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

Bis[aminoguanidinium(1+)] hexa-fluorozirconate(IV): redeterminations and normal probability analysis

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The crystal structure of bis[aminoguanidinium(1+)] hexa-fluorozirconate(IV), (CH3N4)2[ZrF6], 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+) penta-fluorozirconate (CH3N4)2[ZrF5] + 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, 2(CH3N4)2[ZrF6]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+) hexa-fluorozirconate, CH3N42+[ZrF6]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 deviations between all atomic coordinates varied in sets 1 and 2 and (ii) the corresponding deviations for all F-atom y coordinates, are shown in Fig. 1.

The Q exp(–)Q norm(–) plot of the 45 ordered atomic position coordinate deviates for sets 1 and 2 (Q exp(–) = ||ξ(1) − ξ(2)||/ [σ2[ξ(1)] + σ2[ξ(2)]]1/2, where ξ(i) is the ith atomic coordinate magnitude from set 1 and ξ(2) is the ith magnitude from set 2, against the ordered normal ith 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 F-atom y deviations for sets 1 and 2 in the Q exp–Q norm plot of Fig. 1(b) contain eight outliers, viz. Zr(U33), Zr(U33), F2(U33), F3(U33), F2(U33), Zr(U33), F3(U33) and F1(U33), 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(U33)] and Zr(U33)], are probably related to residual inaccuracies in the absorption corrections.

The [ZrF6]2– coordination octahedra are located on inversion centers (see Fig. 2a), with three unique Zr–F bonds (Table 1), leading to an overall bond valence (Brown &
Altermatt, 1985) of 3.91 valence units (v.u.), in good agreement with the formal ZrIV 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) indicates a significant elongation of the Zr(Uij) ellipsoid along the b axis (U11:U22:U33 = 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 (Umin/Umax = 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. 2c) being similar to previous observations of the anions in CH8N4[ZrF6], H2O, CH8N4[SiF6] and (CH7N4)2[SiF6]2H2O (Ross et al., 1998, 1999). Both the N1-C-N3 and the N2-C-N3 angles in CH7N4[ZrF5] (Ross et al., 2002), however, are 119.1 (2)°.

The C(Uij) ellipsoid is relatively isotropic (Umin/Umax = 0.73), while for the N atoms, Umin/Umax is in the range 0.35–0.46, with Umax roughly normal to the plane of the cation as well as the bond axis, as expected.

The packing of the CH7N4+ and [ZrF6]2− ions in the unit cell is illustrated in Fig. 2(a). The anionic polyhedra occupy inversion centers and the interstitial CH7N4+ cations are oriented with the ionic plane roughly normal to the b axis at (y = 0 and 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 ZrF6 structure to X-radiation greatly exceeds that of CH7N4+·ZrF5− (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 ZrF6 (average 0.079 v.u.) are stronger than the average 0.060 v.u. hydrogen bond in CH7N4+·ZrF5−. 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

Figure 1
(a) A normal probability Qexp-Qnorm plot of the 45 atomic coordinate deviates determined with crystals 1 and 2 of (I). (b) A normal probability Qexp-Qnorm plot of the 57 Uij variable deviates determined with crystals 1 and 2 of (I). (c) A normal probability Qexp-Qnorm plot of the 45 atomic coordinate deviates determined with crystal 1 and by Bukvetskii et al. (1990).

Figure 2
(o) The packing of the aminoguanidinium(1+) and [ZrF6]2− ions in the unit cell of (I). (b) The [ZrF6]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).
metal-organic compounds

RISC-caused atomic displacements in \( \text{CH}_3\text{N}_4^+\text{ZrF}_5^- \), 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

\((\text{CH}_3\text{N}_4)_2\text{[ZrF}_6]\)

\(M_r = 355.43 \)

Monoclinic, \(P2_1/c\)

\(a = 6.3705 (4) \) Å

\(b = 6.3288 (9) \) Å

\(c = 14.5630 (8) \) Å

\(\beta = 99.606 (4)\)

\(V = 578.91 (10) \) Å³

\(Z = 2\)

\(D_\text{m} = 2.039 \) Mg m⁻³

Mo Kα radiation

Cell parameters from 25 reflections

\(\theta = 24.5\text{–}28.5^\circ\)

\(\mu = 1.03 \) mm⁻¹

\(T = 283 (2) \) K

\(\text{Block, colorless}\)

\(\text{Symmetry codes: (i)}\)

\(N1 \rightarrow C, \quad N2 \rightarrow C, \quad N3 \rightarrow C, \quad N4 \rightarrow C\)

\(\text{Hydrogen bond lengths (Å) and angles (°).}\)

**Table 1**

<table>
<thead>
<tr>
<th>Selected geometric parameters (Å, °) for (I).</th>
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<tbody>
<tr>
<td>Zr–F₁</td>
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<td>Zr–F₂</td>
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<tr>
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<td>F₂–Zr–F₃</td>
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**Table 2**

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<tr>
<th>Hydrogen bond lengths (Å) and angles (°).</th>
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**Bond valence (v.u.) calculated according to Brown & Altermatt (1985).**

\(\text{N–H} \rightarrow \text{F}^\dagger\)

\(\text{H} \rightarrow \text{N} \rightarrow \text{H} \rightarrow \text{F}^\dagger\)

\(\text{N} \rightarrow \text{H} \rightarrow \text{N} \rightarrow \text{F}^\dagger\)

\(\text{N} \rightarrow \text{H} \rightarrow \text{N} \rightarrow \text{F}^\dagger\)

\(\text{N} \rightarrow \text{H} \rightarrow \text{N} \rightarrow \text{F}^\dagger\)

\(\text{N} \rightarrow \text{H} \rightarrow \text{N} \rightarrow \text{F}^\dagger\)

\(\text{N} \rightarrow \text{H} \rightarrow \text{N} \rightarrow \text{F}^\dagger\)

\(\text{N} \rightarrow \text{H} \rightarrow \text{N} \rightarrow \text{F}^\dagger\)

\(\text{N} \rightarrow \text{H} \rightarrow \text{N} \rightarrow \text{F}^\dagger\)

\(\text{N} \rightarrow \text{H} \rightarrow \text{N} \rightarrow \text{F}^\dagger\)

**References**

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