Structure of a Twin Initially Solved from a Partial Data Set: Di-μ-chlorobis-[di-n-butyl-dithiocarbamato]dipalladium

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Abstract

This compound crystallizes as twins, monoclinic, space group $P2_1/a$. There being no systematic hkl absences, the chosen cell was primitive. All reciprocal lattice points hkl with $h = 0$ or $\pm 3n$ from the twins overlap. From the non-overlapping reflexions, the ratio of the masses of the two twins was obtained, but it proved impossible to partition satisfactorily the observed intensities of the overlapping reflexions between the twins. Accordingly they were deleted from the data set. The remaining data did not lead to a structure solution; very small average E^2 values were obtained for all hkl reflexions when $(h + l)$ was odd, implying a (non-Bravais) B-centred monoclinic cell. The data from the larger twin were reindexed to give a primitive cell. Using direct methods, the structure was solved, showing the original cell to be B-centred, even though reflexions hkl with $(h + l)$ odd were observed. This is because these (weak) reflexions all originate from the other twin. Accordingly, the reflexions hkl with $h = \pm 3n$ do not overlap, as had originally been supposed. These data were restored, forming a complete data set and were used to refine further the structure already obtained. The centrosymmetric dinuclear complex has a chelating dithiocarbamate ligand on each Pd atom with chloride bridges.

1. Introduction

The material was generated by the research group of Dr S. D. Robinson of these Laboratories, as part of a study of dialkyldithiocarbamato complexes of the chlorides of single and mixed transition elements. The composition of the sample was uncertain but could be assumed to contain Pd and/or Cu, Cl and the di-n-butyldithiocarbamate moiety.

2. Experimental

The red–brown material could only be obtained as thin fragile plates. Slow evaporation from benzene yielded the best crystals.

No satisfactory orientation matrix could be obtained on the diffractometer. Accordingly, Weissenberg and precession photographs were taken. These also proved difficult to interpret, but it was finally clear that the crystal was twinned, the components belonging to the monoclinic system. The only systematic absences were $0k0$ for k odd and $h0l$ for h odd, although $h0l$ for l odd were also very weak or absent. There were no systematic absences in the hkl reflexions. All reflexions could be accounted for on the basis of a primitive cell, space group $P2_1/a$.* Fig. 1 shows the mutual orientation of the crystal axes of the cells; x and y axes for twin (I) being collinear with $-x$ and $-y$ of twin (II), respectively. The reciprocal lattices of the components (Fig. 2) show that all $0kl$ reflexions overlap, as do hkl with $h = \pm 3n$. Data collection (Grant & Gabe, 1974) was carried out for one twin on a Picker diffractometer (see Table 1 for details). Data collection was stopped before completion and collection restarted using the orientation matrix for the other twin. This collection was also stopped prematurely and the raw intensities of a number of strong non-overlapping reflexions from the two data sets compared. A simole plot of *ca* ten or so raw intensities showed that those of the second data set were 6.0 times as intense as those of the first. Accordingly, collection of the second data set was continued and no further use was made of the incomplete first set. On completion, the intensities of all the $0kl$ reflexions (which are exactly overlapped from the twins and have the same F_c values) were scaled by 6/7. Knowing the mass ratio of the twins it was thought that the intensities of the other reflexions which overlap, *i.e.* those with $h = \pm 3n$ (but having different F_c values) could be partitioned between the twins. No self-consistent results could be obtained, however. Therefore, it was decided advisable at this stage to remove all hkl reflexions having $h = \pm 3n$ from the data set. Following data reduction (*NRCVAX*; Gabe, Le Page, Charland, Lee & White, 1989), an attempt was made to solve the structure by direct methods using *SOLVER* (*NRCVAX*; Gabe *et al.*, 1989). Although some of the eight phase sets yielded

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* Equivalent positions: x, y, z; $\frac{1}{2} - x, \frac{1}{2} + y, -z$; $-x, -y, -z$; $\frac{1}{2} + x, \frac{1}{2} - y, z$.

