

derivatives (Sakurai, Sundaralingam & Jeffrey, 1963; Trotter, Whitlow & Zobel, 1966). Thus C(10)–N(3) is much shorter than a single bond, and N(2)–C(7), while longer than C(10)–N(3), is significantly shorter than C(4)–N(1). C(9)–C(10) and C(10)–C(11) are the longest bonds in the ring, C(8)–C(9) and C(11)–C(12) are the shortest, and C(7)–C(8) and C(7)–C(12) have intermediate values. (These differences are, however, of marginal significance.) In contrast, bond distances in the other ring are equal.

The coordination of the sodium atom is distorted octahedral, with Na–O distances ranging from 2.37 to 2.48 Å. The octahedron is made up of two water molecules at opposite corners, three sulphonate oxygen atoms, each from a different group, and the oxygen atom of the ethanol molecule. Adjacent octahedra share water molecules, and are linked in endless chains parallel to *c*. The structure is stabilized by two sets of O–H...O bonds, linking the water molecule to O(1), and the ethanol molecule to O(3). The hydrogen-bonding potential of the structure is not fully realized, however, as one aqueous hydrogen atom [H(*WB*)] and one sulphonate oxygen atom [O(2)] do not participate.

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References

- AHMED, F. R. (1970). *Crystallographic Computing*, p. 279. Copenhagen: Munksgaard.
- AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1966). NRC Crystallographic Programs for the IBM/360 System. *World List of Crystallographic Computer Programs*, 2nd Ed. Appendix p. 52.
- BROWN, C. J. (1966). *Acta Cryst.* **21**, 146–152.
- CAREY, P. R., SCHNEIDER, H. & BERNSTEIN, H. J. (1972). *Biochem. Biophys. Res. Commun.* **47**, 588–595.
- HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- PINNOCK, P. R., TAYLOR, C. A. & LIPSON, H. (1956). *Acta Cryst.* **9**, 173–178.
- SAKURAI, T., SUNDARALINGAM, M. & JEFFREY, G. A. (1963). *Acta Cryst.* **16**, 354–363.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- TROTTER, J., WHITLOW, S. H. & ZOBEL, T. (1966). *J. Chem. Soc. (A)*, pp. 353–356.

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The Crystal Structure of Cesium Nonfluorodiuranate(IV), CsU₂F₉*

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Cesium nonfluorodiuranate(IV) is monoclinic, space group *C2/c*, with $a=15.649$ (3), $b=7.087$ (1), $c=8.689$ (2) Å, $\beta=118.11^\circ$ (2), and $Z=4$. The structure was refined by full-matrix least squares techniques, using data collected with a Picker four-circle diffractometer, to an *R* value of 4.8%. Uranium is coordinated to eight fluorines in polyhedra which share edges to form (U₄F₁₆) sheets parallel to (100). The full uranium coordination approximates a tri-capped trigonal prism, the ninth corner of the polyhedron being a half-filled eightfold set of fluorines so that the coordination number is effectively 8½. The U–F distances span the range from 2.28 to 2.42 Å, with an average value of 2.33 Å.

The compound CsU₂F₉ was obtained by L. B. Asprey from a 40% aqueous HF solution from which crystals of CsUF₆ had been previously obtained. On being allowed to stand in contact with air, disproportionation of the remaining U(V) slowly occurred, yielding U(VI) and U(IV). Deep green, tabular crystals of

CsU₂F₉ up to 2 × 1 × 0.2 mm crystallized from this solution together with a number of other phases. The measured density, by pycnometer, of this impure material was approximately 6.4 g cm⁻³. Optically the monoclinic crystals are biaxial negative, with $2V_x$ approximately 54°. The optical axes display marked symmetrical dispersion with $v > r$. The refractive indices, optical orientation and pleochroism, for white light are as follows:

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$$\begin{aligned} N_x &\sim \perp(100) & 1.542 \pm 0.0005 & \text{yellow green} \\ N_y &= b & 1.569 \pm 0.0005 & \text{green} \\ N_z & & 1.576 \pm 0.0005 & \text{green.} \end{aligned}$$

Single-crystal precession photographs show systematic extinctions compatible with the monoclinic space groups Cc and $C2/c$, i.e. hkl : $h+k=2n$ and $h0l$: $l=2n$. The unit-cell dimensions obtained by least-squares refinement of room temperature measurements (24°C) of the setting angles of 10 high-order reflections that had been centered on an automated four-circle Picker diffractometer using $\text{Mo } K\alpha_1$ radiation ($\lambda = 0.70930 \text{ \AA}$) are: $a = 15.649 \pm 0.003$, $b = 7.087 \pm 0.001$, $c = 8.689 \pm 0.002 \text{ \AA}$, $\beta = 118.11 \pm 0.02^\circ$. The measured density suggests that four formula units per unit cell is the correct value. The calculated density for $Z=4$ is 6.09 g cm^{-3} .

