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Neutron Diffraction Study of $[Pt(en)_2][Pt(en)_2I_2](ClO_4)_4$ at 20 K: Structure and Evidence of a New Phase Transition

J.-F. Bardeau,[a]* A. Bulou,[a] W. T. Klooster,[b] T. F. Koetzle,[b] S. Johnson,[c] B. Scott,[c] B. I. Swanson[c] and J. Eckert[d]

[a]Laboratoire de Physique de l'Etat Condensé, CNRS URA No. 807, Maine University, 72017 Le Mans CEDEX, France, [b]Brookhaven National Laboratory, Chemistry Department, PO Box 5000, Upton, Long Island, NY 11973, USA, [c]Los Alamos National Laboratory, Spectroscopy and Biochemistry Group, Los Alamos, NM 87545, USA, and [d]Los Alamos National Laboratory, Lansce, Los Alamos, NM 87545, USA.
E-mail: pec_bardeau@aviion.univ-lemans.fr

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Abstract

The structure at 20 K of fully deuterated $[Pt(en)_2][Pt(en)_2I_2](ClO_4)_4$, where en = ethylenediamine, has been determined by neutron diffraction on a single crystal. It is shown that the symmetry is monoclinic with cell parameters $a = 16.650(7)$, $b = 5.760(2)$, $c = 14.751(2)$ Å and $\beta = 99.19(1)°$, that is, with respect to the previously reported room-temperature structures, a doubling of the c parameter is observed. The space group is $C2/c$ and the refinements lead to an R value of 0.0374. All the bond lengths (C—C, C—N, C—D, N—D and Cl—O) and angles are consistent with the expected values and the main difference with respect to the previously reported room-temperature structures results in an ordering of the stacking of the ethylenediamines. The iodines are distributed over two sites, which gives two Pt—I distances, 2.712 (3) Å, attributed to the Pt^{IV}—I bond, and 3.048 (3) Å, attributed to Pt^{II}—I. Actually, very weak diffraction peaks that provide evidence for an additional doubling of the a and b parameters are also observed and a space group $C2$ is therefore proposed. This could result from a very slight ordering of the chains with respect to one another, but, due to the weakness of such signals and the large number of atoms to be considered, no reliable refinement has been obtained in $C2$. On the other hand, on heating the crystal the diffraction peaks with l odd greatly decrease in intensity between 150 and 160 K, which unambiguously argues for the existence of a phase transition presumably connected to an order–disorder of the ethylenediamines.

1. Introduction

For many years, extensive studies have been carried out on the $[M(L\text{-}L)_2][MX_2(L\text{-}L)_2]Y_4$ systems (usually denoted by $MX/L\text{-}L/Y$), where M represents a mixed-valence metal (Pt, Pd, Ni, ...), X a halogen (Cl, Br, I), Y a counterion (ClO_4, I) and ($L\text{-}L$) a ligand with two N atoms, such as ethylenediamine or cyclohexanediamine. These compounds can be described in terms of an alternate stacking of tetragonal-bipyramidal $M^{IV}N_4X_2$ of the $M(L\text{-}L)_2X_2$ units and square-planar $M^{II}N_4$ of $M(L\text{-}L)_2$, with the counterions separating these infinite chains (Campbell, Clark & Turtle, 1978; Keller, 1982). The main interest of these structures comes from the presence of the quasi-one-dimensional linear and straight infinite chains of alternating metal (M) and halogen (X) atoms, the metallic ions along the chains being alternately in the oxidation states $M^{3-\delta}$ and $M^{3+\delta}$; the charge disproportion δ varies from 0 to 1 so that the MX chains can be considered as CDW (charge-density wave) systems (Baeriswyl & Bishop, 1988). One-dimensional models successfully described the electronic properties of the chains (Huang, Batistic & Bishop, 1993) as well as the longitudinal vibrational properties (Bulou, Donohoe & Swanson, 1991), even in the case of the isotopically disordered $^{35}Cl/^{37}Cl$ system (Love, Worl, Donohoe, Huckett & Swanson, 1992; Bardeau, Bulou & Swanson, 1995). Their interest is also due to the fact that valence defects (polarons, bipolarons *etc.*), stable at low temperature, can be generated by photolysis (Donohoe, Tait & Swanson, 1990).

Some of the most studied compounds are PtX/en/ClO_4 where 'en' indicates ethylenediamine ($C_2H_8N_2$). The first structural studies on these materials began at the end of the seventies. While PtCl/en/ClO_4 (Matsumoto, Yamashita, Ueda & Kida, 1978) and PtBr/en/ClO_4 (Endres, Keller, Martin & Traeger, 1979) are orthorhombic in their high-temperature forms, PtI/en/ClO_4 is monoclinic and it has been the object of several X-ray investigations at room temperature with different conclusions:

(1) According to Matsumoto, Yamashita, Kida & Ueda (1979) the cell parameters are $a = 16.914(2)$, $b = 5.820(1)$, $c = 7.429(1)$ Å and $\beta = 98.48(1)°$, with

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the space group $C2$, but diffuse layer scattering indicates that the real value of b is 11.640 Å.

(2) According to Endres, Keller, Martin, Nam Gung & Traeger (1979) the cell parameters are $a = 17.031\,(10)$, $b = 5.827\,(4)$, $c = 7.440\,(4)$ Å and $\beta = 97.94(4)^\circ$, with the space group $C2/m$.

(3) According to Weinrach, Ekberg, Conradson, Swanson & Hochheimer (1990), in a crystal grown at elevated pressures (7×10^8 Pa), the cell parameters are $a = 16.908\,(2)$, $b = 5.818\,(1)$, $c = 7.436\,(1)$ Å and $\beta = 98.55\,(1)^\circ$ with the space group $C2$.

On the other hand, in a recent investigation of the lattice dynamics of PtI/en/ClO_4 at room temperature by inelastic neutron scattering (Bardeau, Swanson, Hennion & Bulou, 1994), we observed the existence of 'superstructure' lines that witness for a doubling of both the a and b parameters which indicated that the real structure is actually another one. The existence of such extra lines has been confirmed by the X-ray investigations of Scott *et al.* (1996) with space group $C2/m$.

It is clear that the determination of the structure of PtI/en/ClO_4 by X-ray diffraction is a difficult task and moreover that polymorphism may be present (Keller, Müller, Ledezma & Martin, 1985; Huckett *et al.*, 1993). This can be imputed to the fact that the compound is made of very heavy atoms (Pt, I), from which the scattering signal is much higher than that of hydrogen or even carbon, nitrogen or oxygen. On the other hand, for neutron diffraction, the scattering lengths of the various atoms are of the same order of magnitude and it can be expected that a neutron diffraction study provides a reliable structure. In this article we report on such an investigation performed on a fully deuterated sample to avoid the incoherent scattering of hydrogen and at low temperature (20 K) in order to minimize possible disorder.

