

Aminoguanidinium(2+) Hexafluorozirconate Monohydrate: A Co-Product of Preparing the Ferroelectric Anhydrous Salt

C. R. ROSS II,^{a,b,†} B. L. PAULSEN,^{c,‡} R. M. NIELSON^c AND S. C. ABRAHAMS^{d,*}

^aDepartment of Chemistry, University of Nebraska–Lincoln, Lincoln, NE 68577-0304, USA, ^bDepartment of Structural Biology, St Jude Children's Research Hospital, 332 North Lauderdale St, Memphis, TN 38105-2794, USA, ^cChemistry Department, Southern Oregon University, Ashland, OR 97520, USA, and ^dPhysics Department, Southern Oregon University, Ashland, OR 97520, USA. E-mail: sca@mind.net

(Received 22 August 1997; accepted 22 December 1997)

Abstract

Preparation of anhydrous aminoguanidinium(2+) hexafluorozirconate, $\text{CN}_4\text{H}_8\text{ZrF}_6$, shown previously to satisfy the structural criteria for ferroelectricity [Abrahams *et al.* (1996). *Acta Cryst.* B52, 806–809], generally results in the co-formation of a series of related fluorozirconates. The structure of the monohydrate salt, one of the co-products, has been redetermined to improve understanding of the preparation pathway, locate the H atoms and compare corresponding atom positions [Gerasimenko *et al.* (1989). *Koord. Khim.* 15, 130–135]. The positions of the H atoms were not established in the latter study. All 16 H atoms in the two symmetry-independent $\text{CN}_4\text{H}_8(2+)$ ions are now located and refined, with $R_1 = 0.0299$ and $S = 1.119$. Both independent water molecules are disordered. Normal probability analysis reveals uncompensated error and/or underestimated uncertainty associated with ten non-H-atom position coordinates. The relative concentrations of HF, $\text{CN}_4\text{H}_7\text{Cl}$ and H_2ZrF_6 are among the major variables controlling the formation of the related fluorozirconates.

1. Introduction

Anhydrous aminoguanidinium(2+) hexafluorozirconate, $[(\text{NH}_2)_2\text{C}(\text{NHNH}_3)]\text{ZrF}_6$ or $\text{CN}_4\text{H}_8\text{ZrF}_6$, has been shown to satisfy the structural criteria for ferroelectricity (Abrahams *et al.*, 1996). Preparation and crystal growth of $\text{CN}_4\text{H}_8\text{ZrF}_6$, in anticipation of making the physical measurements necessary for verification of the predicted ferroelectric property, led to an initial crop of crystals identified as containing aminoguanidinium(1+) pentafluorozirconate, $\text{CN}_4\text{H}_7\text{ZrF}_5$. Structural redetermination (Ross II *et al.*, 1998) of $\text{CN}_4\text{H}_7\text{ZrF}_5$ revealed that one F atom, assigned to a special position in an earlier study by Bukvetskii *et al.* (1992), in fact occupies a general position. The CN_4H_7^+ cation was found to be

planar, except for the two H atoms bonded to the terminal N atom.

Many crystals grown in later preparations were identified as $\text{CN}_4\text{H}_8\text{ZrF}_6 \cdot \text{H}_2\text{O}$, the structure of which had been studied by Gerasimenko *et al.* (1989), hereafter referred to as GBDK. Redetermination of this structure was appropriate both in the course of investigating the different products obtained by small variations in the preparation pathway and in view of the above results on $\text{CN}_4\text{H}_7\text{ZrF}_5$. The new structural results, a comparison of the two sets of $\text{CN}_4\text{H}_8\text{ZrF}_6 \cdot \text{H}_2\text{O}$ atomic coordinates by normal probability analysis and a brief account of the factors affecting the preparation of specific members of this $\text{CN}_4\text{H}_8\text{ZrF}_6$ family are presented below.

2. Experimental

2.1. Preparation and crystal growth

Bukvetskii *et al.* (1990), hereafter referred to as BGD, identified several different aminoguanidinium(2+) polyfluorozirconates formed by the reaction between equimolar proportions of $\text{CN}_4\text{H}_7\text{Cl}$ and H_2ZrF_6 in aqueous solution followed by subsequent dissolution of the reactant in H_2O and slow evaporation at room temperature. The commercial availability of H_2ZrF_6 (Alfa Aesar, 45% solution in H_2O , 99%) allowed the use of a variant of this method in which 10.09 g (21.9 mmol) was slowly added, with stirring, to a solution of 2.423 g (21.9 mmol) of aminoguanidine hydrochloride (Aldrich, > 98%) dissolved in 20 ml (~550 mmol) of 48% aqueous HF solution (Aldrich, 48–51%) at room temperature. The resulting fine white precipitate was filtered, redissolved in water and allowed to evaporate at room temperature over 2 d. Transparent colorless single crystals, with maximum dimensions *ca.* $6 \times 5 \times 3$ mm, could be separated microscopically from other crystals by means of their characteristic columnar pseudohexagonal morphology. The presence of other compounds in the preparation, see §4.5, is apparent from its X-ray diffraction powder pattern.

† Present address: St Jude Children's Research Hospital.

‡ Present address: Genentech Inc., 460 San Bruno Blvd, South San Francisco, CA 94080, USA.

