Structures and Isomerization in Diamminedichloropalladium(II)

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Abstract

Three forms (*cis*-, *trans*-, *β-trans*-) of $[Pd(NH_3)_2Cl_2]$ were obtained as pure single-phase powder materials. *Ab initio* structure determinations using X-ray powder diffraction were carried out. The *cis*-$Pd(NH_3)_2Cl_2$ [$a = 6.3121(2)$, $b = 6.4984(2)$, $c = 3.3886(1)$ Å, $\alpha = 96.604(4)$, $\beta = 97.290(4)$, $\gamma = 104.691(2)°$, $Z = 1$, space group $P\bar{1}$] and *trans*-$Pd(NH_3)_2Cl_2$ [$a = 6.5398(3)$, $b = 6.8571(4)$, $c = 6.3573(3)$ Å, $\alpha = 103.311(5)$, $\beta = 102.454(3)$, $\gamma = 100.609(4)°$, $Z = 2$, space group $P\bar{1}$] phases have a typical layer-column structure, while *β-trans*-$Pd(NH_3)_2Cl_2$ [$a = 8.1540(2)$, $b = 8.1482(2)$, $c = 7.7945(1)$ Å, $Z = 4$, space group $Pbca$] is described as a parquet-like layer structure. Both *trans* phases demonstrate the order–disorder phenomenon. The possible ways of phase transitions are discussed. It is noted that the *cis* phase can transform into *trans* in the solid state without destroying the crystal body. Further transformation to *β-trans* follows through a break up of the crystal body.

1. Introduction

In spite of impressive results obtained over the last decades in the chemistry of precious metals, this field shows many white spots even regarding rather simple compounds. No doubt this is caused by some obvious difficulties. One is the problem of the structural investigation of powdered materials, which are typical for precious metals compounds. The present study has become possible due to recent developments in powder diffraction techniques in X-ray structure analysis. The paper deals with the simplest complex compounds such as $[Pd(NH_3)_2Cl_2]$. Smirnov, Volkova, Chumakov & Volkov (1981) gave a primary description of three forms of this compound. In contrast with the chemical data there is extremely limited crystal structure information on these and related compounds. Only crystal data are available on *cis*- and *trans*-$[Pt(NH_3)_2Cl_2)]$ (Porai-Koshits, 1954; Milburn & Truter, 1966). Powder data generated from the latter reference are, by the way, not in agreement with the powder data available in the PDF [Powder Diffraction File (1993).]
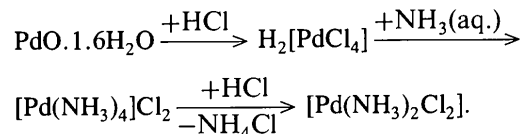
Preparation methods have been developed to obtain pure powders of *cis*-, *trans*- and *β-trans*-diamminedichloropalladium(II), making it possible to solve the crystal structures from X-ray powder data. Some obstacles which interfere with obtaining perfect single crystals were revealed in this process. The crystal structure information obtained gives a basis for understanding the mechanism of phase transitions in $[Pd(NH_3)_2Cl_2]$.

2. Experimental

2.1. *Preparations*

The starting material for the synthesis of *cis*-$[Pd(NH_3)_2Cl_2]$ was $[Pd(NH_3)_2C_2O_4]$, which was synthesized as described previously (Chernyaev, 1964). The oxalate was placed in an agate mortar and HCl was added in 10–20% excess. The mixture was ground until the colour changed from pale yellow to brown–yellow, which took ~3 min at room temperature. The salt obtained was washed with ethanol and then dried. The chemical analysis of the product showed Pd 50.52 (50.40), Cl 33.40 (33.49)%. Although this method never produces a single crystal material, it provides the most pure substance.

trans-$[Pd(NH_3)_2Cl_2)]$ was prepared according to the same source (Chernyaev, 1964) from $PdO.1.6H_2O$. The following chain of transformation was carried out:

$$PdO.1.6H_2O \xrightarrow{+HCl} H_2[PdCl_4] \xrightarrow{+NH_3(aq.)}$$

$$[Pd(NH_3)_4]Cl_2 \xrightarrow[-NH_4Cl]{+HCl} [Pd(NH_3)_2Cl_2].$$

The result was a fine yellow powder. Chemical analysis: Pd 50.50 (50.40), Cl 33.41 (33.49)%. The *trans* compound could also be prepared by thermal transformation of *cis*-$[Pd(NH_3)_2Cl_2)]$ at ~523 K, but in this case the product is contaminated by other isomers.

