Copper(II) Oxydiacetate Hemihydrate: Crystal Structure and Twinning

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The structure of $[Cu\{O(CH_2CO_2)_2\}],0\cdot5H_2O$ has been determined by Fourier and least-squares methods from diffractometer data. Crystals, all of which are twinned by reflection across the (101) twin plane or by a 90° rotation about [010], are orthorhombic with $a = 9\cdot263(6)$, $b = 14\cdot283(5)$, $c = 9\cdot283(6)$ Å, $Z = 8$, space group *Pbcn*. Volume fractions of the twin components were deduced from the ratios of intensities observed at space-group forbidden positions. The structure of the major component, which represents 88% of the twin volume, was refined to R 0·88 for 1042 reflections.

The Cu atoms are co-ordinated by four carboxy-oxygen atoms, two from the two ends of a chelating oxydiacetate ligand and one from each of two neighbouring $Cu\{O(CH_2CO_2)\}$ groups, with Cu–O 1·941(9)—1·952(8) Å. Longer contacts to the ether oxygen of the chelating ligand [Cu–O 2·488(8) Å] and to a statistically disordered water molecule [Cu–O 2·73(2) Å] complete a distorted octahedral arrangement. A pseudo-mirror plane passing through Cu, H_2O, and the ether O atom relates the halves of the oxydiacetate group and results in markedly similar packing schemes in the *ab* and *bc* unit-cell projections. Stacking faults in the packing along *b* account for the occurrence of the twinning.

THE chelate structures formed between complexing agents and metal ions are of concern in evaluating alternatives to phosphate in washing products. Following our studies of nitrilotriacetic acid complexes with calcium and copper[1] we now report on the complex formed between copper and oxydiacetic (otherwise called diglycolic) acid. In oxydiacetic acid itself, the carboxy-groups are related by a two-fold axis passing through the central oxygen atom of the molecule.[2] The present structure analysis was performed to determine the extent of chelation in the copper oxydiacetate complex. We wanted to examine the conformational changes the ligand would undergo to facilitate multidentate-complex formation. A strongly chelated structure might include an ether oxygen–copper bond. When we discovered all crystals to be twinned, an explanation of the twinning became an additional objective.

EXPERIMENTAL

Crystal Data.—$C_4H_5O_{11/2}Cu$, $M = 204\cdot6$, Orthorhombic, $a = 9\cdot263(6)$, $b = 14\cdot283(5)$, $c = 9\cdot283(6)$ Å, $U = 1228\cdot2$ Å^3, $D_m = 2\cdot21$ (flotation), $Z = 8$, $D_c = 2\cdot21$ g cm^{-3}, $F(000) = 816$. Space group, *Pbcn* (D_{2h}^{14}, No. 60). Mo-$K_{\alpha1}$ radiation ($\lambda = 0\cdot70926$ Å) for cell dimensions and Mo-K_α radiation ($\lambda = 0.71069$ Å) for intensity measurements; μ(Mo-K_α) = 27·97 cm^{-2}.

The royal-blue complex was prepared by adding excess of oxydiacetic acid to basic copper carbonate, and recrystallized from water as either square or rectangular plate-like crystals. Atomic-absorption analysis gave 32·0% by weight for copper indicating a 1 : 1 copper–ligand ratio.

All crystals are twinned in varying degrees. *X*-Ray photographs of square crystals showed pseudotetragonal symmetry and those for rectangular ones orthorhombic symmetry. Photographs of each type had unusual systematic absences but yield similar lattice parameters. For all crystals twinning occurs either by reflection across the (101) twin plane or by a 90° rotation about the [010] direction so that the *a* and *c* axes become interchanged. The pseudotetragonal symmetry of the square crystals is caused by *ca.* 50% twinning, while the rectangular crystals are twinned to a lesser (but variable) degree. All the unusual systematic absences could be accounted for by the symmetry elements of the orthorhombic space group *Pbcn* in conjunction with these twin operations.

