A Revision of the Structure of (Bipyridyl-N,N')dicyanoplatinum(II)

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Abstract

In a previous X-ray crystallographic study of crystals of Pt(bpy)(CN)$_2$ (bpy = 2,2'-bipyridine) the planar molecules were reported to be exactly eclipsed, stacked directly on top of one another with a spacing of 3.33 Å so as to form a linear Pt···Pt···Pt chain. A reinvestigation shows this structure to be incorrect. The presence of weak intermediate layer lines indicates that the repeat distance along the stacking direction is 6.66 Å rather than 3.33 Å. Successive molecules within the stack are rotated by 180° and the resulting Pt-atom chain is slightly zigzag with a Pt···Pt···Pt angle of 168.6 (1)°. The implications are discussed of the determination and refinement of an apparently satisfactory, although grossly wrong, structure that was based on an incorrect unit cell and an incorrect space group.

1. Introduction

Stacking of square-planar platinum(II) complexes in the solid state to form approximately linear chains of closely spaced (< 3.5 Å) Pt atoms is a well known phenomenon and leads to highly anisotropic physical and spectroscopic properties (Miller, 1982). Although there are many examples of such materials, we have found few structural reports of platinum(II) diimine compounds forming such chains [Osborn & Rogers, 1974; Che, He, Poon & Mak, 1989; Coyer, Herber & Cohen, 1990, 1991 (see Marsh, 1994); Biedermann, Gliemann, Klement, Range & Zabel, 1990]. In all but one of these reported structures, successive platinum diimine molecules are rotated by 180° about the chain axis, so that eclipsing of the ligands is avoided and the Pt···Pt···Pt chain is slightly zigzag. The exception to this pattern was (bipyridyl-N,N')dicyanoplatinum(II) (and its palladium analogue), which was reported to crystallize with adjacent molecules exactly eclipsed (Che et al., 1989). This structure was described in the polar orthorhombic space group Cm2m (no. 38) with a very short c axis (3.33 Å) and it occurred to us that a doubling of this axis could well lead to the more usual staggered arrangement of stacked complexes along the chain axis. The doubling could occur if systematically weak reflections with l odd had been overlooked in the original investigation: we

imagined a structure, perhaps in space group Cmcm [as found by Osborn & Rogers, 1974, for the dichloro-bipyridyl compound and by Coyer et al., 1991 (see also Marsh, 1994), for the bis-isocyanato-4,4'-dimethylbipyridyl compound] with successive Pt atoms approximately but not exactly superposed. We report here a re-investigation of the structure, which confirms our suspicions.

This re-investigation also serves as an interesting case study. Although accidental halving of a unit cell will, typically, lead to the conclusion that the structure is disordered, in the present case no disorder was apparent in the original Cm2m structure. This result illustrates that, in certain instances, suspicious disorder arising from halving a unit cell may be eliminated by refinement in a non-centrosymmetric space group. The resulting model may appear crystallographically reasonable, but is grossly incorrect.

2. Experimental

Pt(bpy)(CN)$_2$ was prepared according to the published protocol (Che et al., 1989). Crystals suitable for X-ray diffraction studies were grown by slow cooling of a hot solution of dimethylformamide. Preliminary oscillation photographs about the c axis clearly showed weak, odd-order layer lines, confirming that this cell edge must be twice that reported previously (Che et al., 1989); see Table 1. Data were then collected using an Enraf–Nonius CAD-4 diffractometer (Mo Kα radiation). The unit-cell dimensions were obtained from the setting angles of 25 reflections (11 < θ < 13°); intensities were measured for two separate octants (+h, ±k, +l). Systematic absences (hkl, h + k = 2n + 1; h0l, l = 2n + 1) were consistent with space groups Cmcm (no. 63), Cmc2$_1$ (no. 36) and C2cm (an alternative setting of Ama2, no. 40); the structure was successfully described in the centrosymmetric Cmcm. The Pt atom was located with the help of a Patterson map and the remaining atoms from ensuing structure-factor Fourier calculations; H atoms were positioned by calculation (C—H, 0.95 Å) and were assigned isotropic B's 1.15 times that of the attached C atom. Weights were taken as $1/\sigma^2(F_o^2)$; individual variances $\sigma^2(I)$ were derived from counting statistics plus an additional term (0.014I)^2, while variances of the merged intensities