β-trans-$[Pd(NH_3)_2Cl_2)]$ was obtained by thermal transformation of *trans*-$[Pd(NH_3)_2Cl_2)]$. The latter compound was heated in water at 363–368 K for 4 h. The orange coloured product was washed and dried. Chemical analysis: Pd 50.45 (50.40), Cl 33.40 (33.49)%. The *trans* isomer is insoluble in water.

Water promotes the transformation and makes it possible to obtain the material without traces of the initial substances.

2.2. *Thermal decomposition*

A thermoanalysis system MOM Q 1500D was used for the thermogravimetric and thermographic investigations. Analysis in the range 298–773 K, in a static atmosphere of decomposition products and with a heating rate of $10\,\mathrm{K\,min^{-1}}$, indicate a thermal stability up to 563 and 593 K for the *cis* and *trans* isomers, respectively. TG curves show a loss of weight of ~50.8 and 50.2% at one stage in the temperature range up to 678 K. This corresponds to the full decomposition of the compounds to pure Pd powders and Cl_2 and NH_3 as gaseous products. DTA curves, on the other hand, indicate that the process of decomposition consists of two stages. The first less energetic stage seems to be a partial release of NH_3. There are no clear thermal effects associated with phase transitions. Fig. 2 presents both TG and DTA curves.

The thermal transformation was also studied by the high-temperature X-ray diffraction technique in air with a thin layer of powder sample. It was found that the powder pattern of the *cis* isomer gradually transformed into the powder pattern of the *trans* isomer in the temperature range 403–453 K. The decomposition was detected at temperatures higher than 523 K, but not even traces of *β-trans*-[Pd(NH₃)₂Cl₂] could be observed.

2.3. *X-ray powder structure investigation*

The structures of all the compounds were studied with the technique described in detail elsewhere (Solovyov, Blokhina, Kirik, Blokhin & Derikova, 1996). The X-ray diffraction data were collected on a DRON-4 diffractometer using monochromatic (flat graphite) $Cu K\alpha$, $\lambda_1 = 1.54056$, $\lambda_2 = 1.54439\,\text{Å}$ radiation. The measurements for the crystal structure investigations were performed at room temperature. Selected patterns to study the thermal transformation were obtained on heating in air in a high-temperature chamber. The X-ray powder data have been deposited at ICDD-JCPDS (PDF 44-573, 46-877).*
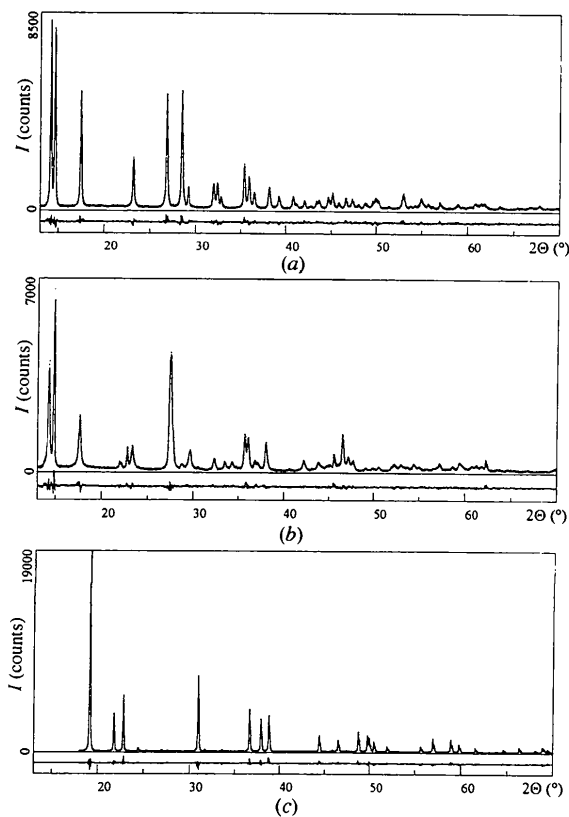
Fig. 1. The final Rietveld plots for (*a*) *cis-*, (*b*) *trans-* and (*c*) *β-trans*-[Pd(NH₃)₂Cl₂].
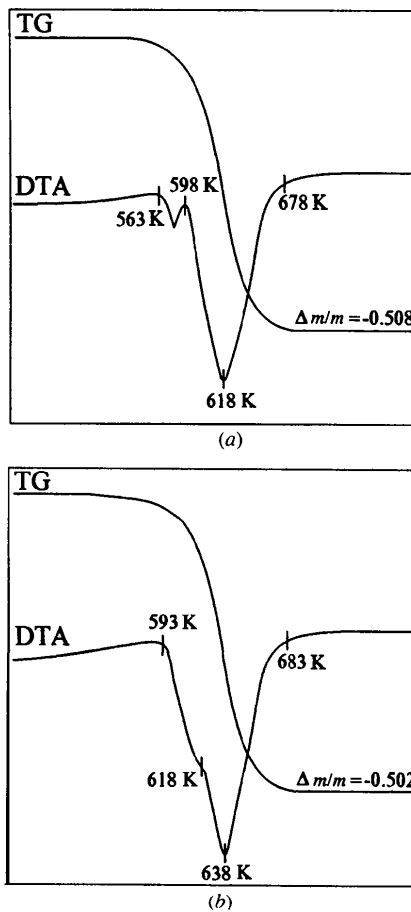

