

Twinning and Pseudo-Symmetry in Two Complexes of Uranyl Chloride with Dibenzylideneacetone

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Abstract

The complexes $C_{34}H_{28}Cl_2O_4U$, $UO_2Cl_2(DBA)_2$ [DBA = dibenzylideneacetone, $(C_6H_5-CH=CH)_2CO$] and $UO_2Cl_2(DBA)_2 \cdot 2CH_3COOH$ both show twinning leading to pseudo-symmetry and possible false assignment of space group; this is made more significant by the presence of a heavy atom at the origin and by molecular symmetry.

It has been previously reported (Alcock, Herron, Kemp & Shoppee, 1975) that $UO_2Cl_2(DBA)_2 \cdot 2CH_3COOH$ crystallizes in space group $C2/m$ with $Z = 4$. The structure was solved and refined in that space group to $R = 0.121$. Only two molecules whose U atoms are at $0,0,0$ and $\frac{1}{2}, \frac{1}{2}, 0$ could be found and refined, and it appeared that the two other molecules in the middle of the cell at $c \simeq \frac{1}{2}$ were disordered. It was also reported that the unsolvated form of the same complex crystallizes in space group $C2$ with $Z = 2$, the U atoms being located on diad axes. Solution and refinement of the structure led to $R = 0.081$, but several interatomic distances and temperature factors were not satisfactory. Both structures have now been reinvestigated, and the refinement problems shown to be due to twinning. The structural results will be reported elsewhere (Alcock, de Meester & Kemp, 1978). For this note we discuss the twinning and pseudo-symmetry encountered. For both crystals these problems were complicated by the presence of a very heavy atom at the origin and by molecular symmetry.

Pseudo-symmetry and twinning in $UO_2Cl_2(DBA)_2 \cdot 2CH_3COOH$

This form of the complex is so photo-sensitive that severe decomposition occurs after exposure to daylight for about 1 h. Preliminary Weissenberg photographs revealed a cell with apparent monoclinic symmetry. Using a fresh crystal (for which no photographs could be taken), least-squares refinement of 15 reflections on the Syntex $P2_1$ diffractometer gave the following cell

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constants at 291 K: $a_2 = 9.671$ (5), $b_2 = 17.745$ (9), $c_2 = 21.54$ (2) Å, $\alpha_2 = 90.78$ (5), $\beta_2 = 91.93$ (5), $\gamma_2 = 89.52$ (4)° and $U_2 = 3694$ Å³ (cell II). The deviations of α_2 and γ_2 from 90° were thought to be a result of the large w -spread of the crystal, which was consequently treated as having monoclinic symmetry. Study of the data collected with this crystal gave the refinement problems noted above. On reinvestigation with a new crystal, a triclinic cell was found of one quarter the volume of the original monoclinic cell. Refinement in $P1$, using this cell, proceeded very smoothly (to $R = 0.035$). The cell constants at 118 K are $a_1 = 11.851$ (2), $b_1 = 10.023$ (3), $c_1 = 11.668$ (3) Å, $\alpha_1 = 103.57$ (2), $\beta_1 = 129.20$ (2), $\gamma_1 = 103.48$ (2)° and $U_1 = 900.4$ Å³ (cell I). On reindexing, these give $a_2 = 9.593$ (2), $b_2 = 17.679$ (6), $c_2 = 21.245$ (4) Å, $\alpha_2 = 89.31$ (2), $\beta_2 = 91.14$ (1), $\gamma_2 = 90.45$ (2)° and $U_2 = 3602.0$ Å³, corresponding to the original cell used (cell II). This cell (II) is therefore a quadruply-centred triclinic cell. In Fig. 1, the unit cells and lattice points of cells (I) and (II) are shown, demonstrating their relationship. In cell (II), the U atoms of the four molecules are located at $0,0,0$ and $\frac{1}{2}, \frac{1}{2}, 0$ (C-centre) and

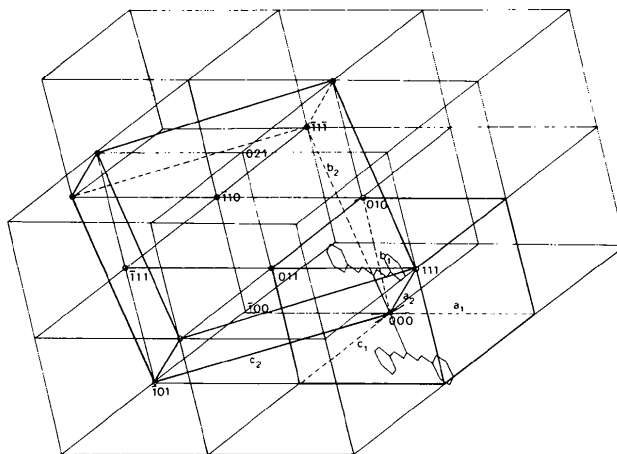


Fig. 1. $UO_2Cl_2(DBA)_2 \cdot 2CH_3COOH$, showing several unit cells of the lattice based on the primitive cell (I) and how the quadruple cell (II) is generated. Indices of lattice points of cell (I) are given.

