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The Crystal Structure of Ammonium Heptafluorocerate(IV) Monohydrate; Hydrogen Bonding to the Dimer $Ce_2F_{14}^{6-}$*

By R. R. Ryan and R. A. Penneman

Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico 87544, *U.S.A.*

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The crystal structure of ammonium heptafluorocerate(IV) monohydrate, $(NH_4)_3CeF_7.H_2O$, has been determined from counter measurements of 1029 reflections and refined by full-matrix least-squares methods to an unweighted R value of 0·018. The space group is $P2_1/n$ with unit-cell dimensions of $a=$ 11·064 (2), $b=12·104$ (2), $c=7·134$ (1) Å, and $\beta=95·704$ (8)°. Observed and calculated densities are ($Z=4$) $D_x=2·41$, $D_m=2·38$ g.cm^{-3}. Cerium is 8-coordinated in dimeric $Ce_2F_{14}^{6-}$ units. The fluorine coordination polyhedron about the Ce atom can best be described as a dodecahedron with triangular faces. All hydrogen atoms have been located and are in positions reasonable for bonding to oxygen and fluorine in the structure.

Introduction

Monoclinic $(NH_4)_4CeF_8$, space group $C2/c$, is formed in the CeF_4–NH_4F–H_2O system at NH_4F concentrations greater than 28·9% by weight. At slightly lower NH_4F concentrations (24 to 28·9% by wt.), a monohydrate of composition $(NH_4)_3CeF_7.H_2O$ occurs. This phase is also monoclinic, space group $P2_1/n$, and is unstable (on loss of hydrate water) with respect to $(NH_4)_2CeF_6$ and $(NH_4)_4CeF_8$ (Penneman & Rosenzweig, 1969). In both of these latter compounds, the cerium is 8-coordinated; in $(NH_4)_2CeF_6$, chains of antiprisms are found (Ryan, Larson & Kruse, 1969), while in $(NH_4)_4CeF_8$ isolated MF_8^{4-} antiprisms exist (Rosenzweig & Cromer, 1970). Thus, $(NH_4)_3CeF_7.H_2O$ could retain 8-coordination, with H_2O occupying a position in the coordination sphere. Compounds having a 3:1 mole ratio of alkali metal fluoride to actinide tetrafluoride are common but are rare for NH_4F. Thus, the structure of $(NH_4)_3CeF_7.H_2O$ is interesting since it is one of the few having a 3:1 NH_4F:MF_4 mole ratio, and it is a hydrate.

Experimental

Crystals of $2/m$ symmetry, with chemical analysis corresponding to $(NH_4)_3CeF_7.H_2O$, were obtained from a 26% NH_4F solution which had been saturated with CeF_4 at slightly above room temperature, filtered, and allowed to cool. Developed faces were of the prisms {011} and {110}. A crystal was selected, mounted near the c axis, and was coated with Fluorolube (Hooker Chemical Corp.) to arrest an apparent slow loss of hydrate water. Maximum distances between plane intersections were $180\times180\times250$ μ.

Precession photographs taken with Mo $K\alpha$ radiation showed monoclinic symmetry with the following systematic absences: $0k0$ reflections, k odd, $h0l$ reflections, $h+l$ odd. Thus, the space group is uniquely $P2_1/n$. Cell constants at room temperature were obtained by least-squares fitting of the angles of 10 high-order reflections measured on an automatic Picker diffractometer using Mo $K\alpha_1$ radiation ($\lambda=0·70930$ Å); parameters are: $a=$ 11·064 (2), $b=12·104$ (2), $c=7·134$ (1) Å, $\beta=95·704$ (8)°, where the numbers in parentheses are the least-squares errors. For $Z=4$, $D_x=2·41$ g.cm^{-3}. Experimental density, as measured by flotation methods, was 2·38 g.cm^{-3}.

Intensity measurements were made on hkl and $hk\bar{l}$ planes using a Picker, computer-controlled four-circle diffractometer similar to the one described by Busing, Ellison, Levy, King & Roseberry (1967). Zr-filtered Mo $K\alpha$ radiation, θ–2θ scan, bisecting positions, and a take-off angle of 5° were used to collect data on all reflections for which $2\theta\le45°$. The scan was taken over a 2°–2θ range in steps of 0·05° with a two-second count time at each step. Background was counted for 20 seconds at each end of the scan.