Fig. 2. TG and DTA curves for (*a*) *cis-* and (*b*) *trans*-[Pd(NH₃)₂Cl₂].

The unit-cell parameters were found using the programs of Visser (1969) and Kirik, Borisov & Fedorov (1979). Refinement of the unit-cell parameters was carried out with an iterative whole powder-pattern fitting procedure (unpublished) incorporated in the program *DBWS-9006PC* (Wiles & Young, 1981). After some improvements (addition of split-FWHM asymmetry correction and individual FWHM refinement, where FWHM is full width at half-maximum), this program was used for structure refinement by the Rietveld (1969) method. The procedure of fitting the whole powder pattern was also used to extract the integrated intensities and to find the initial peak-shape parameters.

In all cases the structure models were provided by a three-dimensional Patterson synthesis calculated using sets of 120, 175 and 135 reflections, respectively, for the *cis*, *trans* and *β-trans* isomer. The Patterson maps revealed the positions of the Pd atoms and the principal arrangement of the Cl atoms. The N atoms were located from successive $\Delta\rho$ maps. The H atoms were not located, but were introduced in the structure model and rigidly fixed near the N atoms. This gave more reasonable interatomic distances and lower levels of R factors than without H atoms added. The $\Delta\rho$ and Patterson maps for the *trans* and *β-trans* isomers also showed some additional features which were attributed to crystal imperfections. A detailed discussion of these features is given below.

The Pearson VII function was chosen for the simulation of the peak shape for the *cis* and *β-trans* isomers. The angular dependence of the FWHM for the *cis* and the *β-trans* phases was refined with three parameters using the formula of Caglioti, Paoletti & Ricci (1958). A split-FWHM approach (Solovyov *et al.*, 1996) was applied to the symmetry correction. The background was defined as a fifth-order polynomial in 2θ.

A marked *hkl*-dependent peak broadening was found in the powder pattern of the *trans* isomer. This broadening may be interpreted as a consequence of crystal imperfections. Some additional difficulties were met in the course of processing these data. The positions of the main atoms were found from the Patterson map. Nevertheless, the refinement faced a difficulty in the N-atom location. The problem was solved by analysing a difference-Fourier map. Two additional positions ($\frac{1}{2}, 0, 0$ and $\frac{1}{2}, \frac{1}{2}, 0$) with occupancies equivalent to 0.07 Pd were revealed. The inclusion of the additional positions into the structure model made it possible to locate the N atoms and obtain a reliable molecular geometry and molecular arrangement. Some correlations between the additional occupied positions in the crystal and the indexes of the broadened peaks were noticed. However, an uncertainty in the model of the

imperfection did not allow us to find a satisfactory analytical representation of the *hkl*-dependence for FWHM.

The Thompson–Cox–Hastings pseudo-Voigt profile function was used to simulate the shape of the peaks. It has some advantages over the Pearson VII for individual peak refinement, because only one parameter can be used to control both the shape and the width of the peak. The reflections having odd k indexes were found to be weak and almost free from anisotropic broadening. The angular dependence of FWHM for these reflections was conventionally refined with two parameters representing the Gaussian and Lorentzian parts of the peak. The Lorentzian parts for the remaining reflections were allowed to vary individually within certain restrictions.

Due to correlation between the background, occupancies and thermal parameters because of a lack of experimental data, restrictions were introduced on the occupancies and thermal parameters in the final stage of refinement. The restrictions did not aim to meet stoichiometry requirements, because of an incompleteness of the model of the real structure. However, the difference between the Pd(1) and Pd(2) occupancies was within two standard deviations, so these occupancies were set equal. As for the large values of the thermal parameters of the N atoms (Table 2), they should not be considered as real physical values, but as a consequence of the correlations mentioned above.