A crystal containing only a small amount of the minor twin component was selected for intensity-data collection. Its dimensions were 0·21 × 0·09 × 0·03 mm with the *c* direction elongated and the (010) face prominent. Crystal data were measured by use of a computer-controlled four-circle Picker diffractometer. Cell dimensions and estimated standard deviations were calculated by least-squares methods from the positions of 40 high-angle reflections. Intensity data for reflections with $2\theta \leqslant 60°$ were collected by the θ—2θ scan technique at 2° min^{-1}. The scan range was $(1\cdot3 + 0\cdot7 \tan \theta)°$ with 10 s backgrounds measured either side of the scan. No splitting of reflections due to twinning was observed. There was no appreciable decomposition of the crystal and periodic measurements of three standard reflections varied <5%. Least-squares standard deviations based on counting statistics and instrument stability were assigned to the reflections.[3] Where the net count was < the 10% significance level, a reflection was classified unobserved; of the 2080 reflections measured (including *ca.* 300 systematic absences) 1145 were thus considered significant.

The degree of twinning was estimated from intensity measurements made at space-group forbidden positions. Reflections are generally superimposed, each intensity being made up of the *hkl* reflection of one twin component plus the corresponding *lkh* reflection of the other. But at the space-group systematically absent positions ($h0l$, $l = 2n + 1$; $hk0$, $h + k = 2n + 1$; $0kl$, $k = 2n + 1$) the intensity is due to only one of the twin orientations, *e.g.* the intensity at the 320 position comes only from the 023 reflection of the minor twin component; comparison of this with the intensity measured at the 023 position provides an estimate of the respective volume ratios. From a comparison of *ca.* 40 zero-level pairs of intensities the smaller twin fragment was initially found to have 14·5% of the volume of the major component.

Corrected intensities, I', for the major component of the twin were obtained from the observed intensities I_{hkl} by the formula: $I' = [I_{hkl} - x(I_{lkh})]/(1 + x^2)$, where x is the

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[1] S. H. Whitlow, *Acta Cryst.*, 1972, **B28**, 1914; *Inorg. Chem.*, 1973, **12**, 2286.

[2] G. Davey and S. H. Whitlow, *J. Cryst. Mol. Struct.*, 1973, **3**, 193.

[3] E. J. Gabe, J. P. Glusker, J. A. Minkin, and A. L. Patterson, *Acta Cryst.*, 1967, **22**, 366.

volume fraction of the minor twin component. The value of x was adjusted so that the minimum I' values were within the range ($\pm$) of the 10% significance level of the net count [*i.e.* $x(I_{lkh}) = I_{hkl}$ for unobserved reflections]. The final value of x was 12·0%. Reflections with net counts $(I') < 5$ were coded unobserved, those having a negative I' were set equal to zero. Of the **1145** reflections considered observed for the bulk crystal, there were **1042** significant reflections due to the major twin component. The corrected intensities, now fully consistent with the space group *Pbcn*, were used in the subsequent structure determination. A procedure for handling superimposed reflections in cadmium chloroapatite has recently been described in which the volume ratio was adjusted in each cycle of least-squares and each crystal in the twin was refined.[4] We chose not to refine the smaller twin component because the proportionally weaker intensities would be unreliable after data manipulation. At stages in our refinement different volume-fraction parameters were used but these did not improve the model.

Intensities, corrected for Lorentz and polarization effects, but not absorption or extinction, were scaled by Wilson's method.[5] Scattering factors were taken from ref. 6, the anomalous dispersion correction being included for copper. Most of the calculations were performed with the '*X*-Ray' system of crystallographic programs; [7] the structural Figures (showing 50% probability ellipsoids) were drawn by use of the program ORTEP.[8]

Structure Determination.—The position of the copper atom was deduced from a sharpened Patterson synthesis. A subsequent Fourier synthesis gave positions for the atoms of the oxydiacetate ligand. A peak, half the height of the oxygen atoms of the ligand, occurred *ca.* 0·7 Å from the two-fold axis at $x = 0{\cdot}25$, $z = 0{\cdot}5$, on the section $y = 0{\cdot}10$. This peak, the oxygen atom of a water molecule, was assigned an occupancy factor of 0·5 (the other 'half' of the oxygen atom being related by the two-fold axis). A structure-factor calculation, with thermal parameters U of 0·04, and 0·05 Å^2, respectively, for copper and the remaining non-hydrogen atoms, gave R 0·225.