Table 1. Comparison of the present unit-cell dimensions with those reported by GBDK

GBDK exchanged *b* and *c* axes and labeled the monoclinic angle γ ; their cell is relabeled below.

	This work	GBDK
<i>a</i> (Å)	12.3770 (7)	12.376 (2)
<i>b</i> (Å)	9.7522 (6)	9.741 (2)
<i>c</i> (Å)	13.8543 (11)	13.840 (2)
β (°)	97.326 (6)	97.35 (2)
<i>V</i> (Å ³)	1658.60 (4)	1654.8 (9)

2.2. Structure determination and refinement

The unit-cell dimensions of the present preparation are compared in Table 1 with those reported by GBDK. Symmetry-related reflections corresponded to Laue group $2/m$ and space group $P2_1/n$, thereby confirming the earlier report. Intensity data were measured using graphite-monochromated Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å, and scan width $(0.6 + K\alpha/K\alpha_2)^\circ$. Reflections measured, using XSCANS software (Siemens, 1993), corresponded to a limiting resolution of 0.77 Å. Absorption corrections decreased R_{int} less than 20%, leading to a final value of 0.022, see also Table 2.†

Structure solution by direct methods (Siemens, 1995) revealed all non-H atoms, except for the water O atom. Use of SHELXL5.03 (Siemens, 1995) led to two independent high-residual electron densities after the first four refinement cycles; these were identified as water O atoms and added to the refinement model with isotropic atomic displacement parameters (ADP's). Further refinement of the N1,N2—C1—N3—N4 and ZrF₆²⁻ moieties gave additional improvement, whereupon H atoms were added to the N atoms in a simple riding mode, assuming only $d_{\text{N-H}} = 0.86$ Å within each refinement cycle. H-atom positions were, however, modified between cycles to maintain $\angle\text{C-N3-H3} = \angle\text{N4-N3-H3}$, with the H atoms in terminal $X = \text{NH}_2^+$ groups constrained to lie in the plane of the nearest substituents on the X atom. The angles in the —N4H₃ group were constrained to be ideally tetrahedral, varying only the C1—N3—N4—H1 torsion angle in both A and B ions. $U(\text{H})$ parameters were constrained to be $1.2 \times U_{\text{iso}}(\text{coordinating atom})$, except for NH₃ H atoms where $U(\text{H}) = 1.5 \times U_{\text{iso}}(\text{coordinating atom})$. Parameters in the Siemens (1995) weights, see Table 2, were evaluated by analysis of variance.

Examination of the resulting residual electron density distribution showed the water molecules OW1 and OW2 to be poorly modeled using single atoms with isotropic ADP's. The distribution was, however, suggestive of

† Lists of atomic coordinates, anisotropic displacement parameters, structure factors, principal mean-square atomic displacements and additional bond lengths and angles have been deposited with the IUCr (Reference: BR0070). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Experimental details

Crystal data	
Chemical formula	CN ₄ H ₈ ZrF ₆ H ₂ O
Chemical formula weight	299.33
Cell setting	Monoclinic
Space group	$P2_1/n$
Unit-cell dimensions	See Table 1
<i>Z</i>	8
D_x (Mg m ⁻³)	2.397
D_m (Mg m ⁻³)	2.31 (4)
Density measured by	Pycnometry at 295 K
Radiation type	Mo $K\alpha$
Wavelength (Å)	0.71073
No. of reflections for cell parameters	14
θ range (°)	12.0–12.5
μ (mm ⁻¹)	1.402
Temperature (K)	295 (2)
Crystal form	Prismatic
Crystal size (mm)	0.36 × 0.36 × 0.3
Crystal color	Colorless
Data collection	
Diffractometer	Siemens P4
Data collection method	θ - 2θ scans
Absorption correction	Psi scans (Siemens, 1993)
T_{min}	0.422
T_{max}	0.473
No. of measured reflections	4811
No. of independent reflections	3798
No. of observed reflections	3434
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.0220
θ_{max} (°)	27.49
Range of <i>h</i> , <i>k</i> , <i>l</i>	–1 → <i>h</i> → 16 –1 → <i>k</i> → 12 –17 → <i>l</i> → 17
No. of standard reflections	3
Frequency of standard reflections	Every 100 reflections
Intensity decay (%)	5
Refinement	
Refinement on	F^2
$R[F > 4\sigma(F^2)]$	0.0299
$wR(F^2)$	0.0842
<i>S</i>	1.119
No. of reflections used in refinement	3798
No. of parameters used	243
H-atom treatment	Riding
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0390P)^2 + 1.7484P]$, where $P = (F_o^2 + 2F_c^2)/3$ (Siemens, 1995)
$(\Delta/\sigma)_{\text{max}}$	0.005
$\Delta\rho_{\text{max}}$ (e Å ⁻³)	0.744
$\Delta\rho_{\text{min}}$ (e Å ⁻³)	–0.692
Extinction method	None
Source of atomic scattering factors	International Tables for Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Computer programs	
Data collection	XSCANS2.1 (Siemens, 1993)
Cell refinement	XSCANS2.1 (Siemens, 1993)
Data reduction	XSCANS2.1 (Siemens, 1993)