Tables 1–3 summarize the crystal data, the results of the Rietveld refinements and the structure parameters obtained correspondingly for *cis*-, *trans*- and *β-trans*-[Pd(NH$_3$)$_2$Cl$_2$].* The observed, calculated and difference profiles are shown in Fig. 1.

3. Results and discussion

3.1. Crystal structure of cis-[Pd(NH$_3$)$_2$Cl$_2$]

cis-[Pd(NH$_3$)$_2$Cl$_2$] as well as the other isomers studied have a molecular type of structure (Fig. 3), which is not isostructural to the Pt analogue (Milburn & Truter, 1966). Practically planar molecules have the form of a slightly distorted regular trapezoid. All angles differ from right angles. The molecular geometry is in good agreement with that described for *cis*-[Pt(NH$_3$)$_2$Cl$_2$]. The molecules are stacked along the c axis parallel to one another. Each successive molecule in the stack is translationally related to the previous one ('one-side packing'). This is in contrast to *cis*-[Pt(NH$_3$)$_2$Cl$_2$], where every two successive complexes are centrosymmetrically related. 'One-side packing' does not significantly affect the Pd—Pd distance, which is equal to c [3.3886(1) Å] and close to Pt—Pt [3.372(2) and 3.409(2) Å]. This means that the Cl···Cl and

Table 1. *Experimental details*

	cis	*trans*	*β-trans*
Crystal data			
Chemical formula	[PdCl₂(NH₃)₂]	[PdCl₂(NH₃)₂]	[PdCl₂(NH₃)₂]
Chemical formula weight	211.39	211.39	211.39
Cell setting	Triclinic	Triclinic	Orthorhombic
Space group	$P1$	$P\bar{1}$	$Pbca$
a (Å)	6.3121 (2)	6.5398 (3)	8.1540 (2)
b (Å)	6.4984 (2)	6.8571 (4)	8.1482 (2)
c (Å)	3.3886 (1)	6.3573 (3)	7.7945 (1)
α (°)	96.604 (4)	103.311 (5)	
β (°)	97.290 (4)	102.454 (3)	
γ (°)	104.691 (2)	100.609 (4)	
V (Å³)	131.78	262.63	517.87
Z	1	2	4
D_x (Mg m⁻³)	2.6632	2.6732	2.711
Radiation type	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$
Wavelength (Å)	1.5418	1.5418	1.5418
No. of reflections for cell parameters	40	40	40
θ range (°)	6.5–35	6.5–31.5	9–37.5
μ (mm⁻¹)	36.445	36.581	37.098
Temperature (K)	293	293	293
Crystal form	Thin powder	Thin powder	Thin powder
Crystal color	Brown–yellow	Yellow	Orange
Data collection			
Diffractometer	DRON-4	DRON-4	DRON-4
Data collection method	θ–2θ scans	θ–2θ scans	θ–2θ scans
Absorption correction	None	None	None
No. of estimated reflections	120	175	135
No. of independent reflections	120	175	135
No. of observed reflections	120	175	135
R_{int}	0.033	0.030	0.046
θ_{max} (°)	35	31.5	37.5
Range of h, k, l	$0 \rightarrow h \rightarrow 4$	$0 \rightarrow h \rightarrow 4$	$0 \rightarrow h \rightarrow 6$
	$-4 \rightarrow k \rightarrow 4$	$-4 \rightarrow k \rightarrow 4$	$0 \rightarrow k \rightarrow 5$
	$-2 \rightarrow l \rightarrow 2$	$-4 \rightarrow l \rightarrow 4$	$0 \rightarrow l \rightarrow 5$
Intensity decay (%)	<1	<1	<1
Refinement			
Refinement on	Powder pattern profile	Powder pattern profile	Powder pattern profile
R_p	0.097	0.094	0.111
R_{wp}	0.083	0.091	0.109
S	1.58	1.61	1.81
No. of reflections used in refinement	120	175	135
No. of parameters used	26	32	32
H-atom treatment	H-atom parameters not refined	H-atom parameters not refined	H-atom parameters not refined
Weighting scheme	$w = 1/Y$	$w = 1/Y$	$w = 1/Y$
Source of atomic scattering factors	*DBW*3.2S (Wiles & Young, 1981)	*DBW*3.2S (Wiles & Young, 1981)	*DBW*3.2S (Wiles & Young, 1981)

$NH_3\cdots NH_3$ repulsions are quite insensitive to the packing. Many authors consider the observed Pd—Pd distance to show some type of metal–metal interaction (Porai-Koshits & Kukina, 1974), which is a characteristic feature of many Pd- and Pt-containing complex compounds.