Table 1. *Experimental details*

Crystal data	
Chemical formula	$[Pt(C_2D_8N_2)_2][Pt(C_2D_8N_2)_2I_2](ClO_4)_4$
Chemical formula weight	1313.98
Cell setting	Monoclinic
Space group	$C2/c$
a (Å)	16.650 (7)
b (Å)	5.760 (2)
c (Å)	14.751 (2)
β (°)	99.19 (1)
V (Å^3)	1396.5 (1)
Z	2
D_x (Mg m^{-3})	3.1242
Radiation type	Neutron
Wavelength (Å)	1.0462 (1)
No. of reflections for cell parameters	32
θ range (°)	20–25
μ (mm^{-1})	0.01535
Temperature (K)	20
Crystal form	Parallelepiped
Crystal size (mm)	3.0 × 2.2 × 0.9
Crystal color	Opaque, golden brown
Data collection	
Diffractometer	Four-circle
Data collection method	ω–2θ scans
Absorption correction	ψ scan (Meulenaar & Tompa, 1965; Templeton & Templeton, 1973)
T_{min}	0.968
T_{max}	0.986
No. of measured reflections	5118
No. of independent reflections	5018
No. of observed reflections	2608
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.019
θ_{max} (°)	55
Range of h, k, l	$-25 \rightarrow h \rightarrow 26$ $0 \rightarrow k \rightarrow 9$ $-23 \rightarrow l \rightarrow 0$
No. of standard reflections	2
Frequency of standard reflections	Every 50 reflections
Intensity decay (%)	None
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0374
$wR(F^2)$	0.0501
S	2.9291
No. of reflections used in refinement	2608
No. of parameters used	170
H-atom treatment	All H-atom parameters refined
Weighting scheme	$1/\sigma^2$
Extinction method	Isotropic type I (Becker & Coppens, 1974)
Extinction coefficient	0.15787×10^4
Source of atomic scattering factors	Sears (1992)

2. Experimental

A fully deuterated crystal of volume 6.0 mm^3, synthesized at the Spectroscopy and Biochemistry Group of the LANL, was sealed under a helium atmosphere in an aluminium container. The container was placed in a close-cycle helium refrigerator (Displex Model CS-202, APD Cryogenics, Inc.) and mounted on a four-circle diffractometer at port H6M of the High-Flux Beam Reactor at Brookhaven National Laboratory. The neutron beam, monochromated by Be(002) planes in transmission geometry, was of wavelength 1.0462 (1) Å, as calibrated against a KBr crystal ($a_0 = 6.6000$ Å at 295 K). The sample temperature was maintained at 20.0 ± 0.05 K during the experiment and unit-cell parameters were determined by a least-squares fit of $\sin^2\theta$ values for 32 reflections in the range $40 < 2\theta < 50^\circ$. Intensity data were obtained over one quadrant of reciprocal space by means of ω–2θ scans. The intensities of two reflections were monitored during the data collection and showed no systematic variations throughout. Integrated intensities I_0 and variances $\sigma^2(I_0)$ were derived from the scan profiles. Lorentz factors were applied, as well as an absorption correction. The transmission factors ranged from 0.968 to 0.986, which is close to the expected value of 0.92 calculated from the absorption cross sections of the components (Sears, 1992) and the volume of the sample. Averaging over 200 symmetry-related pairs of reflections resulted in an internal agreement factor of 0.019 and yielded 5018 independent observations.

3. Results

3.1. *Preliminary remarks*

With regard to the results reported above, all the data have been collected considering the monoclinic unit cell with $a_{LC} = 33.33$, $b_{LC} = 11.52$, $c_{LC} = 14.75$ Å and $\beta_{LC} = 99.19°$, which will be termed in the following the 'large cell' (LC). Measurements over 19 reflections showed systematic extinctions that indicate this cell is C centered. However, it appeared that the sum of the intensities of the peaks, such that h_{LC} and k_{LC} are odd, are very weak (less than 0.2% those of the main peaks) and so, none of these reflections were collected for 2θ greater than 60°. Moreover, due to their weakness and width, the attribution of these signals to diffraction peaks may be questionable (see §3) and, in a first step, an analysis in a cell with $a = 16.65$, $b = 5.76$ and $c = 14.75$ Å (and $\beta = 99.19°$) has been carried out; in the following this cell will referred to as the 'small cell' (SC), which still has c double with respect to the reported ambient-temperature cells.

For the refinements, the neutron scattering lengths (in fm) were taken to be $b_{Pt} = 9.6$, $b_I = 5.28$, $b_{Cl} = 9.577$, $b_O = 5.803$, $b_N = 9.36$, $b_C = 6.646$ and $b_D = 6.671$ (Sears, 1992). Least-squares refinements were carried out by a full-matrix procedure (Lundgren, 1982), minimizing $\Sigma wtg(|F_o|^2 - k^2|F_c|^2)^2$, where wtg, F_o, k and F_c represent the weight of an individual reflection in the refinement, the observed structure-factor amplitude, the scale factor and the calculated structure-factor amplitude, respectively. The reliability factors are defined by

$$R = \Sigma\big||F_o|^2 - k^2|F_c|^2\big|/\Sigma(|F_o|^2) \text{ and}$$
$$wR = [\Sigma wtg(|F_o|^2 - k^2|F_c|^2)^2/\Sigma wtg(|F_o|^2)^2]^{1/2}.$$

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

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	Site	x	y	z	B_{eq}
Pt	4(*e*)	0.0	0.49933 (14)	1/4	0.10 (1)
I(1)	4(*e*)	0.0	−0.02986 (48)	1/4	0.22 (5)
I(2)	4(*e*)	0.0	0.02845 (49)	1/4	0.18 (5)
N(1)	8(*f*)	0.88137 (3)	0.49400 (11)	0.18363 (4)	0.31 (1)
N(2)	8(*f*)	0.05301 (3)	0.50213 (11)	0.13365 (4)	0.30 (1)
C(1)	8(*f*)	0.82865 (5)	0.42021 (14)	0.25119 (6)	0.42 (2)
C(2)	8(*f*)	0.14236 (5)	0.54466 (14)	0.15969 (5)	0.43 (2)
Cl	8(*f*)	0.85858 (3)	0.98300 (10)	0.01553 (3)	0.28 (1)
O(1)	8(*f*)	0.81565 (6)	0.96835 (17)	0.09289 (6)	0.57 (2)
O(2)	8(*f*)	0.08517 (6)	0.21012 (16)	−0.01919 (7)	0.53 (2)
O(3)	8(*f*)	0.80256 (6)	0.97397 (17)	−0.06908 (6)	0.68 (2)
O(4)	8(*f*)	0.90366 (6)	0.19942 (16)	0.02100 (7)	0.54 (2)
D(1)	8(*f*)	0.86405 (6)	0.65516 (19)	0.15772 (7)	1.37 (2)
D(2)	8(*f*)	0.87475 (6)	0.38355 (19)	0.12834 (7)	1.36 (2)
D(3)	8(*f*)	0.76515 (6)	0.46039 (19)	0.22458 (7)	1.16 (2)
D(4)	8(*f*)	0.83558 (6)	0.23199 (17)	0.25983 (7)	1.23 (2)
D(5)	8(*f*)	0.15061 (6)	0.73266 (17)	0.16811 (7)	1.23 (2)
D(6)	8(*f*)	0.17460 (6)	0.48727 (21)	0.10511 (6)	1.20 (2)
D(7)	8(*f*)	0.04394 (7)	0.34826 (19)	0.09858 (7)	1.33 (2)
D(8)	8(*f*)	0.02861 (6)	0.62944 (19)	0.08922 (7)	1.32 (2)