Table 1. *A comparison of cell dimensions found herein with those reported by Che et al. (1989)*

	This work	Che *et al.* (1989)
Space group	*Cmcm*	*Cm2m*
a (Å)	18.142 (5)	18.154 (5)
b (Å)	9.361 (2)	9.357 (2)
c (Å)	6.659 (1)	3.3296 (4)
V (Å^3)	1130.9 (4)	565.6 (2)
Z	4	2
D$_x$ (g cm^{-3})	2.369	2.368*

* Che *et al.* (1989) actually reported $D_x = 3.368$, $D_m = 3.39$ g cm^{-3}.

included propagation of error plus another additional term $(0.014\langle I \rangle)^2$. Pertinent data are collected in Table 2; final parameters are given in Table 3.*

3. Description of the structure

The neutral Pt(bpy)(CN)$_2$ molecules lie on mirror planes at $z = 1/4$ and $3/4$ and have crystallographic symmetry *mm*2; the bonding about Pt is approximately square planar. A drawing of the molecule is shown in Fig. 1(*a*) and bond lengths and angles are given in Table 4.

The cyanide ligands are linearly coordinated to Pt, with a normal C—N bond length of 1.152 (9) Å (Orpen, Brammer, Allen, Kennard, Watson & Taylor, 1989); the Pt—C distance, 1.949 (7) Å, is close to the values 1.92 (1) and 1.94 (1) Å reported for the related linear-chain compound Pt(bpym)(CN)$_2$ (bpym = 2, 2'-bypyr-imidine; Biedermann *et al.*, 1990). The Pt—N(bpy) distance of 2.059 (5) Å is also in satisfactory agreement with the values 2.042 (8) and 2.057 (7) Å reported by Biedermann *et al.* (1990). These Pt—N distances in complexes with *trans* π-acceptor ligands are understandably longer than those found in related compounds with *trans* π-donor ligands, such as the red and yellow forms of Pt(bpy)Cl$_2$ [2.001 (6) and 2.01 (11) Å; Osborn & Rogers, 1974; Herber, Croft, Coyer, Bilash & Sahiner, 1994] and Pt(bpy)I$_2$ [2.020 (7) Å; Connick & Gray, 1994].

The crystal packing is illustrated in Fig. 2. The complexes stack along the *c* axis to form an approximately linear chain of Pt atoms; consecutive molecules along the chain are related by the *c*-glide perpendicular to *b* and consequently are rotated by 180° about *c*. This arrangement leads to a staggered, rather than an eclipsed, arrangement of ligands in adjacent molecules, while still accommodating relatively close Pt···Pt contacts. The Pt atoms along the chain are slightly offset from the *c* axis, by 0.1662 (3) Å along *b*, resulting in a Pt···Pt···Pt chain angle of 168.6 (1)°. [It is the proximity of this *y* coordinate to 0.0 which is

* Lists of anisotropic displacement parameters, atomic coordinates, complete geometry and structure factors have been deposited with the IUCr (Reference: BK0031). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Experimental details*

