Acta Crystallographica Section C
**Crystal Structure
Communications**
ISSN 0108-2701

Bis[aminoguanidinium(1+)] hexafluorozirconate(IV): redeterminations and normal probability analysis

C. R. Ross II,[a] M. R. Bauer,[b]† R. M. Nielson[b]‡ and S. C. Abrahams[c]*

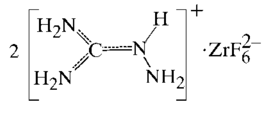
[a]Department of Structural Biology, St Jude Children's Research Hospital, 332 North Lauderdale St., Memphis, TN 38105-2794, USA, [b]Chemistry Department, Southern Oregon University, Ashland, OR 97520, USA, and [c]Physics Department, Southern Oregon University, Ashland, OR 97520, USA.
Correspondence e-mail: sca@mind.net

Received 2 November 2003
Accepted 27 November 2003
Online 13 December 2003

The crystal structure of bis[aminoguanidinium(1+)] hexafluorozirconate(IV), $(CH_7N_4)_2[ZrF_6]$, originally reported by Bukvetskii, Gerasimenko & Davidovich [*Koord. Khim.* (1990), **16**, 1479–1484], has been redetermined independently using two different samples. Normal probability analysis confirms the reliability of all refined parameter standard uncertainties in the new determinations, whereas systematic error detectable in the earlier work leads to a maximum difference of 0.069 (6) Å in atomic positions between the previously reported and present values of an F-atom *y* coordinate. Radiation-induced structural damage in aminoguanidinium polyfluorozirconates may result from minor displacements of H atoms in weak N—H···F bonds to new potential minima and subsequent anionic realignment.

Comment

Single crystals of aminoguanidinium(1+) pentafluorozirconate ($CH_7N_4{}^+\cdot ZrF_5{}^-$) have recently been shown to undergo small but highly significant radiation-induced structural changes (RISC) under X-ray diffraction investigation (Ross *et al.*, 2002). The relative stability of the title compound, $2CH_7N_4{}^+\cdot ZrF_6{}^{2-}$, (I), to X-radiation was not discussed in the original structural study of Bukvetskii *et al.* (1990) but is of interest in view of the common cation and closely related anions in the two materials. Since crystals of (I) were grown during an investigation of the ferroelectric properties of aminoguanidinium(2+) hexafluorozirconate, $CH_8N_4{}^{2+}\cdot ZrF_6{}^{2-}$ (Bauer *et al.*, 1999), the present study was undertaken. The structures of two crystals (1 and 2) of (I) were determined independently and refined. Evidence for radiation damage was undetectable, with a variation in the standard reflections of less than 1% on average and less than 5% maximum. The results of normal probability analysis (Abrahams & Keve, 1971), based on (i) the deviates between all atomic coordinates varied in sets 1 and 2 and (ii) the corresponding deviates for all U^{ij} magnitudes, are shown in Fig. 1.



(I)

