

Calculations were performed on a FACOM 230-75 computer at this Institute using the UNICS III program system (Sakurai & Kobayashi, 1979) for the crystallographic calculations, and MMB80 (Sakurai, 1978) for the conformational-energy calculation.

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Structure of Bis(ethylenediamine)palladium(II) Dichlorobis(ethylenediamine)palladium(IV) Tetraperchlorate* and Remarks Concerning the Structures of Analogous Mixed-Valence Platinum Compounds

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Abstract

$[\text{Pd}(\text{C}_2\text{H}_8\text{N}_2)_2][\text{Pd}(\text{C}_2\text{H}_8\text{N}_2)_2\text{Cl}_2](\text{ClO}_4)_4$, $\text{C}_8\text{H}_{32}\text{Cl}_2\text{N}_8\text{Pd}_2^+ \cdot 4\text{ClO}_4^-$, is orthorhombic, space group *Ibam*, $a = 9.665$ (2), $b = 13.636$ (3), $c = 10.715$ (7) Å, $Z = 2$ [$\text{Pd}(\text{en})_2$][$\text{PdCl}_2(\text{en})_2$](ClO_4)₄ units per cell (en = ethylenediamine, $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$). The structure was solved in space group *Ibam* and refined to a conventional *R* factor of 0.033 for 573 nonzero reflections. The crystal contains infinite stacks of roughly planar $\text{Pd}(\text{en})_2$ units perpendicular to the chain axis and bridged by the halogens. Bridging is clearly unsymmetrical [$\text{Pd}-\text{Cl} = 2.324$ (3) and 3.033 (3) Å], leading to four-coordinate Pd^{II} species alternating with *trans* octahedral Pd^{IV} groups along the chain. The chains are separated by sheets of ClO_4^- ions parallel to the *ac* plane at $y \sim 1/4$ and $\sim 3/4$. Each ClO_4^- anion is

bridging successive $\text{Pd}(\text{en})_2$ units by using two of its oxygen atoms to form H bonds with coordinated ethylenediamine. The anion is found in two disordered orientations differing by their interactions with the rest of the structure. The presence of diffuse background under the normal Bragg diffraction spots for the odd layer lines in the oscillation diagram of the crystal mounted along the *c* axis indicates that the bridging halogens are disordered over two sites along the chain axis, as is usually found for similar halide-bridged $\text{Pt}^{\text{II}}-\text{Pt}^{\text{IV}}$ mixed-valence complexes.

Introduction

Mixed-valence metal compounds have been known for a long time (Smith & Sterns, 1976). In many cases, the color, spectra, electrical and magnetic properties, and not very common semiconductive and temperature

* Alternative name: *catena-μ-chloro-bis(ethylenediamine)palladium(II, IV) tetraperchlorate*.

variations of these properties, have been explained by intervalence charge transfer between the two metal oxidation states (Burns & Vaughan, 1975). These minerals usually contain various transition elements as constituents in the II and IV oxidation states. The common pattern in the crystals of these compounds is the presence of discrete linear chains.

The linear chain complexes show unusual resonance Raman spectra and electronic properties (Clark, 1980; Papavassiliou, Layek & Theophanides, 1980). These compounds possess intense characteristic mixed-valence electronic transitions in the visible region and if the crystals are irradiated with exciting radiations which fall within the contours of such bands, resonance Raman spectra are obtained which show enormous enhancement of the Raman band associated with the halogen-bridging fundamental vibration $\nu(M-X \cdots M)$.