'structures' akin to those anticipated, none would refine. At this stage it was noted that the average value of E^2 among the parity groups, as given in the data reduction output, showed that reflexions having $(h + l)$ odd were systematically weaker than the others, almost to the point of being completely absent. This implies a (non-Bravais) B-centred monoclinic lattice, in apparent contradiction to the lack of systematic absences in the hkl reflexions. Nevertheless, an extra lattice point was added at the centre of the B-face of the cell and the intensity data reindexed on the basis of a primitive cell (see Fig. 3). This reindexing, of course, removes all reflexions with original indices $(h + l)$ odd. After reduction, SOLVER was reimplemented. The phase set having the highest f.o.m. (figure of merit) yielded the structure, which refined anisotropically to an R of 0.055. This successful structure solution based on the incomplete data set shows without doubt that the cell originally chosen is not primitive, but is genuinely B-centred. This seeming contradiction with the observations is readily explained. If the original cell is taken as B-centred (Fig. 4), reflexions hkl with $h = \pm 3n$ no longer overlap. Those with $(h + l)$ even for one twin appear exactly in positions corresponding (with different values of $h = \pm 3n$) to $(h + l)$ odd of the other. Thus, the systematic absence hkl for $(h + l)$ odd is only apparently violated, the apparent violations arising entirely from the other twin. Accordingly, reflexions hkl with $h = \pm 3n$, which had been removed from the data, do not overlap and were restored, and, using the newly reduced complete data set, the structure further refined. Full anisotropic refinement of the non-H atoms was uneventful. The final ΔF map showed small peaks in regions where H atoms are expected. The actual hydrogen coordinates used were theoretical using C—H 1.08 Å. Final fractional atomic coordinates are given in Table 2 and derived bond lengths and angles of interest are given in Table 3. An ORTEP (Johnson, 1965) depiction of the molecule is given in Fig. 5.

3. Discussion

The molecule is centrosymmetric. The crystal structures of four dialkylthiocarbamatopalladium complexes are known: with alkyl groups propyl-, n-butyl-, isobutyl and trifluoroethyl (Riekkola, Pakkanen & Niinisto, 1983). They all lack the central dichoro bridge possessed by the current molecule, whose presence appears to have a small effect on the Pd—S bond length. Thus, without the chlorine bridge, Pd—S ranges from 2.313 to 2.329 Å, compared with here where it is shorter at 2.239–2.248 Å. The same moiety, albeit with the Pd atom also bonded to another metal atom, occurs in some of the mixed-metal complexes studied by Ebihara, Tokoro, Maeda, Ogami, Imaeda, Sakurai, Masuda & Kawamura (1994). Again, the Pd—S lengths are somewhat longer than in the compound studied here. Otherwise, the stereochemistry

Table 1. *Experimental details*

Crystal data	
Chemical formula	$C_{18}H_{36}Cl_2N_2Pd_2S_4$
Chemical formula weight	692.2
Cell setting	Monoclinic
Space group	$P2_1/a$
a (Å)	16.393 (7)
b (Å)	9.235 (8)
c (Å)	11.176 (12)
β (°)	128.01 (7)
V (Å^3)	1333 (2)
Z	2
D_x (Mg m^{-3})	1.73
Radiation type	Mo $K\alpha$
Wavelength (Å)	0.7107
No. of reflections for cell parameters	14
θ range (°)	5–11
μ (mm^{-1})	1.87
Temperature (K)	293
Crystal form	Very thin plate
Crystal size (mm)	1.1 × 0.3 × 0.01
Crystal colour	Red–brown
Data collection	
Diffractometer	Picker
Data collection method	θ–2θ
Absorption correction	None
No. of measured reflections	2325
No. of independent reflections	2325
No. of observed reflections	1547
Criterion for observed reflections	$I > 2.5\sigma(I)$
θ_{max} (°)	25
Range of h, k, l	$-19 \to h \to 14$
	$0 \to k \to 8$
	$0 \to l \to 13$
No. of standard reflections	1
Frequency of standard reflections	100
Intensity decay (%)	<1
Refinement	
Refinement on	F
R	0.053
wR	0.060
S	2.43
No. of reflections used in refinement	1547
No. of parameters used	127
H-atom treatment	H atoms placed in calculated positions
Weighting scheme	Weights based on counting statistics
$(\Delta/\sigma)_{max}$	0.106
$\Delta\rho_{max}$ (e Å^{-3})	0.84
$\Delta\rho_{min}$ (e Å^{-3})	−0.45
Extinction method	None
Source of atomic scattering factors	NRCVAX (Gabe et al., 1989)

