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Two phases of bis(tetraethylammonium) di-μ-chloro-bis[dichloropalladium(II)]

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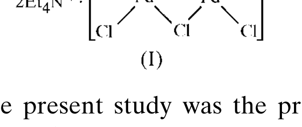
A phase transition was found to occur at ~153 K in the title compound, $(C_8H_{20}N)_2[PdCl_6]$. The structures of the two phases are reported at 292 and 130 K. The low-temperature phase is twinned. The phase transition is accompanied by a minor displacement of the ions. There are C—H···Cl interactions as short as ~2.80 Å, indicating the existence of hydrogen bonds, and this was confirmed by vibrational spectroscopy. The $[Pd_2Cl_6]^{2-}$ anion occupies sites of *mmm* and 2/*m* symmetry in the room-temperature and low-temperature phases, respectively.

Comment

The present study was prompted by the occurrence of phase transitions in chemically related compounds, for example $(NH_4)_2PdCl_4$ (*e.g.* Adams & Berg, 1976; Prager & Badurek, 1986; Gesi, 2001) and $[N(CH_3)_4]_2PdCl_4$ (*e.g.* Sato *et al.*, 1987; Vaněk *et al.*, 1993; Fábry *et al.*, 2004). Larger cations can cause condensation of $[PdCl_4]^{2-}$ into $[Pd_2Cl_6]^{2-}$ or even larger anions, as in $Cs_2Pd_2Cl_6$ (Schüpp & Keller, 1999) or $[N(C_4H_9)_4]_2Pd_2Cl_6$ (Bouquillon *et al.*, 1999). These latter authors isolated a mononuclear compound, $[N(C_4H_9)_4]_2PdCl_4$, in the form of a powder from which $[N(C_4H_9)_4]_2Pd_2Cl_6$ was recrystallized.



(I)

The aim of the present study was the preparation of bis(tetraethylammonium) tetrachloropalladium(II), $(Et_4N)_2PdCl_4$, or of $(Et_4N)_2[PdCl_4(\mu\text{-}Cl)_2]$, the detection of plausible phase transitions in the prepared compound, and the structure determination of pertinent phases. The structure analyses at 292 and 130 K showed that the sample under study corresponded to the latter formula, hereafter (I). The structural motifs and views of the unit cells of the low- and room-temperature structures are shown in Figs. 1 and 2.

A phase transition was detected by differential scanning calorimetry at ~153 K, as well as by the splitting of reflections except those of the 0*kl* type below the phase transition temperature (see *Experimental*). The phase transition is accompanied by a change of the crystal system from orthorhombic to monoclinic during cooling. To facilitate the comparison of the two phases, the low-temperature phase is

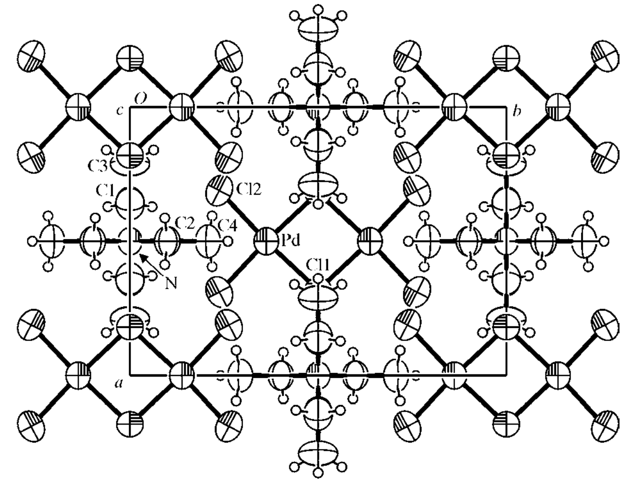


Figure 1
A view of the unit cell of (I) at 292 K along the *c* axis. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