Crystal data	
Chemical formula	C$_{12}$H$_8$N$_4$Pt
Chemical formula weight	403.30
Cell setting	Orthorhombic
Space group	*Cmcm*
a (Å)	18.142 (5)
b (Å)	9.361 (2)
c (Å)	6.659 (1)
V (Å^3)	1130.9 (4)
Z	4
D$_x$ (Mg m^{-3})	2.369
Radiation type	Mo *K*α
Wavelength (Å)	0.71073
No. of reflections for cell parameters	25
θ range (°)	11–13
μ (mm^{-1})	12.4
Temperature (K)	295
Crystal form	Rectangular needle
Crystal size (mm)	0.40 × 0.12 × 0.04
Crystal color	Red–orange
Data collection	
Diffractometer	Enraf–Nonius CAD-4
Data collection method	ω
Absorption correction	ψ scan
T_{min}	0.59
T_{max}	1.00
No. of measured reflections	2721
No. of independent reflections	1364
R_{int}	0.031
θ_{max} (°)	35
Range of *h, k, l*	$0 \rightarrow h \rightarrow 25$
	$-13 \rightarrow k \rightarrow 13$
	$0 \rightarrow l \rightarrow 9$
No. of standard reflections	2
Frequency of standard reflections	60
Intensity decay (%)	Within counting statistics
Refinement	
Refinement on	F^2
R^*	0.0453
$wR\dagger$	0.072
GOF$\ddagger$	1.56
No. of reflections used in refinement	1363
No. of parameters used	54
H-atom treatment	Calculated
Weighting scheme	$w = 1/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{max}$	<0.01
$\Delta\rho_{max}$ (e Å^{-3})	2.9
$\Delta\rho_{min}$ (e Å^{-3})	−2.9
Extinction method	Secondary (Larson, 1967)
Extinction coefficient	0.18 (2) × 10^{-6}
Source of atomic scattering factors	Cromer (1974) and Cromer & Waber (1974)
Computer programs	
Structure solution	*CRYM Crystallographic Computing System* (Duchamp, 1964)
Structure refinement	*CRYM Crystallographic Computing System* (Duchamp, 1964)
Molecular graphics	*ORTEPII* (Johnson, 1976)
Electron-density maps	*XP/PC Molecular Graphics Software* (1989)

* $R = \Sigma||F_o| - |F_c||/\Sigma F_o$. $\dagger wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(F_o^2)^2]^{1/2}$. $\ddagger$ GOF $= [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where *n* and *p* are the numbers of observations and parameters, respectively.

responsible for the relatively weak intensities of reflections with *l* odd – the reflections that were over-looked in the earlier work of Che *et al.* (1989).] In the red form of Pt(bpy)Cl$_2$, which is isostructural with the

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

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

	x	y	z	U_{eq}
Pt	0.0	0.01776 (3)	1/4	0.0274 (1)
N1	0.0728 (3)	−0.1511 (5)	1/4	0.0337 (12)
N2	0.1209 (4)	0.2518 (7)	1/4	0.0526 (17)
C1	0.1469 (4)	−0.1405 (7)	1/4	0.0442 (17)
C2	0.1916 (4)	−0.2605 (9)	1/4	0.0539 (21)
C3	0.1590 (5)	−0.3930 (9)	1/4	0.0580 (21)
C4	0.0835 (5)	−0.4032 (7)	1/4	0.0507 (18)
C5	0.0399 (4)	−0.2820 (6)	1/4	0.0382 (14)
C6	0.0749 (4)	0.1671 (7)	1/4	0.0380 (15)

Table 4. *Selected geometric parameters (Å, °)*

Pt—N1	2.059 (5)	C1—C2	1.385 (11)
Pt—C6	1.949 (7)	C2—C3	1.374 (12)
N1—C1	1.349 (9)	C3—C4	1.373 (11)
N1—C5	1.363 (8)	C4—C5	1.383 (10)
N2—C6	1.152 (9)	C5—C5^i	1.448 (9)
N1—Pt—C6	96.0 (2)	C2—C1—N1	121.6 (7)
N1—Pt—N1^i	79.8 (2)	C3—C2—C1	118.7 (7)
C6—Pt—C6^i	88.3 (3)	C4—C3—C2	119.5 (8)
Pt—C6—N2	177.7 (6)	C5—C4—C3	120.9 (7)
Pt—N1—C1	125.7 (4)	C4—C5—N1	119.2 (6)
Pt—N1—C5	114.2 (4)	C5^i—C5—N1	115.9 (6)
C5—N1—C1	120.2 (6)	C5^i—C5—C4	124.9 (6)

