Fig. 1. Projection suivant c de quatre mailles cristallines de la structure du carbonate d'argent.
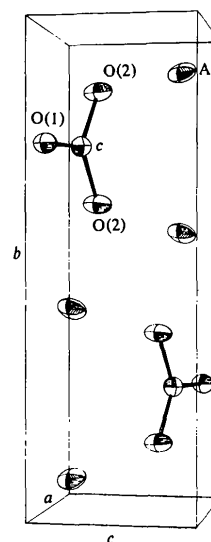
Tableau 2. *Distances interatomiques* (Å) *et angles des liaisons* (°)

Ag–O(1)	2,254 (7)	O(1)–Ag–O(2)	158,6 (2)
Ag–O(2)	2,239 (7)	O(1)–Ag–O(2)	83,7 (2)
Ag–O(2)	2,479 (7)	O(1)–Ag–O(2)	120,4 (2)
Ag–O(2)	2,697 (7)	O(2)–Ag–O(2)	90,7 (2)
Ag–Ag	2,907 (2)	O(2)–Ag–O(2)	78,1 (2)
Ag–Ag	3,124 (2)	O(2)–Ag–O(2)	77,8 (2)
Ag–Ag	3,284 (2)		
Ag–Ag	3,483 (2)		

Groupement CO_3^{2-}

C–O(1)	1,318 (16)	O(2)–O(1)	2,238 (11)
C–O(2)	1,272 (9)	O(2)–O(2)	2,211 (14)
O(1)–C–O(2)	119,6 (8)	O(2)–C–O(2)	120,8 (8)

Discussion. La structure du carbonate d'argent est représentée en projection suivant c sur la Fig. 1. Les triangles CO_3 forment avec les atomes d'argent des files parallèles aux cotes approximatives $z = \frac{1}{4}, \frac{3}{4}$. Les plans des triangles CO_3 aux cotes $\frac{1}{4}$ sont parallèles aux plans des triangles CO_3 aux cotes $\frac{3}{4}$ par symétrie. Ces plans font un angle de 22° environ avec le plan ab. Si π est un plan passant par la droite b et parallèle aux plans des triangles CO_3, on a $\pi/ab = 22°$.

Le groupement CO_3 forme un triangle presque équilatéral. L'atome d'argent a quatre voisins dont deux à une distance plus courte, mais ce voisinage tétraédrique est très déformé comme le montre les angles $\angle O(i)$–Ag–$O(i)$ (Tableau 2). L'ensemble des atomes

Fig. 2. Perspective de la structure mettant en évidence la direction préférentielle de vibration thermique de l'ensemble des atomes.

d'argent et d'oxygène vibrent suivant une direction propre à peu près normale au plan π.

La Fig. 2, représentant une perspective de la structure réalisée à l'aide du programme *ORTEP* de Johnson (1965), met en évidence le phénomène global de vibration thermique des atomes d'argent et d'oxygène suivant une direction commune privilégiée normale au plan π.

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Ammonium Tetrafluoroberyllate(II)

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Abstract. $(NH_4)_2BeF_4$, orthorhombic, *Pnma*, $a = 7.6367$ (3), $b = 5.9072$ (2), $c = 10.4316$ (3) Å, $V = 470.56$ Å^3, $Z = 4$, $D_c = 1.707$ Mg m^{-3}, $M_r = 120.97$. The structure has been refined by X-ray diffraction data to a conventional reliability index R ($= \Sigma \|F_o\| - |F_c\|/\Sigma |F_o|$) of 0.049. The BeF$_4$ ion forms an almost

regular tetrahedron; the average Be—F bond length, after thermal-vibration correction, is 1·551 (5) Å, and the average F—Be—F bond angle is 109·5 (3)°. The NH_4^+ tetrahedra are not very regular.