In this study, we report an X-ray crystallographic analysis on such a compound. No crystallographic study has been carried out so far on the ethylenediamine (en) compound $[Pd(en)_2][PdCl_2(en)_2](ClO_4)_4$, but the corresponding $[Pt(en)_2][PtX_2(en)_2](ClO_4)_4$ compounds ($X = Cl, Br, I$) have been investigated (Matsumoto, Yamashita, Ueda & Kida, 1978; Endres, Keller, Martin, Traeger & Novotny, 1980; Bekaroglu, Breer, Endres, Keller & Gung, 1977) and they follow the trends observed for this class of mixed-valence compounds (Clark, 1980). Indeed, they consist of infinite linear chains of roughly planar $Pt(en)_2$ units, perpendicular to the chain axis and bridged by halide ions. Bridging by chlorine is usually clearly unsymmetrical, producing an alternation of oxidation states $Pt^{II} \cdots Cl - Pt^{IV} - Cl \cdots Pt^{II} \cdots Cl - Pt^{IV} - Cl \cdots$ along the chain. Heavier halogens tend to sit closer to the midpoint between successive Pt atoms, thus attenuating the distinction between oxidation states. The chains are parallel and any given chain is ordered. However, some chains are randomly advanced by one Pt-Pt distance with respect to the others and the ideal crystal periodicity is destroyed in the direction perpendicular to the chain axis. This effect is apparent from continuous layer lines interleaving normal Bragg layers in the rotation photographs of a crystal mounted along the chain axis. Diffuse layer lines were observed for $[Pt(en)_2][PtI_2(en)_2](ClO_4)_4$ (Bekaroglu *et al.*, 1977; Endres *et al.*, 1980) and presumably for the isostructural Br analog. On the other hand, $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$ appears to be one of the first mixed-valence compounds of this type for which continuous layer lines were not found in oscillation photographs. A complete structural analysis was performed and the structure was solved in terms of a completely ordered model in space group $I222$ (Matsumoto, Yamashita, Ueda & Kida, 1978). Very recently, the structure of an alternative modification of $[Pt(en)_2][PtBr_2(en)_2](ClO_4)_4$, which is isomorphous with the Cl compound, was similarly interpreted (Endres *et al.*, 1980).

At the beginning of the present study, the cell dimensions and the I -centered orthorhombic lattice deduced from Weissenberg photographs clearly indicated that $[Pd(en)_2][PdCl_2(en)_2](ClO_4)_4$ and its Pt analog were isostructural. However, we noted two sets of systematic absences for glide planes ($0kl, k \neq 2n$ and $h0l, h \neq 2n$), which pointed to $Ibam$ and $Iba2$ as possible space groups. In fact, the same pair of space groups had been first proposed for $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$ on the basis of Weissenberg and powder diffraction measurements (Bekaroglu *et al.*, 1977).^{*} These conditions were not listed or discussed in the full structural determination of the chloro compound, the authors simply stated that the systematic absences were consistent with space groups $I222$, $Imm2$ and $Immm$. It is not clear why $I2_12_12_1$, which has the same set of absences, was not included (Matsumoto, Yamashita, Ueda & Kida, 1978).

Owing to the ambiguity in space groups and the presence of other unusual structural features, such as high thermal motion for two perchlorate oxygens, we felt that a complete structure determination of the Pd compound would be worthwhile, in spite of the fact that it was isostructural with the Pt compound. We expected the light-atom portion of the structure to be better defined than in the Pt analog, where the scattering power of Pt outweighs those of the remaining atoms.

As the interpretation was in progress, it became obvious that the choice of the space group was connected with questions concerning three structural aspects of this compound:

(a) are the bridging Cl atoms three-dimensionally ordered, or are they involved in disorder as observed with most of these compounds?

(b) what is the origin of the high thermal motion of two perchlorate oxygens?

(c) as the Pt-en chelate ring is not planar, does ring puckering lead to a $Pt(en)_2$ unit with 222 symmetry as found in $[Pt(en)_2]Cl_2$ (Wiesner & Lingafelter, 1966 and references therein) or with $2/m$ symmetry as in $[Pt(en)_2]$ (*R*)-tartrate (Freeman, 1976)? How is this pattern repeated along the chain?

We feel that the present work provides satisfactory answers to these questions.

Crystal data

$C_8H_{32}Cl_2N_8Pd_2^{4+} \cdot 4ClO_4^-$, $M_r = 905.69$, orthorhombic, space group $Ibam$, $a = 9.665(2)$, $b = 13.636(3)$, $c = 10.715(7)$ Å, $V = 1412.2$ Å³; $Z = 2$, $D_{calc} = 2.130$ Mg m⁻³; $\mu(Mo K\alpha) = 1.906$ mm⁻¹, $\mu(Cu K\alpha) = 16.66$ mm⁻¹; $\lambda(Mo K\alpha) = 0.71067$ Å, $\lambda(Cu K\alpha) =$

^{*} The cell used by Matsumoto, Yamashita, Ueda & Kida (1978) has its a and c axes interchanged with respect to those used here. In the cell used by Endres *et al.* (1980), b and a are interchanged.