Symmetry code: (i) $-x, y, z$.

present compound, the Pt atoms are offset by a slightly greater distance – 0.2818 (4) Å – and the Pt···Pt···Pt chain angle is 161.2 (1)° (Osborn & Rogers, 1974). The interplanar spacing between molecules along the chain is somewhat greater in that dichloro compound (3.40 Å)

than in the present dicyano compound (3.33 Å) and hence the Pt···Pt distance is greater – 3.448 (1) *versus* 3.3461 (5) Å.

4. The earlier *Cm2m* structure

The structure of this compound, which was reported earlier by Che *et al.* (1989), was based on a unit cell half as large; reflections with *l* odd, which are systematically weak because of the almost linear arrangement of Pt atoms, were apparently overlooked during the diffractometer search for orienting reflections. Such events have surely occurred before (Asker, Hitchcock, Moulding & Seddon, 1990; see also Marsh, 1995). The usual result is that the incorrect structure, based on too small a cell, is disordered; in effect, the two molecules in each stack shown in Fig. 2 must be superposed in order to create the appearance of a smaller cell. In the present case, however, the structure reported by Che *et al.* (1989) seemed to show no such disorder; the only hint of possible trouble was a somewhat large and elongated (along *b*) U_{ij} ellipsoid for the Pt atom and, perhaps, some slightly peculiar bond lengths and angles. Why was there no apparent disorder?

The answer is that Che *et al.* (1989) chose to describe the structure in a non-centrosymmetric space group,
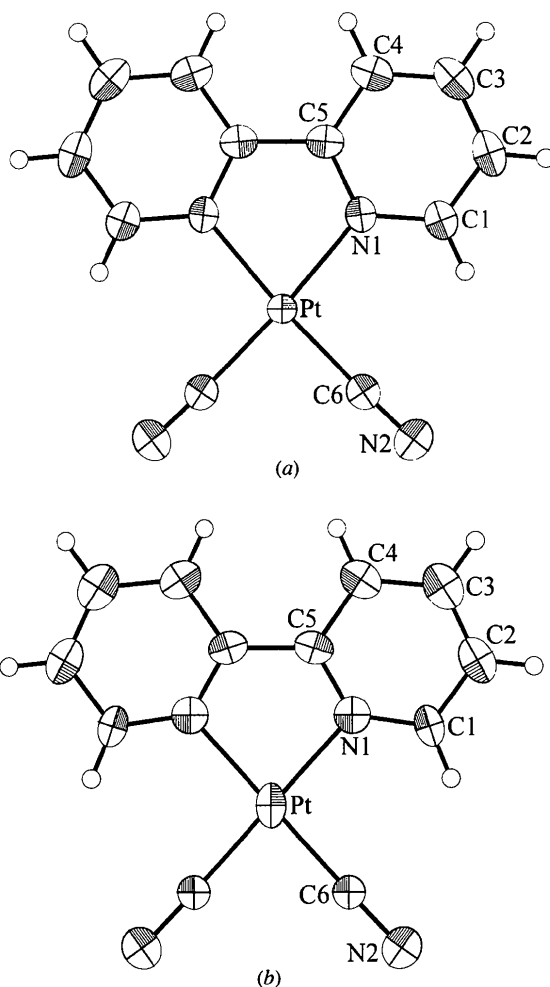