The $Q_{\exp(i)}$–$Q_{\mathrm{norm}(i)}$ plot of the 45 ordered atomic position coordinate deviates for sets 1 and 2 ($Q_{\exp(i)} = |[\xi_i(1) - \xi_i(2)]|/\{\sigma^2[\xi_i(1)] + \sigma^2[\xi_i(2)]\}^{1/2}$, where $\xi_i(1)$ is the *i*th atomic coordinate magnitude from set 1 and $\xi_i(2)$ is the *i*th magnitude from set 2, against the ordered normal *i*th deviates, Q_{norm}, is presented in Fig. 1(*a*). The magnitudes of Q_{norm} were calculated using the program *NORMPA* (Ross, 2003). Departures from linearity in the plot are minor, indicating that the residual systematic error is small. The slope of 0.69 (3) and intercept of −0.07 (3), as determined by linear regression, suggest that the joint standard uncertainty (j.s.u.) is overestimated by ~30%. The 57 U^{ij} deviates for sets 1 and 2 in the $Q_{\exp}$–Q_{norm} plot of Fig. 1(*b*) contain eight outliers, *viz*. Zr(U^{13}), Zr(U^{33}), F2(U^{33}), F3(U^{13}), F2(U^{13}), Zr(U^{11}), F3(U^{33}) and F1 (U^{13}), with respective values of 7.42, 4.98, 2.87, 2.78, 2.22, 2.08, 2.02 and 1.81. The remaining 49 $Q_{\exp}$ values are close to linear, with a slope of 1.02 (1) and an intercept of −0.09 (12), indicative of j.s.u. values that are well estimated. Fig. 1(*c*) compares the positional coordinates in set 1 with those determined by Bukvetskii *et al.* (1990), hereafter referred to as set 3. Excluding the two outliers in Fig. 1(*c*), *viz*. F1(*y*) and F3(*z*) at 12.11 and 4.37, respectively, the departure from linearity is significantly greater than that in Fig. 1(*a*). The slope in Fig. 1(*c*) is 2.01 (4), with an intercept of −0.11 (4). The corresponding plot for coordinates from sets 2 and 3 is very similar to Fig. 1(*c*) and is available as part of the supplementary material (Fig. S1); the corresponding deviations are 12.09 for F1(*y*) and 4.22 for F3(*z*), and the slope and intercept are 2.15 (8) and −0.10 (7).

The atomic coordinates in sets 1 and 2 are hence closely comparable, each differing systematically from those in set 3, particularly F1(*y*), with a difference of 0.069 (6) Å [by comparison, the difference between F1(*y*) coordinates in sets 1 and 2 is 0.0001 (10) Å]. The small systematic underestimate of standard uncertainties in the final positional parameters for sets 1 and 2 is indicative of realistic weight assignments, the close approach to linearity in Fig. 1(*a*) eliminating the possibility that RISC is observable in either. The largest outliers, $Q_{\exp}$[Zr(U^{13}) and Zr(U^{33})], are probably related to residual inaccuracies in the absorption corrections.

The $[ZrF_6]^{2-}$ coordination octahedra are located on inversion centers (see Fig. 2*a*), with three unique Zr—F bonds (Table 1), leading to an overall bond valence (Brown &

---

† Present address: Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287-1604, USA.
‡ Deceased 27 November 1998.

DOI: 10.1107/S0108270103027264

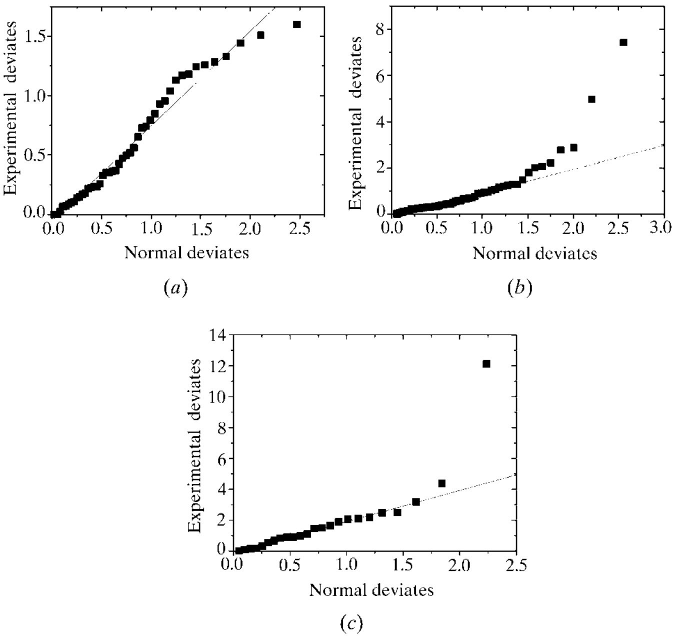
Altermatt, 1985) of 3.91 valence units (v.u.), in good agreement with the formal Zr^{IV} state. The octahedron is nearly ideal, with a quadratic elongation of 1.0003 and an angle variance of 1.091. Examination of the anisotropic displacement parameters (Fig. 2*b*) indicates a significant elongation of the $Zr(U^{ij})$ ellipsoid along the *b* axis (U^{11}:U^{22}:U^{33} = 0.62:1:0.56). Since the bonding environment of the Zr atom is nearly isotropic, this result is consistent with a residual inaccuracy in the absorption correction, as noted above. The F-atom anisotropic displacement parameter values show moderate elongation (U_{min}/U_{max} = 0.28–0.48) normal to the bond axis, as expected.