The structure was refined by use of a full-matrix least-squares procedure to minimize $\Sigma(w|F_o| - |F_c|)^2$. Initially the weight, w, was unity and in the final refinement $w = 1/(70 + 0{\cdot}003\ F_o^2)$. An electron-density difference synthesis calculated after isotropic refinement (R 0·12) showed positions of the hydrogen atoms of the oxydiacetate ligand. It was not possible to locate those of the water molecule because of the fractional occupancy of the oxygen atom and the probable disorder of the hydrogen atoms. The positions of the located hydrogens were optimized (assuming C–H 1·0 Å), and they were included as constants (U 0·045 Å^2) in subsequent calculations. Refinement was continued with anisotropic thermal parameters until the maximum shift in any parameter was $<0{\cdot}1\sigma$. The final values for R, based on 1042 reflections, and $R' \{= [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}\}$ were 0·088 and 0·116, respectively. Final atomic co-ordinates and thermal parameters are given, with estimated standard deviations, in Table 1. Calculated and observed structure factors are listed in Supplementary Publication No. SUP 21280 (10 pp., 1 microfiche).*

TABLE 1

Final positional and thermal parameters, with estimated standard deviations in parentheses

(*a*) Atomic fractional cell parameters

Atom	x	y	z
Cu	0·2707(2)	0·2980(1)	0·4707(2)
O(1)	0·2489(11)	0·2392(6)	0·2827(10)
O(2)	0·1943(10)	0·1229(6)	0·1371(9)
O(3)	0·2185(8)	0·1299(5)	0·5179(8)
O(4)	0·4584(8)	0·2397(6)	0·4987(11)
O(5)	0·6005(8)	0·1252(6)	0·5667(10)
O(6) †	0·454(2)	0·392(1)	0·291(3)
C(1)	0·2096(12)	0·1566(9)	0·2616(13)
C(2)	0·1770(14)	0·0925(9)	0·3859(14)
C(3)	0·3545(12)	0·0947(8)	0·5718(14)
C(4)	0·4768(12)	0·1588(8)	0·5418(12)
H(1)	0·70	0·080	0·390
H(2)	0·229	0·032	0·371
H(3)	0·374	0·031	0·523
H(4)	0·346	0·082	0·678

(*b*) Anisotropic vibrational parameters ($\times 10^3$) in the form: $\exp\,[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{23}klb^*c^*\cos\alpha^*)]$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	24(1)	24(1)	28(1)	1(1)	−1(1)	0(1)
O(1)	43(5)	28(4)	34(5)	0(4)	1(4)	3(4)
O(2)	39(5)	30(5)	28(5)	−1(4)	−2(4)	−2(4)
O(3)	16(3)	21(3)	27(4)	5(3)	−1(3)	1(3)
O(4)	19(4)	22(4)	49(6)	0(3)	7(4)	8(4)
O(5)	17(4)	28(4)	50(6)	0(3)	−5(4)	5(4)
O(6)	68(20)	40(10)	83(25)	−1(10)	−50(16)	12(12)
C(1)	16(6)	37(6)	23(5)	5(4)	2(4)	−5(5)
C(2)	38(7)	27(6)	29(6)	−10(5)	−9(6)	−7(5)
C(3)	20(5)	23(5)	31(6)	0(4)	−6(5)	6(5)
C(4)	20(5)	34(6)	12(5)	1(4)	3(4)	3(5)

† Atom at half occupancy.

RESULTS AND DISCUSSION

Co-ordination.—Each copper atom is bonded to an oxydiacetate ligand *via* the carboxylate groups and (to a lesser extent) the ether oxygen atom. To facilitate terdentate chelation the ligand configuration is changed from that in the parent acid,[2] with the carboxy-groups above and below the central COC plane, to one with both carboxy-groups extending on the same side. The present configuration is different also from the nearly planar form found [9] in $Ca[O(CH_2CO_2)_2],6H_2O$ where terdentate bonding is present between calcium and the oxydiacetate ligand. The intramolecular bond lengths and angles of the ligand (Table 2) are similar to those previously reported for the free ligand and in the calcium salt; the configuration of the ligand and the environment of the copper atom are shown in Figure 1. The halves of the oxydiacetate ligand are related by the pseudo-mirror plane passing through Cu, O(3), and the

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

[4] K. Sudarsanan, R. A. Young, and J. D. H. Donnay, *Acta Cryst.*, 1973, **B29**, 808.

[5] A. J. C. Wilson, *Nature*, 1942, **150**, 152.