1.54178 Å, $T = 297$ K; crystal dimensions: 0.04 [between faces (110) and ($\bar{1}\bar{1}0$)] \times 0.04 [(1 $\bar{1}0$) and ($\bar{1}10$)] \times 0.68 mm [(001) and (00 $\bar{1}$)]; transmission coefficient (Cu $K\alpha$) = 0.16–0.60.

Experimental section

The compound was prepared as described previously (Matsumoto, Yamashita & Kida, 1978a).

Camera work was carried out on three specimens, which all gave identical results. Oscillation photographs taken along the needle axis clearly revealed a perpendicular Laue mirror. The even layers were much stronger than the odd layers and the latter appeared to consist only of discrete diffraction spots on a normally exposed photograph. At the end of the work, overexposed photographs revealed that, for the odd layers, the discrete spots were superimposed on weak, continuous layer lines, but this was not detected at this stage. Weissenberg photographs (levels $l = 0, 1$ and 2) clearly showed the crystal to be orthorhombic and the space groups *Ibam* and *Iba2* were consistent with the systematic absences ($hkl, h + k + l \neq 2n; 0kl, k \neq 2n; h0l; h \neq 2n$). Diffractometer intensity measurements subsequently confirmed that the last two classes of reflections were indeed systematically absent.

Intensity data were measured with an Enraf–Nonius CAD-4 diffractometer using Mo then Cu radiation. The orientation matrix and accurate cell parameters were obtained by least-squares refinement on the setting angles of 25 centered reflections randomly distributed in the hkl octant. Three standard reflections were monitored every hour as a check on instrument and crystal stability. They showed fluctuations $< \pm 2\%$ for both sets of data. Crystal orientation was also checked every 100 measurements by recentering three axial reflections. In no case was crystal recentering necessary.

The intensities were measured by the $\omega/2\theta$ scan technique. The scan range was $\omega = (1.0 + k \tan \theta)^\circ$, extended 25% on each side for background counts ($k = 0.35$ for Mo $K\alpha$ and 0.14 for Cu $K\alpha$). The scan speed was adjusted, after a prescan at $6.7^\circ \text{ min}^{-1}$, to make $I/\sigma(I)$ equal to 100, but a maximum scan time of 100 s was imposed. The intensities were corrected for the effects of Lorentz, polarization and absorption (Gaussian integration, grid $8 \times 8 \times 8$).

A first set of 1174 independent reflections was collected using Mo $K\alpha$ radiation (hkl octant, $h + k + l = 2n, 2\theta \leq 60^\circ$). All reflections found to be weak [$I \leq \sigma(I)$] during the fast prescan were not remeasured at slow speed. 573 nonzero reflections were retained for structure determination on the basis of the criterion $I \geq 3\sigma(I)$. It is noteworthy that none of the reflections of classes $0kl, k \neq 2n$ and $h0l, h \neq 2n$ were found in this set of nonzero intensities, in agreement with film work.

However, since slow scans had not been performed on the weak data, we felt that the status of the presumably absent reflections was not unambiguously settled. We decided to collect a new set of intensities in which special care would be taken to measure at slow speed the presumably absent reflections. In this case, the cleaner and stronger Cu $K\alpha$ radiation was preferred.

710 measurements were collected ($hkl, h + k + l = 2n, 2\theta \leq 140^\circ$) and a slow scan was performed even if the reflection had been found to be weak at the prescan stage. After data reduction [$I \geq 3\sigma(I)$], 621 nonzero reflections remained, none of which corresponded to the systematic absences mentioned above. Consequently, there were no indications from intensity data that the space group could be different from *Ibam* or *Iba2*. From that point on, the Cu $K\alpha$ data were retained, because they included a greater number of non-zero reflections and they improved the proportion of weak data, in which most of the l -odd reflections were found. All the steps initially made with the Mo $K\alpha$ data were repeated on this new set, with essentially identical results and a slight improvement of the R factor.