The aminoguanidinium cations are in general positions; although unconstrained, their geometry is nearly ideal. The C and three N atoms of the guanidine core are slightly cupped, the deviation of the C atom from the plane containing all four atoms being 0.0042 (10) Å, whereas that of the N atoms is 0.0014 (3) Å. The deviation of the remaining N atom (N4) from this plane is 0.081 (2) Å, indicating a slight twist about the C—N3 bond; the N2—C—N3—N4 torsion angle is 4.46 (17)°. Each N—C—N bond angle (see Fig. 2*c*) is near the expected value of 120°, the largest deviation [117.9 (2)° in the N1—C—N3 angle] being similar to previous observations of the anions in $CH_8N_4{\cdot}ZrF_6{\cdot}H_2O$, $CH_8N_4{\cdot}SiF_6$ and $(CH_7N_4)_2{\cdot}SiF_6{\cdot}2H_2O$ (Ross *et al.*, 1998, 1999). Both the N1—C—N3 and the N2—C—N3 angles in $CH_7N_4{\cdot}ZrF_5$ (Ross *et al.*, 2002), however, are 119.1 (2)°.

The $C(U^{ij})$ ellipsoid is relatively isotropic (U_{min}/U_{max} = 0.73), while for the N atoms, U_{min}/U_{max} is in the range 0.35–0.46, with U_{max} roughly normal to the plane of the cation as well as the bond axis, as expected.

The packing of the $CH_7N_4^+$ and $[ZrF_6]^{2-}$ ions in the unit cell is illustrated in Fig. 2(*a*). The anionic polyhedra occupy inversion centers and the interstitial $CH_7N_4^+$ cations are oriented with the ionic plane roughly normal to the *b* axis (at $y = 0$ and $\frac{1}{2}$). Details of the hydrogen bonds between the H and F atoms are given in Table 2. Individual calculated N—H···F bond strengths (Brown & Altermatt, 1985) are small, but these bonds are numerous enough to suggest that they may make a significant contribution to the energy of crystallization.

