

## Bis( $\mu$ -pyridine-2-thiolato)- $\kappa^4$ S:N;N:S-bis[(pyridine-2-thiolato- $\kappa$ S)(2-pyridylphenyl- $\kappa^2$ N,C<sup>2</sup>)platinum(III)](Pt—Pt): the non-solvated and acetonitrile-solvated forms

Tamami Koshiyama and Masako Kato\*

Division of Materials Science, Graduate School of Humanities and Sciences, Nara Women's University, Nara 630-8506, Japan

Correspondence e-mail: kato@cc.nara-wu.ac.jp

Received 17 December 2004

Accepted 14 February 2005

Online 11 March 2005

The title dinuclear platinum(III) complex, [Pt<sub>2</sub>(C<sub>11</sub>H<sub>8</sub>N)<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>NS)<sub>4</sub>], forms two crystal structures, *viz.* the non-solvated and acetonitrile-solvated (C<sub>2</sub>H<sub>3</sub>N) forms. For both forms, two (2-pyridylphenyl)platinum units are bridged by two pyridine-2-thiolate (pyt) anions in a head-to-tail configuration, and the other two pyridine-2-thiolate anions occupy the axial position, coordinated through their S atoms. The most remarkable difference between the two forms is the orientation of the axial monodentate ligands. Those for the solvated form are located over the 2-pyridylphenyl ligands, being related by a twofold axis which lies through the centre of the Pt—Pt bond, while the axial pyt ligands for the non-solvated form are oriented irregularly, which is attributable to the dimeric arrangement in the crystal.

### Comment

We recently reported a luminescent dinuclear platinum(II) complex, [Pt<sub>2</sub>(ppy)<sub>2</sub>(pyt)<sub>2</sub>] (where Hppy is 2-phenylpyridine and Hpyt is pyridine-2-thiol; Koshiyama *et al.*, 2004). Because of the strong ligand field of the ppy ligand, this platinum complex was found to have a short Pt...Pt distance [2.8491 (4) Å] for the divalent state of platinum and could be oxidized easily. For example, the divalent complex formed the trivalent complex [Pt<sub>2</sub>Cl<sub>2</sub>(ppy)<sub>2</sub>(pyt)<sub>2</sub>] immediately on dissolution in chloroform. We then investigated the redox properties of [Pt<sub>2</sub>(ppy)<sub>2</sub>(pyt)<sub>2</sub>] and the possibility of the formation of trivalent complexes with various axial ligands. In the course of the study, the pyt ligand itself was found to act as an axial ligand. This compound is remarkable for containing such an asymmetric ligand as both bridging and terminal ligands, although various dinuclear platinum(III) complexes with bridging ligands have been reported (Umakoshi & Sasaki, 1993; Roundhill *et al.*, 1989; Lippard, 1982). We report here the title trivalent complex, [Pt<sub>2</sub>(ppy)<sub>2</sub>(pyt)<sub>4</sub>], which could be

produced either by heating the reaction solution at 343 K or in the presence of an excess of pyt ligand. Two crystal structures, a non-solvated form, (I), and an acetonitrile-solvated form, (II), were found.

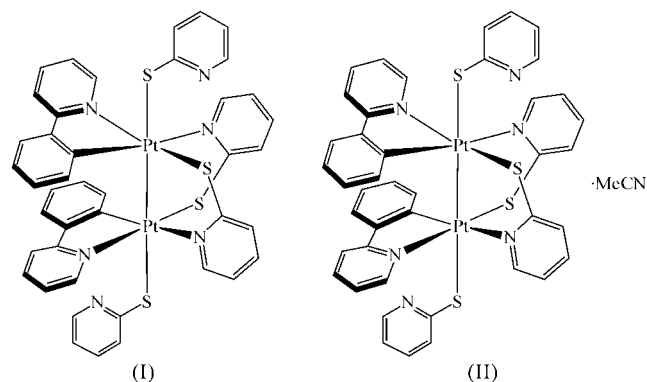
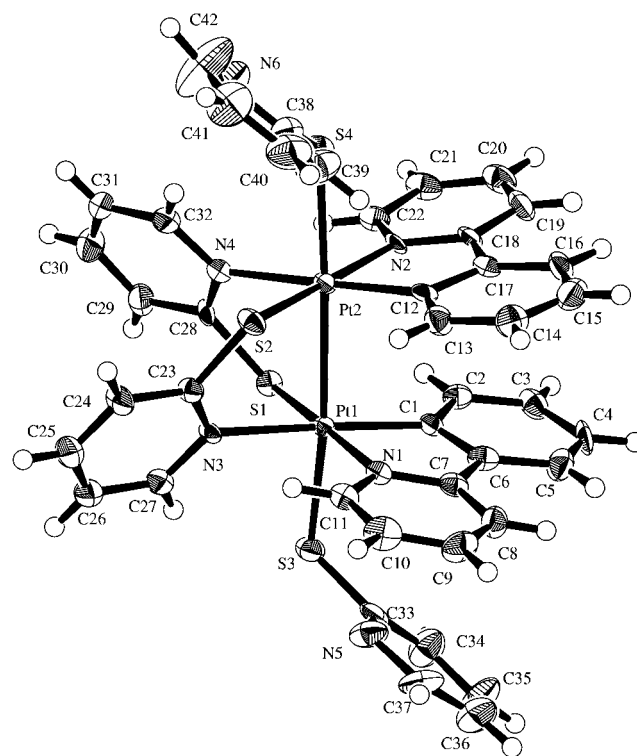


