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Structure cristalline de Rb₂UO₂F₄.H₂O. Par HENRY BRUSSET, NGUYEN QUY DAO et ANNE RUBINSTEIN-AUBAN,

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The crystal structure of $Rb_2UO_2F_4.H_2O$ has been determined from single-crystal X-ray intensity data as orthorhombic, space group *Pbca* with 8 molecules in the unit cell. The lattice parameters are $a=8\cdot881$ (3), $b=14\cdot547$ (6), $c=11\cdot975$ (4) Å, $d_{exp}=4\cdot8$ g.cm⁻³, $d_{th}=4\cdot6$ g.cm⁻³. The structure is composed of $U_2O_4F_8^{4-}$ ions, Rb⁺ ions and water molecules showing hydrogen bonding of medium strength.

Parallèlement à l'étude structurale du composé $Cs_2UO_2F_4$. H_2O (Nguyen Quy Dao, 1972), nous avons étudié la structure cristalline de $Rb_2UO_2F_4$. H_2O par diffraction des rayons X sur un monocristal. Les cristaux ont été préparés conformément à la méthode signalée dans la littérature (Davidovich, Sergienko & Kalacheva, 1968), soit en laissant évaporer lentement à l'air une solution contenant une mole de UO_2F_2 pour 3 moles de RbF. Ils ont ensuite été identifiés parmi les composé définis existant dans le système ternaire UO_2F_2.RbF.H_2O en dosant le rubidium et l'uranium par fluorescence X et en comparant son spectre infrarouge avec celui donné dans la littérature (Sergienko & Davidovich, 1970). La technique expérimentale utilisée pour la détermination de la structure est identique à celle exposée pour le composé homologue $Cs_2UO_2F_4$. H_2O.

Les caractéristiques de maille de $Rb_2UO_2F_4$. H_2O sont les suivantes:

$$a= 8,881 \pm 0,003 \text{ Å}$$
$$b= 14,547 \pm 0,006$$
$$c= 11,975 \pm 0,004$$

Groupe spatial *Pbca*

$$d_{exp}=4,8 \text{ g.cm}^{-3} \quad d_{th}=4,6 \text{ g.cm}^{-3}$$

8 groupements formulaires par maille.

La position de l'atome d'uranium a été déterminée grâce aux projections de la fonction de Patterson parallèlement aux trois de la maille. Les positions des atomes de rubidium ont été déterminées par la fonction de densité électronique tridimensionnelle. Les positions des atomes de fluor et d'oxygène ont été repérées sur la série différence tridimensionnelle. L'affinement général de la structure, supposant isotropes les facteurs d'agitation thermique des atomes, conduit à un coefficient de reliabilité R de 0,16. Cette valeur relativement élevée est due au fait que la correction d'absorption n'a pu être menée de façon rigoureuse. En effet, la forme irrégulière du cristal ne s'y prête pas. Nous avons été obligés d'effectuer la correction d'absorption en assimilant le cristal de forme allongée à un cylindre de longueur infinie. En raison de cette approximation nous n'avons pas jugé nécessaire de pousser plus avant l'étude structurale du composé. Le Tableau 1 donne les valeurs des coordonnées atomiques et le Tableau 2 indique les distances et angles interatomiques de la structure. La Fig. 1 représente la projection de la structure parallèlement à l'axe *c*. Les chiffres entre parenthèses indiquent la cote de l'atome. On peut constater sur cette figure, que la structure est composée d'ions $U_2O_4F_8^{4-}$, d'ions Rb⁺ et de molécules d'eau reliant les ions bicondensés par des ponts hydrogène (distances $H_2O-F(3)=2,78$ Å, $H_2O-F(2)=2,92$ Å). L'ion $U_2O_4F_8^{4-}$ possède approximativement la symétrie D_{2h}. Le groupement UO_2 est linéaire. La distance moyenne U–O est de $1,84 \pm 0,08$ Å. Les 8 atomes de fluor se trouvent approximativement dans un plan perpendiculaire à l'axe O–U–O. Les distances U–F varient entre 2,13 et $2,41 \pm 0,10$ Å. La distance entre deux atomes d'uranium d'un même dimère est de $4,000 \pm 0,005$ Å, tandis que la plus courte distance entre deux atomes d'uranium appartenant à deux dimères différents est de $5,898 \pm 0,005$ Å.