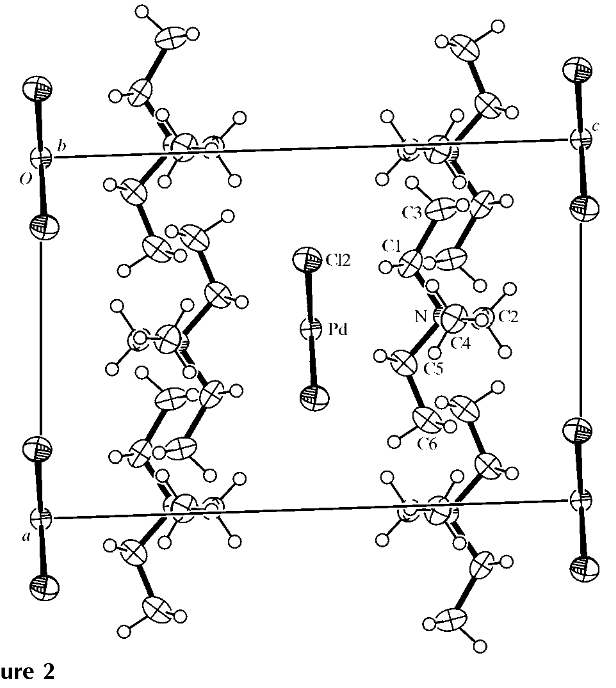


Figure 2
A view of the unit cell of (I) at 130 K along the *b* axis. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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described in the space group *I*2/*m*, a non-standard setting of *C*2/*m*. The lattice parameters relating to the standard space-group setting and the corresponding coordinates are included in the archived CIF, as is a detailed description of the twinning which was observed in the low-temperature phase.

The geometrical parameters of the $[Pd_2Cl_6]^{2-}$ anion in (I) (Tables 1 and 3) correspond very well with the values obtained from nine compounds found in the Cambridge Structural Database (CSD, November 2002 release, Version 5.24, and addenda up to the end of 2003; Allen, 2002), as well as with those of the only inorganic structure known to contain the $[Pd_2Cl_6]^{2-}$ anion, *viz*. $Cs_2Pd_2Cl_6$ (Schüpp & Keller, 1999). In these structures, the $[Pd_2Cl_6]^{2-}$ anion is usually situated on an element of symmetry; most often it lies across a centre of inversion, in accordance with Kitaigorodskii's rule (Kitaigorodskii, 1955). However, in $[N(C_4H_9)_4]_2Pd_2Cl_6$ (Bouquillon *et al.*, 1999), the anion occupies a general position in space group $P\overline{1}$.

In the title compound, the $[Pd_2Cl_6]^{2-}$ anion occupies sites of *mmm* and 2/*m* symmetry in the room-temperature and low-temperature phases, respectively. Therefore, the anion is strictly planar, in accordance with the findings by Pérez *et al.* (2002), who observed that the $[Pd_2(\mu\text{-}Cl)_2]$ core is usually planar.

In the studied structures, the ethyl group containing atoms C1 and C3 (atoms C5 and C6 in the low-temperature phase) differs from that containing atoms C2 and C4 by its orientation with respect to the $[Pd_2Cl_6]^{2-}$ anion. Consequently, these pairs of ethyl groups interact differently with the Cl atoms. The equivalent displacement parameters U_{eq} of atoms C1 and C3 are somewhat larger than those of the respective atoms C2 and C4 or C5 and C6, especially in the room-temperature phase (Table 5 and Fig. 2). The displacement parameters of the methyl C atoms are larger than those of the methylene C atoms, in accordance with expectations. On the other hand, the C—C distances are somewhat shorter in the high-temperature phase than the corresponding distances in the low-temperature phase (Tables 1 and 3). This indicates libration of the methyl groups.

It can be deduced that these features may be related to the phase transition. The phase transition is accompanied by displacements of the atoms by several tenths of an Å and by a moderate rotation of the methyl group around the C2—C4 bond by several degrees. These changes in the geometric parameters are concomitant with the disappearance of some mirror planes in accordance with the change of symmetry of the room- and low-temperature phases. The sections of the difference electron-density maps through the methyl H atoms show ordered methyl groups at room temperature. At low temperature, the difference electron-density map is not so clear, due to the twinning and hence the rejection of some unmatched reflections, as well as due to errors in data collection caused by the twinning. Despite this, the methyl H atoms also seem to be ordered in the low-temperature phase.

As a result of the phase transition, some H atoms are closer to the Cl atoms at low temperature (*cf*. Tables 2 and 4). It is worthwhile stressing that the methylene H atoms are closer to the Cl atoms than the methyl H atoms. This situation is similar to that in $[N(C_4H_9)_4]_2Pd_2Cl_6$ (Bouquillon *et al.*, 1999). In the latter structure, the closest $H_{methylene}\cdots Cl$ distance is 2.5767 (7) Å, while the closest $H_{methyl}\cdots Cl$ distance is 3.1455 (7) Å.