The intensity of a standard reflection, sampled after every 25 reflections, was found to decrease continuously during the roughly 50 hours required for data collection. At the end of the data collection process it was about 50% of its original value. The crystal was checked periodically for orientation and centering. Reduction in intensity was probably due, primarily, to crystal damage from the X-rays, since a control crystal mounted and coated in the same way as the data crystal showed no signs of decomposition over the same period of time. Multiplicative correction factors for the data were derived from a least-squares fit of a sixth-order polynomial (of intensity *vs.* time) to the standard spot ($hkl=10, 0, 0$). The order of the polynomial was determined from significance tests based on the residual error. Of the 1029 reflections measured, 921 were judged to be observed according to the criterion $I_m=f(t)\,(T-$

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$KB) \geq 3\sigma(I_m)$, where $\sigma(I_m) = [f^2(t)\{(T+KB+\sigma_s^2(T-KB)^2\}]^{\frac{1}{2}}$, T is the total count, KB is the normalized background, $f(t)$ is the time dependent correction factor. The quantity σ_s^2 is the percentage variance of the standard reflection after correction by the least-squares polynominal, minus the percentage variance expected on the basis of counting statistics; this was $2{\cdot}2 \times 10^{-4}$ for the structure.

Absorption corrections were made by the Busing & Levy (1957) method using Burnham's (1962) program modified for the appropriate geometry (Larson, Cromer & Roof, 1964). The linear absorption coefficient is 49·3 cm^{-1}, and the calculated transmission factors vary from 0·603 to 0·558.

Structure determination and refinement

A three-dimensional Patterson function revealed the Ce position to be $x \simeq 0{\cdot}60$, $y \simeq 0{\cdot}36$, $z \simeq 0{\cdot}52$. After least-squares refinement of the Ce position and its isotropic temperature factor, the crystallographic R value ($R = \sum ||F_o| - |F_c^*|| / \sum |F_o|$) was 0·24. A difference Fourier map clearly showed the positions of all light atoms except hydrogen. Positions and temperature factors were refined initially using fluorine scattering factors. Of the 11 independent nonhydrogen light atoms, 7 were now assumed to be fluorine, based on their temperature factors and/or proximity to the Ce position. Of the remaining four light atoms, one was assumed to be oxygen, based on the distance and angles to nearby atoms; the other three were then assigned as nitrogen atoms. A difference Fourier map, phased on the resulting model, showed all the hydrogen positions.

A full-matrix least-squares refinement of all positions and nonhydrogen temperature factors was carried out. The quantity minimized was $\sum w(|F_o| - |F_c^*|)^2$ where w is $1/\sigma^2\ (F_o)$ (Evans, 1961) and

$$F_c^* = KF_c / \left\{ 1 + g\,\mathrm{Lp}\left[\frac{2(1+\cos^4 2\theta)}{(1+\cos^2 2\theta)^2}\right] F_c^2 \right\}^{\frac{1}{2}}$$

in which K = scale constant, g = extinction factor (Zachariasen, 1963; Larson, 1967), Lp = Lorentz-polarization factor, and F_c = structure factor calculated in the usual way. Scattering factors given in *International Tables for X-ray Crystallography* (1962) were used for the light (non-hydrogen) atoms, and Cromer & Waber's (1965) scattering factors were used for cerium. Cromer's (1965) anomalous dispersion terms were used for cerium ($\Delta f' = -0{\cdot}42$, $\Delta f'' = 3{\cdot}04$). Hydrogen scattering factors were those of Stewart, Davidson & Simpson (1965).

The final unweighted R value with all nonhydrogen temperature factors anisotropic is 0·018 (hydrogen temperature factors were held fixed at 3·0). The R value with the hydrogen atoms removed from the model was 0·026. The hypothesis that the hydrogen atoms do not contribute to the intensities can be rejected at the 0·005 confidence level (Hamilton, 1965). Root-mean-square variance of an observation of unit weight is 1·33.

Observed and calculated structure factors are listed in Table 1. Final parameters are listed in Table 2, and selected distances and angles are listed in Table 3. A final difference Fourier map showed peaks of *ca.* ±0·4 e.Å^{-3} in the vicinity of the Ce atom; the maximum electron density elsewhere was 0·2 e.Å^{-3} with $\sigma(\varrho) = 0{\cdot}1$ e.Å^{-3} (Cruickshank, 1949, 1950, 1954).

Table 1. *Observed and calculated structure factors*

Column headings are *l*, F_o/K and $|F_c^*/K|$.