Structure determination

The three-dimensional Patterson synthesis was fully consistent with the arrangement of Pd and perchlorate Cl atoms found in the corresponding Pt–Cl and Pt–Br compounds (Matsumoto, Yamashita, Ueda & Kida, 1978; Endres *et al.*, 1980). This pattern can be described either in the space groups suggested by film work (*Iba2* or *Ibam*), or in any of the I -orthorhombic space groups without systematic absences (*I222, I2,2,2, I, Imm2* or *Immm*). However, only in space group *I222* is it possible to divide the Pd atoms into two sets, corresponding to Pd^{II} and Pd^{IV}, as would be required in a nondisordered structure. Since the latter space group had been used for the Pt compounds, we decided to try it first.

All refinement was carried out by full-matrix least squares in order to maintain correlations between the parameters, an effect that was eliminated in the refinement of the Pt compounds by block-diagonal least squares.

Space group *I222*

The starting parameters taken from the [Pt(en)₂]-[PtX₂(en)₂](ClO₄)₄ structures (Matsumoto, Yamashita, Ueda & Kida, 1978; Endres *et al.*, 1980) were refined. In spite of high correlations, convergence was reached with $R = \sum | |F_o| - |F_c| | / \sum |F_o| = 0.087$ (two Pd and two Cl anisotropic, two C, two N and four O isotropic). Two of the oxygens had very high temperature factors (12 and 16 Å²) as noted for the Pt compounds. A difference Fourier (ΔF) synthesis showed three regions of residual electron density:

(a) Two peaks of $\sim 2 \text{ e } \text{Å}^{-3}$ at $\sim 1.5 \text{ Å}$ from Cl_I^* in the same plane as the oxygens having high thermal motion. This would be consistent with a ClO_4^- ion involved in a twofold disorder, with alternative positions for the above oxygens, and displacements of Cl_I and the remaining oxygens too small to produce resolved components.

(b) A third peak of $\sim 3 \text{ e } \text{Å}^{-3}$ on the c axis, symmetrically located with respect to the Cl_B atoms already present, across the midpoint of the Pd–Pd vector. The height of this peak increased when the ΔF map calculation included the unobserved reflections, which is one way of introducing an influence by the absent $0kl$ and $h0l$ reflections. It was then concluded that $[\text{Pd}(\text{en})_2][\text{PdCl}_2(\text{en})_2](\text{ClO}_4)_4$, like most compounds of this type, contains Cl_B atoms equally distributed on two sites.

In a first step, the split oxygens were described as four half-oxygens and their coordinates and temperature factors were refined. This reduced R to 0.063. The ΔF map still contained the high peak along c . Thus, two half-chlorines were used instead of a single ordered Cl_B atom. Refinement of the scale factor reduced R to 0.049, but it was not possible to refine the coordinates because of high correlations. Indeed, as Cl_B is no longer ordered, the Pd atoms become equivalent and the actual symmetry of the cell is very close to $Ibam$. Consequently, refinement in space group $I222$ was abandoned.

Space group $Ibam$

In this space group, all Pd atoms are symmetrically equivalent, occupying equipoint 4(a) with 222 site symmetry. The Cl_B atoms are on the twofold axis [equipoint 8(h)] with occupancy factors of 0.50 by symmetry. The ClO_4^- ion has its Cl_I and the disordered oxygens confined to a mirror plane. Refinement in this space group proceeded without parameter correlations. The R factor decreased to 0.040 (anisotropic, except for the four disordered half-oxygens). The highest residuals in the ΔF map all corresponded to H atoms of ethylenediamine, which were introduced into the structure and isotropically refined. This reduced the R factor to 0.035. In the final cycles, individual weights based on counting statistics were applied and a secondary extinction coefficient was refined. The final R factor was 0.033 whereas $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ was 0.049. The residual on an observation of unit weight was 1.40. As a check, the occupancy factors of the 'half-oxygens' were refined as well for a few cycles and converged to values in the range 0.42–0.46 ($\sigma = 0.05$). They were left at their ideal values of 0.50.

* In the following discussion, Cl_B designates the bridging Cl atom, and Cl_I the Cl atom of the ClO_4^- ion.