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a^i a^j \mathbf{a}_i \cdot \mathbf{a}_j.$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Zr1	0.81610 (2)	0.11839 (2)	0.50967 (2)	0.01500 (9)
Zr2	1.00976 (2)	0.12107 (2)	0.33245 (2)	0.01572 (9)
F1	0.69060 (13)	-0.0125 (2)	0.44744 (13)	0.0253 (4)
F2	0.7249 (2)	0.2399 (2)	0.41729 (15)	0.0357 (4)
F3	0.82696 (14)	0.3029 (2)	0.58486 (14)	0.0314 (4)
F4	0.9453 (2)	0.0933 (2)	0.63250 (14)	0.0297 (4)
F5	0.8612 (2)	-0.0943 (2)	0.54993 (13)	0.0288 (4)
F6	0.71618 (15)	0.0937 (2)	0.61477 (13)	0.0297 (4)
F7	0.87391 (15)	0.0252 (2)	0.38562 (13)	0.0303 (4)
F8	0.95740 (14)	0.2174 (2)	0.46324 (12)	0.0277 (4)
F9	1.13241 (15)	0.0878 (2)	0.25012 (13)	0.0321 (4)
F10	0.93397 (14)	0.0228 (2)	0.21130 (12)	0.0273 (4)
F11	0.89490 (15)	0.2570 (2)	0.26995 (13)	0.0300 (4)
F12	1.09076 (14)	0.3069 (2)	0.33685 (15)	0.0315 (4)
C1A	0.8714 (2)	0.5836 (3)	0.3628 (2)	0.0243 (6)
N1A	0.7975 (2)	0.4940 (3)	0.3275 (2)	0.0311 (6)
N2A	0.9760 (2)	0.5534 (3)	0.3741 (2)	0.0355 (6)
N3A	0.8421 (2)	0.7123 (3)	0.3859 (2)	0.0321 (6)
N4A	0.7329 (2)	0.7355 (3)	0.4014 (2)	0.0280 (5)
C1B	0.4462 (2)	0.1623 (3)	0.3476 (2)	0.0249 (6)
N1B	0.5157 (2)	0.2566 (3)	0.3275 (2)	0.0331 (6)
N2B	0.4791 (2)	0.0457 (3)	0.3861 (3)	0.0441 (8)
N3B	0.3383 (2)	0.1831 (3)	0.3315 (2)	0.0379 (7)
N4B	0.2927 (2)	0.2993 (3)	0.2851 (2)	0.0381 (7)
O1W1	0.6907 (3)	0.5284 (4)	0.5399 (3)	0.0419 (9)
O2W1	0.7439 (15)	0.5543 (18)	0.5504 (13)	0.044 (4)
O1W2	0.5191 (4)	0.3162 (5)	0.5584 (4)	0.0723 (12)
O2W2	0.5003 (17)	0.390 (2)	0.5397 (14)	0.068 (5)

disorder; an 80–20% occupancy split between O1W1 and O2W1, also between O1W2 and O2W2, was necessary to yield comparable U_{iso} values for each fractional O atom. The orientation of the OW1 split is approximately along [120], that of OW2 along [010]. Earlier trials with different, but fixed, occupancies of O1W2 and O2W2 had little effect upon the refinement indicators within wide occupancy limits, the change in occupancy being compensated for by correlated variations in the isotropic ADP's. In the final refinements, O1W1 and O2W1 were assigned anisotropic ADP's, but attempts to model O1W2 and O2W2 similarly were unsuccessful. Since the remaining two highest excess electron density peaks (0.74 and 0.65 $e \text{\AA}^{-3}$) are closely associated with OW2, the model for this second water molecule in Table 3 is clearly only an approximation to its actual disorder.

Final methyl group torsion angles are 172.96° for the *A* and 176.50° for the *B* cation; uncertainties could not be determined by Siemens' (1995) software. Water H atoms were not included in the final refinement.

3. Normal probability comparison

The atomic coordinates determined by GBDK may be compared quantitatively with those in Table 3 using the normal probability method (Abrahams & Keve, 1971; Abrahams, 1997), although the present ADP's for the

non-H atoms and the positional coordinates for the H atoms must be excluded from the comparison since these values were not reported by GBDK. Following transformation of their x_1, y_1, z_1 coordinates to the form $x_2, z_2, \frac{1}{2} + y_2$, see Table 1, the method orders the 78 experimental deviates $\delta\xi = [|\xi_G| - |\xi_R|]/[\sigma^2\xi_G + \sigma^2\xi_R]^{1/2}$, where ξ_G is the value of an atomic coordinate refined by GBDK, ξ_R is the value of the same coordinate determined by the present authors and $\sigma^2\xi_G, \sigma^2\xi_R$ are the corresponding evaluated variances for each ξ coordinate. The major water components O1W1 and O1W2 (see Table 3) were included, the minor water components excluded, in forming the $\delta\xi$ deviates.