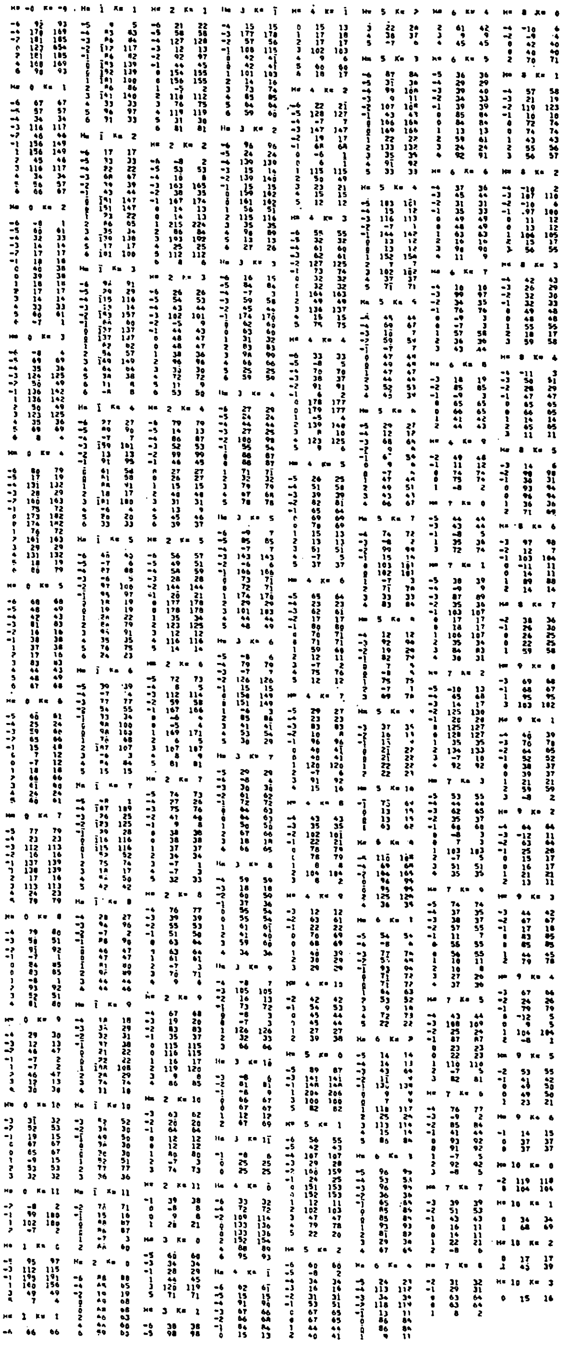

Table 2. *Fractional coordinates and anisotropic temperature factors with their respective least-squares errors*

Anisotropic temperature factors are defined by exp $[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$

	x	y	z	β_{11}	β_{22}	β_{23}	β_{12}	β_{13}	β_{23}
Ce	0·60388 (3)	0·36477 (2)	0·51868 (4)	26·5 (0·5)	23·5 (0·4)	71·9 (1·1)	4·9 (0·5)	7·8 (0·8)	−0·1 (0·6)
F(1)	0·4459 (2)	0·4698 (2)	0·6346 (4)	53 (3)	36 (2)	117 (7)	29 (4)	18 (8)	55 (7)
F(2)	0·7834 (3)	0·4429 (2)	0·4753 (4)	32 (3)	53 (3)	128 (7)	−16 (4)	−8 (8)	−7 (7)
F(3)	0·6792 (3)	0·4264 (3)	0·7943 (4)	55 (3)	69 (3)	105 (7)	−15 (5)	−16 (8)	−55 (8)
F(4)	0·6353 (3)	0·3365 (3)	0·2144 (4)	46 (3)	74 (3)	100 (7)	−6 (5)	25 (8)	−70 (7)
F(5)	0·4359 (3)	0·2955 (2)	0·3702 (4)	31 (3)	55 (3)	110 (7)	−16 (5)	−8 (8)	−25 (7)
F(6)	0·5189 (3)	0·2538 (2)	0·7244 (4)	53 (3)	38 (2)	127 (7)	−9 (5)	10 (8)	46 (7)
F(7)	0·7089 (3)	0·2167 (3)	0·5345 (5)	67 (4)	51 (3)	320 (11)	73 (5)	83 (11)	50 (9)
N(1)	0·2025 (5)	0·3287 (5)	0·4775 (8)	55 (7)	41 (4)	117 (15)	−23 (10)	26 (15)	−11 (13)
N(2)	0·8656 (5)	0·4179 (5)	0·1173 (8)	52 (7)	51 (5)	114 (13)	−4 (9)	34 (14)	2 (14)
N(3)	0·4113 (5)	0·3961 (5)	0·0040 (8)	45 (6)	51 (4)	76 (12)	−25 (8)	25 (13)	11 (13)
O	0·9848 (4)	0·4082 (5)	0·7215 (8)	66 (6)	54 (4)	276 (16)	−40 (9)	−91 (13)	55 (14)
H(1)	0·201 (5)	0·402 (5)	0·509 (7)						
H(2)	0·156 (6)	0·320 (5)	0·398 (9)						
H(3)	0·263 (6)	0·326 (5)	0·437 (9)						
H(4)	0·193 (5)	0·289 (4)	0·586 (8)						
H(5)	0·942 (6)	0·411 (7)	0·671 (11)		$g=2{\cdot}2\ (0{\cdot}6)\times10^{-7}$				
H(6)	0·962 (5)	0·342 (4)	0·762 (8)						
H(7)	0·814 (6)	0·406 (5)	0·194 (8)						
H(8)	0·906 (5)	0·469 (5)	0·150 (9)						
H(9)	0·840 (6)	0·420 (5)	0·000 (9)						
H(10)	0·921 (5)	0·355 (4)	0·137 (8)						
H(11)	0·386 (5)	0·464 (5)	0·079 (8)						
H(12)	0·420 (5)	0·414 (4)	0·886 (9)						
H(13)	0·467 (6)	0·372 (5)	0·066 (9)						
H(14)	0·358 (6)	0·343 (4)	0·003 (8)						

