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

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Abstract

The complexes \( \text{C}_{34}\text{H}_{28}\text{Cl}_2\text{O}_4\text{U}, \text{UO}_2\text{Cl}_2(\text{DBA})_2 \) [\( \text{DBA} = \text{dibenzylideneacetone, (C}_6\text{H}_5-\text{CH}==\text{CH})_2\text{CO} \)] and \( \text{UO}_2\text{Cl}_2(\text{DBA})_2.2\text{CH}_3\text{COOH} \) 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.

Pseudo-symmetry and twinning in \( \text{UO}_2\text{Cl}_2(\text{DBA})_2.2\text{CH}_3\text{COOH} \)

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 constants at 291 K: \( a_2 = 9.671 \text{ (5)}, b_2 = 17.745 \text{ (9)}, c_2 = 21.54 \text{ (2)} \text{ Å}, \alpha_2 = 90.78 \text{ (5)}, \beta_2 = 91.93 \text{ (5)}, \gamma_2 = 89.52 \text{ (4)}^\circ \) and \( U_2 = 3694 \text{ Å}^3 \) (cell II). The deviations of \( \alpha_2 \) and \( \gamma_2 \) 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 \( a_1 = 11.851 \text{ (2)}, b_1 = 10.023 \text{ (3)}, c_1 = 11.668 \text{ (3)} \text{ Å}, \alpha_1 = 103.57 \text{ (2)}, \beta_1 = 129.20 \text{ (2)}, \gamma_1 = 103.48 \text{ (2)}^\circ \) and \( U_1 = 900.4 \text{ Å}^3 \) (cell I). On reindexing, these give \( a_2 = 9.593 \text{ (2)}, b_2 = 17.679 \text{ (6)}, c_2 = 21.245 \text{ (4)} \text{ Å}, \alpha_2 = 89.31 \text{ (1)}, \beta_2 = 91.14 \text{ (1)}, \gamma_2 = 90.45 \text{ (2)}^\circ \) and \( U_2 = 3602.0 \text{ Å}^3 \), 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 \( 1_2,0,0 \) (C-centre) and...
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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 \(h + k = 2m + 1\), 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 \(a^*_2\) and \(a^*_3\) is \(180^\circ - 2\beta^\circ\). The rows with \(h = 2, 6, 10, \ldots\) (all single peaks) have twice as many spots as rows with \(h = 4, 8, 12, \ldots\) (all double peaks). Treating the lattice as single, the two first spots on row

Fig. 2. \(\text{UO}_2\text{Cl}_2\text{(DBA)}_2\), 2CH₃COOH, showing the \(hk0\) zone of cell (II). Unindexed reflections are \(C\)-centring absences, those with one index are absences of the type \(h - k = 2l + 4m\), 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 $c \approx 21 \text{ Å}$, would be indexed 200 and 201 instead of 200 (crystal 1) and 202 (crystal 2), resulting in no apparent absences in the $h0l$ zone. In the $h1l$ zone, not shown here, the $c$ axis appears doubled ($c \approx 42 \text{ Å}$), 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 $a = 12.397 (5)$, $b = 11.587 (3)$, $c = 21.950 (5) \text{ Å}$, $\beta = 97.89 (2)^{\circ}$.

**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 pseudosymmetry. 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. UO₂Cl₄(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.](image)

**APPENDIX**

**Transformation matrices and systematic absences for UO₂Cl₄(DBA)₂·2CH₃COOH**

(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

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

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:

$$(0,0,0; \frac{1}{4}, \frac{1}{4}, 0) +$$

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

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

Its structure factor can be expressed as:

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

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

$$\times \sin 2\pi \left( \frac{h - k + 2l}{8} \right].$$

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**

