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Crystal Structure of Ferroelectric Guanidinium Uranyl Sulphate Trihydrate

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(*Received* 19 *October* 1976; *accepted* 7 *May* 1977)

The crystal structure of the ferroelectric title compound has been determined from three-dimensional X-ray data, and refined by full-matrix least-squares calculations to an R value of 6·9%. Although physical evidence required a non-centrosymmetric space group, convergence could only be achieved in the centrosymmetric monoclinic space group $C2/c$. The U coordination polyhedron is a pentagonal bipyramid with the uranyl O atoms at the apices. Sulphate groups, acting as bridging ligands, join polyhedra together to form a tightly bound two-dimensional network parallel to (001). A fairly complex H bonding pattern holds layers together, *via* the guanidinium groups and the water of crystallization. [Crystal data: $a = 11\cdot220$ (8), $b = 8\cdot027$ (4), $c = 18\cdot681$ (8) Å, $\beta = 101°$ (4′), $U = 1652$ (1) Å^3.]

Introduction

As part of a general study of the relationship between crystal structure and electrical properties of uranyl compounds, we report here the crystal and molecular structure of guanidinium uranyl sulphate trihydrate (hereinafter GUSH), as obtained from three-dimensional X-ray photographic data.

Interest in this study was stimulated by the fact that the material has been found to be ferroelectric (de Benyacar, de Dussel & de Wainer, 1977).

Experimental

The material used throughout this investigation was synthetized following Canneri (1925). After recrystallization from a saturated water solution at room temperature, well developed thick plates were obtained which, under optical investigation, showed a biaxial interference figure corresponding to an orthorhombic, or lower, symmetry (X-ray diffraction patterns showed later that the true lattice symmetry was monoclinic).

A crystal suitable for X-ray analysis was mounted along **b**, and *hk*0 and 0*kl* precession photographs were taken with Mo $K\alpha$ radiation, from which accurate cell dimensions were measured and later confirmed by the least-squares fit of a calibrated powder diagram (Table 1).

Table 1. *Indexed powder diagram of GUSH*

$h\,k\,l$	d_{obs} (Å)	d_{cal} (Å)
0 0 2	9·158	9·169
1 1 1	6·349	6·344
1 1 1	5·912	5·910
2 0 2	5·177	5·177
1 1 2	5·038	5·036
1 1 3	4·723	4·721
0 0 4	4·584	4·585
2 0 2	4·368	4·368
1 1 3	4·220	4·219
0 2 1	3·916	3·921
0 2 2	3·678	3·677
1 1 4	3·560	3·560
3 1 1	3·389	3·390
1 1 5	3·357	3·358
0 2 3		3·355
2 2 0	3·245	3·243
2 2 2	3·172	3·172
3 1 3		3·171
0 0 6	3·054	3·056
2 2 2	2·955	2·955
3 1 4		2·954
2 0 6	2·919	2·919
1 3 2	2·529	2·531
1 1 7		2·530
0 0 8	2·293	2·292
4 0 6	2·273	2·273
4 2 0		2·270

Crystal data

Guanidinium uranyl sulphate trihydrate, $(SO_4)_2$-$UO_2.[C(NH_2)_3]_2.3H_2O$. $M_r = 636{\cdot}3$, $F(000) = 1200$. Monoclinic, $a = 11{\cdot}220\,(8)$, $b = 8{\cdot}027\,(4)$, $c = 18{\cdot}681\,(8)$ Å, $\beta = 101°\,(4')$, $U = 1652\,(1)$ Å^3. $D_m = 2{\cdot}53$ (pycnometric), $D_x = 2{\cdot}55$ g cm^{-3}. μ(Mo $K\alpha$) = 122 cm^{-1}. Maximum crystal dimensions: 0·2 × 0·4 × 0·2 mm. Space group: *Cc* or *C*2/*c* (from systematic absences *hkl*: $h + k = 2n + 1$, *h*0*l*: $l = 2n + 1$). Although the structure could only be refined in the centrosymmetric space group *C*2/*c* (to an *R* value of 6·9%), this is in contradiction with the known ferroelectric character of the material.

Canneri (1925) reported the compound to be a tetrahydrate, but a better match between our calculated and measured densities was obtained if three water molecules were assumed. Moreover, a thermogravimetric analysis of the material showed, as its only distinctive feature, a sharp loss of three water molecules per formula unit at about 65 °C. This result was later confirmed by the structure determination.