Table 1. Refined coordinates ($\times 10^4$, for H $\times 10^3$) and equivalent isotropic temperature factors ($\times 10^3$, for Pd, Cl $\times 10^4$) for space group $Ibam$

$$U_{\text{eq}} = |U_{11} + U_{22} + U_{33} + 2U_{12}a^*b^*ab \cos \gamma + 2U_{13}a^*c^*ac \times \cos \beta + 2U_{23}b^*c^*bc \cos \alpha|/3.$$

	x	y	z	$U_{\text{eq}} (\text{Å}^2)$
Pd	0	0	2500	242 (2)
Cl(1)	785 (2)	7021 (1)	0	502 (6)
Cl(2)	0	0	4669 (3)	348 (10)
O(1)	165 (6)	7361 (4)	−1093 (4)	78 (2)
O(31)	384 (13)	5963 (9)	0	55 (3)*
O(32)	1984 (22)	7803 (16)	0	110 (6)*
O(41)	2180 (18)	6996 (15)	0	90 (5)*
O(42)	1678 (20)	6202 (13)	0	98 (5)*
N	1577 (5)	996 (3)	2479 (4)	37 (1)
C	2879 (6)	494 (5)	2819 (6)	50 (2)
H(1)	140 (6)	145 (4)	296 (6)	42 (16)*
H(2)	161 (6)	126 (4)	169 (6)	45 (16)*
H(3)	361 (7)	92 (5)	262 (5)	47 (17)*
H(4)	285 (5)	50 (4)	375 (5)	40 (14)*

* Isotropic values.

The final ΔF map contained a few peaks of 0.4–0.5 $\text{e } \text{Å}^{-3}$ near the disordered oxygens, while the general background was $< \pm 0.18 \text{ e } \text{Å}^{-3}$. The coordinates are listed in Table 1.*

The scattering factors used were those of Cromer & Waber (1965), except for hydrogen (Stewart, Davidson & Simpson, 1965). The real and imaginary contributions to anomalous dispersion (Cromer, 1965) were included in structure factor calculations for Pd and Cl. The computer programs used are listed elsewhere (Hubert & Beauchamp, 1980).

Space group $Iba2$

Although space group $Ibam$ led to satisfactory results, we checked whether a significant improvement would occur upon refining the structure in the noncentric $Iba2$ space group. In this case, a twofold axis remains along c , which means that the $\text{Pt}(\text{en})_2\text{-Cl}_B$ chain has to remain essentially as it was in $Ibam$, except for certain equivalences between N or C atoms which are now relaxed. The ClO_4^- ion could also be somewhat displaced, because the mirror plane through Cl_I is no longer present.

Refinement in this space group converged with some difficulties because of high correlations. The H atoms could not be unambiguously located and they were fixed at their calculated positions. The final R factor

* Lists of structure factors and anisotropic thermal parameters, as well as the coordinates refined in space group $Iba2$, have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36562 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester, CH1 2HU, England.

reached the same value as above (0.033) for the same kind of refinement. The refined coordinates in space group *Iba2* are provided in the supplementary material.*

The only significant differences between the *Ibam* and the *Iba2* models are detected for one N and two O atoms (4–6 σ on their *z* coordinates). Since the use of many extra variables in *Iba2* did not reduce the *R* factor and only minor differences existed between the two models, there were no reasons not to retain the centric *Ibam* space group.

Description of the structure

The unit-cell contents are shown in Fig. 1. Linear chains of chlorine-bridged Pd(en)₂ units run along the *c* direction, through the cell corners and the middle of the *ab* face. These chains are interleaved with sheets of ClO₄⁻ ions, parallel to the *ac* plane, at $y \sim \frac{1}{4}$ and $\sim \frac{3}{4}$.

* See previous footnote.

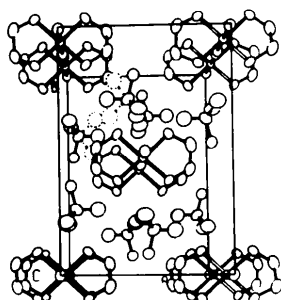


Fig. 1. A view of the unit cell down the *c* axis. The ellipsoids correspond to 50% probability. Hydrogens are omitted. The alternative oxygen positions of the disordered ClO₄⁻ ion are represented by dashed spheres for some of the ions.