[6] P. A. Doyle and P. S. Turner, *Acta Cryst.*, 1968, **A24**, 390.

[7] J. M. Stewart, G. L. Kruger, H. L. Ammon, and S. R. Hall, 'The *X*-Ray System,' Computer Science Centre Report, University of Maryland, Technical Report TR 192, 1972.

[8] C. K. Johnson, 'ORTEP,' Report ORNL 3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1965.

[9] V. A. Uchtman and R. P. Oertel, *J. Amer. Chem. Soc.*, 1973, **95**, 1802.

H_2O molecule (Table 3). Similar halves of the ligand are also found in the alkali-metal hydrogen oxydiacetates.[10]

TABLE 2

Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Distances

Cu–O(1)	1·948(9)	C(1)–O(1)	1·25(2)
Cu–O(4)	1·946(8)	C(1)–O(2)	1·26(1)
Cu–O(2^{I})	1·941(9)	C(2)–O(3)	1·39(2)
Cu–O(5^{II})	1·952(8)	C(3)–O(3)	1·45(1)
Cu–O(3)	2·488(7)	C(4)–C(3)	1·48(2)
Cu–O(6)	2·73(2)	C(4)–O(4)	1·23(1)
C(1)–C(2)	1·50(2)	C(4)–O(5)	1·26(1)

(*b*) Angles

O(1)–Cu–O(3)	73·8(3)	O(6)–Cu–O(2^{I})	95·5(6)
O(1)–Cu–O(4)	91·6(4)	O(6)–Cu–O(5^{II})	96·6(5)
O(1)–Cu–O(6)	74·3(6)	O(2^{I})–Cu–O(5^{II})	87·1(4)
O(1)–Cu–O(2^{I})	169·0(4)	O(1)–C(1)–O(2)	122·4(11)
O(1)–Cu–O(5^{II})	89·9(4)	O(1)–C(1)–C(2)	120·8(11)
O(3)–Cu–O(4)	74·7(3)	O(2)–C(1)–C(2)	116·7(11)
O(3)–Cu–O(6)	134·7(5)	C(1)–C(2)–O(3)	112·8(10)
O(3)–Cu–O(2^{I})	116·9(3)	C(4)–C(3)–O(3)	112·7(9)
O(3)–Cu–O(5^{II})	114·6(3)	O(4)–C(4)–O(5)	122·7(10)
O(4)–Cu–O(6)	74·9(5)	O(4)–C(4)–C(3)	122·2(10)
O(4)–Cu–O(2^{I})	89·6(4)	O(5)–C(4)–C(3)	115·1(10)
O(4)–Cu–O(5^{II})	170·5(3)	C(2)–O(3)–C(3)	114·3(9)

Roman numerals as superscripts refer to atoms in the positions:

I $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$ II $-\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$

TABLE 3

Equation of the (pseudo-mirror) plane through Cu, O(3), and O(6) with distances (Å) of atoms from the plane

$$0{\cdot}707X - 0{\cdot}013Y + 0{\cdot}707Z = 4{\cdot}806\,^*$$

O(1) −1·37, O(2) −2·66, C(1) −1·75, C(2) −1·13, O(4) 1·42, O(5) 2·82, C(4) 1·84, C(3) 1·25

* *X*, *Y*, *Z* are co-ordinates in Å related to the orthogonal crystal axes, and the coefficients are the direction cosines.

The copper atom has a (4 + 1 + 1) co-ordination of oxygen atoms with four shorter and nearly equal carboxy-bonds [mean 1·947(5) Å], an intermediate ether bond [2·488(7) Å], and a more distant water contact [2·73(2) Å]. These Cu–O bond lengths are all within accepted ranges for, respectively, ' short ' and ' long ' Cu–O bonds.[11] The stereochemistry about copper can be described as a distorted tetragonal bipyramid or distorted octahedron, the distortion being due to constraints imposed by chelation. Although the angle between the axial bonds is only 135°, the four equatorial atoms are more regularly disposed and nearly planar. The copper is displaced slightly (0·17 Å) towards the ether oxygen. Such a shift of metal towards the shorter axial bond in a (4 + 1 + 1) co-ordination is common and occurs in *e.g.* $[Cu_3\{AsO_4(OH)_3\}]$.[12] While complex formation involving bonds between copper and non-terminal nitrogen atoms is frequent (see *e.g.* copper