Introduction. $(NH_4)_2BeF_4$ has been the subject of considerable interest since the discovery of its ferroelectric transition at 175 K (Pepinsky & Jona, 1957) and, more recently, of its non-ferroelectric transition at 182 K (Makita & Yamauchi, 1974). The three phases have very different and interesting properties which can be understood fully only when the detailed crystal structure in all three phases is known. Keeping this in mind, we have determined the crystal structure of $(NH_4)_2BeF_4$ at room temperature in the paraelectric phase. Crystals were grown from a saturated solution by slow evaporation. A colourless needle-shaped crystal was employed for the X-ray structure determination. Preliminary studies were carried out both photographically and with a GE XRD-6 diffractometer. Precession photographs show orthorhombic symmetry and reflections only for $hk0$, $h = 2n$, $0kl$, $k + l = 2n$, indicating space group $Pnma$ or $Pn2_1a$. Since the crystal of $(NH_4)_2BeF_4$ is isomorphous with $(NH_4)_2SO_4$ (Singh, 1962), the former space group was assumed and later confirmed by statistical tests on normalized structure factors (program *NORMSF*) and by satisfactory refinement.

Intensity data were collected on a Syntex $P2_1$ automatic diffractometer at the Materials Research Center, McMaster University, Canada. X-ray intensities for 1267 reflections up to $2\theta = 55°$ in the octants hkl and $hk\bar{l}$ were measured, from a crystal ground into the shape of a cylinder of radius 0·075 mm and length (along **b**) 0·30 mm, using graphite-crystal-monochromated Mo $K\alpha$ radiation ($\lambda = 0·71069$ Å). Two reference reflections were monitored throughout the data collection (at intervals of 14 reflections) and their intensities showed random fluctuations of less than 10% in one case and 1% in the other. Background intensity was measured on either side of and 1° removed from each peak. The scan rate depended upon peak intensity. The intensities were corrected for Lorentz and polarization effects. No absorption correction was applied ($\mu = 0·28$ mm^{-1}). Averaging equivalent reflections gave 673 unique reflections, 411 of which were coded as observed [$I > 3\sigma(I)$] (based on counting statistics).

The trial parameters were taken from Singh (1962). The refinement of the structure was performed on the CDC 6400 computer at McMaster University Computer Centre, using the locally written least-squares program *CUDLS*. The least-squares refinement with isotropic temperature factors converged at $R = 0·141$. At this stage anisotropic temperature factors with restrictions imposed by symmetry (Peterse & Palm,

1966) were introduced. The refinement was stopped when shifts in all parameters were less than a quarter of the corresponding standard deviations. R at this stage was 0·064. A difference synthesis calculated with the final parameters showed small peaks at the expected H positions. The H atoms as indicated by the difference synthesis were therefore introduced in the structure. They were assigned the anisotropic temperature factors of the atoms to which they are bound. After three cycles of least-squares refinement a final $R = 0·049$ and weighted R $\{= [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}\} = 0·044$ were obtained.* At this stage all the shifts were less than the corresponding standard deviations, the maximum and the average being $0·17\sigma$ and $0·02\sigma$ respectively.

Discussion. The multiplicity of the general position in $Pnma$ is eight and there are only four formula units per cell. Both the N atoms, the Be atom, two F atoms and four H atoms lie on the mirror plane at $y = \frac{1}{4}$; the remaining atoms occupy general positions. The positions of all atoms are listed in Table 1. The lengths and directions of the principal axes of the thermal ellipsoids for atoms other than H are listed in Table 2. There is large anisotropy in the thermal motion of the F atoms as compared to those of the other atoms; therefore an interpretation of the anisotropic temperature factors in terms of librational motion of the BeF_4 group has been attempted. On the assumption that BeF_4 is a rigid body (Cruickshank, 1956), the radial ($\overline{U_r^2}$) and tangential ($\overline{U_t^2}$) component of mean square vibration $\overline{U^2}$ have been calculated at each F atom. Since $\overline{U_t^2}$ is larger than $\overline{U_r^2}$ for each atom, the minimum vibration for each atom is essentially along the bond and the maximum