H atoms were not located. However, judging from N$\cdots$Cl distances and Pd—N$\cdots$Cl angles, the contacts N(1) $(1 + x, y, z)\cdots$Cl(2) and N(2) $(1 + x, y, z)\cdots$Cl(2) (Table 3) could possibly be referred to as hydrogen bonds.

3.2. *Crystal structure of trans-[Pd(NH₃)₂Cl₂]*

In the case of *trans*-[Pd(NH₃)₂Cl₂)] (Fig. 4) the packing resembles *cis*-[Pt(NH₃)₂Cl₂)] (Milburn & Truter, 1966), but is quite different from *trans*-[Pt(NH₃)₂Cl₂)] (Porai-Koshits, 1954). In contrast to the Pt compound, the *trans* isomer shows stacking along the *b* axis. The stacks consist of a sequence of flat complexes, which are approximately perpendicular to the *ac* plane. There are two independent molecules in the triclinic cell, so every two successive complexes in a stack are symmetrically independent. Every second complex is rotated ~90° with respect to the first. However, the expected decrease of the repulsion between complexes due to this rotation does not influence the Pd—Pd distances [3.4285 (2) Å], which are even longer than in the *cis* isomer.

The complexes have a rhombic form. The interatomic distances (Table 2) in the two independent complexes correspond quite well to the average distances known for this type of bond (Porai-Koshits & Kukina, 1974). The most probable system of hydrogen bonds analysed from distances and angles is presented in Fig. 4. It consists of two Cl$\cdots$N contacts.

Table 2. *Fractional atomic coordinates, occupancy and equivalent isotropic temperature parameters (Å²)*

	x	y	z	B_{iso}	Occupancy factor
cis form					
Pd	0.0	0.0	0.0	1.36 (7)	1.00
Cl(1)	0.270 (2)	0.312 (2)	0.157 (5)	1.2 (3)	1.00
Cl(2)	0.238 (2)	−0.214 (2)	−0.015 (5)	1.2 (3)	1.00
N(1)	−0.254 (6)	−0.267 (4)	−0.100 (10)	2.0	1.00
N(2)	−0.253 (5)	0.159 (5)	0.070 (10)	2.0	1.00
trans form					
Pd(1)	0.0	0.0	0.0	1.86 (6)	1.00
Pd(2)	0.0	1/2	0.0	1.86 (6)	1.00
Pd(3)	1/2	0.0	0.0	1.86 (6)	0.070 (2)
Pd(4)	1/2	1/2	0.0	1.86 (6)	0.070 (2)
Cl(1)	−0.196 (2)	0.068 (2)	0.262 (2)	2.0 (3)	1.00
Cl(2)	0.328 (2)	0.569 (2)	0.267 (2)	2.0 (3)	1.00
N(1)	0.276 (3)	0.078 (4)	0.250 (5)	4.7 (8)	1.00
N(2)	−0.149 (4)	0.574 (5)	0.250 (5)	4.7 (8)	1.00
β-trans form					
Pd	0.0	0.0	0.0	0.89 (8)	1.00
N	0.026 (3)	0.021 (3)	0.253 (1)	1.9 (5)	1.00
Cl	0.196 (1)	0.210 (1)	−0.011 (1)	2.0 (2)	0.71 (1)
Cl(1)	−0.210 (1)	0.196 (1)	0.011 (1)	2.0 (3)	0.29 (1)

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

cis form			
Pd—Cl(1)	2.26 (2)	Pd—N(2)	2.13 (4)
Pd—Cl(2)	2.29 (2)	Cl(2)—N(1')	3.37 (5)
Pd—N(1)	1.99 (4)	Cl(2)—N(2')	3.47 (5)
Cl(1)—Pd—Cl(2)	94.4 (7)	N(1)—Pd—Cl(2)	88 (1)
N(1)—Pd—N(2)	85 (2)	N(2)—Pd—Cl(1)	92 (1)
trans form			
Pd(1)—Cl(1)	2.33 (2)	Pd(2)—N(2)	2.05 (4)
Pd(2)—Cl(2)	2.32 (2)	Cl(1ⁱⁱ)—N(1)	3.58 (6)
Pd(1)—N(1)	2.02 (4)	Cl(1ⁱⁱⁱ)—N(2)	3.49 (6)
N(1)—Pd(1)—Cl(1)	90 (1)	N(2)—Pd(2)—Cl(2)	90 (1)
β-trans form			
Pd—Cl	2.35 (1)	N—Clᵛ	3.18 (4)
Pd—N	1.99 (2)	N—Clᵛⁱ	3.47 (4)
Pdⁱᵛ—Cl	3.42 (1)		
Cl—Pd—N	84 (1)		

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

The distances from the extra Pd(3) and Pd(4) positions to the nearest atoms are in the 2.15–2.35 Å range. It is a substantial argument that these positions are not occupied by N, O or Cl atoms, because such distances are too short to be van der Vaals contacts. As for the Pd atom, these distances correspond well to the Pd—Cl and Pd—N bonds.