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

	x	y	z	B_{iso}*
Pd	0.08671 (7)	0.50010 (13)	0.19341 (9)	4.05 (5)
Cl	0.0834 (3)	0.4092 (5)	−0.0076 (3)	6.3 (2)
S1	0.1068 (2)	0.5668 (4)	0.4036 (3)	4.4 (2)
S2	0.2477 (2)	0.4302 (4)	0.3850 (3)	4.7 (2)
C1	0.2297 (8)	0.4981 (15)	0.5094 (10)	3.7 (6)
N	0.2958 (6)	0.4978 (12)	0.6558 (9)	3.9 (5)
C2	0.4009 (9)	0.4367 (15)	0.7362 (13)	4.5 (7)
C3	0.4813 (10)	0.5572 (16)	0.7943 (15)	5.3 (8)
C4	0.4751 (10)	0.6399 (17)	0.6729 (17)	6.0 (10)
C5	0.5671 (12)	0.7335 (19)	0.7333 (22)	7.8 (14)
C6	0.2679 (9)	0.5507 (14)	0.7504 (13)	4.5 (8)
C7	0.2364 (16)	0.4270 (20)	0.8044 (21)	8.1 (17)
C8	0.190 (3)	0.3098 (23)	0.733 (3)	16.0 (4)
C9	0.1600 (16)	0.1936 (18)	0.7870 (23)	8.2 (16)

* B_{iso} = mean of the principal axes of the thermal ellipsoid.

Table 3. *Selected geometric parameters (Å, °)*

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Pd—Cl	2.368 (4)	N—C6	1.470 (14)
Pd—Cl^i	2.379 (5)	C2—C3	1.53 (2)
Pd—S1	2.247 (4)	C3—C4	1.50 (2)
Pd—S2	2.238 (4)	C4—C5	1.49 (2)
S1—C1	1.710 (11)	C6—C7	1.52 (2)
S2—C1	1.709 (11)	C7—C8	1.28 (3)
N—C1	1.291 (12)	C8—C9	1.46 (2)
N—C2	1.479 (14)		
Cl—Pd—Cl^i	88.12 (15)	C2—N—C6	116.9 (8)
Cl—Pd—S1	172.66 (13)	S1—C1—S2	107.1 (5)
Cl—Pd—S2	97.46 (15)	S1—C1—N	126.1 (8)
Cl^i—Pd—S1	98.87 (15)	S2—C1—N	126.8 (9)
Cl^i—Pd—S2	174.15 (13)	N—C2—C3	110.9 (11)
S1—Pd—S2	75.62 (15)	C2—C3—C4	115.1 (11)
Pd—Cl—Pd^i	91.88 (15)	C3—C4—C5	113.4 (13)
Pd—S1—C1	88.5 (4)	N—C6—C7	111.6 (11)
Pd—S2—C1	88.8 (4)	C6—C7—C8	127.2 (15)
C1—N—C2	121.7 (9)	C7—C8—C9	126.1 (19)
C1—N—C6	121.4 (9)		