3.2. *Results in the 'small cell'*

With respect to the SC, a total of 2608 reflections with $I > 2.00\sigma(I)$ were considered for the refinement. It appears, with respect to this cell, that the peaks (i) with $h + k$ odd and (ii) $h0l$ with l odd are as weak and broad as the peaks that would suggest considering the LC. As a consequence, in this SC corresponding to an average structure (see below) the centrosymmetric space group is $C2/c$. The initial coordinates were obtained by direct methods (Main *et al.*, 1978) and all the atoms, including the deuteriums, were taken into account (19 independent atoms). Platinum and iodine do not stand on a symmetry center (actually the symmetry centers are between the chains and no atom is located on them); note also that in this space group, with such a value of the b parameter, it is not possible to account for a $Pt^{3+\delta}$/$Pt^{3-\delta}$ alternance, *i.e.* the PtI chains cannot be ordered with respect to one another (as in the previously reported room-temperature structures). Under these conditions, the best refinements with isotropic thermal parameters showed an R value of 10.54% (0.1054) and the different solutions with anisotropic thermal parameters revealed that these parameters for iodine are strongly anisotropic and large. With regard to this result, to the observation of the (weak) reflections that provide evidence for a doubling of the lattice parameter along the chain axis (b) and to the structures already reported, refinements with I atoms distributed over two half-occupied positions around the positions determined above have been undertaken. In this case, with anisotropic temperature factors for the 20 independent atoms and an isotropic extinction correction (type I; Becker & Coppens, 1974), $R = 0.0374$ and $wR = 0.0501$ for a total of 170 refined independent parameters. The atomic coordinates for this model are reported in Table 2 together with isotropic displacement parameters; the maximum difference between atomic coordinates refined with isotropic and anisotropic displacement parameters does not exceed 2×10^{-3} for the iodine coordinates (y) and 5×10^{-4} for all the other atoms.* The structure is shown in Fig. 1. It appears that there are two different orientations for consecutive ethylenediamines along **c** (Fig. 1*a*), which is the main origin of the doubling of the c parameter with respect to the room-temperature structures reported in the literature; this doubling is also due to a slight difference in the 'rocking' of the successive ClO_4's around the c axis (Figs. 1*b* and *c*). On the other hand, in this structure

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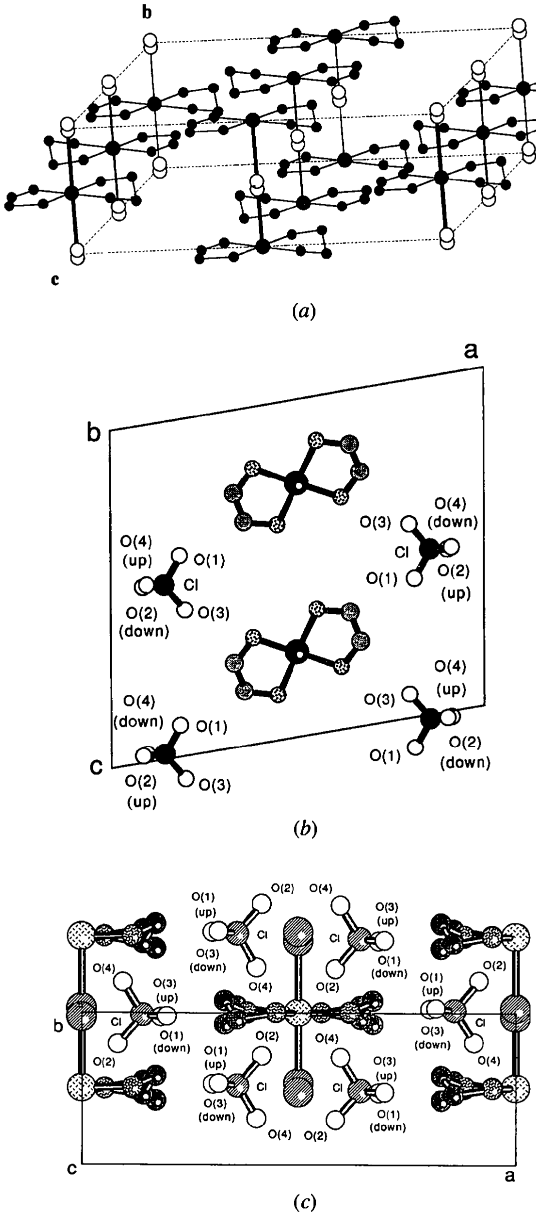
* Lists of anisotropic displacement parameters and structure factors have been deposited with the IUCr (Reference: DU0404). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

there is only one type of chain since they all have the same neighborhood.

The more significant bond lengths and angles are listed in Table 3. There are two types of PtI distances, each being determined from the positions of two independent atoms [I(1), I(2)] and (surprisingly!) are equivalent; the average values are 2.712 (3) and 3.048 (3) Å. Each of these values is of the same magnitude as the sum of the platinum and iodine ionic radii calculated in the approximation of coordination VI (Shannon, 1976), *i.e.* 2.825 and 3.00 Å for the Pt^{2+}—I and Pt^{4+}—I distances, respectively. It is often admitted that the ratio ρ of the $M^{3+\delta}$—X distance to $M^{3-\delta}$—X is a measure of the charge disproportion δ (or the CDW strength). In the present case, this ratio is $\rho = 0.890\,(2)$, which remains close to the values deduced from the room-temperature structures of Matsumoto, Yamashita, Kida & Ueda (1979), 0.868, Endres, Keller, Martin, Nam Gung & Traeger (1979), 0.919, and especially Weinrach, Ekberg, Conradson, Swanson & Hochheimer (1990), 0.886, but significantly higher than in PtCl/en/ClO_4, 0.75 (Matsumoto, Yamashita, Ueda & Kida, 1978), and PtBr/en/ClO_4, 0.83 (Endres, Keller, Martin & Traeger, 1979). Concerning the bond lengths in the organic molecule, there is good agreement between the N—D distances [1.023 (1)–1.028 (1) Å] and the C—D distances [1.088 (1)–1.096 (1) Å] found in this work and those deduced by Yokoseki & Kuchitsu (1971) from gathering results obtained by X-ray diffraction of crystals containing ethylenediamine and from gas electron diffraction of ethylenediamine [1.03 and 1.10 (1) Å for N—H and C—H, respectively]; more recently, Siam, Van Alsenoy & Schäfer (1990) obtained similar values [1.00 and 1.083 (1) Å] from *ab initio*



(*a*)

(*b*)

(*c*)

Fig. 1. Structure of PtI/en/ClO_4 as determined in the $C2/c$ space group ('small cell'). (*a*) Overview of the Pt—I chains with carbons and nitrogens of the ethylenediamine; (*b*) and (*c*) projection in the *ac* and *ab* planes of the Pt—I chains with ethylenediamine (without deuteriums) and ClO_4, showing their implication in the 'doubling' of the *c* parameter.