Smirnov, Rumin & Blokhina (1985) admit the presence of defects in the substance, which are the result of a transformation yielding dimers (or even polymers) and releasing ammonia according to

$$2[Pd(NH_3)_2Cl_2] \rightarrow [Pd_2(NH_3)_2Cl_4] + 2NH_3.$$
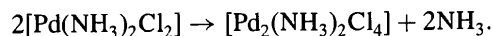
Having the sizes compatible with the lattice sizes, dimers could be built into the structure, causing tolerable tensions. However, the chemical analysis of *trans*-[Pd(NH₃)₂Cl₂] and data on thermal stability

incline us to reject this model of the phenomenon, *e.g.* the expected loss of weight in 7% of defects is ∼1.5%, which is in contradiction to the thermal and chemical analysis data.

It is well known that the anisotropy of FWHM is the evidence of stretched defects in crystals. In the powder pattern of *trans*-[Pd(NH₃)₂Cl₂] the reflections with even *k* indexes were found to be anisotropically broadened so that the 00*l* peaks were the narrowest and the peaks with odd *h* indexes were the broadest.

Thus, we suppose that the most probable model of the observed order–disorder phenomenon is the presence of layer-packing defects. It is quite reasonable to assume that approximately 7% of the layers in the *ac* or *ab* plane are randomly translated on *a*/2. Unfortunately, we did not succeed in refining the real atomic
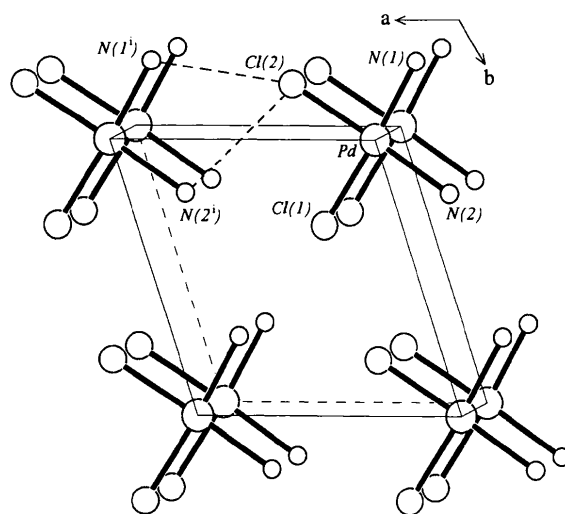
Fig. 3. Crystal structure of *cis*-[Pd(NH₃)₂Cl₂].
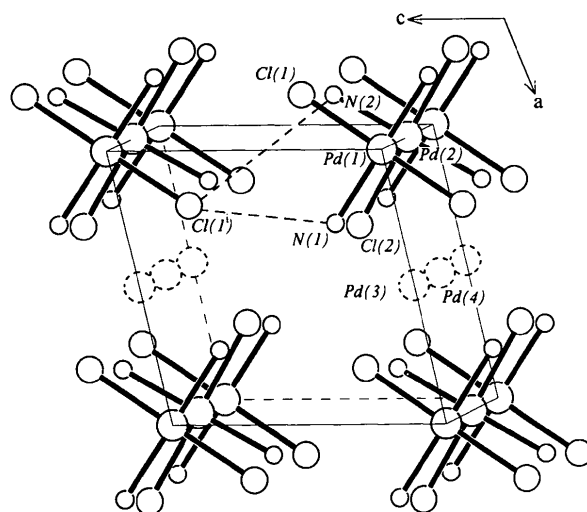
Fig. 4. Crystal structure of *trans*-[Pd(NH₃)₂Cl₂]. The extra Pd positions are shown by dotted circles.

environments of the Pd(3) and Pd(4) positions because of the low level of electron density for these atoms (7% Cl and 7% N), which was the reason why the stoichiometric model was not used for the refinement of the structure.

3.3. Crystal structure of β-trans-[Pd(NH₃)₂Cl₂]

The first crystal structure determination of *β-trans*-[Pd(NH₃)₂Cl₂] was carried out from X-ray powder data not long ago (Kirik, Kruglik, Yakimov & Krapivko, 1991). It was repeated here to obtain more details of the order–disorder phenomena.