Intensity measurements were made using a Picker computer-controlled diffractometer similar to that described by Busing, Ellison, Levy, King & Roseberry (1967). Zirconium-filtered $\text{Mo } K\alpha$ radiation, θ - 2θ scan, bisecting positions, and a 5° take-off angle were used to collect data on all reflections for which $2\theta \leq 50^\circ$ and $h \geq 0$. Scans were taken in 0.05° steps with two sec counting at each step over a range of 2° plus the α_1 - α_2 dispersion. The background was counted for 20 sec at each end of the scan. A standard reflection

whose intensity was monitored after every 25 reflections showed no signs of degradation during the course of the data collection process. Of the 1487 reflections measured, 1075 were considered as observed according to the criterion $[T-KB] \geq 3\sigma(I)$, where T is the total count, KB is the normalized background, and $\sigma(I) = (T+KB)^{1/2}$. The crystal used was a ground sphere of $56 \mu\text{m}$ radius. The linear absorption coefficient, computed by using the calculated density, is 510 cm^{-1} ; the transmission factors applied varied from 0.029 to 0.046.

The approximate uranium and cesium positions were obtained from a 3-dimensional Patterson map. Uranium was placed in the eightfold general position with $x \approx 0.71$, $y \approx 0.09$, $z \approx 0.79$; cesium was placed in the fourfold special position $0, y, \frac{1}{2}$ with $y \approx 0.90$. A difference Fourier map obtained following three cycles of least-squares refinement of the uranium and cesium parameters, revealed the approximate position of the fluorines. All peaks in the difference Fourier map were in general positions (eightfold) of space group $C2/c$. None were found in fourfold sets as expected from the assumed cell contents; this suggests that one of the eightfold sites is only half-occupied.

Least-squares refinement of all atomic positions, using anisotropic thermal parameters for all atoms except the fluorine in the half-occupied site, F(5), yielded the positional and thermal parameters listed in Tables 1 and 2, respectively. The function minimized was $\sum_i \omega_i^2 (F_o - F_c)^2$ where $\omega_i = 1/\sigma_i(F)$ and $F_c^* = kF_c \{1 + g \text{Lp} [2(1 + \cos^4 2\theta)/(1 + \cos^2 2\theta)] F_c^2\}^{1/2}$ in which k is a scale constant, Lp is the Lorentz-polarization factor, g is the extinction coefficient (Zachariasen, 1967; Larson, 1967) and F_c is the structure factor calculated in the usual way. The scattering factors of Doyle & Turner (1968) were used for the neutral atoms fluorine, uranium and cesium with appropriate

Table 1. Fractional coordinates and associated least-squares errors ($\times 10^4$)

	<i>x</i>	<i>y</i>	<i>z</i>
U	7129 (1)	955 (1)	7937 (1)
Cs	0 (0)	8968 (5)	2500 (0)
F(1)	3310 (9)	2227 (18)	2775 (19)
F(2)	1686 (10)	1751 (18)	4340 (17)
F(3)	1603 (9)	1087 (22)	1385 (16)
F(4)	3144 (9)	469 (15)	9851 (17)
F(5)	4554 (13)	823 (29)	8503 (22)

Table 2. Anisotropic temperature factors ($\times 10^4$)

Defined by $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
U	17.1 (0.5)	44.8 (1.7)	48.8 (1.5)	1.1 (2.6)	31.2 (1.3)	-1.9 (4.3)
Cs	26 (2)	151 (6)	130 (5)	0 (0)	42 (4)	0 (0)
F(1)	12 (8)	57 (28)	129 (31)	22 (24)	46 (27)	100 (51)
F(2)	24 (9)	86 (31)	85 (29)	-5 (26)	53 (27)	-7 (46)
F(3)	15 (7)	86 (29)	96 (26)	34 (31)	34 (23)	46 (58)
F(4)	25 (9)	25 (33)	101 (29)	2 (22)	35 (27)	-8 (42)
F(5)*	$B = 4.63 (0.42) \text{ \AA}^2$					

* Isotropic thermal parameter only.