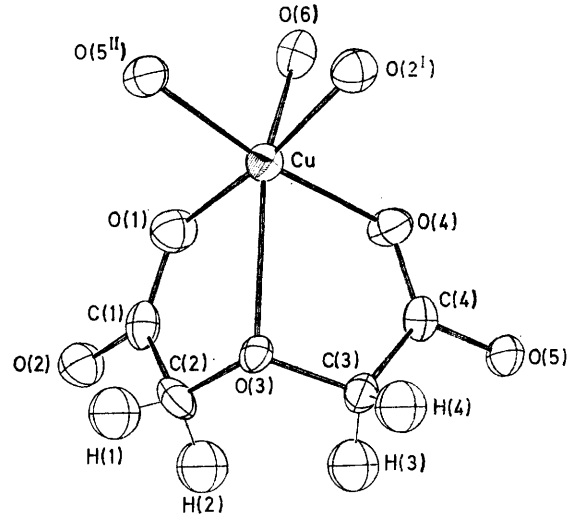

FIGURE 1 A view of the molecule showing the copper environment and the pseudo-mirror plane through O(6), Cu, and O(3); the atom numbering system is also illustrated

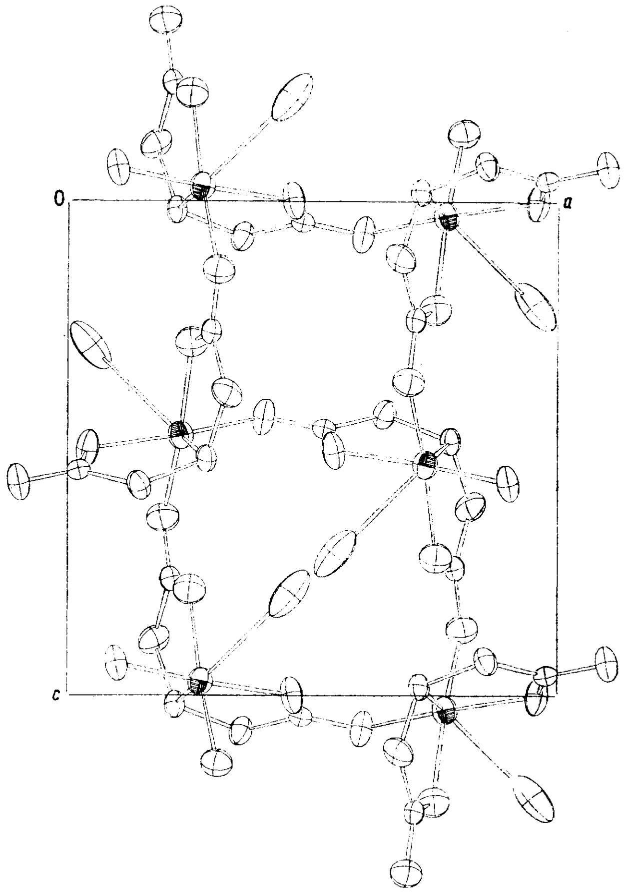

FIGURE 2 An *ac* projection (of half the unit cell) showing the layers perpendicular to *b*

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[10] J. Albertsson, I. Grenthe, and H. Herbertsson, *Acta Cryst.*, 1973, **B29**, 1885; 2839.

[11] B. J. Hathaway, *Co-ordination Chem. Rev.*, 1970, **5**, 143.

[12] S. Ghose, M. Fehlmann, and M. Sundaralingam, *Acta Cryst.*, 1965, **18**, 777.

monoglycylglycine trihydrate[13]), no other copper–ether bonds have been reported. The bonding overlap between copper and oxygen presumably utilizes the lone-pair electrons on the ether oxygen. The metal–ether bond, here and in $[Ca\{O(CH_2CO_2)_2\}],6H_2O$,[9] is evidence of the strong chelating power of the oxydiacetate ligand.

Twinning.—The twinning operation could not be determined unambiguously even after close examination of *h0l* photographs for a number of different crystals. The similarity of the *a* and *c* axial dimensions is such that a maximum angular separation of only 15′ can occur between related reflections. On one photograph this splitting may have been present, which would suggest that the [101] direction of one component coincides with the [$\bar{1}$01] direction of the other. Twinning would then be due to reflection across the (101) twin plane. However, a 90° rotation about [010] so that *b* becomes a four-fold axis is also possible, and either or both symmetry operations could produce the observed twinning.

