

SHORT STRUCTURAL PAPERS

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Disodium Uranium(IV) Fluoride

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Abstract. δ -Na₂UF₆, hexagonal, *P*3, $a = 6.112$ (2), $c = 7.240$ (2) Å, $Z = 2$. Intensities were measured diffractometrically. There are two uranium ions in the asymmetric unit and each of these ions has nine nearest-neighbour fluorine ions at the corners of capped trigonal prisms. The U–F distances range from 2.23 (1) to 2.42 (1) Å. There are four independent Na ions. Two are in the same type of crystallographic site and are also in the same type of polyhedron as the uranium ions. The other two have six coordination. The Na–F distances range from 2.25 (2) to 2.73 (2) Å.

Introduction. In connexion with a more general study of the crystal chemistry of mixed fluorides containing an actinide element, we first considered the phases appearing in binary LiF–AF₄ and NaF–AF₄ ($A = \text{Th, U, Np, Pu}$). For a NaF/AF₄ ratio of 2/1, we observed that the compound corresponding to Np was isotopic with the compound known as δ -Na₂UF₆. Because of the similarities in behaviour of Np and U, and in order to study the physical properties of these elements, we felt it appropriate to undertake the complete crystal structure analysis of δ -Na₂UF₆.

Single crystals were obtained by the flux-growth method (Cousson, Pagès, Cousseins & Vedrine, 1977). A eutectic mixture of sodium chloride and zinc chloride was used. The best results were obtained for: 2NaF + UF₄ + 2(NaCl + ZnCl₂). After degassing under high vacuum, the different compounds, mixed together, were heated to 913 K in a controlled atmosphere. From this temperature, slow cooling was programmed (5 K h⁻¹). Abundant single crystals appeared as green regular hexagons.

Lattice parameters and systematic absences were determined first by a study of single crystals with a

Weissenberg camera and precession photographs, and then a powder using a focusing goniometer: $a = 6.112$, $c = 7.240$ Å; hkl no conditions. Cu $K\alpha$ and Mo $K\alpha$ radiations were used.

The density of the crystals, measured by picnometry in *o*-xylene, corresponded to two formula units per cell ($D_{\text{exp}} = 5.640$, $D_{\text{calc}} = 5.645$ Mg m⁻³).

The 1/3 stoichiometry ratio for Na/F was confirmed using fast γ -ray spectrometry (Borderie, Pinault & Barrandon, 1977).

The single crystal used for the measurement of intensities was a regular hexagonal prism (0.180 × 0.180 × 0.140 mm). Data collection was made with the Nonius CAD-4 four-circle diffractometer of the Centre de Mesures Physiques de Clermont-Ferrand. Data-collection conditions were: Mo $K\alpha$ wavelength with graphite monochromator, ω - 2θ scan, $\theta_{\text{max}} = 50^\circ$, scanning range (1.2 + 0.35 tg θ)°. All 1924 reflexions out to $2\theta = 100^\circ$ were recorded. The intensities of three standard reflexions were checked hourly and their orientation every 100 reflexions (standard reflexions: 300, 030, 0.0.10). The relative standard deviation is 0.02. After Lorentz-polarization correction, 1735 positive reflexions remain. Maximum indices are 13 for h and k , 15 for l .

The linear absorption coefficient for Mo $K\alpha$ is 33.16 mm⁻¹. Absorption corrections were made using de Meulenaer & Tompa's (1965) analytical method, with the program *AGNOST* (Ahmed, 1976) (minimum absorption correction 0.015, maximum 0.092).

Packing was determined by classical methods. A three-dimensional Patterson map yielded the positions of all atoms. First, the positions of the heavy atoms belonging to group *P*321 were refined by placing them in the 2(d) site. With this data, a difference Fourier

synthesis determined the positions of all F and Na atoms and matched the results obtained with the Patterson map. We noted that the two U atoms were not correlated. We saw on this difference Fourier synthesis that one of the two U atoms was not completely eliminated. A centrosymmetric distribution could not lead to a satisfactory value of R ; for example, we obtain $R = 0.098$ in group $P\bar{3}$. We then distributed them in group $P3$, which is the only group in which the U atoms may be independent. The origin was set at U(1). Taking into account the anomalous dispersion, we give the absolute configuration for this structure.