The collection of three-dimensional data was undertaken with an integrating Weissenberg camera, using equi-inclination techniques. Levels *h*0*l* to *h*7*l* were recorded with Mo *Kα* radiation ($\lambda = 0{\cdot}7107$ Å) and 1713 non-zero reflexions were measured on a manual microdensitometer. Data were corrected for geometrical and absorption factors, and after correlation with *hk*0 cross-level data, a Patterson map was computed and evaluated in the lower-symmetry group *Cc*.

Structure determination

The highest Harker peaks unambiguously showed the positions of the U atom. The rest could not be easily interpreted in terms of the usual octahedral coordination of the U atom in uranyl compounds, so a cycle of Fourier synthesis was performed until the whole structure could be recognized. The final *F* map showed a very nearly centrosymmetric distribution for non-H atoms, with the U atoms surrounded by a pentagonal bipyramid, the base formed by four O atoms from the sulphate groups and a fifth oxygen from a water of crystallization. The latter, as well as the U atom, lay on a quasi-twofold axis which bisected the pentagonal base. To check, by means of refinement-convergence arguments, if that symmetry element was genuine (which would imply that the whole structure was centrosymmetric, in conflict with the physical properties previously found) a cycle of full-matrix least-squares refinement was begun in space group *C*2/*c*, with the atomic coordinates, temperature factors and a separate scale factor for each layer as variables. The process converged fairly smoothly in a few cycles to an *R* value of 8·9% when individual isotropic temperature factors were used. Refinement was pursued with an overall scale factor and anisotropic temperature factors for the heavier atoms and, afterwards, for those atoms not directly coordinated to them (which showed the largest isotropic temperature factors). The latter were included to see if any anomalous behaviour attributable to some kind of disorder could be detected, but the results obtained seemed to rule out this possibility. The *R* value decreased to 7·3%. Up to this stage of refinement, each reflexion had been given unit weight.

An attempt was made to refine the structure in the non-centrosymmetric space group *Cc*, but it resulted in very unreliable parameter shifts and therefore in bond distances with no chemical sense. This behaviour seemed to preclude the possibility of detecting any departure from a centrosymmetric arrangement for non-H atoms. However, the fairly low figures attained for *R* during the refinement in space group *C*2/*c*

Table 2. *Final parameters*

The anisotropic temperature factor is defined as $\exp(-\Sigma\, h_i h_j \beta_{ij})$. When both isotropic and anisotropic temperature factors are reported, $B_{\rm iso}$ refers to the value it had at the time the isotropic refinement had converged.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	$B_{\rm iso}$
U	0·5000*	0·2906 (2)	0·2500*	12 (0)	33 (2)	8 (0)	0 (*)	1 (0)	0 (*)	0·85
S	0·7805 (4)	0·4592 (8)	0·2078 (2)	19 (3)	29 (16)	12 (1)	7 (5)	6 (2)	−4 (5)	1·28
N(1)	0·3011 (21)	0·0408 (39)	0·4115 (10)	87 (21)	246 (98)	14 (6)	4 (37)	4 (10)	22 (28)	3·12
N(2)	0·1801 (19)	0·0660 (37)	0·5031 (12)	67 (18)	163 (92)	29 (9)	31 (33)	16 (11)	7 (33)	3·52
N(3)	0·3554 (21)	−0·0981 (33)	0·5189 (12)	75 (18)	42 (76)	23 (8)	−1 (29)	6 (10)	−16 (30)	3·33
C	0·2774 (21)	0·0081 (44)	0·4769 (15)	40 (16)	134 (96)	24 (9)	2 (30)	7 (10)	−3 (35)	2·66
W(2)	0·4844 (14)	0·7646 (36)	0·4065 (9)	49 (11)	352 (98)	28 (7)	−30 (30)	3 (7)	27 (31)	3·20
W(1)	0·5000*	0·6023 (28)	0·2500*	12 (10)	25 (41)	43 (9)	0 (*)	−1 (7)	0 (*)	1·84
O(*A*)	0·4757 (10)	0·2923 (27)	0·1546 (6)							2·04
O(1)	0·6224 (11)	0·0503 (19)	0·2435 (8)							1·43
O(2)	0·8367 (13)	0·3165 (22)	0·1783 (8)							2·34
O(3)	0·6981 (11)	0·3983 (21)	0·2552 (7)							1·72
O(4)	0·7836 (13)	0·0590 (24)	0·3538 (8)							2·34

* Parameters fixed by symmetry.