Symmetry code: (i) $-x, 1 - y, -z$.
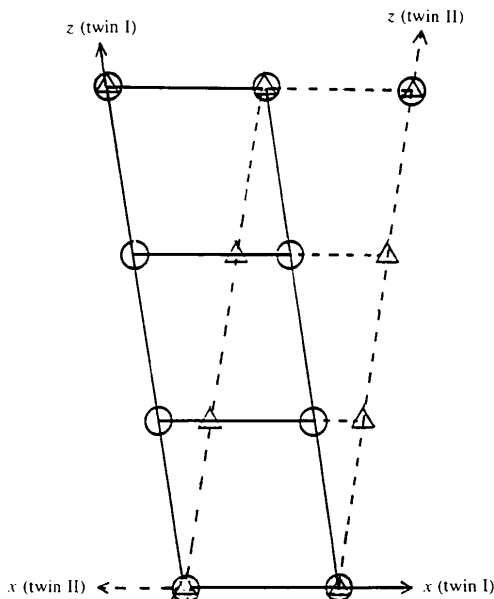
Fig. 1. *y*-Projection of the original choice of primitive unit cells, showing the mutual orientation of the axes. Lattice points of twin (I) are circles, of twin (II) triangles.
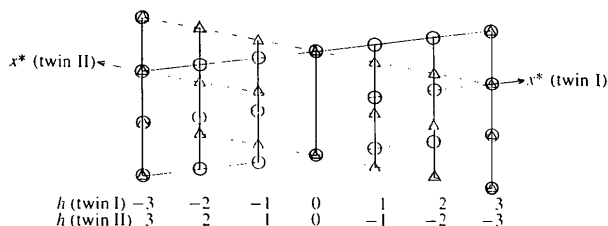
Fig. 2. Section of fixed *k* of reciprocal lattices (twin I circles, twin II triangles) corresponding to Fig. 1. Note the exact overlap of reciprocal points $0kl$ and hkl, where $h = \pm 3n$.
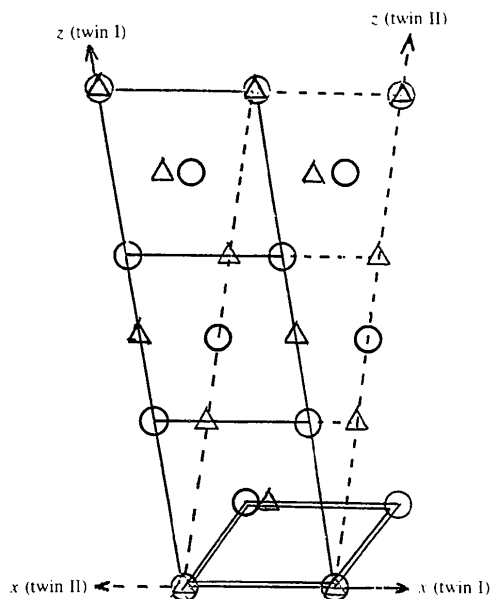
Fig. 3. As in Fig. 1, with lattice points added to make the cells *B*-centred. Double lines show the chosen new primitive cell of twin (I).
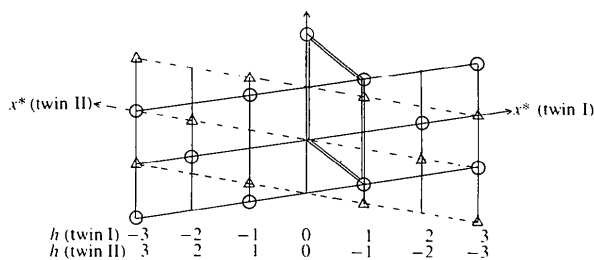
Fig. 4. As in Fig. 2, but for the centred cells in Fig. 3. Note that now only the $0kl$ reflexions overlap. Double lines show the new reciprocal cell corresponding to the new primitive cell of twin (I).
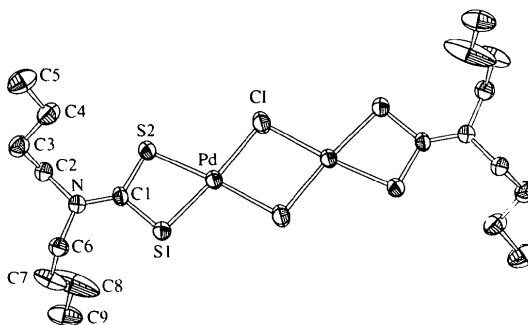
Fig. 5. *ORTEP* (Johnson, 1965) plot of the molecule with 30% probability ellipsoids.

of all these molecules is virtually identical. The C(8) atom appears to be in a disordered location, having an unacceptable distance of 1.28 (3) Å from C(7) and a very large thermal factor. No attempt was made to resolve the disorder. It is striking that in all five molecules the
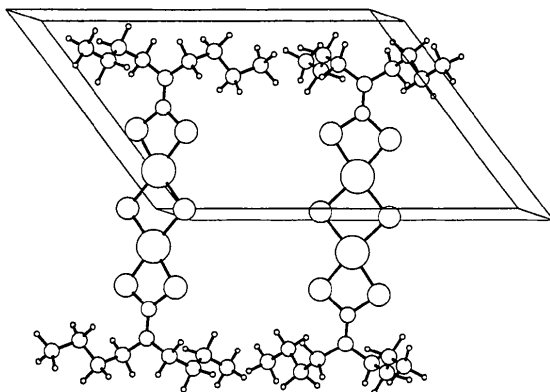

Fig. 6. Packing diagram in approximate *y*-projection.

formally single C—C bonds are shorter than 1.54 Å. However, libration may play a role in this shortening.

The whole of the central part of the molecule is planar [maximum deviation at C(6), 0.0651 Å], a fact that can readily be seen from Table 2, all these atoms lying very close to $y = 0$. The molecular packing is shown in Fig. 6. The *n*-butyl groups are aggregated together in layers, the H· · ·H contacts all being normal.

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