The shortest C—H···Cl distances and angles in (I) indicate the existence of hydrogen bonds which can be considered intermediate or long, even for the N—H···Cl moiety (*i.e.* with a more electronegative donor), where the Cl atom is bonded to a metal (Desiraju & Steiner, 1999; Aullón *et al.*, 1998). Some H atoms, such as H12 (Table 2), and H12 and H22 (Table 4), are involved in a bifurcated interaction with the surrounding Cl atoms. The vibrational spectroscopic data can serve as the criterion (*e.g.* James *et al.*, 1996) for deciding whether a hydrogen bond really exists, due to a decrease in a pertinent frequency of a *D*—H bond. Therefore, both IR and Raman spectra were recorded in order to confirm the existence of C—H···Cl hydrogen bonds in the title crystal structures (see *Experimental*). The observed lowering of the νCH_2 and νCH_3 frequencies is clear evidence of the formation of C—H···Cl hydrogen bonds.

Experimental

Our intention was to prepare $[N(C_2H_5)_4][PdCl_4]$ from stoichiometric amounts of $[N(C_2H_5)]_4Cl$ and $PdCl_2$ according to the following equations:

$$[N(C_2H_5)]_4OH + HCl \rightarrow [N(C_2H_5)]_4Cl + H_2O \ (1)$$

$$2[N(C_2H_5)]_4Cl + PdCl_2 \rightarrow [N(C_2H_5)]_4[PdCl_4] \ (2).$$

Accordingly, aqueous $[N(C_2H_5)_4]OH$ (2.3767 *M*; Aldrich) was neutralized with a stoichiometric amount of HCl (Lachema) to yield $[N(C_2H_5)_4]Cl$ (2 g). A stoichiometric amount of $PdCl_2$ (1.070 g; Fluka) was then added to the solution; the colour of the solution changed to dark-red–brown during dissolution of the $PdCl_2$. Water was added to bring the volume of the mixture to 300 ml the resulting mixture was allowed to stand for 12 h. The mixture was then stirred for 2 h in order to dissolve all remaining solid matter, followed by heating at 323 (5) K for another 2 h. The resulting wine-red solution (about 50 ml) was decanted into another beaker in order to obtain the red–brown precipitate. Water (about 45 ml) was then added and all solid matter dissolved. After one month at 292 (2) K, crystals of (I) several mm in size were formed. The preparation was successfully repeated with stoichiometric amounts of the reagents, according to the reaction

$$2[N(C_2H_5)_4]Cl + 2\ PdCl_2 \rightarrow [N(C_2H_5)_4]_2Pd_2Cl_6.$$

In all cases, the lattice parameters corresponded to the phase that is described in this article.

The calorimetric experiments were performed on a PerkinElmer DSC 7 differential scanning calorimeter using *PYRIS Software* (PerkinElmer, 2001), with m = 28 mg, a temperature interval of 93–323 K and a scanning rate of 10 K min^{-1}. The experiment showed a λ-type anomaly which indicated a structural phase transition at about 153 K. A melting point was detected at 449 K, ΔH = 57 J g^{-1}. The structural phase transition was observed even in previously melted and solidified samples. After several cycles of cooling and heating, the phase-transition temperature tended to be lower by 2–4 K, according to three experiments on different samples.

The phase transition was also recognized by the splitting of reflections from several single crystals. Preliminary measurements showed that the reflections *hk*0 were split, while 0*kl* were not. By careful centring of the reflections using narrow slits on the point detector, it was possible to determine the lattice parameters with the prevailing contribution to the diffraction of just one of the domain states.

The orientation matrices relating the respective domain states of the low-temperature phase were determined experimentally and correspond well with an idealized twinning matrix:

$$\begin{pmatrix} h_2 & k_2 & l_2 \end{pmatrix} = \begin{pmatrix} h_1 & k_1 & l_1 \end{pmatrix} \begin{pmatrix} -1 & 0 & -(2c/a)\cos\beta \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

Finally, the reversibility of the phase transition was determined experimentally. After collecting data on the low-temperature phase, the data collection on the room-temperature phase proved the reversibility of the phase transition. (The room-temperature phase was determined on several crystals.)