Diagrams of the unit cell help explain, on a packing basis, why twinning occurs so readily. The *ac* projection (Figure 2) shows four of the eight equivalent units in the cell. (The other four have been omitted for clarity; they can most easily be generated from the centre of symmetry at 0·5,0·5,0·5.) The two-fold axes along *b*, which approximate four-fold axes, and the pseudo-mirror planes parallel to (101) and ($\bar{1}$01) are evident on this diagram. The copper atoms are singly bonded to two other ligands in addition to the terdentate one so that rather similar chains extend in the *a* and *c* directions. This network perpendicular to *b*, forms well defined layers of copper atoms, oxydiacetate groups, and water molecules. There are, however, no chemical contacts between adjacent layers. The closest non-hydrogen interlayer contact is 3·42 Å between O(5) and C(3) at $1 - x, -y, 1 - z$. By contrast, within the layers the shortest intermolecular contact is 2·68 Å between O(5) and O(2) at $1 - x, y, 0{\cdot}5 - z$, and there are seven other O · · · O, Cu · · · O, or Cu · · · C contacts of 2·74—3·0 Å. Views down the *a* and *c* axes (Figure 3) are necessarily complicated because of the atom density of the sheets, but illustrate the well-defined edges of the layers (many of the atoms after undergoing symmetry operations have similar *y* co-ordinates). Figure 3 also shows the marked similarity between the *bc* and *ac* projections. Because of the pseudo-mirror plane, the *x* co-ordinate of an atom plus 0·25 is nearly equal to its *z* co-ordinate (or of a related atom having the same *y* value in the other half of the molecule). Therefore, translation of all atoms in the *ab* projection by 0·25 produces a view almost superposable with the *bc* projection.

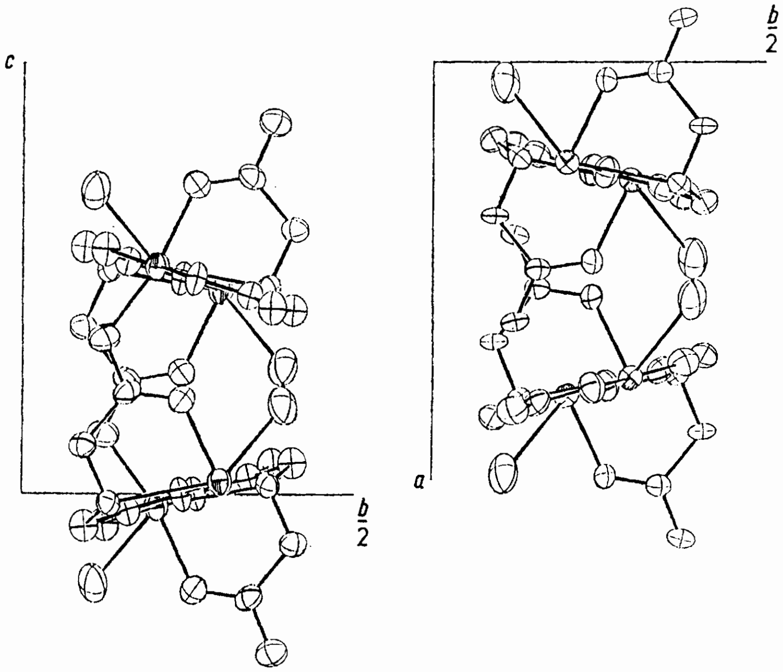

FIGURE 3 Views looking down *a* and *c* (each of half the unit cell) showing the well-defined layers and the similarity of the projections

The twinning found in all crystals of the compound can thus be accounted for in terms of stacking faults which occur as the crystal grows. Layers of molecules perpendicular to *b* have only van der Waals attractions between them. If a newly-formed layer is reflected across (101) or it is turned 90° and shifted slightly it

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[13] B. Strandberg, I. Lindqvist, and R. Rosenstein, *Z. Krist.*, 1961, **116**, 266.

becomes virtually identical to the substrate. As the crystal grows, the scheme of propagation in the *b* direction is variable and this results in the different degrees of twinning found.

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