$\pm(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ corresponding to the lattice points 000, 010, 011 and 110 of cell (I) (see Appendix). The U—O=C line is precisely along the b_2 axis, and thus the *trans*-octahedral coordination of the U atom virtually gives the molecules $2/m$ symmetry relative to this axis (the 000 site symmetry in $P2/m$). However, the final refinement showed slight twists in the dibenzylideneacetone groups, giving a dihedral angle of 7.8° between the phenyl rings, which would be related by a twofold axis.

It is also useful to compare cells (I) and (II) in reciprocal space. Fig. 2 shows the $hk0$ net (cell II) which also contains b^* of cell (I). The points common to both lattices (I) and (II) are shown with their two indices, the lower corresponding to cell (II), the upper to cell (I). The unindexed spots are C -centring absences (cell II). Those given one index would occur with a normal C -centred cell, but are also systematically absent in cell (II) with an untwinned crystal because they do not fulfil the condition $h - k + 2l = 4n$ (which also excludes the C -centred reflections), and thus have non-integer indices in cell (I) (see Appendix). However, they do occur in the inverse twin of cell (I) obtained by a rotation of 180° about a_2^* . Reflections of this type were observed in the first data set collected. This gives unambiguous proof that the crystal was twinned; as noted above, no photographs could be taken of it.

We can also consider if there is any relationship in intensity between observed reflections in cell (I), since

refinement with the first crystal in space group $C2/m$ was partly successful. In Fig. 2, two $h \pm kl$ reflections, for example 220 and $\bar{2}\bar{2}0$ (cell II), should have the same intensity if this cell has $C2/m$ symmetry. A modified version of *DATCO5* in the XRAY 76 system (Stewart, 1976) was used for this purpose. Cell (I) to cell (II) index transformation was performed on all hkl , and observed F_{hkl} values were averaged with $F_{h\bar{k}l}$; as Fig. 2 shows, only half of the reflections in cell (I) can be averaged, since half of them are systematically absent. This half of the data produced $R = 0.05$ $\{R = \sum [(F_{hkl} - F_{h\bar{k}l})/2(F_{hkl} + F_{h\bar{k}l})]\}$, with about 10% rejected where $\Delta F > 5\sigma(F)$. This strikingly good agreement reflects the pseudo $2/m$ symmetry of the molecule.

The crystal habit, in combination with the twinning rule, complicates the problem further. The crystals are plates, elongated along a_2 (cell II) and their obvious mounting is about this axis rather than along any of the axes of cell (I). The zero layer for this axis ($0kl$ of cell II) contains *only* reflections which all have pseudo-symmetric equivalents; thus the apparent symmetry is extremely close to mm . This is not affected by twinning, which merely adds an equal additional intensity to each of a pair of spots. On the first layer, the pseudo-symmetry is retained for half the spots, as shown above, while for a twinned crystal, the spots of the second component fill in the gaps in the pattern that would otherwise reveal absences in the complex lattice. Therefore the only significant deviation from the apparent higher symmetry is in the intensity relationship between these pairs of spots. Thus, in the obvious mounting, the zero layer does not easily reveal the twinning, and only on very close examination of high-quality photographs of the first or higher layers can it be detected.

Twinning in $UO_2Cl_2(DBA)_2$

This complex crystallizes as perfect prisms of hexagonal section, with faces of the type $\{001\}$ and $\{111\}$. The twinned crystal used in the first data collection showed no absences other than $h + k = 2n + 1$, indicating space groups $C2$, Cm or $C2/m$. The structure was solved and refined in space group $C2$, but the results were not satisfactory. Later, when this complex was reinvestigated, precession and Weissenberg photographs showed that *all* crystals are twinned in a perfect manner, in the sense that they are made of two single crystals with the true space group $C2/c$. Fig. 3 shows the $h0l$ zone, indexed in terms of the two lattices. The two single crystals share their ab plane, but their c^* axes are pointing in opposite directions and the angle between a_1^* and a_2^* is $180^\circ - 2\beta^*$. The rows with $h = 2, 6, 10, \dots$ (all single peaks) have twice as many spots as rows with $h = 4, 8, 12, \dots$ (all double peaks). Treating the lattice as single, the two first spots on row