Tableau 1. *Coordonnées atomiques de* $Rb_2UO_2F_4.H_2O$ *(données en fraction de bord de maille)*

	X	σX	Y	σY	Z	σZ	B	σB
U	0,0926	0,0005	0,1210	0,0003	0,0418	0,0003	1,17	0,10
Rb(1)	0,104	0,002	0,107	0,001	0,441	0,001	2,40	0,30
Rb(2)	0,163	0,002	0,814	0,001	0,262	0,001	2,50	0,24
F(1)	0,150	0,010	0,260	0,004	0,097	0,005	1,5	1,0
F(2)	0,169	0,010	0,101	0,004	1,207	0,005	2,0	1,3
F(3)	0,019	0,010	0,034	0,005	0,089	0,006	2,6	1,5
F(4)	0,070	0,016	0,209	0,006	0,101	0,008	5,0	2,2
O(1)	−0,09	0,01	0,150	0,005	0,11	0,01	3,0	1,9
O(2)	0,27	0,01	0,084	0,005	−0,017	0,005	1,0	1,3
O(3)	0,09	0,02	0,460	0,005	0,19	0,01	4,0	2,3

Tableau 2. *Distances et angles interatomiques avec leurécart type*

U(1)—U(1')	4,005	(0,005) Å	U(1)-Rb(1)	4,78	(0,02) Å
U(1)—U(2)	5,898	(0,005)	U(1)-Rb(2)	4,55	(0,02)
U(1)—O(1)	1,88	(0,08)	U(1)-Rb(3)	4,34	(0,02)
U(1)—O(2)	1,80	(0,08)	U(1)-Rb(4)	4,13	(0,02)
			U(1)-Rb(5)	4,08	(0,02)
U(1)—F(1)	2,19	(0,07)	U(1)-Rb(6)	4,47	(0,02)
U(1)—F(2)	2,13	(0,07)	U(1)-Rb(7)	4,43	(0,02)
U(1)—F(3)	2,41	(0,07)	U(1)-Rb(8)	4,31	(0,02)
U(1)—F(4)	2,15	(0,07)			
U(1)—F(3')	2,26	(0,07)	O(1)-U(1)-O(2)	178	(4)°
			F(1)-U(1)-F(2)	76	(3)