The structure was refined by iterative least-squares adjustment using *AFFINE*, a modification of the

Table 1. Atomic positional parameters ($\times 10^4$) and isotropic temperature factors

	Position	x	y	z	B (\AA^2)
U(1)	1(b)	3333	6667	8579	0.4
U(2)	1(c)	6667	3333	1394 (1)	0.1
Na(1)	1(a)	0	0	313 (26)	1.6
Na(2)	1(a)	0	0	5111 (41)	1.7
Na(3)	1(b)	3333	6667	4141 (19)	0.5
Na(4)	1(c)	6667	3333	6213 (19)	0.7
F(1)	3(d)	3166 (22)	9191 (21)	1083 (15)	0.5
F(2)	3(d)	7157 (24)	911 (24)	3459 (16)	0.9
F(3)	3(d)	924 (34)	3946 (34)	6354 (25)	1.1
F(4)	3(d)	6991 (35)	800 (33)	9029 (23)	1.0

Table 2. Interatomic distances (\AA)

	Number at this distance		σ (\AA)
F(1)—F(4)	1	2.52	0.02
F(1)—F(4)	1	2.63	0.02
F(1)—F(4)	1	2.65	0.02
F(1)—F(2)	1	2.70	0.02
F(1)—F(2)	1	2.73	0.02
F(1)—F(1)	1	1.765	0.03
F(1)—F(2)	1	2.81	0.02
F(2)—F(2)	2	2.86	0.03
F(2)—F(3)	1	2.98	0.02
F(3)—F(3)	2	2.73	0.03
F(3)—F(4)	2	2.86	0.03
F(3)—F(4)	1	2.93	0.02
F(4)—F(4)	2	2.87	0.04
Na(1)—F(1)	3	2.29	0.02
Na(1)—F(4)	3	2.32	0.02
Na(2)—F(3)	3	2.36	0.02
Na(2)—F(2)	3	2.39	0.02
Na(3)—F(3)	3	2.25	0.02
Na(3)—F(2)	3	2.52	0.01
Na(3)—F(1)	3	2.73	0.02
Na(4)—F(3)	3	2.44	0.02
Na(4)—F(2)	3	2.59	0.02
Na(4)—F(4)	3	2.63	0.02
U(1)—F(3)	3	2.25	0.02
U(1)—F(1)	3	2.415	0.012
U(1)—F(4)	3	2.42	0.01
U(2)—F(2)	3	2.23	0.01
U(2)—F(1)	3	2.371	0.009
U(2)—F(4)	3	2.38	0.02

Busing, Martin & Levy (1962) computer program. The scattering factors are those of *International Tables for X-ray Crystallography* (1974).

With a series of three-dimensional refinements on the heavy atoms only, the scale factor k , the coordinates and the individual isotropic temperature factors were successively corrected, in three different cycles.

The evolution of the calculations is matched by the variation of the two agreement coefficients: $R = \sum (|F_o| - k|F_c|) / \sum |F_o|$ and $R_w = [\sum w(|F_o| - k|F_c|)^2 / \sum w|F_o|^2]^{1/2}$, where F_o and F_c are, respectively, the observed and calculated structure factors, k is the scale factor and w a statistical weight given to each F_o [$w = 1/\sigma^2(F_o)$, $\sigma(F_o) = \sigma(F_o^2)/2F_o$]. A second series of refinements was made on all the atoms, each given first an individual isotropic temperature factor, then anisotropic. After leaving out the planes with $I < 3\sigma(I)$, we obtain $R = 0.056$ and $R_w = 0.077$ for the remaining 1504 reflexions.*

Discussion. Atomic parameters are listed in Table 1 and interatomic distances in Table 2. Fig. 1 is an ideal projection of the structure in the $(x,y,0)$ plane.

In this structure, although they are located in different types of sites, the U atoms have similar polyhedra: trigonal tricapped prisms. The characteristic of this structure is that Na(3) and Na(4) are located in polyhedra identical to that of U: they are at the centres of trigonal tricapped prisms.

On the one hand, there is a piling up of Na and U [Na(3),U(1)] and, on the other hand, a piling up of U and Na [U(2),Na(4)]. Infinite chains are formed along c . Seen along c , these prisms share a triangular base.