Fig. 1. *ORTEPII* (Johnson, 1976) diagrams with 50% probability ellipsoids showing the Pt(bpy)(CN)₂ molecule described in space groups (*a*) *Cmcm* and (*b*) *Cm2m*. H atoms are shown as spheres of arbitrary size.
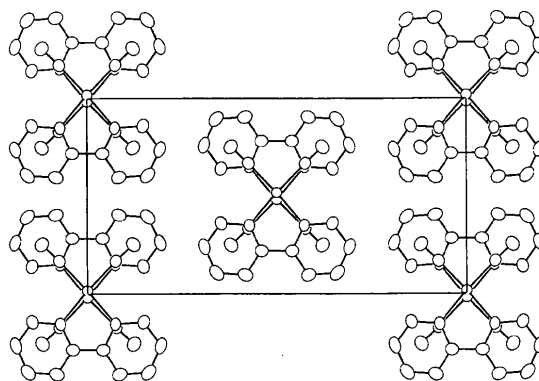

Fig. 2. View of the crystal packing along the *c* axis and perpendicular to the *ab* plane; the *a* axis is horizontal. H atoms are not shown.

Table 5. *Selected data refinements in Cmcm, Cmmm and Cm2m*

	Cmcm (no. 63)	*Cmmm* (no. 65)	*Cm2m* (no. 38) (Enantiomorph *A*)	*Cm2m* (no. 38) (Enantiomorph *B*)
a (Å)		18.142 (5)		
b (Å)		9.361 (2)		
c (Å)	6.659 (1)	3.329 (1)	3.329 (1)	3.329 (1)
V (Å³)	1130.9 (4)	565.4 (3)	565.4 (3)	565.4 (3)
No. of reflections	1363	762	1450	1450
No. of reflections $F_o^2 > 0$	1287	741	1394	1394
No. of reflections $F_o^2 > 3\sigma(F_o^2)$	1096	641	1142	1142
No. of parameters	54	47*	47*	47*
GOF	1.56	1.88	1.68	1.71
R	0.0453	0.0444	0.0516	0.0514
$R[F_o^2 > 3\sigma(F_o^2)]$	0.0349	0.0359	0.0397	0.0397
Pt U_{eq} (Å² × 10⁴)	274 (1)	394 (1)	390 (1)	390 (1)
N1 U_{eq} or U_{iso} (Å² × 10⁴)	337 (12)	379 (49)	398 (38)	360 (35)
C5 U_{eq} (Å² × 10⁴)	382 (14)	404 (23)	391 (20)	399 (21)
C6 U_{eq} or U_{iso} (Å² × 10⁴)	380 (15)	328 (47)	318 (37)	352 (39)
Pt—N1 (Å)	2.059 (5)	1.92 (2)	2.04 (2)	1.96 (2)
Pt—C6 (Å)	1.949 (7)	2.08 (2)	1.95 (2)	2.04 (2)
N2—C6 (Å)	1.15 (1)	1.15 (2)	1.27 (2)	1.18 (2)
N1—C5 (Å)	1.363 (8)	1.36 (2)	1.29 (2)	1.34 (2)
N1—Pt—N1ⁱ (°)	79.8 (2)	88.0 (7)	83.9 (7)	85.4 (7)
C6—Pt—C6ⁱ (°)	88.3 (3)	80.5 (8)	83.9 (7)	81.9 (8)
Pt—C6—N2 (°)	177.7 (6)	171.8 (17)	178.0 (14)	175.0 (16)

Symmetry code: (i) $-x$, y, z.   * Due to the severe correlation between N1 and C6, these atoms were assigned isotropic *B*'s.

Cm2m. (It was actually cast in a different setting, *C2mm*; both are conventionally described as *Amm2*, no. 38.) As a result, an 'imaginary' out-of-phase component – a *B* term when the Pt atom is positioned at $y = 0$, as chosen by Che *et al.* (1989) – was introduced into each of the F_c values; this *B* term is due, almost entirely, to contributions from the lighter atoms and hence is relatively small. Since the Pt atoms lie very close to the origin of the cell, the 'real' terms, A_c, are almost invariably large; accordingly, the relatively small B_c terms have little influence on the resulting values of $|F_c|$. However, these *B* terms can reflect appreciable asymmetry in the apparent arrangement of the lighter atoms; in effect, they resolve the centrosymmetric superposition of two molecules (Fig. 2) into a single polar molecule.