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

Pt—I(1^{i})	2.712 (3)	Cl—O(1)	1.443 (1)
Pt—I(1)	3.048 (3)	Cl—O(2^{iv})	1.450 (1)
Pt—I(2)	2.712 (3)	Cl—O(3)	1.435 (1)
Pt—I(2^{i})	3.048 (3)	Cl—O(4^{i})	1.451 (1)
Pt—N(1^{ii})	2.0599 (9)	O(2)—D(7)	2.122 (2)
Pt—N(2)	2.0515 (7)	O(2)—D(8^{v})	2.210 (1)
N(1)—C(1)	1.491 (1)	O(4)—D(2)	2.027 (2)
N(2)—C(2)	1.496 (1)	O(4)—D(8^{iv})	2.339 (2)
C(1)—C(2^{iii})	1.507 (1)	O(1)—D(1)	2.138 (2)
N(1)—D(1)	1.028 (1)	O(1)—D(6^{vi})	2.387 (2)
N(1)—D(2)	1.027 (1)	O(3)—D(3^{vii})	2.419 (1)
N(2)—D(7)	1.025 (1)	O(3)—D(5^{viii})	2.442 (1)
N(2)—D(8)	1.023 (1)	O(1)—N(1)	3.160 (1)
C(1)—D(3)	1.092 (1)	O(2)—N(2)	2.930 (1)
C(1)—D(4)	1.096 (1)	O(3)—N(1^{vii})	3.258 (2)
C(2)—D(5)	1.096 (1)	O(4)—N(1)	3.010 (1)
C(2)—D(6)	1.088 (1)		
I(1^{i})—Pt—N(1^{ii})	90.85 (3)	D(5)—C(2)—D(6)	108.4 (1)
I(1^{i})—Pt—N(2)	89.55 (3)	D(3)—C(1)—C(2^{iii})	111.68 (9)
I(2)—Pt—N(1^{ii})	89.15 (3)	D(4)—C(1)—C(2^{iii})	110.86 (9)
I(2)—Pt—N(2)	90.45 (3)	D(5)—C(2)—C(1^{iii})	110.74 (8)
N(1^{ii})—Pt—N(2)	96.34 (3)	D(6)—C(2)—C(1^{iii})	111.95 (9)
D(1)—N(1)—D(2)	106.0 (1)	D(5)—C(2)—N(2)	107.00 (8)
D(7)—N(2)—D(8)	106.6 (1)	D(4)—C(1)—N(1)	107.31 (9)
D(1)—N(1)—C(1)	110.24 (9)	D(3)—C(1)—N(1)	109.80 (9)
D(2)—N(1)—C(1)	110.76 (9)	D(6)—C(2)—N(2)	110.38 (8)
D(7)—N(2)—C(2)	109.36 (8)	N(1)—D(1)—O(1)	172.71 (9)
D(8)—N(2)—C(2)	108.90 (8)	N(1)—D(2)—O(4)	159.47 (11)
D(1)—N(1)—Pt^{ix}	110.74 (7)	N(2)—D(7)—O(2)	134.14 (9)
D(2)—N(1)—Pt^{ix}	111.10 (8)	O(1)—Cl—O(2^{iv})	108.93 (7)
D(7)—N(2)—Pt	111.53 (8)	O(1)—Cl—O(3)	110.52 (7)
D(8)—N(2)—Pt	111.20 (8)	O(1)—Cl—O(4^{i})	108.88 (7)
N(1)—C(1)—C(2^{iii})	107.85 (6)	O(2^{iv})—Cl—O(3)	109.33 (7)
N(2)—C(2)—C(1^{iii})	108.23 (7)	O(2^{iv})—Cl—O(4^{i})	109.38 (7)
D(3)—C(1)—D(4)	109.2 (1)	O(3)—Cl—O(4^{i})	109.77 (7)

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

calculations. The C—C [1.507 (1) Å] and C—N [1.491 (1)-1.496 (1) Å] distances in our work are also close to the values 1.51 and 1.48 Å given by Boudon & Wipff (1991), as determined from an averaging over 48 compounds. Concerning the perchlorates, although the O and Cl atoms are in the general 8(*f*) position, the ions deviate a little from tetrahedral symmetry, since the Cl—O bond lengths range from 1.435 (1) to 1.451 (1) Å and since the O—Cl—O angles range from 108.9 to 110.5°. More precisely, the differences between the Cl—O bond lengths relative to O(2) and O(4) (the closest to the chains - see Fig. 1*c*) are equal within the standard deviations (Table 3), while the two others, and especially Cl—O(3), are significantly shorter. This could be related to the existence of hydrogen bonding since, according to Table 3, O(2) and O(4) are fairly close to two deuteriums belonging to the amino group, while O(1) is close to only one such deuterium. On the other hand, the shortest O(3)· · ·D distances are much larger and the closest occur with deuterium bonded to carbon. The fact that the Cl—O(3) bond is shorter than the others could be related to a much weaker hydrogen bonding.

Therefore, in the proposed structure all bond lengths are in good agreement with the expected values. It can be useful to examine the main differences with respect to the room-temperature structures determined by X-ray diffraction. In the structure proposed by Matsumoto, Yamashita, Kida & Ueda (1979), the C—C [1.50 (4) Å] and C—N [1.55 (3) Å] distances are fairly close to our values, but the Cl—O distances spread over 0.17 Å [from 1.35 (3) to 1.51 (2) Å]; this could argue for a disorder of the oxygens at room temperature since their thermal parameters are also large. In the structure proposed by Endres, Keller, Martin, Nam Gung & Traeger (1979) the C—N distance (1.49 Å) is almost the same as that we found, but the C atoms are disordered along the *c* axis by ~0.61 Å with a C—C distance of 1.47 Å, just a little shorter than we found. Concerning the ClO_4 molecule, there are two types of oxygens, some being in the 4(*i*) symmetry plane, the others being in the general 8(*j*) position, and the Cl—O bond lengths range from 1.41 to 1.42 Å. Finally, according to the structure of the crystal grown at elevated pressures by Weinrach, Ekberg, Conradson, Swanson & Hochheimer (1990) there are two different C—N distances [1.46 (3) and 1.52 (3) Å], the average value being 1.49 Å, as in the structure proposed by Endres, Keller, Martin, Nam Gung & Traeger (1979). However, the Cl—O bond lengths are in a wide range, from 1.32 (3) to 1.51 (4) Å, and the C atoms (C—C) are only distant by 1.39 (4) Å.