There are no direct indications (splitting of lines) of a difference in *a* and *b* parameters in the powder pattern. The whole powder-pattern fitting shows little difference. No data were obtained to distinguish whether it is a real effect or an artifact due to compensation between peak broadening and splitting. The final structure solution without doubt proves an orthorhombic symmetry with non-equivalent *a* and *b* axis.

Due to the complete overlapping of *hkl* and *khl* reflections, Patterson and Fourier maps do not provide any evidence of the non-equivalence of the axes. Parquet-like packing of Cl—Pd—Cl fragments in the basal (*XY*) plane may be stretched along the *a* as well as the *b* axis (Fig. 6). The direction of N—Pd—N in the molecules is close to parallel to the *c* axis. Rietveld refinement of the structure with one of the described complex orientations (see Fig. 5) gave rather good agreement between the experimental and calculated patterns. However, the successive difference-Fourier

and Patterson maps revealed additional peaks at ~2.3 Å from Pd atoms perpendicular to the planes of the molecules. Being rather compact, the parquet-like packing cannot tolerate an order–disorder phenomenon, because of possible short Cl···Cl contacts (~1.12 Å). A reasonable explanation could be found allowing the faults of alternation in the sequence of layers along the *c* axis. The second layer can be obtained from the first by the translation on $\frac{1}{2},0,\frac{1}{2}$ (space group *Pbca*) or $0,\frac{1}{2},\frac{1}{2}$ (related space group *Pcab*). Therefore, if the molecule in the 'correct' layer is oriented with an angle of 133.0 (5)° between the *a* axis and the Cl—Pd—Cl direction (Fig. 6a), then the related molecule in the 'wrong' layer is oriented with an angle of 43.0 (5)° to the *a* axis (Fig. 6b).

The successive Rietveld refinement showed that the concentration of the faults in alternate layers for this sample is ~30%. The previous investigation (Kirik *et al.*, 1991) revealed a 10% concentration of faults. Thus, the degree of crystal imperfection seems to be a function of synthesis and may be changed.
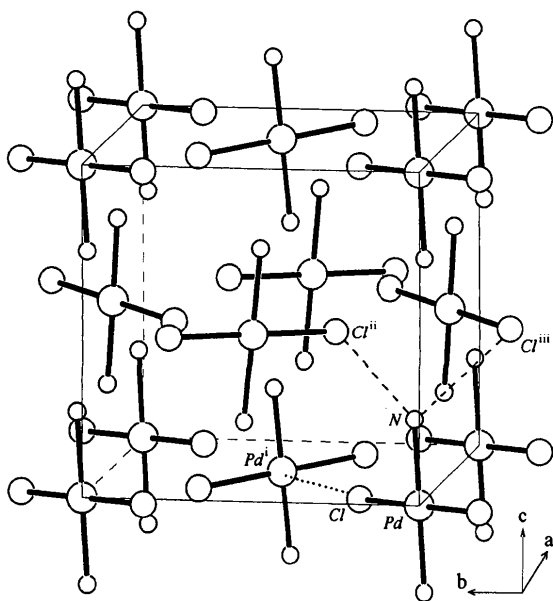

Fig. 5. Crystal structure of *β-trans*-[Pd(NH₃)₂Cl₂]. The disorder is not shown.
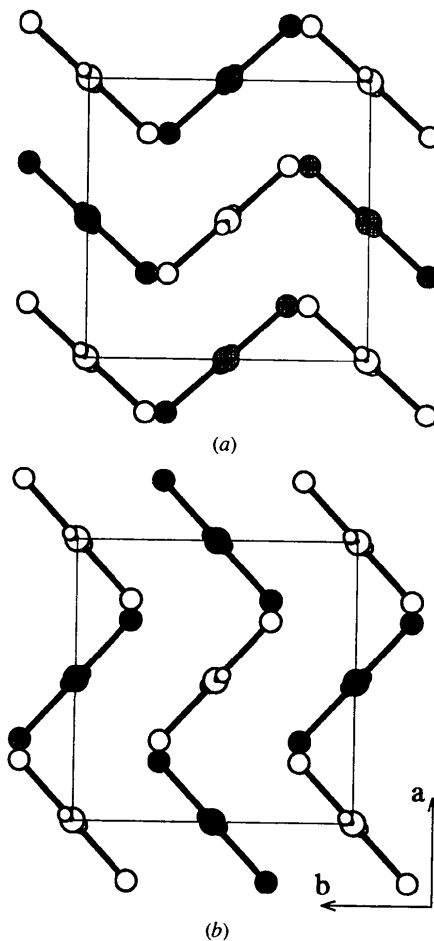

(a)

(b)

Fig. 6. Two possible directions: (a) along the *a* axis and (b) along the *b* axis for the crystal structure stretching in *β-trans*-[Pd(NH₃)₂Cl₂].