Table 3. *Calculated hydrogen positions*

The first digit refers to the nitrogen atom to which the H atoms are bonded.

	x	*y*	*z*
H(11)	0·2438	0·1149	0·3762
H(12)	0·3766	−0·0081	0·3965
H(21)	0·1181	0·1411	0·4715
H(22)	0·1692	0·0344	0·5544
H(31)	0·4267	−0·1474	0·4994
H(32)	0·3426	−0·1287	0·5699

Table 4. *Interatomic distances* (Å) *and angles* (°)

U–*W*(1)	2·503 (22)	*W*(1)–U–O(*A*)	89·6 (6)
U–O(*A*)	1·751 (11)	O(1)–U–O(*A*)	86·2 (6)
U–O(1)	2·385 (15)	O(3)–U–O(*A*)	90·1 (6)
U–O(3)	2·370 (14)	*W*(1)–U–O(3)	68·6 (5)
		O(1)–U–O(3)	75·7 (5)
		O(1)–U–O(1′)	70·8 (5)
		W(1)–U–O(1)	144·0 (5)
S–O(1)	1·474 (15)	O(1)–S–O(2)	107·5 (9)
S–O(2)	1·465 (18)	O(1)–S–O(3)	105·5 (8)
S–O(3)	1·480 (14)	O(1)–S–O(4)	113·9 (9)
S–O(4)	1·473 (17)	O(2)–S–O(3)	109·3 (9)
		O(2)–S–O(4)	108·2 (9)
		O(3)–S–O(4)	112·3 (9)
C–N(1)	1·325 (34)	N(1)–C–N(2)	125·4 (2·7)
C–N(2)	1·361 (35)	N(1)–C–N(3)	115·9 (2·6)
C–N(3)	1·359 (36)	N(2)–C–N(3)	118·8 (2·6)

suggested that such departures, if any, ought to be rather small, and it was accordingly decided to refine the structure in the centrosymmetric space group.

At this stage, the guanidinium H atoms were added at their expected positions, as determined by the molecular geometry assuming an sp^2 bond configuration for each N atom, and a N–H distance of 1·02 Å. Two extra refinement cycles were performed, this time using a weighting scheme of the type

$$\sigma^2 = (A + BF + CF^2)/[D - \exp(-E\rho^2)]$$

where F is the structure amplitude, $\rho = \sin\theta/\lambda$, and $A = 5$, $B = -0{\cdot}5$, $C = 0{\cdot}02$, $D = 1{\cdot}06$, $E = 1{\cdot}8$, which proved to remove to a good extent any systematic trend of $\Sigma w\Delta^2$ as a function of F and ρ. Convergence was considered to have been achieved when parameter shifts were less than $\frac{1}{3}$ of the corresponding e.s.d.'s. The final residual dropped to $R = 6{\cdot}9\%$. A final ΔF synthesis showed no significant peaks attributable to missing atoms. Scattering factors (including anomalous dispersion corrections) used throughout the refinement were taken from *International Tables for X-ray Crystallography* (1968).

The final atomic parameters for non-H atoms are reported in Table 2, and, in Table 3, those for the H atoms included (but not refined) in the last stages of refinement. Table 4 shows the interatomic distances and angles.*

Structure results and discussion

As anticipated the U atom is surrounded by a pentagonal bipyramid of O atoms (Figs. 1, 2). The upper half of the coordination polyhedron is related to the lower half by the twofold axis which bisects the pentagonal

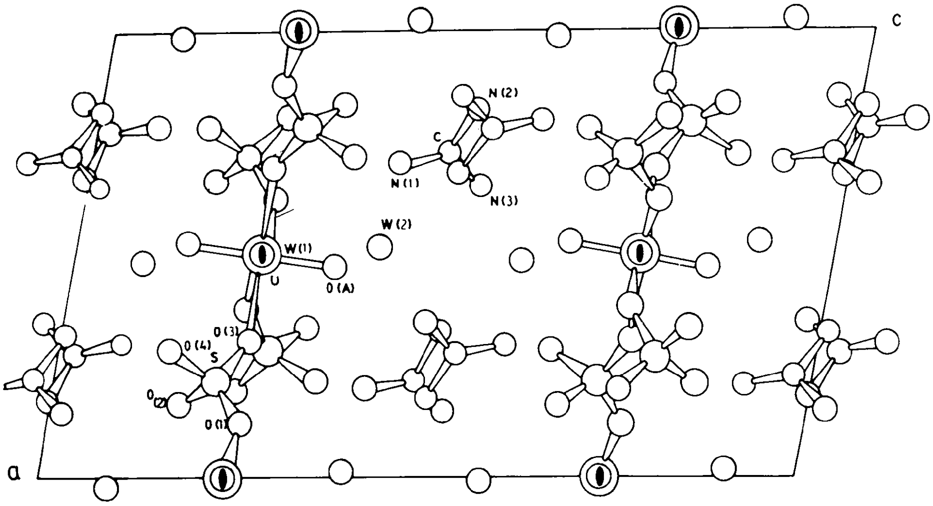

Fig. 1. Projection of the structure down **b**.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32744 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