The isotropic thermal parameters found in the present work also call for some comments, since it can be noted that many of them lie in the same range. For the two nitrogens, which are independent, one obtains 0.31 and 0.30 $Å^2$. The same remark applies to the two carbons (0.42 and 0.43 $Å^2$), the oxygens O(2) and O(4) (0.53 and 0.54 $Å^2$), the four deuteriums linked to nitrogens (1.37, 1.36, 1.33 and 1.32 $Å^2$) and finally the four deuteriums linked to carbons (1.16, 1.23, 1.23 and 1.20 $Å^2$). It can also be noted that the oxygens for which the hydrogen bonding is supposed to play a less important role [O(1) and mostly O(3)] exhibit larger isotropic thermal parameters (0.57 and 0.68 $Å^2$) than the others.

To conclude, the refinement of the structure of $PtI/en/ClO_4$ at low temperature in the space group *C*2/*c* leads to interatomic distances consistent with the expected ones and isotropic thermal parameters that are physically reasonable. The ethylenediamines and the perchlorates are almost undistorted and they are ordered. Such an ordering seems to be the main difference with respect to the structures previously reported for the room-temperature phase. The observation of a phase transition on heating (see §4) supports the hypothesis that the structure determined in this work is the ordered form of the structure at room temperature.

3.3. *Results in the 'large cell'*

As mentioned above, superstructure peaks corresponding to a 'doubling' of the *a* and *b* parameters have been observed and 1263 such reflections specific to the LC have been collected. Actually, their intensities are of the same magnitude as those from the container (aluminium) and their diffraction angles are such that most of them may be contaminated by these lines. A contamination is suggested, for example, by the fact that they may not be strictly centered (Fig. 2*a*) by a strong asymmetry or by the fact that their widths are larger than those of the main reflections (Figs. 2*b*, *c* and *d*). Nonetheless, some reflections where no contamination is possible (either by aluminium or by harmonics) are unambiguously observed and some of these are shown in Fig. 3 (they are collected with twice the standard acquisition time), but the strongest remain 400 times weaker than the main reflections. According to the present data, no systematic extinctions can be detected, except for those resulting from the C centering, and since there is no evidence for the absence of a symmetry center, the *C*2/*m* space group should be proposed. However, with regard to the self consistency of the results obtained in the SC, it is obvious that the space group of the LC must be restricted to the subgroups of *C*2/*c*: since there is no mirror plane in the *C*2/*c* space group, no mirror plane can be present in its subgroups and so the *C*2 space group must be attributed to this structure (actually, starting with the structure determined in the SC, large atomic displacements must be carried out to obtain a mirror plane and the *C*2/*m* space group; under these conditions no refinement was possible).

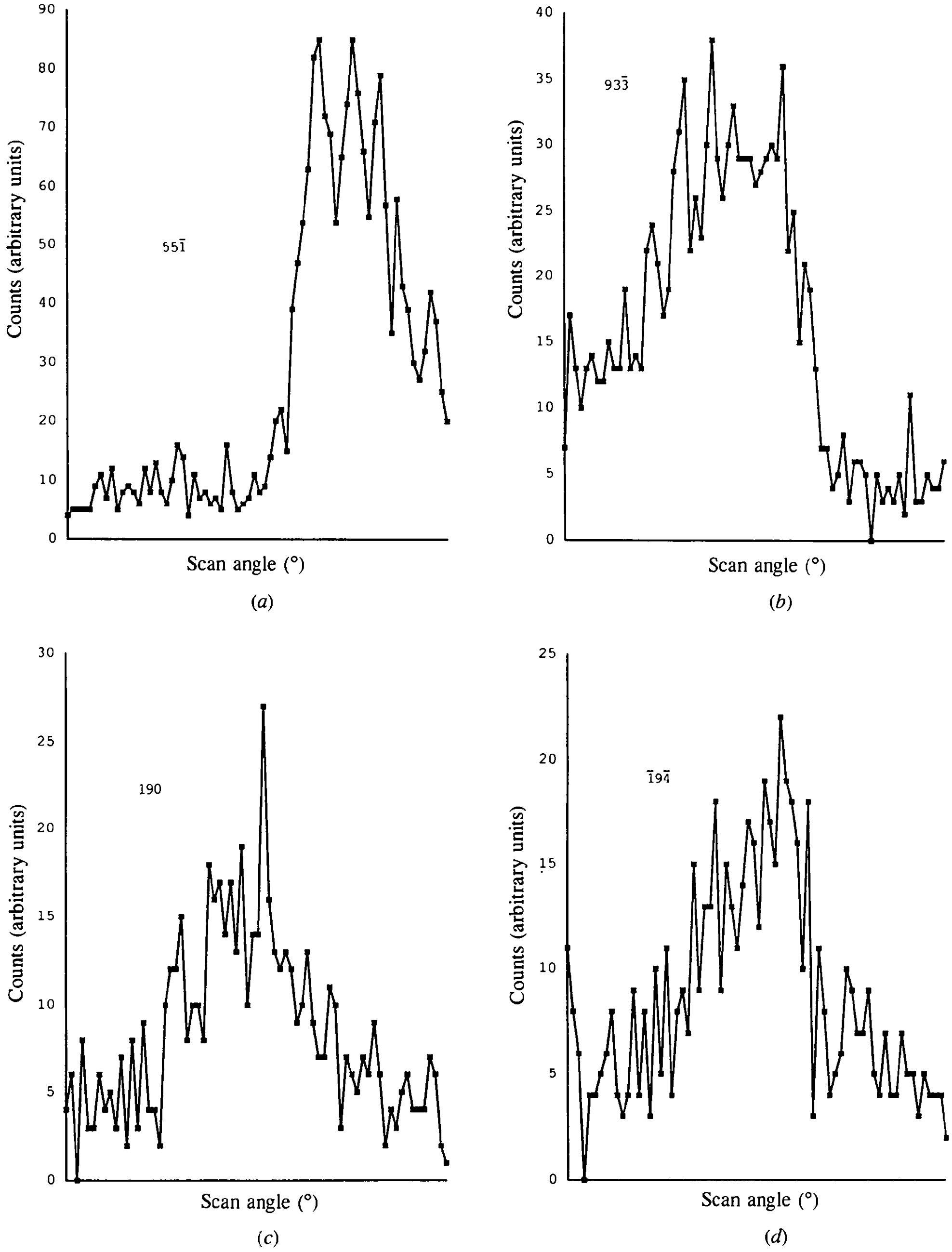


Fig. 2. (*a*)–(*d*) Atypical diffraction peaks specific to the 'large cell'.