The experimental deviates are plotted against the magnitudes of the corresponding normal probability deviates, given by Hamilton (1974), in Fig. 1. The fit by linear regression to line *A* by all 78 deviates has a slope of 1.40 (4), an intercept of -0.14 (4) and a correlation coefficient (*r*) of 0.976. Excluding the ten largest deviates, corresponding to N3A(*z*), O1W1(*z*), N1B(*x*), Zr2(*y*), O1W2(*y*), N2A(*x*), O1W2(*z*), N4B(*x*) and O1W1(*x*) in order of increasing magnitude, the fit of the remaining 68 to line *B* has a slope of 1.097 (12), an

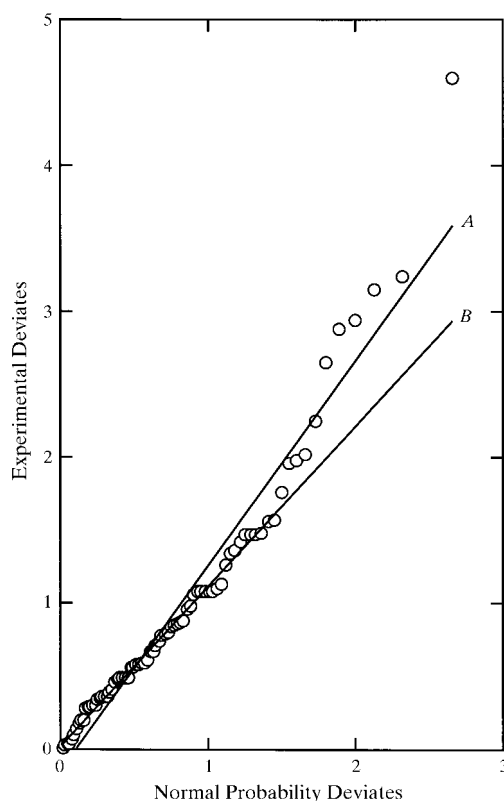


Fig. 1. Normal probability distribution of the 78 non-H atomic coordinate deviates determined both by GBDK and the present authors. Line *A* gives the fit obtained by linear regression to all 78 deviates, line *B* to the 68 deviates that remain after excluding the 10 largest terms.

intercept of 0.02 (1) and $r =$ of 0.996. The 68 deviate array is thus rather linear, whereas the 78-deviate array departs unacceptably from linearity. The slope of line B indicates that the joint distribution of uncertainty in the two determinations is close to normal, but underestimated by $\sim 10\%$, the linearity of the array suggesting little if any uncompensated error; since the uncertainties in the present study are approximately 1/5 those in the former, the underestimation is likely to be associated primarily with the results of GBDK.

Four of the ten outlying deviates are related, unsurprisingly, to the primary components of the disordered water molecules. Coordinates for the secondary (20% occupancy) water components are not available in GBDK's work for comparison. The two largest departures from line B , with $\delta[\text{O1W1}(x)] = 4.60$ and $\delta[\text{N4B}(x)] = 3.24$, are highly significant; correction of GBDK's reported value for $\sigma[\text{O1W1}(x)]$ by the factor 2 and that for $\sigma[\text{N4B}(x)]$ by the factor 1.4, is necessary to satisfy a normal distribution. Further examination of the ten largest experimental deviates, as of the remaining refined parameters, is hindered by the lack of ADP's and their correlation coefficients in the earlier report.

4. Discussion

4.1. Crystal structure

The crystal structure of $\text{CN}_4\text{H}_8\text{ZrF}_6 \cdot \text{H}_2\text{O}$ consists of an array of $\text{CN}_4\text{H}_8^{2+}$ cations forming alternating interstices occupied by bulky $\text{Zr}_4\text{F}_{24}^{8-}$ anions and water molecules, see Fig. 2. Each unit cell contains two anionic clusters, eight cationic molecules and a total of eight water molecules. The significant degree of positional disorder in the water molecules has been modeled by distributing each over two independent positions, with

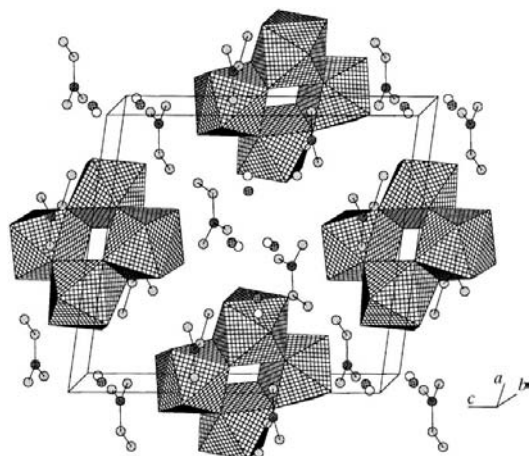


Fig. 2. Contents of the unit cell of aminoguanidinium(2+) hexafluoro-zirconate monohydrate, viewed along the b axis. $\text{Zr}_4\text{F}_{24}^{8-}$ polyhedra are shown as hatched, $\text{CN}_4\text{H}_8^{2+}$ cations in ball-and-stick form. H atoms are omitted for clarity. Water molecules are shown as isolated circles, with hatching representing 80% and open 20% occupation.