Table 3. *Pertinent interatomic distances and angles*

Ce—F(1)	2·375 (3) Å	N(2)—H(7)	0·84 (6) Å
Ce—F′(1)	2·322 (3)	N(2)—H(8)	0·79 (6)
Ce—F(2)	2·249 (3)	N(2)—H(9)	0·86 (6)
Ce—F(3)	2·189 (3)	N(2)—H(10)	0·98 (5)
Ce—F(4)	2·258 (3)		
Ce—F(5)	2·211 (3)	N(3)—H(11)	1·04 (6)
Ce—F(6)	2·262 (3)	N(3)—H(12)	0·89 (6)
Ce—F(7)	2·133 (3)	N(3)—H(13)	0·78 (6)
		N(3)—H(14)	0·87 (5)
F(1)—F′(1)	2·472 (6)		
F(1)—F(2)	2·788 (4)	O—H(5)	0·57 (7)
F(1)—F(3)	2·766 (4)	O—H(6)	0·89 (5)
F(1)—F(4)	2·768 (4)		
F(1)—F(5)	2·825 (4)	H(1)—N(1)–H(2)	107 (6)°
F(1)—F(6)	2·792 (4)	H(1)—N(1)–H(3)	100 (6)
		H(1)—N(1)–H(4)	107 (5)
F(2)—F(3)	2·658 (4)	H(2)—N(1)–H(3)	106 (8)
F(2)—F(4)	2·684 (4)	H(2)—N(1)–H(4)	117 (7)
F(2)—F(7)	2·904 (4)	H(3)—N(1)–H(4)	118 (6)
F(3)—F(6)	2·754 (4)	H(7)—N(2)–H(8)	110 (6)
		H(7)—N(2)–H(9)	117 (6)
F(4)—F(5)	2·614 (4)	H(7)—N(2)–H(10)	103 (5)
F(4)—F(7)	2·758 (4)	H(8)—N(2)–H(9)	113 (6)
		H(8)—N(2)–H(10)	103 (5)
F(5)—F(6)	2·650 (4)	H(9)—N(2)–H(10)	108 (6)
F(6)—F(7)	2·650 (5)	H(1)—N(3)–H(12)	111 (5)
		H(11)–N(3)–H(13)	104 (5)
N(1)—H(1)	0·92 (6)	H(11)–N(3)–H(14)	112 (5)
N(1)—H(2)	0·73 (6)	H(12)–N(3)–H(13)	118 (7)
N(1)—H(3)	0·75 (6)	H(12)–N(3)–H(14)	108 (5)
N(1)—H(4)	0·93 (5)	H(13)–N(3)–H(14)	104 (6)
H(1)—F(2)	1·88 (5)	H(5)—O—H(6)	91 (10)
H(2)—F(6)	2·06 (6)	H(5)—O—H(8)	131 (9)
H(3)—F(5)	2·05 (6)	H(6)—O—H(8)	132 (4)
H(4)—F(4)	1·91 (6)		
H(5)—F(2)	2·17 (7)		