The IR and Raman spectra were recorded on a Nicolet Magna 760 FT–IR spectrometer equipped with a Nicolet Nexus FT–Raman module. The spectra were collected under the following conditions. IR spectrum: fluorolube mull, 2 cm^{-1} resolution, 32 scans, Happ–Genzel apodization; Raman spectrum: polycrystalline sample in glass vial, 2 cm^{-1} resolution, 512 scans, Happ–Genzel apodization, 400 mW Nd:YVO$_4$ laser excitation at 1064 nm, 292 K. Our attention was focused on four observed bands of C—H stretching vibrations. According to a previous spectroscopic study of tetraethylammonium salts (Baran *et al.*, 2000), these bands were assigned to ν_{as}CH$_3$ [IR 3006 cm^{-1} (*w*); Raman 3002 cm^{-1} (*sh*)], ν_sCH$_3$ [IR 2984 cm^{-1} (*s*); Raman 2986 cm^{-1} (*vs*)], ν_{as}CH$_2$ [IR 2973 cm^{-1} (*sh*); Raman 2968 cm^{-1} (*m*)] and ν_sCH$_2$ [IR 2946 cm^{-1} (*m*); Raman 2939 cm^{-1} (*vs*)] vibrations. The frequencies of these bands are shifted to lower wavenumbers in both the IR (4–10 cm^{-1}) and Raman spectra (10–16 cm^{-1}) compared with [N(C$_4$H$_9$)$_4$]HSeO$_4$ (Baran *et al.*, 2000), [N(C$_4$H$_9$)$_4$]SbCl$_6$ (Zeegers-Huyskens & Bator, 1996) and [N(C$_4$H$_9$)$_4$]-Cl·4H$_2$O (Baran *et al.*, 2000).

Compound (I) at 292 K

Crystal data

(C$_8$H$_{20}$N)$_2$[Pd$_2$Cl$_6$]
M_r = 686.04
Orthorhombic, *Immm*
a = 8.7922 (12) Å
b = 12.3094 (16) Å
c = 13.2806 (19) Å
V = 1437.3 (3) Å^3
Z = 2
D_x = 1.585 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 30 reflections
θ = 5.7–14.0°
μ = 1.81 mm^{-1}
T = 292 (2) K
Plate with a trigonal base, red
0.24 × 0.18 × 0.12 mm

Data collection

Kuma XCalibur diffractometer
$\omega/2\theta$ scans
Absorption correction: Gaussian (*JANA*2000; Petříček & Dušek, 2000)
T_{min} = 0.676, T_{max} = 0.737
6309 measured reflections
919 independent reflections
668 reflections with $I > 3\sigma(I)$
R_{int} = 0.029
θ_{max} = 27.0°
$h = -11 \rightarrow 11$
$k = -15 \rightarrow 15$
$l = -16 \rightarrow 16$
3 standard reflections every 100 reflections intensity decay: 2.8%

Refinement

Refinement on F^2
$R(F)$ = 0.025
$wR(F^2)$ = 0.073
S = 1.61
919 reflections
43 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(I) + 0.0009I^2]$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Table 1
Selected interatomic distances (Å) for (I) at 292 K.

Pd—Cl1	2.3233 (9)	N—C2	1.517 (4)
Pd—Cl2	2.2679 (11)	C1—C3	1.473 (7)
N—C1	1.518 (5)	C2—C4	1.495 (6)

Table 2
Geometry of the shortest H···Cl interactions (Å, °) up to 3.5 Å for (I) at 292 K.

D—H···A	D—H	H···A	D···A	D—H···A
C1—H11···Cl2^{i}	0.96	2.84	3.783 (3)	166
C2—H12···Cl1^{ii}	0.96	2.98	3.903 (3)	161
C2—H12···Cl2^{iii}	0.96	3.42	4.186 (3)	139
C3—H23···Cl1^{iv}	0.97	3.18	3.636 (7)	111
C4—H24···Cl2^{v}	0.97	3.13	3.935 (5)	141

Symmetry codes: (i) $x, -y, 1-z$; (ii) $\frac{3}{2}-x, \frac{1}{2}-y, \frac{3}{2}-z$; (iii) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{3}{2}-z$; (iv) $x-\frac{1}{2}, y-\frac{1}{2}, \frac{1}{2}+z$; (v) $1-x, y, z$.