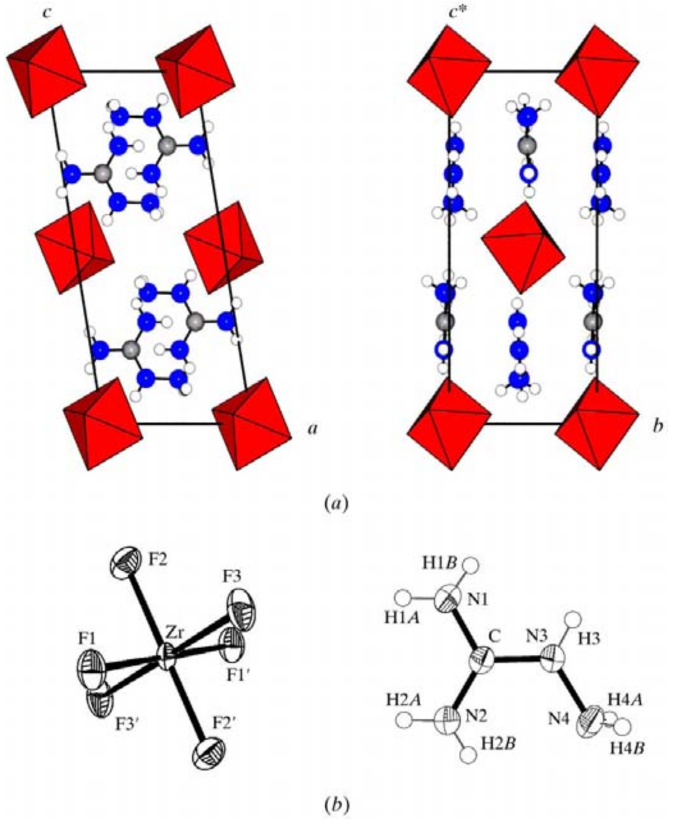
The robustness of this ZrF_6 structure to X-radiation greatly exceeds that of $CH_7N_4^+{\cdot}ZrF_5^-$ (Ross *et al.*, 2002). RISC in the latter results in highly significant unit-cell-parameter variations, together with small but highly significant structural changes. By contrast, significant differences are not detectable either among the lattice constants of all three crystals or in the atomic positions of crystals 1 and 2. The robustness may be related to the fact that the hydrogen bonds in ZrF_6 (average 0.079 v.u.) are stronger than the average 0.060 v.u. hydrogen bond in $CH_7N_4^+{\cdot}ZrF_5^-$. If the reduced bond valence increases the probability that the H atoms can move from their equilibrium growth locations to adjacent potential minima in the structure on exposure to X-radiation, then minor but relative realignment of the fluorozirconate ion would result. The



(*a*) (*b*)

(*c*)

Figure 1
(*a*) A normal probability Q_{exp}–Q_{norm} plot of the 45 atomic coordinate deviates determined with crystals 1 and 2 of (I). (*b*) A normal probability Q_{exp}–Q_{norm} plot of the 57 U^{ij} variable deviates determined with crystals 1 and 2 of (I). (*c*) A normal probability Q_{exp}–Q_{norm} plot of the 45 atomic coordinate deviates determined with crystal 1 and by Bukvetskii *et al.* (1990).



(*a*)

(*b*)

Figure 2
(*a*) The packing of the aminoguanidinium(1+) and $[ZrF_6]^{2-}$ anions in the unit cell of (I). (*b*) The $[ZrF_6]^{2-}$ and aminoguanidinium(1+) ions in (I). Displacement ellipsoids are drawn at the 50% probability level. Atoms marked with a prime are at the equivalent position ($-x$, $-y$, $-z$).

RISC-caused atomic displacements in $CH_7N_4^+\cdot ZrF_5^-$, associated primarily with the Zr atom, are consistent with such a model.

Experimental

Crystals 1 and 2 were grown as described by Bauer *et al.* (1999).

Crystal data

$(CH_7N_4)_2[ZrF_6]$
$M_r = 355.43$
Monoclinic, $P2_1/c$
$a = 6.3705$ (4) Å
$b = 6.3288$ (9) Å
$c = 14.5630$ (8) Å
$\beta = 99.606$ (4)°
$V = 578.91$ (10) Å^3
$Z = 2$

$D_x = 2.039$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 24.5$–28.5°
$\mu = 1.03$ mm^{-1}
$T = 283$ (2) K
Block, colorless
0.50 × 0.42 × 0.20 mm

Data collection

Enraf–Nonius MACH-3 diffractometer
ω–2θ scans
Absorption correction: analytical face-indexed (Mackay *et al.*, 1999)
$T_{\min} = 0.619$, $T_{\max} = 0.815$
3540 measured reflections
1674 independent reflections
1508 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.020$
$\theta_{\max} = 29.9°$
$h = -8 \rightarrow 8$
$k = -8 \rightarrow 8$
$l = -1 \rightarrow 20$
5 standard reflections frequency: 60 min intensity decay: 1%

Table 1

Selected geometric parameters (Å, °) for (I).