The alternate layers model described allows the interpretation of the equality of the a and b axes also. Parquet-like packing does not forbid the equality of a and b axes, although it does not explain it. Nor does the axis equality appear to be a matter of chance, because the same phenomenon is present in β-trans-$[Pd(NH_3)_2Br_2]$ and β-trans-$[Pd(NH_3)_2I_2]$ (to be published).

The geometry of the $[Pd(NH_3)_2Cl_2]$ molecules in the β-trans isomer is quite similar to that in the trans isomer, but the packing is different. Two Cl atoms from neighbouring complexes of the same layer play the role of additional tops to form an octahedron environment for the Pd atom. The Pd$\cdots$Cl distance [3.42 (1) Å] is close to Pd$\cdots$Pd in the cis and trans isomers. A system of hydrogen bonds connects the layers.

3.4. General remarks and phase transitions

The thermal isomerization and stability of $[M(NH_3)_2Cl_2]$, M = Pt,Pd, have been analysed by many authors (see, e.g. Kukushkin, Budanova & Sedova, 1981) using DTA as the main source of data. For the Pt compound it was found that the trans isomer has 12.6 J mol^{-1} less energy than the cis isomer. The cis–trans transition in the Pt case is represented by a distinctive peak in the DTA curve. As for $[Pd(NH_3)_2Cl_2]$, in the present study it was found that visual changes in the powder pattern appeared at 403 K, but it was not followed by any peak on DTA and loss of weight (Fig. 2). The thermal transformations in $[Pd(NH_3)_2Cl_2]$ are irreversible. The β-trans isomer is considered to be the most stable phase and the final point of the transformation if it takes place in a bulk sample or in water.

The structure results obtained and the thermal data provide a good basis to discuss the possible mechanisms of isomerization and phase transitions in $[Pd(NH_3)_2Cl_2]$. The phase transition between the trans and β-trans isomers certainly should follow through destroying the crystal solid body of the trans isomer and recrystallization into the β-trans isomer. This is the only way to decrease the specific volume per molecule of $[Pd(NH_3)_2Cl_2]$ from 131.32 (6) to 129.47 (6) Å^3. Besides the change in specific volume, a transformation is possible when a medium promotes the mass-transition or at a rather high temperature. Since $[Pd(NH_3)_2Cl_2]$ has a low solubility in water, crystallization faults are possible. This could be the reason for the observed layer orientation errors.

In principle, the transformation from the cis to the trans isomer could follow two mechanisms: without a break-up of the crystal body and through such a break-up. Some facts point out that the first mechanism is at hand. A rather small decrease of the specific volume is observed: from 131.78 (6) (cis) to 131.25 (6) Å^3 (trans). The Pd atoms and half of the N and Cl atoms are left

approximately at the same positions and the molecular packing has the same character with only small changes in the unit-cell parameters:

cis		trans
$a = 6.312$ Å	$\rightarrow$	$c = 6.357$ Å
$b = 6.498$ Å	$\rightarrow$	$a = 6.540$ Å
$2c = 6.776$ Å	$\rightarrow$	$b = 6.857$ Å
$\alpha = 96.60°$	$\rightarrow$	$\gamma = 100.61°$
$\beta = 97.29°$	$\rightarrow$	$\alpha = 103.31°$
$\gamma = 104.69°$	$\rightarrow$	$\beta = 102.45°$.

According to our X-ray high-temperature investigation, the closeness in the unit-cell parameters of both phases is maximum at 403 K and no splitting of diffraction peaks is observed.

If we can follow the idea of the solid-state mechanism of the cis–trans transformation, some conclusions on the molecular mechanism of isomerization could also be drawn. Kukushkin et al. (1981) have analysed IR data in a process of solid-state isomerization. They concluded that isomerization of flat complexes proceeded according to an internal mechanism and they proposed that intermediate complexes with a tetrahedral structure may be formed. A specific feature of this mechanism is that the flat complexes change the orientation of the complex plane over 90°. The geometry of the cis and trans isomer lattices for $[Pd(NH_3)_2Cl_2]$ shows that if isomerization takes place in the solid state, the complex planes keep their orientation. Possible tetrahedral intermediate complexes can be formed by rotation of the Cl—Pd—N fragment around the a axis, whereas another Cl—Pd—N fragment keeps its orientation. Thus, most atom displacements occur in the ac plane.

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