A number of refinements in the $C2$ space group have been tried, but none of them lead to R values better than 0.09 for the whole data and 0.40 if limited to the new weak reflections alone (which is related to the fact that the sum of the intensities of these reflections represents less than 0.2% of the sum of intensities of the main reflections). Several reasons may explain such poor results. Some of them arise from the data themselves, since for such weak signals the signal-to-noise ratio is poor, and the contamination by the container plays a significant role together with that by harmonics of the incident wavelength ($\lambda/2$, $\lambda/4$). This can also be related to the origin of these reflections. Actually, the doubling of the a and b parameters has also been observed with a more significant intensity by Scott *et al.* (1996) by X-ray diffraction. This suggests that the superstructure reflections do not result primarily from diffraction by light atoms, since in neutron diffraction (unlike in X-ray diffraction) they contribute almost as much as the heavy atoms. This is also supported by the fact that, with

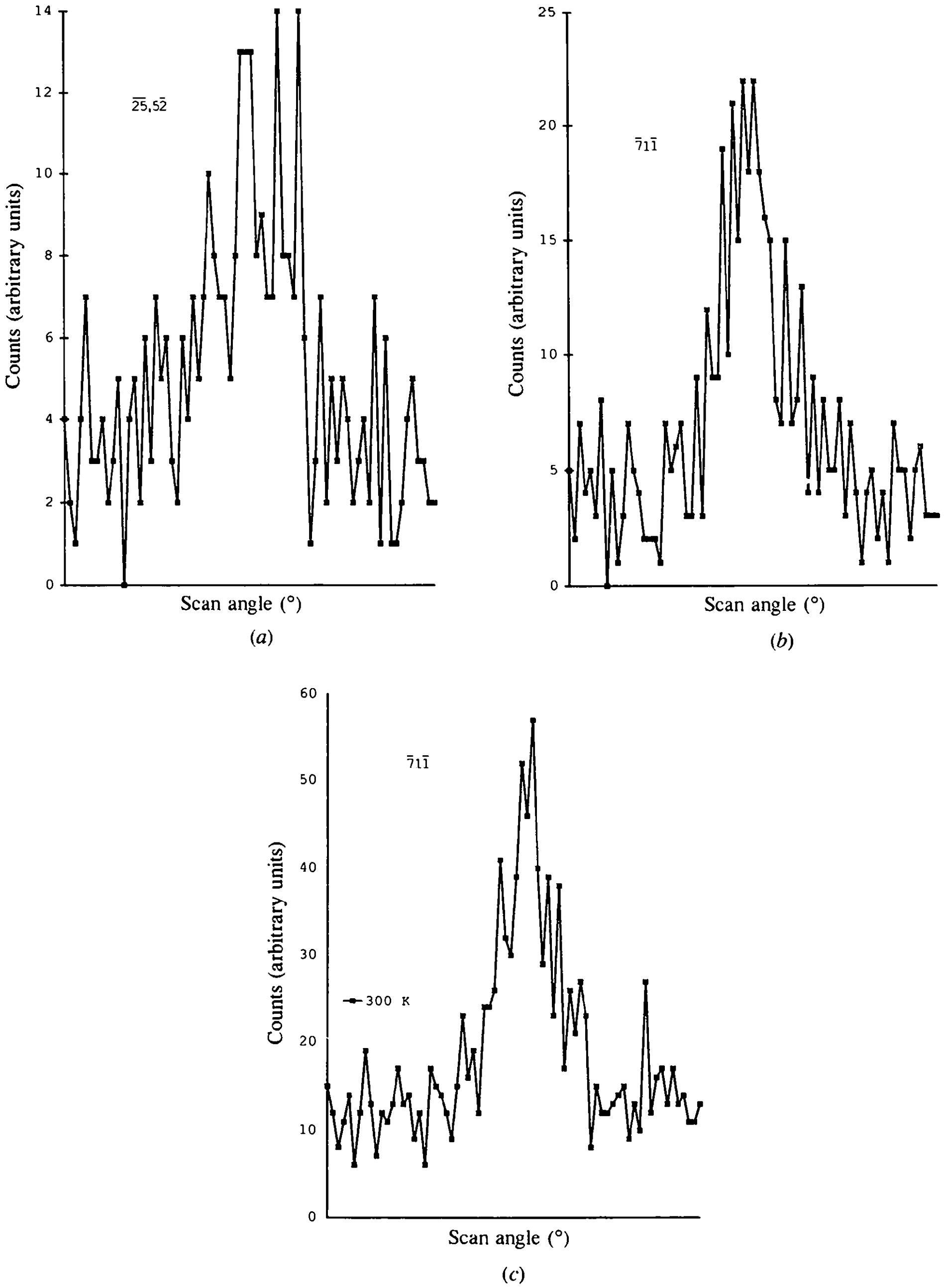


Fig. 3. Diffraction peaks specific to the 'large cell' measured at 20 K [(*a*) and (*b*)] and at room temperature (*c*).

regard to the temperature behavior of a few of these reflections that have been studied on warming up the crystal, no significant variations of intensities were observed at the phase transition (see §4 and Figs. 3*b* and *c*), which presumably results from a disorder of the ethylenediamines, *i.e.* involving most of the light atoms. On the other hand, according to the refinements in the SC, there is no doubt that a charge disproportion of platinums exists along the chains and so the doubling of the *a* (and *b*) parameter(s) can be reasonably attributed to a mutual ordering of the chains. However, with regard to the arrangement of the chains (Fig. 4), a long-range ordering is probably more difficult to establish in the PtI/en/ClO_4 structure than in PtCl/en/ClO_4. In the latter case, as revealed by the body centered character of the cell, there is an ordering of all the chains where each platinum with the highest charge is surrounded by four platinums with the lowest charge (Fig. 4*a*), which presumably results from a minimization of the electrostatic repulsions. In the case of PtI/en/

ClO_4 (Figs. 4*b* and *c*), out of its own chain, a given platinum has only two platinum nearest-neighbors along **c** and there is probably an alternation of the charges [the fact that the $(\bar{7}1\bar{1})$ reflection still exists at room temperature, as shown in Fig. 3*c*, could be the signature for this ordering); on the other hand, the next nearest-neighbors in the $(2a, 2b)$ plane necessarily consist of two platinums with the highest charge and two with the lowest charge (Fig. 4*c*). As a consequence, any mutual ordering of the chains in the (a, b) plane (and several of them can be invoked) probably results from a subtle effect and so it may be very weak and/or very sensitive to various parameters or possibly even the thermal history of the sample. We cannot be sure that the crystals studied by X-ray and neutron diffraction had the same thermal history and it is not obvious that the mutual ordering of the chains is the same. It would be useful to check that the relative intensities of the superstructure reflections are not dependent on external parameters.

