently, Cl was determined by Mohr titration, Fe by atomic absorption, and Cs by neutron activation analysis, giving Cl 35.0, Fe 10.0 and Cs 53.2% compared to expected values for $Cs_2[FeCl_5(H_2O)]$ of Cl 34.28, Fe 10.80, Cs 51.37%. Water was detected from characteristic bands in the infrared spectrum of powdered crystals.

Precession photographs showed orthorhombic symmetry with systematic absences *hkl*: $h + k = 2n + 1$; *h0l*: $l = 2n + 1$ suggesting space groups *Cmcm*, *C2cm* or *Cmc2*. Structure refinement confirms the

choice of *Cmcm*. An acicular crystal elongated along [010] of approximately cylindrical cross section and dimensions 0.125 mm in diameter × 1 mm in length was chosen for diffraction measurements on a Syntex $P2_1$ diffractometer. The crystal was cooled to 243 K in a stream of nitrogen in order to obtain accurate parameters. Cell dimensions were obtained by least-squares refinement of 15 well centred reflections with $2\theta > 20°$ using monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). The intensities of 1330 reflections with $0 \leq h \leq 9, 0 \leq k \leq 22, 0 \geq l \geq -10$ were measured using a $\theta/2\theta$ scan mode. Two standard reflections (131 and 042) measured at regular intervals showed no significant variation. Equivalent reflections were averaged to give 669 unique reflections. Of these, 539 had $I > 3\sigma(I)$ and were classed as observed. Intensities were corrected for Lorentz and polarization effects. Absorption corrections were not considered necessary ($\mu R = 0.52$ for the cylinder; maximum transmission coefficient = 0.45, minimum = 0.37).

The structure was assumed to be similar to $Cs_2[RuCl_5(H_2O)]$ (Hopkins, Zalkin, Templeton & Adamson, 1966) which has the same space group and similar lattice constants: $a = 7.400$ (4), $b = 17.289$ (8), $c = 7.986$ (5) Å. Least-squares refinement of positional and anisotropic temperature parameters of the non-hydrogen atoms and a secondary-extinction coefficient (Larson, 1967) resulted in $R_1 = \sum(||F_o| - k|F_c||)/ \sum |F_o| = 0.023$. Atomic scattering factors, corrected

Table 1. *Fractional atomic coordinates* ($\times 10^4$, $\times 10^3$ *for* H) *with e.s.d.'s and average temperature factors* (Å^2)

	x	y	z	$\langle U_{ii} \rangle$
Cs(1)	0	4711·1 (3)	2500	0·0234 (3)
Cs(2)	0	7548·5 (3)	2500	0·0268 (3)
Fe	0	1218·1 (6)	2500	0·0150 (5)
Cl(1)	0	2540 (1)	2500	0·0259 (10)
Cl(2)	2242 (1)	1115·6 (6)	4596 (1)	0·0264 (4)
O	0	9961 (4)	2500	0·029 (3)
H	0	966 (7)	170 (10)	0·102

for anomalous dispersion, were taken from Cromer & Waber (1974). The H atoms were then located from a difference Fourier synthesis. The positions found are close to those suggested for $Cs_2[RuCl_5(H_2O)]$ (Hopkins, Zalkin, Templeton & Adamson, 1966). Final refinement including the positional and isotropic temperature factors for the H atoms gave the atomic parameters listed in Table 1, with $R_1 = 0 \cdot 021$ and $R_w = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2} = 0 \cdot 027$, where $w = [\sigma^2 + 0 \cdot 0250 F_o)^2]^{-1}$ with σ being the standard error in F_o derived from counting statistics.* The average shift on the final cycle of refinement for all non-hydrogen atoms was 21% of the standard error. All refinements were performed with the local program *CUDLS* (Stephens, 1971).

Discussion. After the completion of our work we became aware of an independent determination of the structure by O'Connor, Deaver & Sinn (1979). The two determinations are in basic agreement although O'Connor *et al.* did not report the positions of the H atoms and their reported standard errors are four to five times larger than ours. The temperature factors in the two determinations, however, show systematic differences. The value of $\Delta = \langle U_a - U_b \rangle$ (where a refers to our results, b to those of O'Connor *et al.* and the average is performed over values for Cs, Fe and Cl) is $+0 \cdot 0059$ for U_{11}, $-0 \cdot 0008$ for U_{22} and $+0 \cdot 0023 \text{ Å}^2$ for U_{33}. Since we worked at low temperatures one would expect Δ to be negative and our neglect of absorption corrections should make Δ_{11} and Δ_{33} slightly more negative ($\lesssim 0 \cdot 0007$) and Δ_{22} more positive ($\lesssim 0 \cdot 0050 \text{ Å}^2$). Since the discrepancy in all cases is in the opposite sense the reason for it must be sought in the results of O'Connor *et al.* Their crystal was an (010) plate about 0·5 mm across and 0·1 mm thick and their transmission coefficients ranged from 0·45 to 0·05. They imply that absorption corrections were made but because of the shape and size of their crystal an error of