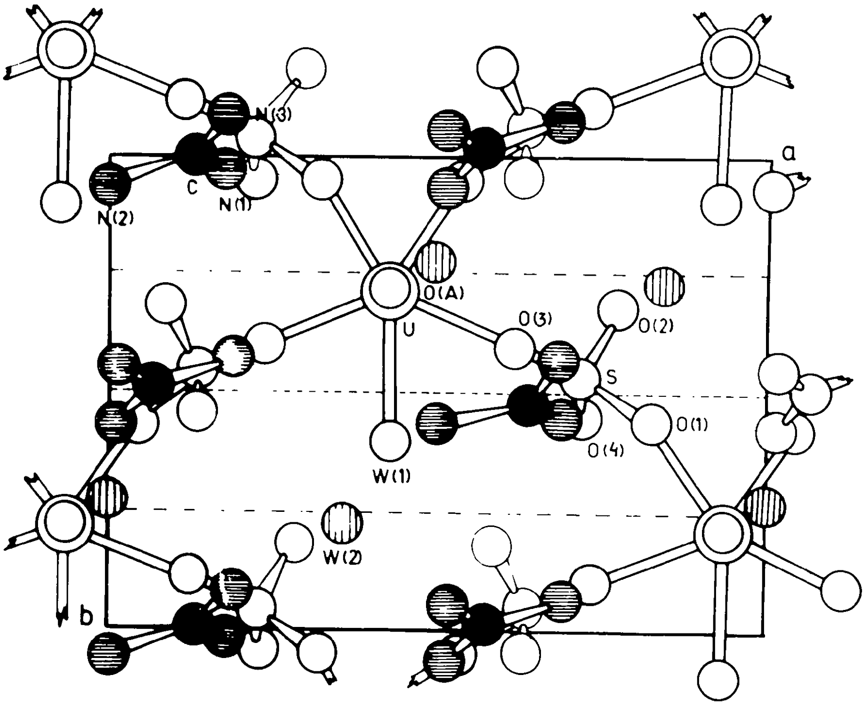

Fig. 2. Projection of the structure down **c***.

Table 5. *Short contacts attributable to* H *bonding*

Atoms involved X–H···Y	Distances (Å) X···Y	H···Y
N(1)–H(11)···O(2)	3·02	2·03
N(1)–H(12)···W(2)	3·04	2·18
N(2)–H(21)···W(2)	3·01	2·03
N(2)–H(22)···O(4)	2·81	1·85
N(3)–H(31)···W(2)	2·98	2·09
N(3)–H(32)··· O(A)	3·06	2·36
O(4)	3·09	2·26
W(1)···O(2)	2·68	
W(2)···O(2)	2·82	
W(2)···O(4)	2·81	

Table 6. *Least-squares planes with deviations from them* (Å)

(*a*) Equatorial plane of the U bipyramidal coordination polyhedron

$$0{\cdot}0066X + 0{\cdot}0001Y - 1{\cdot}0000Z + 4{\cdot}5525 = 0$$

Deviations: U 0·0, W(1) 0·0, O(1) 0·128, O(3) −0·081

(*b*) Guanidinium group

$$0{\cdot}4824X + 0{\cdot}7847Y + 0{\cdot}3893Z + 4{\cdot}1205 = 0$$

Deviations: N(1) 0·004, N(2) 0·004, N(3) 0·003, C −0·016

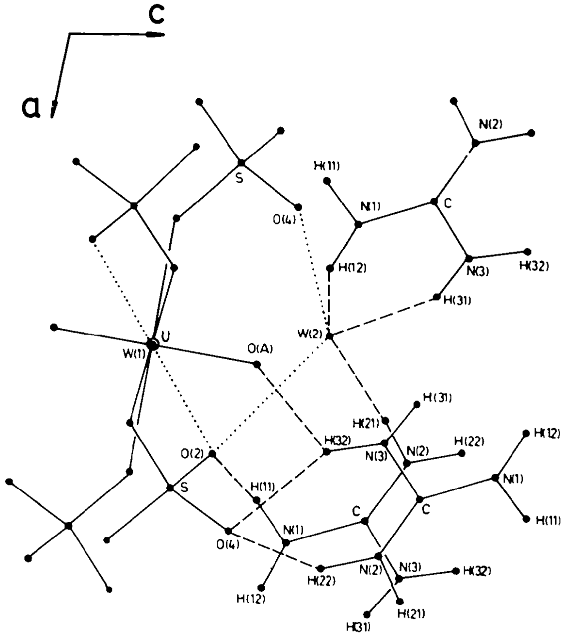

Fig. 3. Schematic partial projection down **b** showing possible H bonds. Dashed lines: short H···O contacts. Dotted lines: short O···O contacts.