Zr—F1	1.9967 (9)	N2—C	1.3158 (17)
Zr—F2	2.0119 (7)	N3—C	1.3307 (17)
Zr—F3	2.0053 (7)	N3—N4	1.3968 (16)
N1—C	1.3279 (17)		
F1—Zr—F2	89.33 (3)	N1—C—N2	121.27 (13)
F1—Zr—F3	91.59 (4)	N1—C—N3	117.86 (13)
F2—Zr—F3	90.10 (3)	N2—C—N3	120.86 (12)
C—N3—N4	119.81 (12)		

Table 2

Hydrogen bond lengths (Å) and angles (°).

Bond valence (v.u.) calculated according to Brown & Altermatt (1985).

N—H···F	H···F	N—H···F	N···F	Bond valence
N1—H1*A*···F1$^{\rm i}$	2.01	170	2.8630 (17)	0.102
N1—H1*B*···F2	2.25	139	2.9492 (16)	0.068
N2—H2*A*···F3$^{\rm ii}$	2.04	164	2.8790 (15)	0.096
N2—H2*B*···F1$^{\rm ii}$	2.13	147	2.8867 (17)	0.082
N3—H3···F2$^{\rm iv}$	2.15	145	2.8926 (15)	0.080
N4—H4*A*···F3$^{\rm v}$	2.26	173	3.1404 (16)	0.067
N4—H4*B*···F2$^{\rm vi}$	2.35	127	2.9648 (16)	0.058

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

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.019$
$wR(F^2) = 0.049$
$S = 1.13$
1674 reflections
81 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0187P)^2 + 0.0859P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.37$ e Å^{-3}
$\Delta\rho_{\min} = -0.58$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.032 (2)

H atoms were allowed for as riding atoms, with N1—H, N2—H and N3—H distances of 0.86 Å and an N4—H distance of 0.89 Å.

For both crystals, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *maXus* (Mackay *et al.*, 1999); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976).

Participation in this work by MRB, an undergraduate student in his senior year at Southern Oregon University at the time, formed part of the requirements for the BS degree. Support of this research by the National Science Foundation (grant Nos. DMR-9708246 and DMR-0137323) and Cancer Center Support (CORE, grant No. P30 CA 21765) is gratefully acknowledged, as is that of the American Lebanese Syrian Associated Charities (ALSAC, to CRR).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1714). Services for accessing these data are described at the back of the journal.

References

Abrahams, S. C. & Keve, E. T. (1971). *Acta Cryst.* A**27**, 157–165.

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

Bauer, M. R., Ross, C. R., Nielson, R. M. & Abrahams, S. C. (1999). *Inorg. Chem.* **38**, 1028–1030.

Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* B**41**, 244–247.

Bukvetskii, B. V., Gerasimenko, A. V. & Davidovich, R. L. (1990). *Koord. Khim.* **16**, 1479–1484.

Enraf–Nonius (1989). *CAD*-4 *Software*. Enraf–Nonius, Delft, The Netherlands.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Mackay, S., Dong, W., Edwards, C., Henderson, A., Gilmore, C., Stewart, N., Shankland, K. & Donald, A. (1999). *maXus User's Manual.* Nonius BV, The Netherlands, MacScience, Japan, and The University of Glasgow, Scotland.

Ross, C. R. (2003). *NORMPA*. Unpublished. Department of Structural Biology, St Jude Children's Research Hospital, Memphis, Tennessee, USA.

Ross, C. R., Bauer, M. R., Nielson, R. M. & Abrahams, S. C. (1999). *Acta Cryst.* B**55**, 246–254.

Ross, C. R., Bauer, M. R., Nielson, R. M. & Abrahams, S. C. (2002). *Acta Cryst.* B**58**, 841–848.

Ross, C. R., Paulsen, B. L., Nielson, R. M. & Abrahams, S. C. (1998). *Acta Cryst.* B**54**, 417–423.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.