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35270 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances* (Å) *and angles* (°)

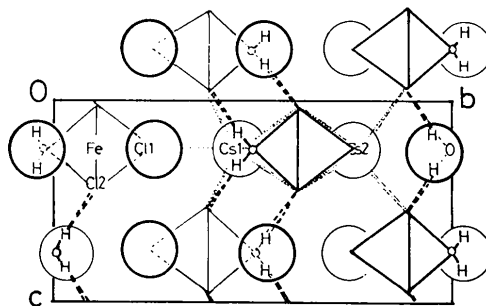|			
Cs(1)–Cl(2)	3·424 (1) × 4	Cs(2)–Cl(2)	3·633 (1) × 4
Cs(1)–Cl(2)	3·600 (1) × 4	Cs(2)–Cl(2)	3·688 (1) × 4
Cs(1)–O	3·738 (2) × 4	Cs(2)–Cl(1)	3·713 (2) × 4
Cs(1)–Cl(1)	3·757 (2)	Cl(2)–Cl(2)	3·380 (1)
Fe–Cl(2)	2·379 (1) × 4	Cl(2)–Cl(2)	3·330 (2)
Fe–Cl(1)	2·288 (2)	Cl(2)–O	3·102 (5)
Fe–O	2·176 (7)	Cl(2)–Cl(1)	3·421 (2)
O–H	0·83 (10)		
H–Cl(2)	2·73 (8) × 2		
H–Cl(2)'	3·20 (10) × 2		
Cl(2)–Fe–Cl(1)	94·3 (1)	H–O–H	102·2 (10)
Cl(2)–Fe–O	85·7 (1)	O–H–Cl(2)*	142·4 (4)
Cl(2)–Fe–Cl(2)	88·9 (1)	O–H–Cl(2)'	76·1 (73)
Cl(2)–Fe–Cl(2)	90·5 (1)		

* Hydrogen bond.

Fig. 1. The structure of $Cs_2[FeCl_5(H_2O)]$ viewed down the a axis. The large circles are Cs. The $[FeCl_5(H_2O)]^{2-}$ ions are shown as octahedra with the O indicated by a small circle. Hydrogen bonds are shown by dashed lines, Cs–Cl bonds by dotted lines. The atoms whose coordinates are given in Table 1 are labelled.

about 10% in its dimensions would give rise to discrepancies of the size observed. When allowance is made for the systematic differences in the temperature factor a δp half-normal-probability plot (Abrahams & Keve, 1971) shows that $\sigma [= (\sigma_A^2 + \sigma_B^2)^{1/2}]$ has been underestimated by a factor of 2. Since σ is determined largely by the larger standard errors of O'Connor *et al.* it is not clear to what extent (if at all) our standard errors have been underestimated. The differences for $Cs(1)y$ ($\delta/\sigma = +5 \cdot 0$) and $Cs(1)U_{33}$ ($\delta/\sigma = +4 \cdot 1$) are significantly greater than those expected for a normal distribution. We conclude that our results are more precise and more reliable than those of O'Connor *et al.* but that systematic errors in our work make the temperature factors uncertain by about $0 \cdot 0050 \text{ Å}^2$.

Bond lengths and angles derived from Table 1 are listed in Table 2 and the structure is illustrated in Fig. 1. The structure contains octahedral $[FeCl_5(H_2O)]^{2-}$ ions bonded together into layers perpendicular to **b** by the bifurcated O–H$\cdots$Cl hydrogen bonds and most of the Cs–Cl and Cs–O bonds. The Fe–Cl and Fe–O bond lengths are significantly longer than the corresponding Ru–Cl and Ru–O bond lengths in $Cs_2[RuCl_5(H_2O)]$

This is probably related to the spin states of the ions. Mössbauer measurements performed here on $Cs_2[FeCl_5(H_2O)]$ indicate the high-spin state for Fe^{III} ($3d^5$) while susceptibility measurements (Buschbeck & Hartmann, 1957) confirm a low-spin state for Ru^{III} ($4d^5$) in $Cs_2[RuCl_5(H_2O)]$.

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