Table 1. *Positional parameters for* $(NH_4)_2BeF_4$ *with standard deviations in parentheses*

	x	y	z
N(1)	0·1804 (6)	0·25	0·0968 (4)
N(2)	0·4687 (6)	0·25	0·8059 (4)
Be	0·2466 (7)	0·25	0·4180 (5)
F(1)	0·0502 (4)	0·25	0·3933 (3)
F(2)	0·2856 (4)	0·25	0·5620 (3)
F(3)	0·3278 (3)	0·0365 (3)	0·3588 (2)
H(1)	0·288 (7)	0·25	0·108 (4)
H(2)	0·109 (7)	0·25	0·156 (5)
H(3)	0·167 (4)	0·115 (5)	0·048 (3)
H(4)	0·491 (7)	0·25	0·739 (5)
H(5)	0·547 (7)	0·25	0·856 (5)
H(6)	0·392 (4)	0·115 (5)	0·823 (3)

Table 2. *The thermal ellipsoids*

q_i: r.m.s. thermal-vibration parameters for the three principal axes of the ellipsoid.

	q_i	Angle with respect to crystal axes				q_i	Angle with respect to crystal axes		
N(1)	0·208	86·7°	90·0°	3·3°	F(1)	0·290	85·4°	90·0°	175·4°
	0·175	90·0	0·0	90·0		0·260	90·0	0·0	90·0
	0·155	3·3	90·0	93·3		0·155	4·6	90·0	85·4
N(2)	0·184	2·6	90·0	87·5	F(2)	0·249	4·3	90·0	94·3
	0·187	90·0	0·0	90·0		0·259	90·0	00·0	90·0
	0·156	87·5	90·0	177·4		0·164	85·7	90·0	4·3
Be	0·166	86·0	90·0	4·0	F(3)	0·265	101·2	74·7	160·9
	0·165	90·0	0·0	90·0		0·224	162·8	105·6	83·1
	0·133	4·0	90·0	94·0		0·183	102·9	22·1	72·3

Table 3. *Interatomic distances* (Å) *and angles* (°)

Numerals 1 and 7 in front of atom symbols indicate symmetry positions x,y,z and $x, \frac{1}{2} - y, z$ respectively.

(a) Environment of Be within a radius of 3·0 Å

1Be—1F(1)	1·522 (6)		1Be—1F(3)	1·535 (4)
—1F(2)	1·531 (6)		—7F(3)	1·535 (4)

1F(1)—1Be—1F(2)	111·0 (4)		1F(2)—1Be—1F(3)	108·4 (2)
—1Be—1F(3)	109·3 (2)		—1Be—7F(3)	108·4 (2)
—1Be—7F(3)	109·3 (2)		1F(3)—1Be—7F(3)	110·5 (3)

(b) Environment of N(1) within a radius of 3·01 Å

1N(1)—1H(1)	0·83 (5)		1N(1)—1H(3)	0·95 (3)
—1H(2)	0·83 (5)		—7H(3)	0·95 (3)

1H(1)—1N(1)—1H(2)	123 (4)		1H(2)—1N(1)—1H(3)	109 (2)
—1H(3)	101 (3)		—7H(3)	109 (2)
—7H(3)	101 (3)		1H(3)—1N(1)—7H(3)	114 (3)

1N(1)—F(2)($\frac{1}{2} - x, \bar{y}, z - \frac{1}{2}$)	2·987 (1)
—F(2)($\frac{1}{2} - x, \bar{y} + 1, z - \frac{1}{2}$)	2·987 (1)
—F(3)($x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} - z$)	3·009 (5)
—F(3)($x - \frac{1}{2}, y, \frac{1}{2} - z$)	3·009 (5)
—F(3)($\frac{1}{2} - x, \bar{y}, z - \frac{1}{2}$)	3·005 (4)
—F(3)($\frac{1}{2} - x, \frac{1}{2} + y, z - \frac{1}{2}$)	3·005 (4)
—F(1)($\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$)	2·826 (6)