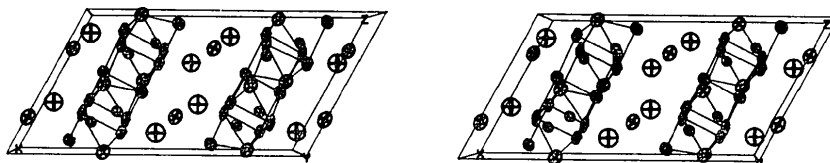


Fig. 1. Stereographic view along the b axis of a unit cell of CsU_2F_9 . Uranium atoms lie within the fluorine polyhedra in the sheets. The isolated ellipsoids represent cesium; the spherical atoms are the statistical fluorines.

dispersion corrections for uranium and cesium (Cromer & Liberman, 1970). *R* for this refinement is 0.048 ($R = \sum |F_o| - |F_c| / \sum |F_o|$). The shifts for the last cycle were less than 0.01 σ for all parameters. Table 3 gives the observed and calculated structure factors for this refinement. Attempts to refine the structure in space group *Cc*, in which all atoms are in fourfold general positions, failed to yield a significantly improved *R*,

or to reduce the rather large thermal parameters of F(5) and cesium.

Table 4 lists the pertinent interatomic distances. Uranium has nine fluorine neighbours arranged to form a tri-capped trigonal prism, but one corner of the prism base is formed by the statistically distributed fluorine, F(5), so that the coordination number may be regarded as $8\frac{1}{2}$. This fluorine is not shared with other uranium atoms. The remaining eight fluorines are shared with a second uranium in such a way as to form sheets of composition (U₄F₁₆) parallel to (100) near $x = \frac{1}{4}, \frac{3}{4}$. The statistically distributed fluorine lies outside these sheets and near the planes of cesium ions at $x = 0, \frac{1}{2}$. These features of the structure are shown in Fig. 1. The U-F distances lie between 2.28 and 2.42 Å with an average of 2.33 Å. Cesium has 12 fluorine neighbors: six in the range 3.03 to 3.12 Å and six in the range 3.43 to 3.69 Å. The rather large thermal parameter of cesium may result from a positional disorder caused by its coordination with the statistically distributed fluorine. The tabular habit of the crystals parallels (100), the orientation of the (U₄F₁₆) sheets.

Table 3. Observed and calculated structure factors

Where *h*, *k* are left blank, they have the preceding value.

Table 3 contains observed and calculated structure factors for CsU₂F₉. The table lists *h* and *k* values and the observed and calculated structure factors. Values less than 1 are indicated by asterisks. The table is truncated in the provided image.

Table 4. Pertinent interatomic distances

U-F(1)	2.31 (1) Å	Cs-2F(1)	3.03 (1) Å
U-F'(1)	2.35 (1)	Cs-2F(2)	3.07 (1)
U-F(2)	2.33 (1)	Cs-2F(3)	3.12 (1)
U-F'(2)	2.29 (1)	Cs-2F(4)	3.43 (1)
U-F(3)	2.42 (2)	Cs-2F(5)	3.69 (1)
U-F'(3)	2.30 (1)	Cs-2F(5)	3.65 (2)
U-F(4)	2.28 (1)		
U-F'(4)	2.38 (1)		
U-F(5)	2.32 (2)		

The structure of CsU₂F₉ is distinctly different from that of KU₂F₉ first reported by Zachariasen (1948) and in greater detail by Brunton (1969). In the potassium compound the U⁴⁺ ion has true 9-coordination with all fluorines shared. Here also there are layers of edge-sharing U⁴⁺ polyhedra, but these layers are linked to one another by corner sharing.

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References

BRUNTON, G. (1969). *Acta Cryst.* B25, 1919-1921.
 BUSING, W. R., ELLISON, R. D., LEVY, H. A., KING, S. P. & ROSEBERRY, R. T. (1967). *The Oak Ridge Computer-Controlled X-ray Diffractometer*. ORNL-4143, Oak Ridge National Laboratory, Tennessee.
 CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* 53, 1891-1898.
 DOYLE, P. F. & TURNER, P. S. (1968). *Acta Cryst.* A24, 390-397.
 LARSON, A. C. (1967). *Acta Cryst.* 23, 664-665.
 ZACHARIASEN, W. H. (1948). *J. Amer. Chem. Soc.* 70, 2147-2151.
 ZACHARIASEN, W. H. (1967). *Acta Cryst.* 23, 558-564.