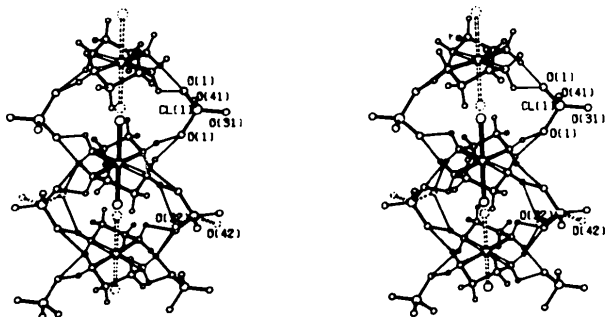


Fig. 2. Portion of the infinite chain along *c*, with surrounding ClO₄⁻ ions. The dashed bonds and spheres along the chain axis represent the disordered positions of the short Pd–Cl bonds in one half of the chains randomly distributed in the cell. The thin lines correspond to H bonds. For some of the ClO₄⁻ ions, the alternative disordered orientation is shown by means of dashed spheres and bonds.

Even though a different space group was used to describe the structures of [Pt(en)₂][PtX₂(en)₂](ClO₄)₄ (*X* = Cl, Br; Matsumoto, Yamashita, Ueda & Kida, 1978; Endres *et al.*, 1980), their general framework is very similar to ours. The present model differs by the twofold disorder of the ClO₄⁻ anion deduced from our data, whereas only high thermal motion had been proposed by the above authors. Our interpretation, as well as theirs, involves a strictly periodic ...Pd...Cl–Pd–Cl...Pd...Cl–Pd–Cl... chain. However, they assumed that the distribution of the bridging halogens is also periodic in the *a* and *b* directions, whereas we propose a disordered model similar to most of the mixed-valence compounds of this class studied so far: for one half of the chains and in a random manner, the pairs of short Cl–Pd–Cl bonds are shifted one step ahead along the chain. The average structure deduced from X-ray diffraction thus shows two half-chlorines close to all the Pd atoms, which consequently appear to be symmetrically equivalent as shown in Fig. 2.

Interatomic distances and bond angles are listed in Table 2. All the Pd atoms have the same 222 site symmetry. Consequently, the Pd–N distances are all equal and the observed distance [2.042 (5) Å] is in good agreement with those reported for similar compounds (Wiesner & Lingafelter, 1966; Ito, Marumo & Saito, 1971; Baggio, Amzel & Becka, 1970). The geometry of the ethylenediamine ring is also usual (Wiesner & Lingafelter, 1966). The two short Pd–Cl_B bonds are equal by symmetry [2.324 (3) Å] and the bridging is clearly unsymmetrical, the long Pd–Cl_B contact being 3.033 (3) Å. These values are not very different from those observed for chloro compounds of Pt, which is the same size as Pd (Matsumoto *et al.*,

Table 2. Interatomic distances (Å) and bond angles (°)

Pd–N	2.042 (5)	C–H(3)	0.94 (6)
Pd–Cl(2)	2.324 (3)	C–H(4)	1.00 (5)
Pd–Cl(2) ⁱ	3.033 (3)	Cl(1)–O(1)	1.395 (5)
N–C	1.478 (8)	Cl(1)–O(31)	1.494 (13)
C–C ⁱⁱ	1.511 (10)	Cl(1)–O(32)	1.575 (21)
N–H(1)	0.82 (6)	Cl(1)–O(41)	1.349 (18)
N–H(2)	0.92 (6)	Cl(1)–O(42)	1.411 (19)
Cl(2)–Pd–Cl(2) ⁱ	180.0	N–C–H(3)	107 (4)
Cl(2)–Pd–N	90.6 (1)	N–C–H(4)	103 (3)
Cl(2)–Pd–N ⁱⁱ	89.4 (1)	H(3)–C–H(4)	103 (4)
N–Pd–N ⁱⁱⁱ	83.4 (2)	H(3)–C–C ⁱⁱ	117 (4)
N–Pd–N ⁱⁱⁱⁱ	96.6 (2)	H(4)–C–C ⁱⁱ	117 (3)
N–Pd–N ^v	178.7 (2)	O(1)–Cl(1)–O(1) ^v	114.2 (3)
Pd–N–C	109.0 (3)	O(1)–Cl(1)–O(31)	102.1 (5)
N–C–C ⁱⁱ	107.6 (5)	O(1)–Cl(1)–O(32)	95.2 (7)
Pd–N–H(1)	110 (4)	O(1)–Cl(1)–O(41)	116.0 (7)
Pd–N–H(2)	107 (4)	O(1)–Cl(1)–O(42)	121.7 (7)
H(1)–N–H(2)	107 (5)	O(31)–Cl(1)–O(41)	103.6 (8)
C–N–H(1)	112 (4)	O(32)–Cl(1)–O(42)	94.9 (9)
C–N–H(2)	112 (4)		