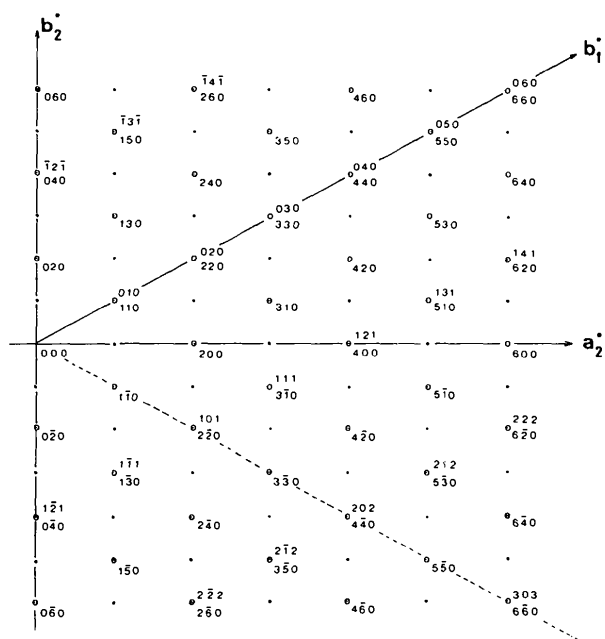


Fig. 2. $UO_2Cl_2(DBA)_2 \cdot 2CH_3COOH$, showing the $hk0$ zone of cell (II). Unindexed reflections are C -centring absences, those with one index are absences of the type $h - k + 2l = 4n$, and those with two indices are the only ones common to both cell (II) (lower index) and cell (I) (upper index).

201, whose separation corresponds to $c \approx 21 \text{ \AA}$, would be indexed 200 and 201 instead of 200 (crystal 1) and 20 $\bar{2}$ (crystal 2), resulting in no apparent absences in the $h0l$ zone. In the $h1l$ zone, not shown here, the c axis appears doubled ($c \approx 42 \text{ \AA}$), because of the perfect twinning, though this was not detected in the first data collection. All peaks on layers with k odd are single (*i.e.* generated either by crystal 1 or 2). Upper layers with k even are similar to the $h0l$ zone, except that all rows have the same number of spots as the 201 rows, and all spots are double. Therefore, one may assume that in the initial structure determination, half of the data collected (those with k odd) were identical to those that would have been given by a single crystal. This, no doubt, explains the low R value achieved. The crystal used in our redetermination of the structure in space group $C2/c$ was obtained by cleavage of a twinned crystal along the ab plane and its photographs were normal. The cell constants are $a = 12.397(5)$, $b = 11.587(3)$, $c = 21.950(5) \text{ \AA}$, $\beta = 97.89(2)^\circ$.

Conclusions

The effect of twinning is well known as a crystallographic trap, but we see here that its effects can be reinforced by molecular symmetry, and particularly by the presence of a heavy atom at the origin. This can even lead to intensity relationships that do not deviate obviously from those expected for the pseudo-symmetry. It is also worth noting the particular danger when a diffractometer is used and photographs of the actual crystal employed either are not or (as in the case of the photo-sensitive crystals) cannot be taken.

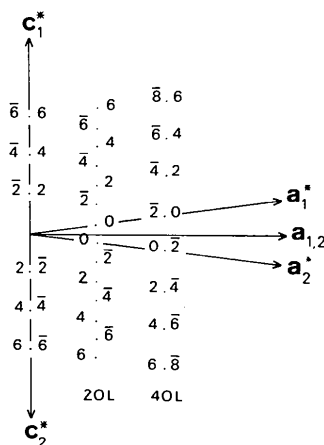


Fig. 3. $\text{UO}_2\text{Cl}_2(\text{DBA})_2$, showing the indexed $h0l$ net of a twinned crystal. The l index of crystal 1 is shown on the right side, that of crystal 2 on the left side.

APPENDIX

Transformation matrices and systematic absences for $\text{UO}_2\text{Cl}_2(\text{DBA})_2 \cdot 2\text{CH}_3\text{COOH}$

(a) The transformation matrix from cell (I) to cell (II) for unit-cell vectors and indices is:

$$A = \begin{pmatrix} 1 & 1 & 1 \\ -1 & 1 & -1 \\ -1 & 0 & 1 \end{pmatrix}$$

with inverse

$$A^{-1} = \begin{pmatrix} \frac{1}{4} & -\frac{1}{4} & -\frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & 0 \\ \frac{1}{4} & -\frac{1}{4} & \frac{1}{2} \end{pmatrix}.$$

The relationship between the two twin members in cell (II) is given by the matrix:

$$B = B^{-1} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}.$$

(b) Cell (II) has eight equivalent positions:

$$(0,0,0; \frac{1}{2}, \frac{1}{2}, 0) +$$

$$x, y, z; \frac{1}{4} + x, \frac{3}{4} + y, \frac{1}{2} + z$$

$$-x, -y, -z; \frac{1}{4} - x, \frac{3}{4} - y, \frac{1}{2} - z.$$

Its structure factor can be expressed as:

$$A = 4 \cos^2 2\pi \left(\frac{h+k}{4} \right) \left[2 \cos 2\pi(hx + ky + lz) \right. \\ \left. \times \cos^2 2\pi \left(\frac{h-k+2l}{8} \right) - \sin 2\pi(hx + ky + lz) \right. \\ \left. \times \sin 2\pi \left(\frac{h-k+2l}{8} \right) \right].$$

It therefore follows that for

$$h - k + 2l \neq 4n \quad A = 0$$

$$h - k + 2l = 4n \quad A = 8 \cos 2\pi(hx + ky + lz).$$

References

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