Table 4. Selected geometric parameters (\AA , $^\circ$)

Zr1—F2	1.987 (2)	Zr2—F7	2.135 (2)
Zr1—F6	2.041 (2)	Zr2—F5 ⁱ	2.147 (2)
Zr1—F3	2.075 (2)	Zr2—F4 ⁱ	2.202 (2)
Zr1—F1	2.108 (2)	Zr2—F8	2.210 (2)
Zr1—F7	2.146 (2)	C1A—N1A	1.313 (4)
Zr1—F8	2.166 (2)	C1A—N2A	1.318 (4)
Zr1—F4	2.195 (2)	C1A—N3A	1.356 (4)
Zr1—F5	2.201 (2)	N3A—N4A	1.414 (4)
Zr2—F9	2.038 (2)	C1B—N2B	1.299 (4)
Zr2—F10	2.053 (2)	C1B—N1B	1.313 (4)
Zr2—F11	2.053 (2)	C1B—N3B	1.340 (4)
Zr2—F12	2.068 (2)	N3B—N4B	1.387 (4)
F2—Zr1—F6	100.59 (9)	F12—Zr2—F5	76.91 (7)
F2—Zr1—F3	78.54 (8)	F7—Zr2—F5	103.13 (8)
F6—Zr1—F3	75.57 (7)	F9—Zr2—F4	77.69 (8)
F2—Zr1—F1	76.67 (7)	F10—Zr2—F4	79.24 (7)
F6—Zr1—F1	74.83 (7)	F11—Zr2—F4	148.01 (7)
F3—Zr1—F1	136.69 (7)	F12—Zr2—F4	135.87 (7)
F2—Zr1—F7	87.52 (8)	F7—Zr2—F4	72.30 (7)
F6—Zr1—F7	144.62 (7)	F5—Zr2—F4	64.82 (7)
F3—Zr1—F7	139.68 (7)	F9—Zr2—F8	147.55 (7)
F1—Zr1—F7	73.71 (7)	F10—Zr2—F8	135.85 (7)
F2—Zr1—F8	87.51 (8)	F11—Zr2—F8	79.14 (7)
F6—Zr1—F8	148.22 (7)	F12—Zr2—F8	78.17 (7)
F3—Zr1—F8	76.07 (7)	F7—Zr2—F8	65.00 (6)
F1—Zr1—F8	136.82 (7)	F5—Zr2—F8	72.37 (7)
F7—Zr1—F8	65.59 (6)	F4—Zr2—F8	108.37 (7)
F2—Zr1—F4	149.73 (7)	N1A—C1A—N2A	121.5 (3)
F6—Zr1—F4	83.20 (8)	N1A—C1A—N3A	120.6 (3)
F3—Zr1—F4	73.34 (7)	N2A—C1A—N3A	117.9 (3)
F1—Zr1—F4	132.49 (7)	C1A—N1A—H1AA	120.0 (2)
F7—Zr1—F4	106.82 (8)	C1A—N1A—H1AB	120.0 (2)
F8—Zr1—F4	75.16 (7)	C1A—N2A—H2AA	120.0 (2)
F2—Zr1—F5	146.11 (7)	C1A—N2A—H2AB	120.0 (2)
F6—Zr1—F5	82.24 (8)	C1A—N3A—N4A	118.3 (2)
F3—Zr1—F5	133.78 (7)	C1A—N3A—H3AA	120.9 (2)
F1—Zr1—F5	71.51 (6)	N4A—N3A—H3AA	120.86 (15)
F7—Zr1—F5	72.79 (7)	N3A—N4A—H1NA	109.47 (14)
F8—Zr1—F5	107.89 (7)	N3A—N4A—H2NA	109.5 (2)
F4—Zr1—F5	64.05 (6)	N3A—N4A—H3NA	109.5 (2)
F9—Zr2—F10	76.31 (7)	N2B—C1B—N1B	121.3 (3)
F9—Zr2—F11	113.08 (8)	N2B—C1B—N3B	117.0 (3)
F10—Zr2—F11	74.75 (7)	N1B—C1B—N3B	121.7 (3)
F9—Zr2—F12	76.31 (8)	C1B—N1B—H1BA	120.0 (2)
F10—Zr2—F12	127.04 (8)	C1B—N1B—H1BB	120.0 (2)
F11—Zr2—F12	75.73 (7)	C1B—N2B—H2BA	120.0 (2)
F9—Zr2—F7	143.01 (7)	C1B—N2B—H2BB	120.0 (2)
F10—Zr2—F7	77.28 (7)	C1B—N3B—N4B	122.6 (3)
F11—Zr2—F7	83.97 (8)	C1B—N3B—H3BA	118.7 (2)
F12—Zr2—F7	140.68 (7)	N4B—N3B—H3BA	118.7 (2)
F9—Zr2—F5	82.55 (8)	N3B—N4B—H1NB	109.5 (2)
F10—Zr2—F5	141.43 (7)	N3B—N4B—H2NB	109.5 (2)
F11—Zr2—F5	143.78 (7)	N3B—N4B—H3NB	109.5 (2)

Symmetry code: (i) $2 - x, -y, 1 - z$.

20 and 80% occupancy, see §2.2. Interatomic distances are given in Table 4.

Each of the symmetry-independent inversion centers in $\text{CN}_4\text{H}_8\text{ZrF}_6 \cdot \text{H}_2\text{O}$, space group $P2_1/n$, is associated with a different molecular group. In the chosen setting, the $\text{Zr}_4\text{F}_{24}^{8-}$ anion is centered at Wyckoff position $2(b)$, i.e. $0, 0, \frac{1}{2}$ and $\frac{1}{2}, 0, 0$. Each of the independent $\text{CN}_4\text{H}_8^{2+}$ cations occurs in pairs related by Wyckoff positions $2(d)$ (cation A at $0, \frac{1}{2}, \frac{1}{2}$ and $\frac{1}{2}, 0, 0$) and $2(c)$ (cation B at $\frac{1}{2}, 0, \frac{1}{2}$ and

Table 5. Hydrogen-bond lengths (Å), valences (v.u.) and angles (°) in $[(\text{NH}_2)_2\text{C}(\text{NHNH}_3)]\text{ZrF}_6 \cdot \text{H}_2\text{O}$ at 295 K

Bond valences from Brown & Altermatt (1985).