base through the U atom and a water molecule coordinated to it, thus forcing the uranyl group to be strictly linear. The sulphate group acts as a bridging ligand, joining bipyramids together with only two kinds of O atoms [namely O(1) and O(3)] involved in the bridging process. This results in two-dimensional networks of U atom coordination polyhedra almost parallel to (001) at heights $z \simeq 0{\cdot}25$ and $z \sim 0{\cdot}75$ (Figs. 1 and 2), with a large number of potentially good acceptors [O(2) and O(4)] for H bonding.

The gap between the layers is filled with guanidinium cations and the remaining water of crystallization (which lies in a general position and accounts for the two missing water molecules in the formula unit). All of them are potentially good donors for H bonds, and so a fairly complex H bonding scheme was expected, connecting layers together into a three-dimensional network.

The presence of the U atom precluded the possibility of detecting the H atoms in a ΔF synthesis, but the well-known configuration of the guanidinium group made it easy to 'guess' the positions of its six H atoms with an accuracy reasonable enough for a discussion of H bonds.

Let us describe such a situation by the scheme X—H$\cdots Y$. Table 5 lists short (estimated) H$\cdots Y$ distances interpreted as H bonds (X is nitrogen, Y is oxygen) as well as the corresponding $X\cdots Y$ distances. Short O$\cdots$O contacts (significantly shorter than the sum of the corresponding van der Waals radii), which could be interpreted as $X\cdots Y$ distances of an X—H$\cdots Y$ bond (X is an O atom from a water molecule, Y is an O atom from a sulphate group), are also shown.

If all these short contacts are accepted as H interactions, a fairly complete H bonding picture is achieved, with each of the nine independent H atoms involved in it. One of them [H(32)] bonds to O(4) and O(A) in a bifurcated mode, with an $X\cdots Y$ distance of 3·09 Å, the longest found in the structure.

Each of O(2), O(4) and W(2) interacts with three different H atoms, thus providing the necessary supply of acceptors.

The fact that the compound dehydrates and loses the water molecule within the U atom coordination polyhedron, W(1), at about the same temperature as W(2) means the latter is at least as firmly attached to the structure as W(1). In fact, Fig. 3 shows that it forms five H bonds with the neighbouring atoms.

The geometry of the chemical groups involved in the structure is quite normal. The uranyl group, forced by symmetry to be linear, is, within experimental error, perpendicular to the least-squares equatorial plane of the U coordination polyhedron (Table 6a), the calculated direction cosine to the normal being 0·999 (3).

U—O distances (1·75 Å to the uranyl O atom, 2·38 Å to sulphate O atoms, and 2·50 Å to the coordinated water) agree well with values previously found, as do the S—O distances in the sulphate group (mean value 1·47 Å) and the O—S—O angles (mean value 109·5°).

The guanidinium anion is almost planar (Table 6b), its only outstanding feature being thc shortening of the O—N(1) bond. Although there are similar examples in the literature (Voliotis & Rimsky, 1975; Voliotis, Rimsky & Faucherre, 1975; Gupta & Dutta, 1975; Adams & Small, 1974) the present case may not be significant, owing to the rather large e.s.d.'s associated with these bond lengths.

Concluding remarks

The original aim of this work was to obtain a model to aid interpretation of the ferroelectric behaviour of GUSH. Although the space group in which we could refine the structure conflicts with this behaviour, we think that it gives a good description of the non-H atom distribution. The non-centrosymmetry associated with ferroelectricity might then be ascribed to the H atoms that we cannot resolve, and it is in this direction that we believe future investigation in the field must evolve.

The following programs were used, and their provision is gratefully acknowledged: A. Zalkin & B. Foxman: general Fourier synthesis, *FORDAP*; C. T. Prewitt & B. Foxman: full-matrix least-squares program, *SFLS*-5; M. E. Pippy & F. R. Ahmed: scan of interatomic distances and angles; M. E. Pippy & F. R. Ahmed: mean-plane calculation.

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