The anionic arrangement is such that if a F atom belongs to the triangular base of a trigonal prism, it

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34265 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

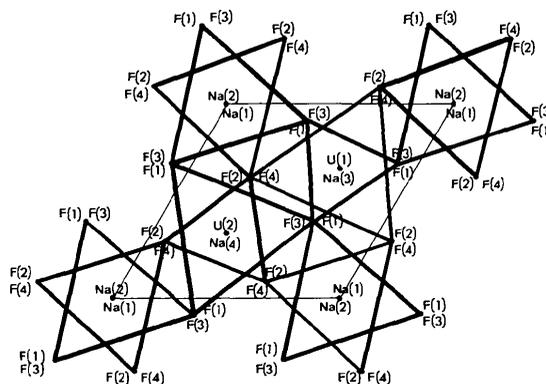


Fig. 1. Ideal projection of the structure in the $(x,y,0)$ plane.

builds a pyramid on one of the rectangular faces of another trigonal prism. Also, the distribution of the prisms is such that they form rings and enclose cavities occupied by Na(1) and Na(2). These cavities are antiprisms with a triangular base. They are not linked to one another.

F(1) and F(4) are, respectively, the bases of the U(1) and Na(3), and of the Na(4) and U(2) polyhedra. They build, respectively, a pyramid on the U(2) and U(1) polyhedra and are linked to Na(1). F(2) and F(3) are, respectively, the bases of the U(2) and Na(4), and of the U(1) and Na(3) polyhedra. They build, respectively, a pyramid on the Na(3) and Na(4) polyhedra and are linked to Na(2). The F atoms are of two types: F(1) and F(4) with a charge of $-(1 + \frac{1}{2})e$ and F(2) and F(3) with a charge of $-(1 - \frac{1}{2})e$.

As can be seen in Fig. 1, each U(1) polyhedron shares three F(3)–F(4) edges with the Na(4) polyhedra, and three F(1)–F(4) edges with the U(2) polyhedra. Each U(2) polyhedron shares the above-mentioned edges with U(1) and three F(1)–F(2) edges with the Na(3) polyhedra.

Several varieties of this compound are known, but no other structural study has been made. This variety is

the most stable form (Barton, Friedman, Grimes, Insley, Moore & Thoma, 1958).

The fact that U and Na atoms occupy the same type of polyhedra is unusual, and the fact that these prisms share triangular bases and edges with their neighbours probably accounts for the particular stability of this compound.

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The Structure of Potassium Tetrachlorozincate

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Abstract. K_2ZnCl_4 , orthorhombic, $Pna2_1$, $a = 26.778$ (6), $b = 12.402$ (2), $c = 7.256$ (2) Å, $Z = 12$, $d_o = 2.29$, $d_c = 2.36$ Mg m⁻³. Crystals prepared from aqueous solution were found to be isomorphous with high-temperature K_2CoCl_4 . The structure was refined by the full-matrix least-squares method to $R = 0.049$.

Introduction. The crystal structure of K_2CoCl_4 has been reported by Vermin, Verschoor & Ijdo (1976) to be closely related to the K_2SO_4 type, containing tetrahedral $CoCl_4^{2-}$ ions. Our crystal structure refinement of K_2ZnCl_4 is a part of the investigation of structures of the type A_2ZnCl_4 .

Clear, colourless crystals were obtained by slow evaporation of an aqueous solution of KCl and $ZnCl_2$ in the ratio 2:1. Since they are deliquescent, the freshly prepared crystals were immediately enclosed in thin-walled capillaries. A crystal of dimensions $0.16 \times 0.22 \times 0.20$ mm was optically centred on the Syntex P1, four-circle diffractometer. The orientation matrix and the cell parameters were determined on the basis of 15 reflections. The intensities of 3081 hkl reflections were measured according to the ω -scan technique (Mo $K\alpha$, graphite monochromator) using a scan range of 1° and a scan speed between 0.5 and $24.0^\circ \text{ min}^{-1}$ depending on the intensity of the measured reflection. In the range $3.0^\circ \leq 2\theta \leq 55.0^\circ$, 2558 reflections hkl with $I > 1.96\sigma(I)$ were obtained which were used for the structure refinement. For the evaluation the XTL system (Syntex, Nova 1200) was employed. An

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