	Bond length	Bond valences	Bond angle
N1A—H1AA···F11	1.930 (3)	0.12	165.22 (10)
N1A—H1AB···F10 ⁱ	2.018 (3)	0.10	166.18 (9)
N2A—H2AA···F12	2.038 (3)	0.10	163.19 (9)
N2A—H2AB···F3 ⁱⁱ	2.013 (3)	0.10	153.12 (10)
N4A—H1NA···F1	1.760 (3)	0.17	168.86 (10)
N4A—H2NA···O1W1	2.024 (5)	0.12	172.24 (14)
N4A—H2NA···O2W1	1.905 (18)	0.15	154.5 (6)
N4A—H3NA···F11 ⁱ	1.854 (3)	0.14	162.92 (9)
N1B—H1BA···F2	1.922 (3)	0.12	156.13 (11)
N1B—H1BB···F10 ⁱ	2.080 (3)	0.09	132.90 (9)
N2B—H2BA···F1	1.855 (3)	0.14	170.45 (12)
N2B—H2BB···F6 ⁱⁱⁱ	1.980 (3)	0.10	152.63 (10)
N4B—H1NB···F12 ^{iv}	1.874 (3)	0.13	157.09 (11)
N4B—H2NB···F6 ^v	2.066 (3)	0.10	123.80 (10)
N4B—H3NB···O1W1 ^{vi}	2.248 (6)	0.08	137.01 (13)
N4B—H3NB···O2W1 ^{vi}	2.226 (18)	0.08	121.6 (5)

Symmetry codes: (i) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $2-x, 1-y, 1-z$; (iii) $1-x, -y, 1-x$; (iv) $x-1, y, z$; (v) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; (vi) $1-x, 1-y, 1-z$.

$0, \frac{1}{2}, 0$). The two independent water molecules are grouped around Wyckoff position $2(a)$ at $0, 0, 0$ and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$.

All but one of the unshared anionic F atoms form hydrogen bonds, with $d_{\text{H}\cdots\text{F}}$ ranging from 1.760 (3) to 2.080 (3) Å and $\angle\text{N}-\text{H}\cdots\text{F}$ from 123.80 (10) to 170.45 (12)°; the bond valences range from 0.09 to 0.17 v.u., see Table 5. The exception is F9, for which hydrogen bonds to H3BA and H1NB are possible, but only with bond strengths of 0.05 v.u. or less. The remaining F4, F5, F7 and F8 atoms shared between two ZrF_8 polyhedra do not form hydrogen bonds. The water O atoms, however, may also form hydrogen bonds to F3, F9, F10 and F12 with $d_{\text{O}\cdots\text{F}}$ distances ranging from

2.678 (18) to 2.999 (7) Å; the disordered water molecules can only form one such hydrogen bond per cation.

4.2. Aminoguanidinium(2+) ion

Each of the two independent aminoguanidinium(2+) ions occupies a general position. The geometry around the central C atom is quite regular. For C1A, the inter-bond angles are 121.5 (3), 120.6 (3) and 117.9 (3)°, whereas for C1B they are 121.3 (3), 121.7 (3) and 117.0 (3)°. In both cases the smallest angle (*ca.* 117°) is between N2—C and N3—C. Although the N2C—N—N cation backbone may be exactly planar, see Fig. 3, interatomic forces result in departures from planarity, both in the coordination about C1 (ideally sp^2) and in the torsion angle about the C1—N3 bond. An indication of bond pyramidalization about C1 is provided by the distance between C1 and the plane formed by N1, N2 and N3, *viz.* 0.013 (3) Å in cation A and 0.010 (4) Å in cation B. The torsion angle about C1—N3, as given by the dihedral angle between the plane defined by N1, C1 and N3 and that defined by C1, N3 and N4, is 19.9 (5)° in cation A and 5.8 (5)° in cation B. The pyramidalization indicates a slight, but possibly significant, deviation from planarity, the torsion angle a deviation of higher significance. The corresponding moiety in the $\text{C}(\text{NH}_2)_2\text{NH.NH}_2^+$ cation is required by symmetry to be strictly planar, as reported for example in aminoguanidinium nitrate (Akella & Keszler, 1994) and in $\text{CN}_4\text{H}_7\text{ZrF}_5$ (Ross II *et al.*, 1998).

4.3. Hexafluorozirconate ion

The hexafluorozirconate ions in $\text{CN}_4\text{H}_8\text{ZrF}_6 \cdot \text{H}_2\text{O}$ form a complex consisting of four Zr atoms in an approximately square-planar arrangement, see Fig. 4, with composition Zr_4F_{24} and formal charge -8 . Each Zr