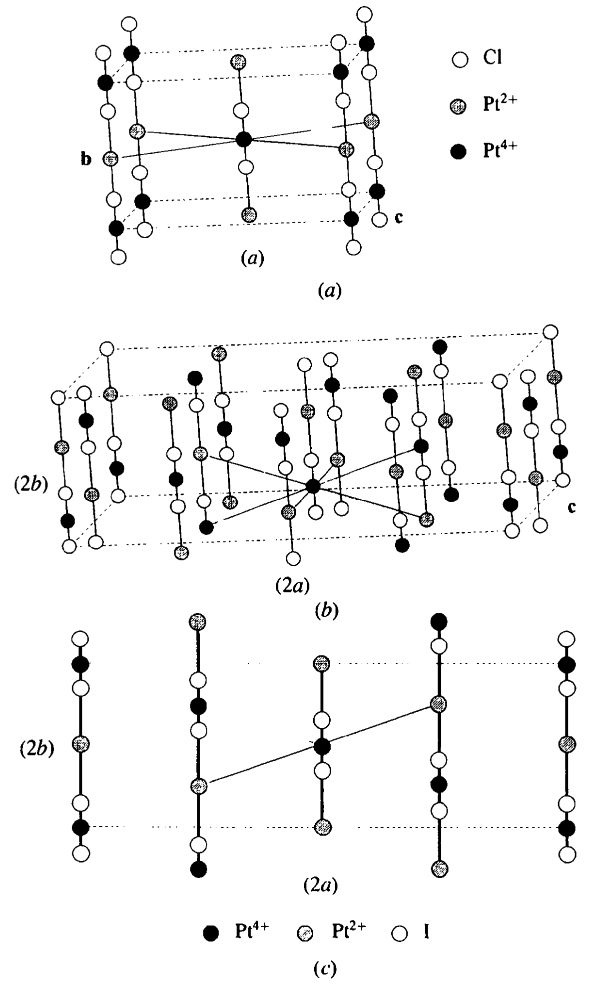


Fig. 4. Schematic view of the platinum and halogen sublattices in $PtCl/en/ClO_4$ (*a*) where the space group is *I*222 (Matsumoto, Yamashita, Ueda & Kida, 1978) and in $PtI/en/ClO_4$ (*b*) and (*c*) for a possible arrangement in the 'large cell'. The dashed lines are guides for the eyes to show, for a given platinum, the nearest platinums of neighboring chains.

4. Phase transition and discussion

On warming the crystal up to room temperature, reflections such that *l* is odd undergo a sudden decrease in intensity between 140 and 170 K (Fig. 5), while a normal behavior is observed for *l* even. The temperature behavior of the intensities of the $(62\bar{5})$ and $(\overline{18},2\bar{1})$ lines with respect to those of a line such that *l* is even is plotted in Fig. 6. Such a behavior provides unambiguous evidence for a phase transition. The temperature behavior of the cell parameters has been determined from three intense reflections and is represented in Fig. 7; their values at room temperature are close to those found recently by X-ray diffraction by Scott *et al.* (1996). No strong singularities are observed, but it can be noted that *b* seems to exhibit a slight plateau in the vicinity of the phase transition. To summarize, on cooling the crystal the phase transition gives rise to a doubling of the *c* parameter, but seems to affect more significantly the *b* parameter, *i.e.* the distance along the chain axis. It must be recalled that

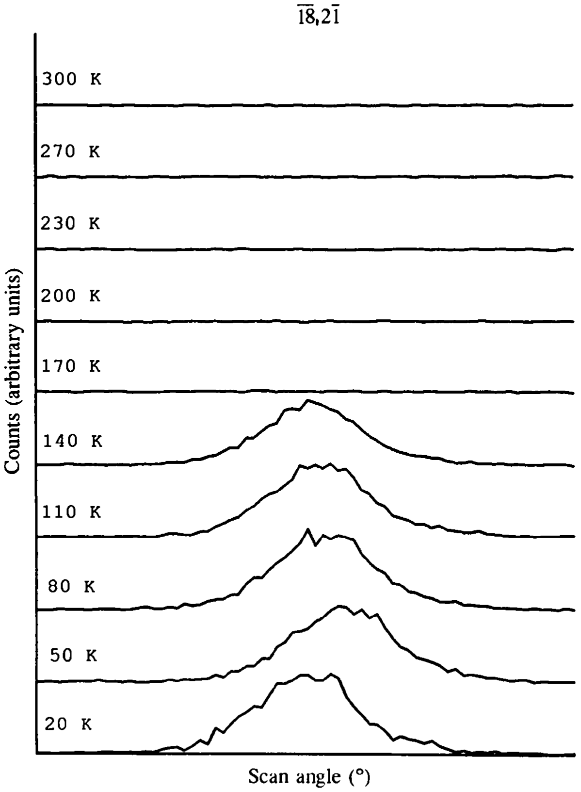


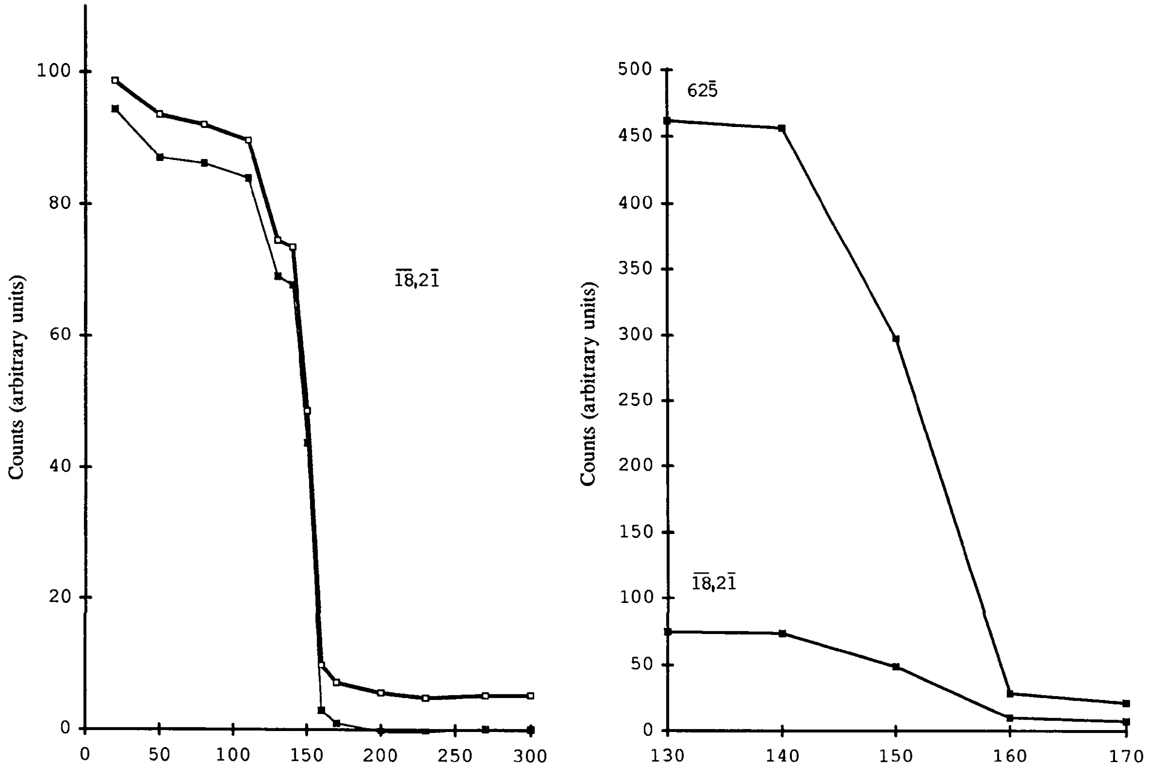
Fig. 5. Temperature behavior of the $(\overline{18},2\bar{1})$ diffraction peak (in the 'large cell').