F(1)-F(2)	2,66	(0,10)	F(1)-U(1)-F(4)	74	(3)
F(2)—F(3)	2,76	(0,10)	F(2)-U(1)-F(3)	74,5	(3)°
F(3)—F(3')	2,35	(0,10)	F(4)-U(1)-F(3)	75	(4)
F(4)—F(3)	2,68	(0,10)	F(3)-U(1)-F(3')	62	(3)
F(4)—F(1)	2,60	(0,10)	F(4)-F(2)-F(3)	160	(4)
			F(2)-F(1)-F(4)	167	(4)
Rb(1)-F(2)	2,85	(0,10)	F(3)-F(3')-F(4)	156	(4)
Rb(1)-F(1)	2,72	(0,10)	F(3)-F(4)-F(1)	163	(4)
Rb(1)-F(4)	2,73	(0,10)	F(3)-O(3)-F(2)	102	(5)
Rb(1)-O(1)	2,83	(0,10)			
Rb(2)-F(1)	2,68	(0,10)			
Rb(2)-F(4)	2,84	(0,10)			
Rb(2)-F(4')	2,89	(0,10)			
Rb(2)-O(1)	2,90	(0,10)			
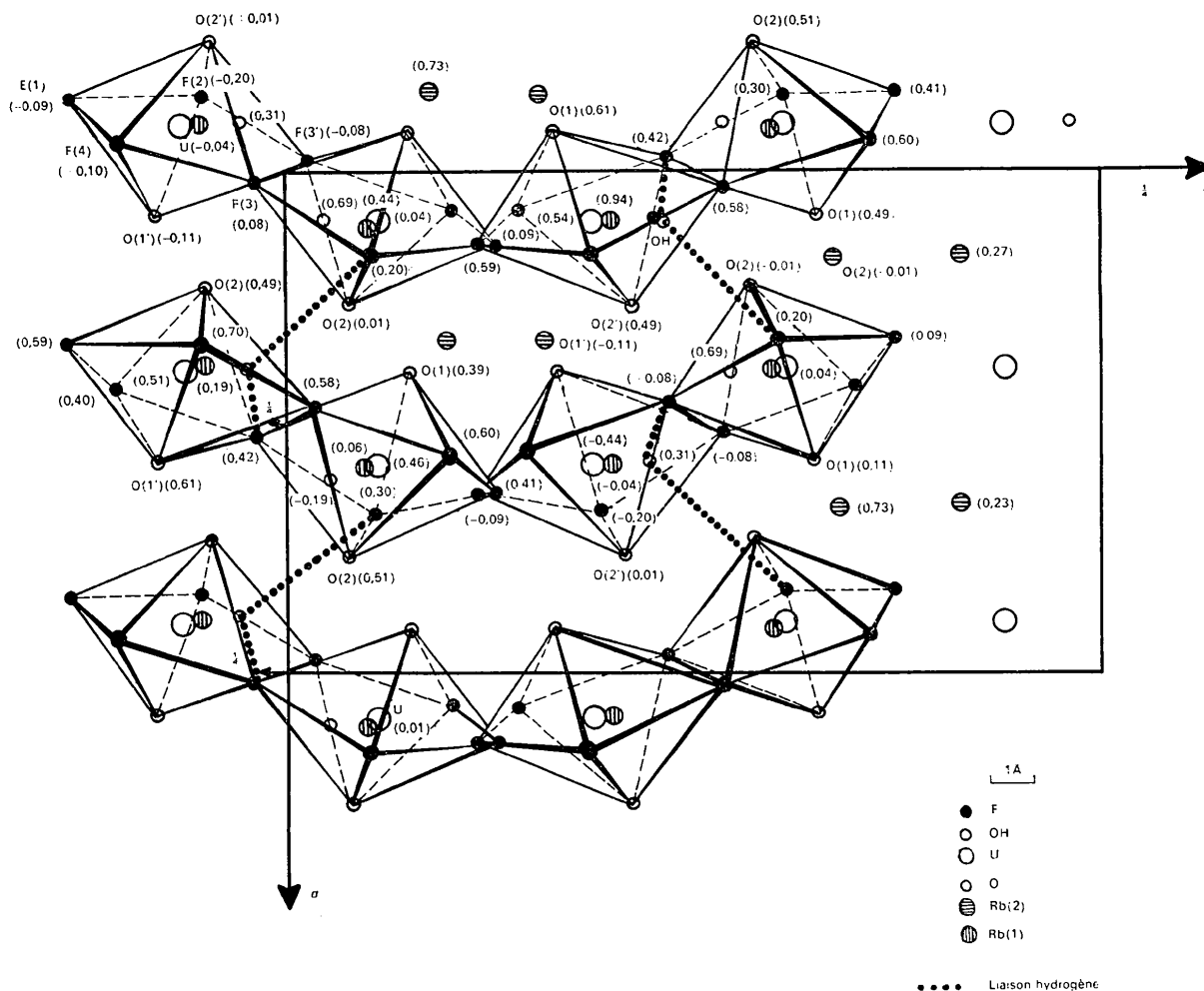
Fig. 1. Structure cristalline de $Rb_2UO_2F_4 \cdot H_2O$ projetée parallèlement à l'axe **c**.

Les atomes de rubidium se répartissent autour de l'ion bicondensé à une distance variant de 4,08 à 4,78 Å de l'atome d'uranium. Les plus proches voisins des atomes de rubidium sont trois atomes de fluor et un atome d'oxygène à une distance moyenne de 2,80 Å.

Les structures de $Rb_2UO_2F_4.H_2O$ et $Cs_2UO_2F_4.H_2O$ présentent des analogies mais elles ne sont pas isotypes.

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On the structures of 2-chlorothiophene and 2-bromothiophene.