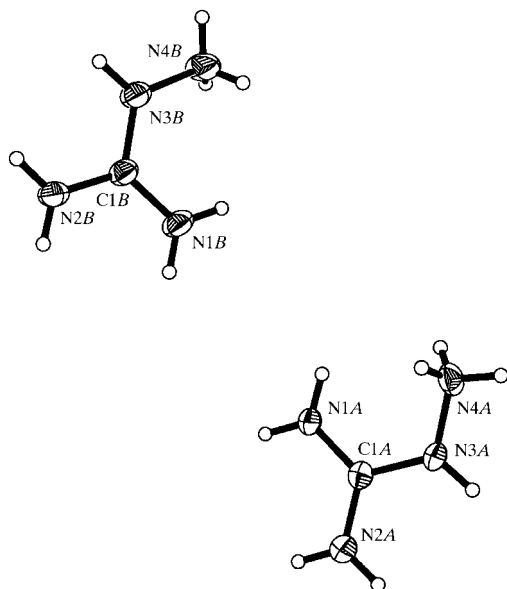


Fig. 3. Atomic arrangement in the two independent aminoguanidinium(2+) ions.

is coordinated by eight F atoms that form a distorted archimedean antiprism about Zr. These coordination polyhedra share square-face edges, so that one-third of the F atoms are shared between two Zr atoms and two-thirds are bonded to a single Zr atom. The anionic $Zr_4F_{24}^{8-}$ complex, in which only two Zr and 12 F atoms occupy unique positions, lies on a center of symmetry and forms an empty parallelepiped, as seen clearly in Fig. 2, of volume $15.74(2) \text{ \AA}^3$. The average shared F—Zr bond length is $2.18(3) \text{ \AA}$ and the average unshared length is $2.05(3) \text{ \AA}$. Comparison of the Zr—F bond lengths with the bond-length—bond-strength tables of Brown & Altermatt (1985) shows excellent agreement with the formal valence of Zr; both Zr1 and Zr2 have a total bond valence of 3.94 v.u. The ZrF_8 coordination polyhedra exhibit typical shared-edge shortening, with two F4—F5 and F7—F8 lengths of 2.33 \AA , whereas the alternating unshared F4—F8 and F5—F7 edges for Zr1 and F4—F7 and F5—F8 edges for Zr2 range from $2.560(3)$ to $2.660(3) \text{ \AA}$ in length. For comparison, the average F—F edge on the completely unshared square face (F1—F2—F3—F6 and F9—F10—F11—F12), averaged over the eight inequivalent bond lengths, is $2.53(2) \text{ \AA}$.

4.4. Water molecules

Major positional disorder is exhibited by both water molecule O atoms. This is not unexpected since the water molecules occupy otherwise void elliptical channels which are parallel to the *b* axis in the molecular packing of the aminoguanidinium and hexafluorozirconate ions. Although the disorder alters intermolecular configurations, a unique model relating alternate molecular positions with bonding patterns was not found. The disorder is accompanied by large thermal or static displacements; the underlying cause appears to be the large number of weak but comparable interac-

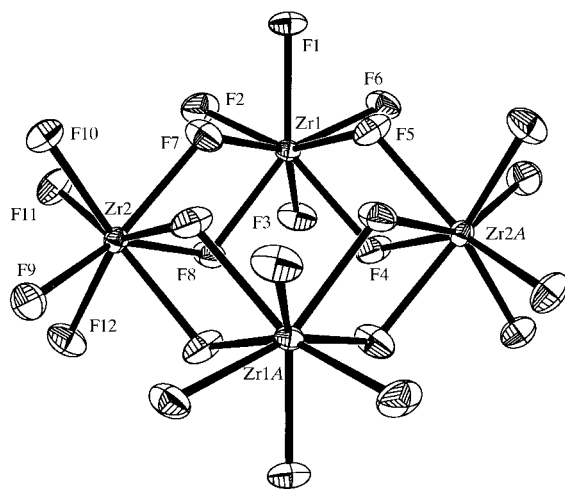


Fig. 4. Atomic arrangement in the hexafluorozirconate, $Zr_4F_{24}^{8-}$, anion.

tions possible between water molecules and channel-wall atoms.

The 20–80% split in occupancy factors for the O atoms gives roughly equal ADP's for the fractional atoms in both molecules, see §2.2. In the case of water 1, resolution of the fractional atoms was sufficient to allow an unconstrained fit of anisotropic ADP's. For both fractions, the ratio U_{\max}/U_{\min} was approximately 1.6, indicating fairly isotropic behavior. In the case of water 2 the electron density was significantly more diffuse, as indicated by larger isotropic ADP's, thereby reducing the ability to resolve the disordered atoms. A refinement of anisotropic ADP's for this pair resulted in non-physically acceptable results, hence isotropic ADP's only were finally refined and reported. Two of the highest residual electron density peaks, see §2.2, in the final model are associated with water 2, indicative of more complex disorder in this molecule. It may be noted that O2W2 is so close to its nearest inversion center that the resulting O2W2—O2W2' distance is only $2.41(4) \text{ \AA}$; the occupancy factor for O2W2 was relatively indeterminate, as noted in §2.2. The rapid increase in H···O valence as the O···O distance decreases toward 2.42 \AA , suggested by Brown & Altermatt (1985), may indicate that only one or other of the two possible O2W2 positions can be occupied simultaneously, *i.e.* the occupancy factor is an average for the crystal, not the unit cell.