Toriumi, Yamashita, Kurita, Murase & Ito (1993) already measured the temperature behavior of hydrogenated PtI/en/ClO_4, but they did not mention any singular behavior of the *b* parameter. This can be attributed to the fact that they limited their investigations to temperatures above 120 K and used large temperature steps (~50 K in this temperature range) or/and to the fact that the phase transition occurs at a lower temperature than in the deuterated sample (which can be possible in the framework of the mechanism proposed below).

According to the present structural determination at 20 K in the SC, the 'doubling' of the *c* parameter with respect to the structures reported at room temperature can unambiguously be mainly attributed to an ordering of the ethylenediamines along **c** (with a slight reorientation of the perchlorates). The vanishing of the lines such that *l* is odd shows that the periodicity along *c* becomes the same as at room temperature and so the ordering vanishes. This is probably connected with motions of deuteriums, presumably those linked to the nitrogens since they still have a significant isotropic temperature factor at 20 K (Table 2). An ordering of deuteriums in this temperature range is not uncommon and it could be attributed to the establishment of hydrogen bonds with oxygens. In this framework the phase transition could be imputed to an ordering in the ethylenediamine–perchlorate sublattice and the singular variation of *b* would be just a consequence. With regard to the temperature behavior of the *b* parameter, it can be thought that the disorder in the high-temperature phase prevents the crystal from a normal contraction on cooling (existence of a plateau), while after ordering the normal behavior is observed. Under such a mechanism, the uncommon behavior of the platinum–iodine distances, and the concomitant change of the CDW would be driven by an order–disorder phase transition. However, a change in the CDW properties of the chain, leading to an uncommon variation of *b* and an ordering of the ethylenediamine, cannot be excluded either. Structural and spectroscopic investigations in the vicinity of the phase transition would be very useful to really explain the driving process.

5. Conclusions

The structure of PtI/en/ClO_4 at 20 K has been solved by neutron diffraction on a single crystal and the space



(*a*) (*b*)

Fig. 6. (*a*) Temperature behavior of the intensity of the $(\bar{1}8,2\bar{1})$ diffraction peak (with respect to the 'large cell') over the whole temperature range studied. The narrow line represents the integrated intensity and the thick line the peak intensity. (*b*) Peak intensities of the $(\bar{1}8,2\bar{1})$ and $(62\bar{5})$ diffraction peaks in the vicinity of the phase transition.

group for an average structure is $C2/c$. All the atomic coordinates, including deuteriums, have been refined and the interionic distances and bond lengths are consistent with the expected values. The perchlorate ions and ethylenediamines are ordered and two types of platinum–iodine distances are found along the chains. However, some very weak superstructure peaks that provide evidence for a doubling of the a and b parameters are also observed (from 20 K to room temperature) and this could be attributed to a mutual ordering of the chains. The corresponding space group would be $C2$, but due to the weakness and the poor signal-to-noise ratio of these extra peaks, no reliable refinement can be proposed. A phase transition has also been observed in the vicinity of 160 K and it is probably mainly associated with an ordering of the ethylenediamines.

The structure determined in this study is probably the ordered form of PtI/en/ClO$_4$. It must be pointed out that, according to the present refinement, (i) it is possible to determine the Pt^{IV}—I and Pt^{II}—I distances (related to the charge disproportions or the CDW strength) with a good precision and (ii) the b parameter and so the sum of the platinum–iodine distances seems to be affected by the phase transition. It appears that structural investigations of PtI/en/ClO$_4$ as a function of temperature and especially in the vicinity of the phase transition could provide essential information on the properties of the PtI chains.

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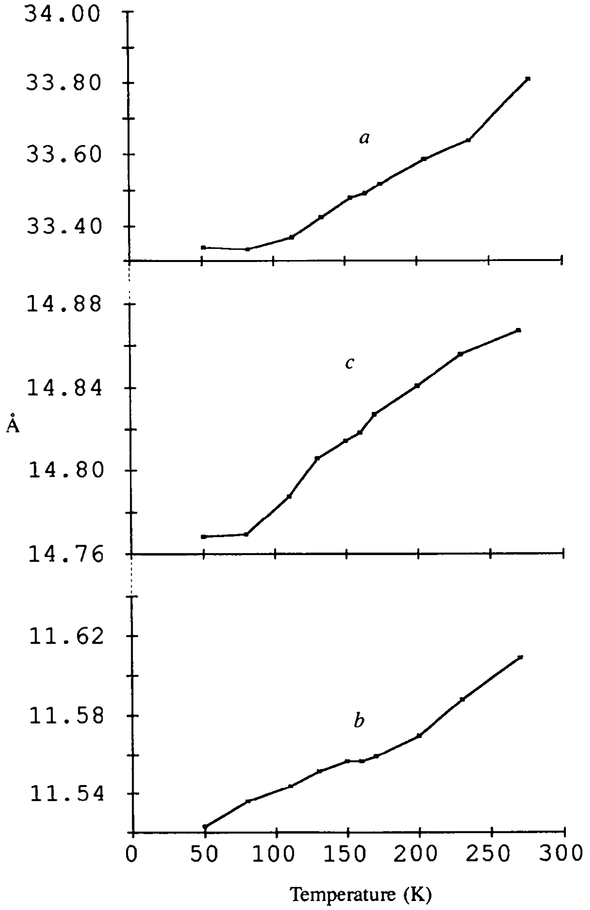

Fig. 7. Temperature behavior of the 'large cell' parameters. The lines are just guides for the eyes.

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