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The original electron diffraction data for the monohalothiophenes (2 position) were reanalyzed, following currently improved procedures. It was again demonstrated that models with undistorted C_4H_4S rings do not fit the scattered intensity functions as well as do the initially proposed models (*A* or *B*), in contrast to conclusions published by Derissen, Kocken and van Weelden.

In a recently published note, Derissen, Kocken & van Weelden (1971) (DKW) reported their reanalysis of our electron diffraction data on the halosubstituted thiophenes, and concluded that structures in which the ring conformed to C_{2v} symmetry are in as good agreement with our molecular scattering intensities as are the initially proposed structures, *A* and *B*. DKW obtained their intensity functions by careful reading of photographic enlargements of our Figs. 5 and 7 (Harshbarger & Bauer, 1970). Such a procedure is highly suspect since it introduces correlations between adjacent points and incorporates a sequence of optical distortions, as well as the assumption that the draftsman was meticulous in reproducing our plotted curves (which were never intended to be a basis for precise data reporting). Indeed, the very low standard deviations they found strongly suggest the presence of large correlations rather than demonstrate an optimum fit of their model. Our original data are on file and will be sent to anyone on request. We consider the procedure followed by DKW to be erroneous and the acceptance of their note prior to submitting it to the original authors for comments to be an oversight by the journal.

It is well known, and it was clearly pointed out in our paper (Harshbarger & Bauer, 1970), that the one-dimensional Fourier transforms derived from gas diffraction data do not necessarily lead to unique molecular structures. For these compounds configurations *A* and *B* fit the molecular scattered intensity functions equally well and the choice must be made on the basis of other information. The question remains whether undistorted ring models or distorted ones are in 'best agreement' with the precise data, subject to certain constraints. In addition to criteria for adequacy of fit between observed and calculated intensities, to within some specified statistical limits, the final distances, bond angles, and root-mean-square amplitudes must fall within acceptable ranges. The symmetric ring structures proposed by DKW fail to meet the latter test. From our tabulated data for the C_{2v} model, values of $I(S-C)$ and $I(C-C)$'s range from 0·059–0·066 Å for the bromocompound, which are too large for such a well-knit structure. In contrast, the distorted models lead to corresponding values (0·045–0·051 Å), in agreement with magnitudes we found for the un-

substituted thiophene. The latter check the values reported by Bonham & Momany (1963), and agree with the calculated spectroscopic estimates by Cyvin, Cyvin, Hagen & Markov (1969). The C_{2v} constraint on chlorothiophene gave unacceptably large bond angles at C(4)C(3)H and C(4)C(5)H (> 140°), and correspondingly small angles at SC(5)H and C(2)C(3)H (< 110°). Finally, in their remarks regarding the structure of the unsubstituted thiophene DKW implied that the parameters reported by us, derived from two sets of data covering the range $6 < q < 125$, were less acceptable than those reported by Bonham & Momany (1963) which covered the smaller data range $15 < q < 90$, because the latter parameters were in slightly better agreement with the microwave structure reported by Bak, Christensen, Hansen-Nygaard & Rastrup-Andersen (1961). DKW failed to recognize that the microwave parameters are r_s values and should not be confused with electron diffraction parameters (r_a); the former are often 0·01 Å smaller than the latter due to the difference in the inherent averaging process by these two structural probes.

To substantiate our response to DKW we undertook a reanalysis of our tabulated data following current techniques, which we believe are superior to those available in 1968 when our previous reduction was completed. The principal innovations are a less subjective manner for drawing in the background function and ease of search for satisfactory structures. Thus, for each model we now have two sets of $qM(q)$ values, the original intensities with Harshbarger's background and the same intensities with Karl's background. It is worth noting that the tabulated data were obtained by averaging over a minimum of three plates for each range in scattering angles, while each plate was scanned several times. Between three to four times as many points were recorded as integral q values used. The standard deviations in measured densities among multiple recordings are generally 0·8 %, and always less than 1·2 %. At any one radial position in the diffraction pattern the polar averaged photometric precision is such that for ten readings the standard deviation is between 3 to 5 parts per 10,000. Discussions of both the random and systematic errors applicable to our operations are given in HB's paper and in other publications from this laboratory (Oberhammer & Bauer,