(c) Environment of N(2) within a radius of 3·01 Å

1N(2)—1H(4)	0·72 (6)		1N(2) -1H(6)	1·01 (3)
—1H(5)	0·79 (5)		—7H(6)	1·01 (3)

1H(4)—1N(2)—1H(5)	117 (5)		1H(5)—1N(2)—1H(6)	109 (3)
—1H(6)	108 (3)		—7H(6)	109 (3)
—7H(6)	108 (3)		1H(6)—1N(2)—7H(6)	105 (2)

1N(2)—F(2)($\frac{1}{2} + x, \frac{1}{2} - y, \frac{3}{2} - z$)	2·785 (5)
—F(2)(x,y,z)	2·903 (5)
—F(3)($\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z$)	2·880 (4)
—F(3)($\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$)	2·880 (4)
—F(3)($1 + \bar{x}, \frac{1}{2} + y, 1 + \bar{z}$)	2·869 (4)
—F(3)($1 + \bar{x}, \bar{y}, 1 + \bar{z}$)	2·869 (4)

1N(2)—F(1)($\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z$)	3·094 (2)
—F(1)($\frac{1}{2} - x, \bar{y} + 1, \frac{1}{2} + z$)	3·094 (2)

perpendicular to it in the xz plane. The mean value of $\overline{U_r^2}$ is 0·0273 Å^2 and $\overline{U_f^2}$ is 0·0893 Å^2; the difference between these values (0·0620 Å^2) corresponds to a r.m.s. libration of 9·3° for the BeF$_4$ ion about the y

axis. This increases (Busing & Levy, 1964) the average Be—F distance from 1·531 to 1·551 Å. The new Be—F bond length agrees well with those in other crystals containing BeF$_4$ ions (Vicat, Tranqui, Aléonard & Richard, 1974; Le Roy & Aléonard, 1972).

Table 3(a) gives the bond lengths and bond angles in the BeF$_4$ ion which show a fairly regular tetrahedral coordination. The mean Be—F distance and mean F—Be—F angle are 1·531 Å and 109·5° respectively. Table 3(b) and (c) shows that the NH$_4^+$ tetrahedra are somewhat distorted and show a large variation in the values of N—H distances and H—N—H angles. In (NH$_4$)$_I$ and (NH$_4$)$_{II}$ tetrahedra, the mean values of the N—H distances are 0·89 and 0·88 Å respectively and the mean value of the H—N—H angle is 109° in each case. Based on the neutron diffraction analysis of (NH$_4$)$_2$SO$_4$, Schlemper & Hamilton (1966) have, for the room-temperature phase, reported the mean N—H distance as 0·97 Å and the H—N—H angle as 109·3°.

The two symmetrically independent N atoms of the unit cell have somewhat different surroundings. Within a sphere of radius 3·01 Å, N(1) has seven and N(2) has six F atoms: average N(1)—F 2·975 Å and N(2)—F 2·964 Å. Around N(1) only one F atom [F(1)] is at a