Compound (I) at 130 K

Crystal data

(C$_8$H$_{20}$N)$_2$[Pd$_2$Cl$_6$]
M_r = 686.04
Monoclinic, *I*2/*m*
a = 8.7249 (12) Å
b = 12.2375 (28) Å
c = 13.0621 (20) Å
β = 91.973 (17)°
V = 1393.8 (4) Å^3
Z = 2
D_x = 1.634 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 39 reflections
θ = 6.8–12.8°
μ = 1.87 mm^{-1}
T = 130 K
Prism, red
0.25 × 0.14 × 0.12 mm

Data collection

Kuma XCalibur diffractometer
$\omega/2\theta$ scans
Absorption correction: Gaussian (*JANA*2000; Petříček & Dušek, 2000)
T_{min} = 0.741, T_{max} = 0.820
7138 measured reflections
2101 independent reflections
1326 reflections with $I > 3\sigma(I)$
R_{int} = 0.113
θ_{max} = 27.0°
$h = -11 \rightarrow 11$
$k = -15 \rightarrow 15$
$l = -16 \rightarrow 16$
3 standard reflections every 100 reflections intensity decay: 1.8%

Refinement

Refinement on F^2
$R(F)$ = 0.029
$wR(F^2)$ = 0.075
S = 1.15
1986 reflections
70 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(I) + 0.0009I^2]$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.43 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 e Å^{-3}

Table 3
Selected interatomic distances (Å) for (I) at 130 K.

Pd—Cl1	2.3225 (9)	N—C5	1.508 (7)
Pd—Cl2	2.2811 (11)	C1—C3	1.514 (8)
N—C1	1.504 (7)	C2—C4	1.507 (5)
N—C2	1.518 (4)	C5—C6	1.497 (8)

Table 4
Geometry of the shortest H···Cl interactions (Å, °) up to 3.5 Å for (I) at 130 K.

D—H···A	D—H	H···A	D···A	D—H···A
C1—H11···Cl2$^{\rm i}$	0.96	2.84	3.797 (4)	176
C2—H12···Cl1$^{\rm ii}$	0.96	2.89	3.806 (4)	161
C2—H12···Cl2$^{\rm iii}$	0.96	3.35	4.101 (4)	137
C2—H22···Cl1$^{\rm iv}$	0.96	3.00	3.915 (4)	159
C2—H22···Cl2$^{\rm v}$	0.96	3.39	4.167 (4)	140
C3—H23···Cl1$^{\rm iv}$	0.97	3.06	3.510 (7)	110
C4—H24···Cl2$^{\rm vi}$	0.97	3.02	3.895 (4)	152
C4—H34···Cl2	0.97	3.12	3.838 (4)	133
C5—H15···Cl2$^{\rm vi}$	0.96	2.80	3.686 (4)	154
C6—H26···Cl1$^{\rm ii}$	0.97	3.16	3.612 (7)	110

Symmetry codes: (i) $x, -y, z$; (ii) $\frac{3}{2}-x, \frac{1}{2}-y, \frac{3}{2}-z$; (iii) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (iv) $x-\frac{1}{2}, y-\frac{1}{2}, \frac{1}{2}+z$; (v) $\frac{1}{2}-x, \frac{1}{2}-y, \frac{3}{2}-z$; (vi) $1-x, y, 1-z$.

Table 5
Equivalent displacement parameters $U_{\rm eq}$ (Å^2) of the room- and low-temperature phases of (I) and their ratio.

$U_{\rm eq} = \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* a_i a_j$.

Atom	$U_{\rm eq}$ at 292 K	$U_{\rm eq}$ at 130 K	Ratio
Pd	0.06373 (13)	0.02878 (14)	2.22 (1)
Cl1	0.0823 (5)	0.0343 (5)	2.40 (4)
Cl2	0.0986 (4)	0.0413 (4)	2.39 (3)
N	0.0686 (13)	0.0302 (15)	2.3 (1)
C1	0.0953 (16)	0.0364 (18)	2.6 (1)
C2	0.0791 (12)	0.0318 (12)	2.5 (1)
C3	0.134 (3)	0.048 (2)	2.8 (1)
C4	0.1021 (18)	0.0416 (15)	2.5 (1)
C5	= C1	0.039 (2)	2.4 (1)
C6	= C3	0.054 (2)	2.5 (1)

Refinement of the low-temperature data was performed on a data set composed of two merged sets of reflections which originated from the domains pertinent to each respective domain state. The exactly superimposed reflections which stem from the domains of both domain states are $0kl$, in accordance with the twinning matrix

$$\begin{pmatrix} h_2 & k_2 & l_2 \end{pmatrix} = \begin{pmatrix} h_1 & k_1 & l_1 \end{pmatrix} \begin{pmatrix} -1 & 0 & -(2c/a)\cos(\beta) \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

The respective reflections linked by the orientation matrix refer to the first and second domain states. The refinement program *JANA*2000 (Petříček & Dušek, 2000) accounts for the systematic superposition of the reflections that occur in accordance with the twinning matrix. The refined domain-state fraction resulted in a value of 0.5008 (9). (The data for each domain state were measured with a standard reflection 006, which is common to both domain states, in order to facilitate further scaling; see the archived CIF for further details.) The extinction correction turned out to be insignificant both for the room- and low-temperature phases.