Table 3 (*cont.*)

H(6)—F(5)	1·87 (5)	
H(7)—F(2)	2·12 (6)	
H(7)—F(4)	2·17 (7)	
H(8)—O	2·07 (6)	
H(9)—F(3)	2·19 (6)	
H(10)–F(6)	1·77 (6)	
H(11)–F(3)	1·80 (6)	
H(12)–F(1)	1·96 (6)	
H(13)–F(4)	2·09 (6)	
H(14)–F(7)	1·83 (6)	
N(1)—F(2)	2·786 (7)	
N(1)—F(4)	2·767 (7)	
N(1)—F(5)	2·795 (7)	
N(1)—F(6)	2·766 (7)	
N(2)—F(2)	2·812 (7)	Bifurcated: H(7)$\left\langle\begin{matrix}\text{F(2)}\\ \text{F(4)}\end{matrix}\right.$
N(2)—F(4)	2·880 (7)	
N(2)—F(3)	2·937 (6)	
N(2)—F(6)	2·743 (7)	
N(2)—O	2·849 (7)	
N(3)—F(1)	2·844 (6)	
N(3)—F(3)	2·825 (7)	
N(3)—F(4)	2·860 (6)	
N(3)—F(5)	2·870 (6)	No hydrogen bond
N(3)—F(7)	2·650 (6)	

Structure and discussion

Each cerium atom is surrounded by eight fluorine atoms to form a slightly distorted dodecahedron with triangular faces. Two dodecahedra are joined along an edge and are related by a center of symmetry to form a $[Ce_2F_{14}]^{6-}$ ion. This anion is shown in Fig. 1 with the fluorine atoms labeled as in Table 2. Dimeric structures are not unknown among the transition metal, lanthanide or actinide halides although few are known with fluorides, *e.g.*, UCl_5 (Smith, Johnson & Elison, 1967), $NbCl_5$ and $TaCl_5$ (Zalkin & Sands, 1958), $MoCl_5$ (Sands & Zalkin, 1959), $Cs_3Tl_2Cl_9$ (Hoard & Goldstein, 1935; Powell & Wells, 1935), $K_3W_2Cl_9$ (Watson & Waser, 1958), and $Na_5Zr_2F_{13}$ (Herak, Makic & Manojlovic, 1965). The present anion is unique among these dimers in metal atom (Ce) and coordination number (8).

Average angles between the twofold axis of the dodecahedron and the two kinds of metal-fluoride distances (Clark, Kepert, Nyholm & Lewis; Hoard & Silverton, 1963; Kepert, 1965) have been used to characterize the dodecahedron. The absence of such an axis in this compound precludes such a calculation. Instead, the angles these distance vectors make with the intersection of the least-squares plane through the two intersecting trapezoids were calculated (see Fig. 2). These angles are $\theta_A = 35°54'$ and $\theta_B = 75°56'$, where θ_A and θ_B refer to the angles that distances of types *A* and *B*, respectively, make with the intersection of the planes (see Hoard & Silverton, 1963). Another parameter of interest is the ratio of the metal–fluoride distance of type *A* to the distance of type *B*, which is 1·032 for this compound. These values for θ_A, θ_B, and CeF_A/CeF_B compare well with the 'most favorable' values (Hoard & Silverton, 1963) of $\theta_A = 35°18'$, $\theta_B = 73°30'$, and $(M-A)/(M-B) = 1{\cdot}03$.

It has been suggested that the angle between the two least-squares planes (containing the trapezoids in the case of the dodecahedron) be used as a criterion for distinguishing between the dodecahedron with triangular faces and the square antiprism (Lippard & Russ, 1968). This angle is 89°25' for this structure as compared to 77·4° for the square antiprism. Note, however, that an angle of 90° is not a sufficient condition for the ideal (D_{2d}) dodecahedron.