4.5. Influence of preparation on composition

All attempts at preparing anhydrous $CN_4H_8ZrF_6$ as the major product from aqueous mixtures of CN_4H_7Cl and H_2ZrF_6 by the method of BGD led to a complex mixture of fluorozirconate compounds. Crystals obtained from the slow evaporation of 25 solutions, each containing different concentrations of HF, CN_4H_7Cl and H_2ZrF_6 , are generally similar but not identical in appearance; they are commonly colorless, but in some preparations are pale yellow. Their morphology is also comparable in most preparations, but not in all. No correlation is found between color or morphology and the relative proportion or concentration of reactants. X-ray diffraction powder patterns reveal striking differences, even from duplicate and triplicate samples prepared under apparently identical reaction conditions. Comparison with predicted patterns from known fluorozirconates suggests the co-formation of several products, including $ZrF_4 \cdot HF \cdot H_2O$, $CN_4H_7ZrF_5$, $CN_4H_8ZrF_6 \cdot H_2O$, $CN_4H_8ZrF_6 \cdot 1/2H_2O$, $CN_4H_8ZrF_6$ and $(CN_4H_7)_2ZrF_6$. A pure product was not obtained in any preparation. The relative proportions of each product could not be correlated either with concentration or percentage of any reactant.

Preferential crystallization of fluorozirconate products by varying reactant concentration or proportion was not achieved. Analysis of the yield of the various compounds formed as a function of other reac-

tion conditions such as pH, temperature and evaporation rate is currently under investigation (Bauer *et al.*, 1998).

The rather minor differences in chemical composition among the aminoguanidinium fluorozirconates is accompanied by wide structural diversity. Both $\text{CN}_4\text{H}_8\text{ZrF}_6 \cdot \text{H}_2\text{O}$ and anhydrous $\text{CN}_4\text{H}_8\text{ZrF}_6$ (BGD) contain distorted antiprisms of edge-sharing ZrF_8 as the repeating structural unit. Short segments of these antiprisms fold back in $\text{CN}_4\text{H}_8\text{ZrF}_6 \cdot \text{H}_2\text{O}$ to form the four-membered rings shown in Fig. 2, whereas they form infinite chains in $\text{CN}_4\text{H}_8\text{ZrF}_6$. Major differences such as this are striking, since the composition of the two compounds differs only by one water molecule. $\text{CN}_4\text{H}_7\text{ZrF}_5$ also forms infinite chains of polyhedra (Ross *et al.*, 1998), as in anhydrous $\text{CN}_4\text{H}_8\text{ZrF}_6$, but with repeating edge-sharing ZrF_7 pentagonal bipyramids rather than ZrF_8 distorted antiprisms. $\text{CN}_4\text{H}_8\text{ZrF}_6 \cdot 1/2\text{H}_2\text{O}$ contains pairs of edge-sharing ZrF_7 and ZrF_8 polyhedra, with edges of the latter shared to form linear units of $\text{Zr}_4\text{F}_{24}^{8-}$ (Gerasimenko *et al.*, 1986). The structure of $(\text{CN}_4\text{H}_7)_2\text{ZrF}_6$ differs significantly from any of the above aminoguanidinium fluorozirconates with its individual ZrF_6 octahedra and lack of shared F atoms (BGD).

The balance among interatomic forces that leads to these various structures is doubtless subtle. The resulting small but important compositional variations such as the presence of water or of additional H or F strongly suggest hydrogen bond interactions play a key role in structure formation.

Participation in this work by B. L. Paulsen, a senior undergraduate student at Southern Oregon University, forms part of the requirements for his B.S. degree. It is a

pleasure to thank Dr R. Jenkins for identifying one of the preparation products from its X-ray diffraction powder pattern. Support of this research by the National Science Foundation (DMR-9708246) is gratefully acknowledged.

References

- Abrahams, S. C. (1997). *Acta Cryst.* **A53**, 673–675.
- Abrahams, S. C. & Keve, E. T. (1971). *Acta Cryst.* **A27**, 157–165.
- Abrahams, S. C., Mirsky, K. & Nielson, R. M. (1996). *Acta Cryst.* **B52**, 806–809.
- Akella, A. & Keszler, D. A. (1994). *Acta Cryst.* **C50**, 1974–1976.
- Bauer, M. R., Pugmire, D. L., Paulsen, B. L., Ross II, C. R., Nielson, R. M. & Abrahams, S. C. (1998). In preparation.
- Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* **B41**, 244–247.
- Bukvetskii, B. V., Gerasimenko, A. V. & Davidovich, R. L. (1990). *Koord. Khim.* **16**, 1479–1484.
- Bukvetskii, B. V., Gerasimenko, A. V. & Davidovich, R. L. (1992). *Koord. Khim.* **18**, 576–579.
- Gerasimenko, A. V., Bukvetskii, B. V., Davidovich, R. L. & Kondratyuk, N. P. (1989). *Koord. Khim.* **15**, 130–135.
- Gerasimenko, A. V., Kondratyuk, N. P., Davidovich, R. L., Medkov, M. A. & Bukvetskii, B. V. (1986). *Koord. Khim.* **12**, 710–714.
- Hamilton, W. C. (1974). *International Tables for X-ray Crystallography*, edited by J. A. Ibers & W. C. Hamilton, Vol. IV, pp. 293–310. Birmingham: Kynoch Press. (Present distributors Kluwer Academic Publishers, Dordrecht.)
- Ross II, C. R., Pugmire, D. L., Bauer, M. R., Nielson, R. M. & Abrahams, S. C. (1998). In preparation.
- Siemens (1993). *XSCANS User's Manual*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1995). *SHELXTL Reference Manual*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.