From the refinement of the low-temperature phase were omitted 125 unmatched reflections for which $|F_o{}^2 - F_c{}^2| > 3\sigma(F_o{}^2)$. The reason for the rejection of these unmatched reflections was inappropriately high indicators for the refinement on 2226 reflections of which 1444 were considered observed $[I > 3\sigma(I)]$: $R_{\rm obs} = 0.047$ and $wR_{\rm obs} = 0.125$, $R_{\rm all} = 0.097$ and $wR_{\rm all} = 0.132$, $S_{\rm all} = 2.08$ and $S_{\rm obs} = 2.45$, and $\rho_{\rm max} = 1.69$ e Å^{-3} and $\rho_{\rm min} = -1.69$ e Å^{-3}. Otherwise the conditions of the refinement were the same as those reported above for the sample at 130 K. From a comparison of the refined parameters of the non-H atoms in both models, it followed that the absolute value of their differences divided by the average of the standard uncertainties did not exceed 5.5 in unique cases.

In order to explain the differences between the observed and calculated intensities of the rejected reflections, it was found that some of these reflections were either split $(10\overline{3})$ or their profile was unsymmetric. The indices of many rejected reflections were of the type $10l$ or $10\bar{l}$. Therefore, it was taken into account that the reason for the rejection of these reflections may be the imperfect superposition of the reflections. Consequently, an alternative procedure was adopted, applying the function CHECKRAN in *JANA*2000. This function calculates the positions of the corresponding reflections stemming from the other domain state for each measured reflection in a bisecting position, taking as its input the orientation matrices pertinent to each domain state.

If the differences $|\Delta\chi|$, $|\Delta\omega|$ and $|\Delta\theta|$ in the setting angles of both reflections were simultaneously lower than 0.7, 0.10 and 0.10°, respectively, then such reflections were considered to be fully overlapped. On the other hand, if at least one of these respective differences of the setting angles was greater than 1.9, 0.15 or 0.15°, then such a reflection was considered to be fully separated. The remaining reflections were considered to be imperfectly separated and were therefore not included in further refinement. The values of the limits for the setting angles were determined by a series of refinements with varying values of these limits. The criteria for adopting the values of the setting-angle limits were the lowest indicators of the refinement. These trial refinements were performed on a data set which was averaged only through the inversion. In the next stage, the reflections which were considered imperfectly overlapped were discarded from the reflection list. Each of the reflection subsets was averaged through the symmetry operations of $2/m$. Hence, the refinement of 2152 diffractions of which 1382 were observed $[I > 3\sigma(I)]$ resulted in $R_{\rm obs} = 0.035$ and $wR_{\rm obs} = 0.082$, $R_{\rm all} = 0.089$ and $wR_{\rm all} = 0.094$, $S_{\rm all} = 1.46$ and $S_{\rm obs} = 1.61$, and $\rho_{\rm max} = 0.71$ e Å^{-3} and $\rho_{\rm min} = -0.49$ e Å^{-3}. Otherwise, the conditions of the refinement were the same as those reported above for (I) at 130 K. This means that the result of the refinement on the data processed by CHECKRAN is inferior to that given above for (I) at 292 K, where the unmatched reflections were simply discarded from the refinement.

From a comparison of the corresponding positional and displacement parameters of the non-H atoms in both models, it followed that the absolute value of their differences divided by the average of the standard uncertainties did not exceed 2.5 and 4.75, respectively, in unique cases. Therefore, neither structure model is influenced too much by omission of the reflections. Thus, the model with the lower R factor is given preference and reported in this article, despite the fact that the rejection of the reflections has not been fully explained.

The structures of the room- and low-temperature phases were determined on different samples. After collecting data on the low-temperature phase, data collection on the room-temperature phase proved the reversibility of the phase transition.

H atoms were placed in geometric positions and treated as riding, with C—H distances of 0.96 or 0.97 Å and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C).

For compound (I) at both temperatures, data collection: *KM*4*B*8 (Gałdecki *et al.*, 1997); cell refinement: *KM*4*B*8; data reduction: *JANA*2000 (Petříček & Dušek, 2000); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *JANA*2000; molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *JANA*2000.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1325). Services for accessing these data are described at the back of the journal.

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