Table 3 shows the two Ce–F distances, Ce–F(1) and Ce–F′(1), are much longer than the average distance of 2·25 Å; also one distance, Ce–F(7), is much shorter than the average. Of the F–F contacts, F(1)–F′(1) is shorter than the average and all nearest-neighbor contacts with F(1) and F′(1) are longer than the average as are distances F(2)–F(7), F(3)–F(6), and F(4)–F(7). All these facts can be considered to be the result of a strong Ce–Ce repulsion with a concomitant attempt on the part of the fluorine atoms to maintain normal F–F contacts (Pauling, 1960). This interaction causes the longer Ce–F distances to bridging fluorine atoms [F(1) & F′(1)] with a resultant shortening of the F(1)–F′(1) contact. The short Ce–F(7) distance is a consequence of the displacement of the Ce atom from the center of the coordination polyhedron and the abovementioned attempt on the part of F(7) to maintain normal F–F contacts. The short Ce–F(7) distance cannot be 'explained' on the basis of temperature factor corrections, even assuming that the atoms concerned have highly correlated antiparallel thermal motion. All other F–F distances in the dodecahedron can also be seen to be consistent with a strongly ionic model.

Average H–N–H angles are reasonably close to the tetrahedral angle with averages for the three different nitrogen atoms being N(1), 109·2°; N(2), 109·0°; and N(3), 109·5°. The average N–H distance of 0·865 Å in the structure is somewhat shorter (*ca.* 0·15 Å) than that found for neutron diffraction results on structures containing this ion, a result which is not unexpected for X-ray studies (*e.g.*, Smith & Lipscomb, 1965). The structure of the water molecule is somewhat more questionable: the H–O–H angle of 91° and the O–H(5) distance of 0·57 Å are markedly smaller than the values determined in several neutron diffraction studies on crystalline hydrates (Hamilton & Ibers, 1968). The O–H angle and distances are probably greatly influenced by systematic errors; however, the hydrogen bonding for both OH---F and N–H---F appears to be physically reasonable, and the hydrogen positions are no doubt meaningful. A stereo view of the packing in the structure is given in Fig. 3.

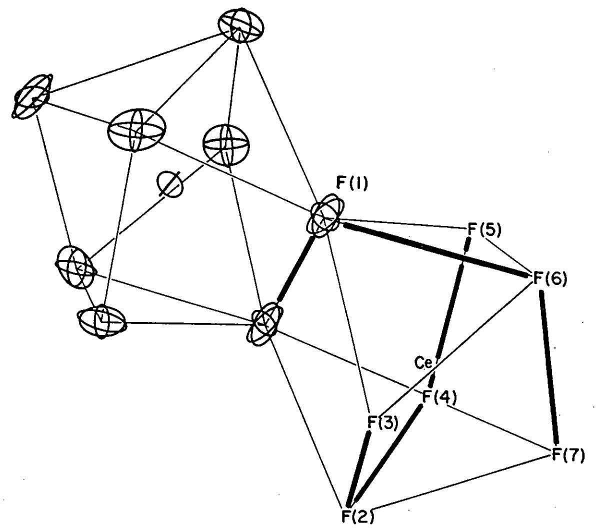

Fig. 1. Perspective view of the $Ce_2F_{14}^{6-}$ dimer. Heavy lines outline the two intersecting trapezoids.

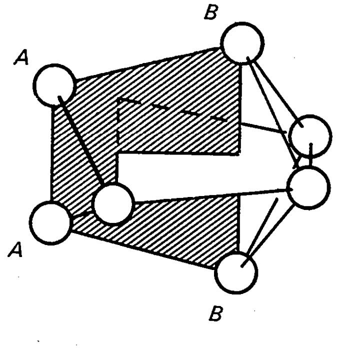

Fig. 2. Idealized polyhedron emphasizing trapezoidal planes. θA and θB, mentioned in the text, are the angles between the Ce atom and F atoms of type *A* and of type *B*, respectively.

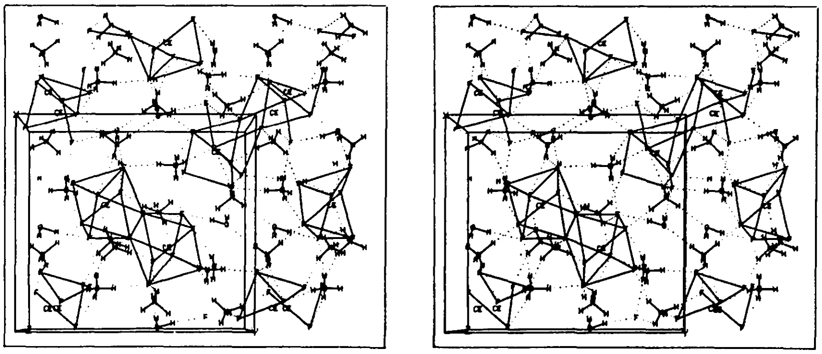

Fig. 3. Stereo view of the packing in the structure as seen looking down the *c* axis.

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