To further understand the situation we have carried out refinements in the space group selected by Che *et al.* (1989), *Cm2m* and also in its centrosymmetric analogue *Cmmm*, based on the sub-cell data containing only *l* even reflections. Thus, we deleted from our data set all reflections with *l* odd and halved the *l* values of the remaining reflections. There resulted 1450 reflections for refinement in *Cm2m* (the averaging of intensities was according to point group *m2m*) and 762 for *Cmmm* (point group *mmm*). For completeness, we repeated the *Cm2m* refinement with the sign of *f″* for Pt reversed, although, in principle, this should have no effect on the outcome. A summary of the results of these refinements is given in Table 5, together with the *Cmcm* results (based on the complete data set, as in Table 2). A drawing of the structure obtained in *Cm2m* is shown in Fig. 1(*b*).

What can be made of these results? First, in terms of the final agreement indices *R* and the goodness-of-fit, there is not a large disparity between the three space groups for this selection of reflections. (Of course, if the *l* odd reflections had been included for the *Cmmm* and *Cm2m* models, with F_c's of 0.0 for all such reflections, the distinction would have been obvious.) Nor is there a clear choice between *Cm2m* and *Cmmm*, the latter showing a slightly better *R* due to the averaging of *hkl* and *hk̄l*, but a slightly worse GOF because of the increased weights. The close similarity of these latter two refinement results clearly demonstrates the small effect of the out-of-phase terms B_c and emphasizes the common difficulty of distinguishing between a disordered centrosymmetric structure and an ordered non-centrosymmetric one (see, *e.g.*, Marsh, 1986).

As a further illustration of the difference between the models, we show in Fig. 3 electron-density projections of the structure onto [001], calculated with the $F(hk0)_o$ values phased according to the final *Cmmm* model (Fig. 3*a*) and to the final *Cm2m* model (Fig. 3*b*). The *Cmmm* map clearly shows, as expected, the superposition of two disordered molecules related by the additional mirror plane passing through the Pt centre. (Except for a factor of 2, this map is identical to that obtained from the complete correct model in *Cmcm*, since only the *hk0* reflections are involved.) In contrast, the *Cm2m* map shows no evidence of disorder and only a single molecule in one orientation. Thus, the antisymmetric components B_c, while not large enough to appreciably affect the magnitudes of F_c, have effectively shifted the entire electron density from one apparent atom site $x, -y, z$ to the other true site x, y, z, completely destroying the mirror plane and creating a seemingly

reasonable, ordered molecule (Fig. 3b). Some evidence for the disorder persists in the elongation, along y, of the electron density associated with the Pt atom; however, the elongation is small (due to the near coincidence of the two superposed Pt atoms) and can be accommodated by an increase in the U_{22} term for Pt; see Fig. 1.

5. Conclusions

So we have here an example in which not only was the unit cell incorrectly assigned (since the weak, odd-order reflections along c were overlooked) but, in addition, the structure was incorrectly presumed to be polar when in fact it is centrosymmetric. What were the effects on the resulting structure? In terms of the *molecular*
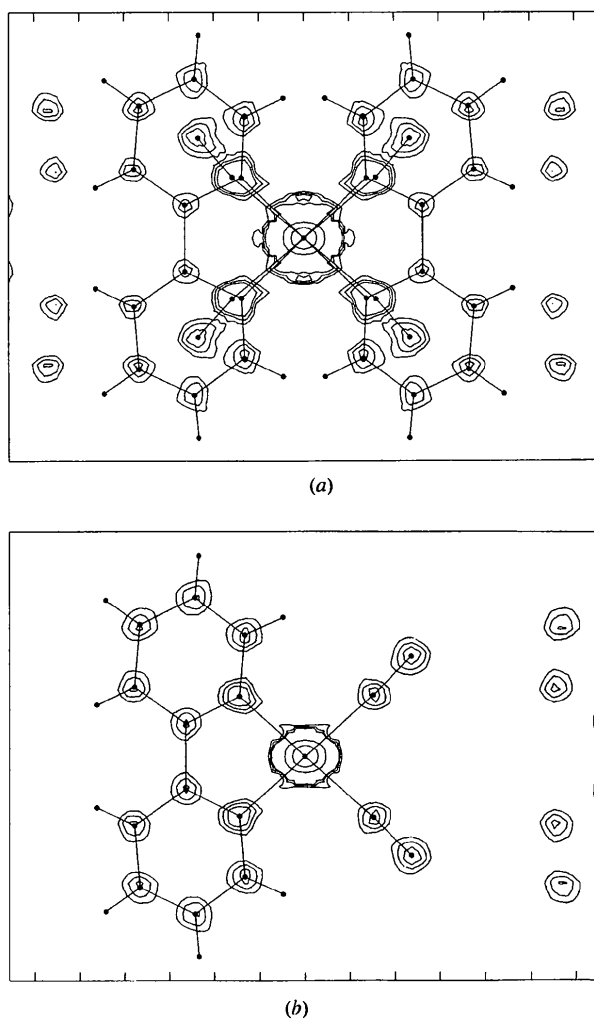