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

1978*a,b*; Craven & Hall, 1961). The values of 1.99 Å and 3.22 Å reported for $[\text{Pd}(\text{NH}_3)_2\text{Cl}_2][\text{Pd}(\text{NH}_3)_2\text{Cl}_4]$ (Wallen, Brosset & Vannenberg, 1962) do not agree with ours. The ratio of the short to the long Pd—Cl bonds is used to determine how unsymmetrical the halogen location is. Our value (0.77) is similar to those found in analogous Pt compounds (Matsumoto *et al.*, 1978*b*).

The ClO_4^- ion appears to be severely distorted (Table 2). This is obviously due to the disorder, which allows two of the oxygens to be refined as distinct components, while Cl, and the two remaining oxygens had to be refined as unresolved atoms. The oxygen positions are sufficiently well defined, however, to discuss their interactions with the rest of the structure. Fig. 2 shows that the anion is H bonded to chelate rings through its two O(1) atoms. Thus it acts as a bridge between successive $\text{Pd}(\text{en})_2$ units along the chain. Details on the geometry of these and other interactions are given in Table 3 and Fig. 3. According to Stout & Jensen (1965), the range of $\text{N}\cdots\text{O}$ distances for an $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond involving an amine is 2.57–3.22 Å with a typical distance of 3.04 Å. The latter value corresponds to one of the H bonds formed by each O(1) atom, which is also involved in a weaker bond with another amino group. These H bonds exist for both orientations *A* and *B* of the disordered ClO_4^- ion. The existence of these two orientations can be understood by comparing their respective interactions (Fig. 3). In orientation *A*, O(41) forms a pair of weak H bonds [$\text{N}\cdots\text{O} = 3.218(12)$ Å], but there is a relatively close van der Waals contact [2.74(2) Å] between O(31) and the corresponding O(31') of an adjacent ion (if it also assumes orientation *A*). In orientation *B*, both O(32) and O(42) form pairs of weak H bonds. In this respect, the second orientation *B* would appear to be more favorable, because it also eliminates the O(31)—O(31') contact. For these reasons, it seems to be likely that adjacent anions assume different orientations, but without following a periodic pattern.

Table 3. *Geometry of the hydrogen bonds*

	$\text{N}\cdots\text{O}$ (Å)	$\text{H}\cdots\text{O}$ (Å)	$\angle\text{N}-\text{H}\cdots\text{O}$ (°)	$\angle\text{H}\cdots\text{O}-\text{Cl}(1)$ (°)
$\text{N}^{\text{I}}-\text{H}(1)^{\text{I}}\cdots\text{O}(1)$	3.037 (7)	2.25 (6)	159 (6)	113 (2)
$\text{N}^{\text{II}}-\text{H}(2)^{\text{II}}\cdots\text{O}(1)$	3.172 (7)	2.62 (6)	119 (4)	136 (1)
$\text{N}^{\text{IV}}-\text{H}(2)^{\text{IV}}\cdots\text{O}(41)$	3.218 (12)	2.38 (6)	152 (5)	120 (2)
$\text{N}^{\text{V}}-\text{H}(2)^{\text{V}}\cdots\text{O}(41)$	3.218 (12)	2.38 (6)	152 (5)	120 (2)
$\text{N}^{\text{I}}-\text{H}(1)^{\text{I}}\cdots\text{O}(32)$	3.183 (12)	2.48 (6)	145 (5)	96 (2)
$\text{N}^{\text{III}}-\text{H}(1)^{\text{III}}\cdots\text{O}(32)$	3.182 (12)	2.48 (6)	145 (5)	96 (2)
$\text{N}^{\text{IV}}-\text{H}(2)^{\text{IV}}\cdots\text{O}(42)$	3.159 (11)	2.45 (6)	134 (5)	113 (2)
$\text{N}^{\text{V}}-\text{H}(2)^{\text{V}}\cdots\text{O}(42)$	3.159 (11)	2.45 (6)	134 (5)	113 (2)