Table 4. *Hydrogen bonds*

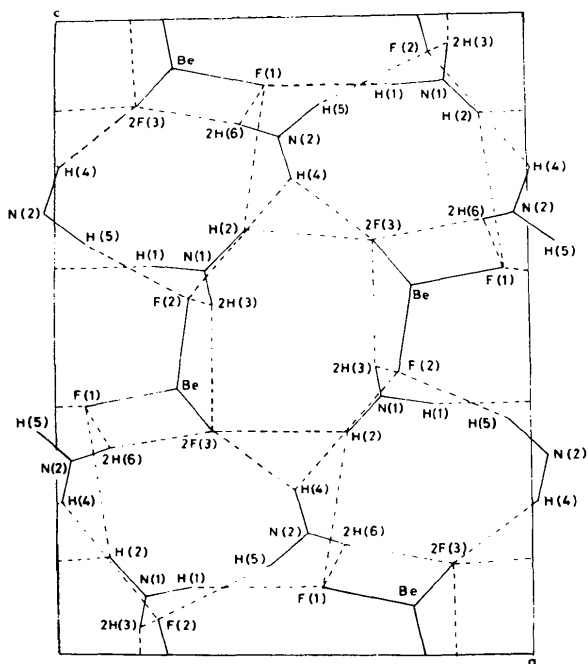|			
F(1)—H(1)	2·01 (5) Å	F(1)···H(1)—N(1)	171 (4)°
—H(2)	2·51 (5)	H(2)—N(1)	149 (4)
—H(6)	2·32 (3)	H(6)—N(2)	133 (2)
—H(6)	2·32 (3)	H(6)—N(2)	133 (3)
F(2)—H(4)	2·43 (5)	F(2)···H(4)—N(2)	126 (5)
—H(5)	2·01 (5)	H(5)—N(2)	164 (5)
—H(3)	2·19 (3)	H(3)—N(1)	141 (2)
—H(3)	2·19 (3)	H(3)—N(1)	141 (2)
F(3)—H(2)	2·49 (4)	F(3)···H(2)—N(1)	122 (3)
—H(3)	2·17 (3)	H(3)—N(1)	146 (2)
—H(4)	2·41 (4)	H(4)—N(2)	123 (3)
—H(6)	1·93 (3)	H(6)—N(2)	155 (3)
F(3)—H(2)	2·49 (4)	F(3)···H(2)—N(1)	122 (3)
—H(3)	2·17 (3)	H(3)—N(1)	146 (2)
—H(4)	2·41 (4)	H(4)—N(2)	123 (3)
—H(6)	1·93 (3)	H(6)—N(2)	155 (3)

Fig. 1. An *xz* projection of a unit cell of $(NH_4)_2BeF_4$. Broken lines indicate hydrogen bonds.

distance of less than 2·9 Å, whereas all six F atoms around N(2) lie within 2·9 Å. If a sphere of radius 3·1 Å is considered, two more F atoms can be added around N(2) but none around N(1). The average N(2)—F distance then becomes 2·922 Å. In Table 4, H···F distances less than 2·6 Å and the corresponding N—H···F bond angles are given. The hydrogen-bonding scheme is depicted by broken lines in the *y* projection of the unit cell which is shown in Fig. 1. Each NH_4^+ tetrahedron is bonded to its neighbouring BeF_4 tetrahedra by eight hydrogen bonds. If H···F distances less than 2·01 Å are considered, then $(NH_4^+)_I$ is strongly hydrogen bonded to its neighbouring BeF_4

tetrahedra by one (2·01 Å) and $(NH_4^+)_{II}$ by three (2·01, 1·93, 1·93 Å) hydrogen bonds. The corresponding distances in $(NH_4)_2SO_4$ (Schlemper & Hamilton, 1966) are 1·97 Å and 1·85, 2·05, 2·05 Å respectively.

Schlemper & Hamilton (1966) have also determined the structure of $(NH_4)_2SO_4$ in the ferroelectric phase. They have attributed the transition to changes in hydrogen bonding. Jain, Bist & Upreti (1973) have, on the basis of spectroscopic evidence, ascribed the ferroelectric transition in $(NH_4)_2SO_4$ to a sudden distortion of sulphate ions at the transition temperature. An accurate crystal structure determination of $(NH_4)_2BeF_4$ in the low-temperature ferroelectric phase should help to reveal the transition mechanism in these crystals.

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Structure of Disilver Chloride Nitrate

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Abstract. Ag_2ClNO_3, $M_r = 313·19$, orthorhombic, *Pnma*, $a = 6·6566 (4)$, $b = 5·1113 (2)$, $c = 12·4887 (14)$ Å, $Z = 4$, $D_x = 4·89$ Mg m⁻³. The structure was refined anisotropically from single-crystal diffractometer data to an R value of 0·028. The Cl atoms are coordinated to five Ag atoms forming trigonal-bipyramidal polyhedra which are linked by edges and corners, creating cavities in which the NO_3 groups are located. Ag_2ClNO_3 is isomorphous with Ag_2BrNO_3.