(a)

(b)

Fig. 3. Electron-density projection maps along the c axis for the structure described in space groups: (a) *Cmmm* with contour levels at 2.4, 3.2, 4.0, 50 and 100 e Å^{-2} (identical to *Cmcm*, except for a factor of 2; see text); (b) *Cm2m* with contour levels at 4.0, 5.6, 7.2, 50 and 100 e Å^{-2}.

structure – that is, the shape and dimensions of an individual molecule – they were only moderately serious: atom connectivity was correct (although, certainly, much of that was assumed *a priori*) and bond lengths and angles were not unreasonable. The most serious errors were in the bond lengths involving the Pt atom: Pt—N was reported as 2.00 (1) Å in the earlier work (Che *et al.*, 1989) whereas we find 2.059 (5) Å, and Pt—C was reported as 2.01 (2) Å whereas we find 1.949 (7) Å. It is surely no coincidence that these two bonds were found to be essentially equal in the earlier work, since the N and C atoms are almost exactly superposed in the disordered structure that results when the odd layer lines are ignored (the *Cmmm* structure discussed earlier; see Fig. 2).

In terms of the entire crystal structure, however, the earlier results were seriously in error, alternating molecules having been rotated by 180° (or reflected across a mirror plane) relative to their correct position. Thus, whereas the earlier structure featured an exact eclipsing of successive molecules with a linear Pt···Pt···Pt chain and, surprisingly, overlap of the ligands, the revised structure shows a slightly zigzag chain and alternating stacking of ligands along the chain. The Pt···Pt distance is slightly increased, from 3.3296 (4) (the length of the c axis in the earlier work) to 3.3461 (5) Å. These features of the structure – the nature of the interactions along the chain of stacked molecules – are of the greatest interest in attempts to understand the properties of materials of this type.

These days when the derivation of the unit cell usually depends on an automated diffractometer search for relatively strong reflections, one should be continually concerned that weak layer lines might have been overlooked. In most cases such weak layer lines evidence a superstructure based on only slight perturbations from an average sub-structure; the sub-structure that results from ignoring the weak layer lines may be entirely reasonable except for some enlarged displacement ellipsoids. In the present case – where a very heavy atom (Pt) is involved – the consequences were far more serious. At the very least, diffractometers should be programmed so as to routinely search for significant intensity at intermediate reciprocal lattice points. However, a far more sensible procedure would be to routinely prepare diffraction photographs so that the entirety of reciprocal space can be examined for sub-cell reflections; the use of area detectors for data acquisition may also be an effective counter-measure. In the current case, and presumably in that of the Pd analogue as well, these additional reflections indicate that very important changes to the sub-structure need to be made. This result underscores a recurrent theme in scientific research: while automation and computation have greatly reduced the time and effort involved in producing results, they have not eliminated the need for

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