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

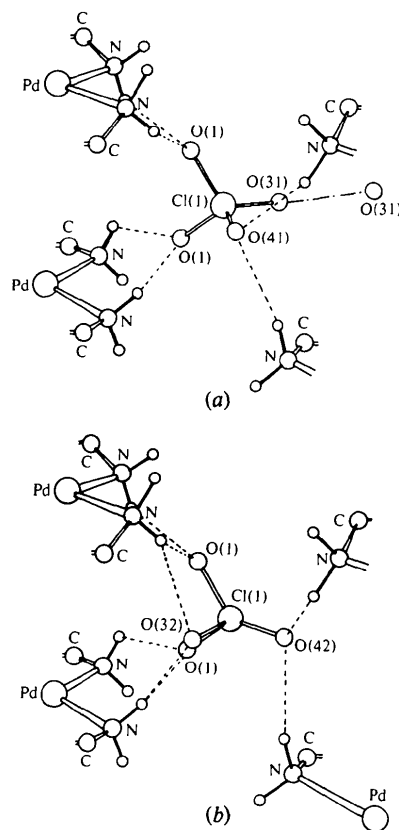


Fig. 3. Details of the interactions involving the ClO_4^- ions in their two possible disordered orientations.

Diffuse scattering

Although the *Ibam* model was quite satisfactory, we were puzzled by the absence of diffuse layer lines in the oscillation photographs to indicate disorder in the bridging halogen. However, the diffuse scattering was subsequently detected. First, it should be noticed that the PdN_4 units alone define a periodicity of $c/2$ only, which means that they do not contribute to the structure factors for the *l*-odd levels. Contributions to these reflections come, to a very small extent, from the C and H atoms of the chelate rings, which are not strictly in the PdN_4 plane and, to a much greater extent, from the ClO_4^- ions. (The disorder of this anion is restricted to planes perpendicular to *c*, so that it has no effect on the periodicity along *c*.) Consequently, the diffusion originating from the C and H atoms and from the ClO_4^- ions should and does, lead to normal Bragg diffraction spots. On the other hand, if the bridging Cl^- ions are disordered, they should produce diffuse layer lines halfway between those corresponding to the Pd—Pd periodicity, as generally found (Endres *et al.*, 1980 and references therein). In the present case, diffuse scattering layers should coincide with the normal Bragg scattering of the *l*-odd levels. We made overexposed oscillation photographs of the crystal

mounted along *c* and we indeed noticed that, for the *l*-odd levels, the Bragg spots were superimposed on a continuous, weak background layer. The weakness of the effect is due to the relatively small scattering power of Cl and to its position being close to *z* = 0.50, where diffuse scattering would totally vanish. In the present case, the presence of the Bragg spots makes the background more difficult to detect, but it is quite clear, especially for layer lines *l* = 3 and 5.

The fact that the present structure contains Pd is likely to make diffuse scattering more noticeable than with compounds containing the heavy Pt atom. However, questions can be raised about the interpretation proposed in terms of completely ordered models. Conceivably, the degree of halogen ordering could vary from compound to compound, or be a function of the method of preparation or the exposure to heat, radiation and other external influences. The presence of some ordering in [Pt(en)₂][PtBr₂(en)₂](ClO₄)₄ (Endres *et al.*, 1980) would be consistent with the diffractometer data, since the structure factor table (Supplementary Publication No. SUP 34773) reports some intensity, although very weak, for one *0kl* and three *h0l* reflections. A similar verification was not possible for the analogous Cl compound (Matsumoto, Yamashita, Ueda & Kida, 1978). At any rate, the present work suggests that special care should be taken to search for diffuse scattering in the odd levels for compounds of this type. It is probably unsafe to rely only on a small number of diffractometer intensities, since the scan might simply be a measure of the higher background in that reciprocal plane. Careful film work is certainly not unnecessary.

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