Fig. 1 shows the molecular structure of (I). As in the case of the [Pt<sub>2</sub>(ppy)<sub>2</sub>(pyt)<sub>2</sub>] and [Pt<sub>2</sub>Cl<sub>2</sub>(ppy)<sub>2</sub>(pyt)<sub>2</sub>] complexes, only the *anti* form, with a head-to-tail configuration of the bridging pyt ligands, was produced for this dinuclear complex, because the strong *trans* influence of the deprotonated C atom in ppy prefers the N atom to the S atom of the pyt ligand at the *trans* position (Koshiyama *et al.*, 2004).

The Pt—C bond distances of (I) are comparable with those reported for other cyclometallated platinum complexes containing ppy (1.98–2.03 Å; Chassot *et al.*, 1984; Mdleleni *et al.*, 1995; Yamaguchi *et al.*, 2004). The pyt ligands at the axial



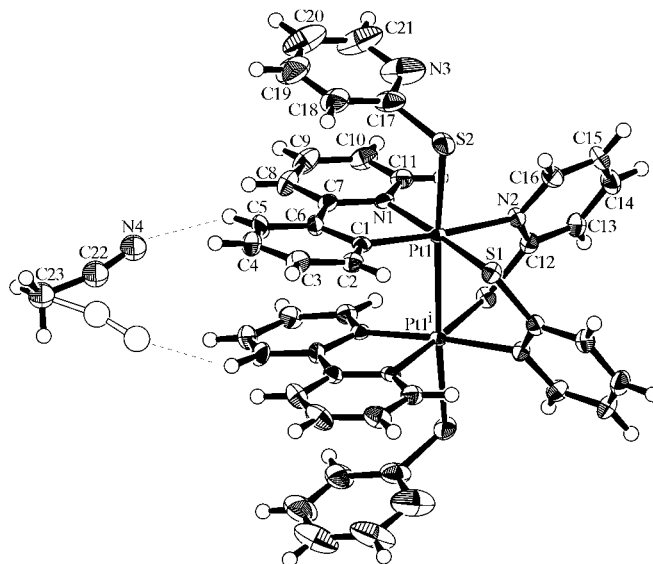
**Figure 1**  
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

sites are coordinated to the respective Pt cations by the S<sup>-</sup> anions. The orientation is likely to be regulated by a dimeric interaction, as shown in Fig. 2. Two complexes related by an inversion centre form a  $\pi$ - $\pi$  stack of pyt ligands, with an interplanar spacing of 3.52 (1) Å.

There are hydrogen bonds (Table 2) between the C—H groups in the aromatic rings and the S or N atoms in the axial pyt ligands. As a result, the pyt ligand containing atom S4 is oriented in the opposite direction to the  $\pi$ - $\pi$  stack, whereas the pyt ligand at the other axial site is located over the ppy ligand. The large displacements for the axial pyridine rings indicate that the monodentate ligands fluctuate easily.

For compound (II), on the other hand, a completely different orientation of the axial pyt ligands was found, as shown in Fig. 3. In this case, both axial pyt ligands are located over the ppy ligands. The complex molecule in (II) has a twofold axis passing through the centre of the Pt—Pt bond. An acetonitrile solvent molecule was found to be disordered, forming hydrogen bonds (Table 4) with the ppy ligands.

Some geometric characteristics for (II) can be seen in connection with the arrangement of the axial pyt ligands. The dihedral angle between two ppy ligands for (II) is much smaller than that for (I) [21.0 (2)° for (I), *cf.* 11.7 (1)° for (II)]. The interplanar spacings, defined as the average distance of the atoms in one ppy from the least-squares plane of the other, are similar [3.4 (1) Å for (I) and 3.30 (7) Å for (II)]. These values indicate that the axial pyt ligands in (II) effectively stabilize the stacking of the ppy ligands. In fact, the dihedral angle and the interplanar spacing between the ppy ligand and the adjacent axial pyt ligand in (II) are 17.3 (1)° and 3.3 (1) Å, respectively, suggesting  $\pi$ - $\pi$  interactions through a pyt-ppy-



**Figure 3**

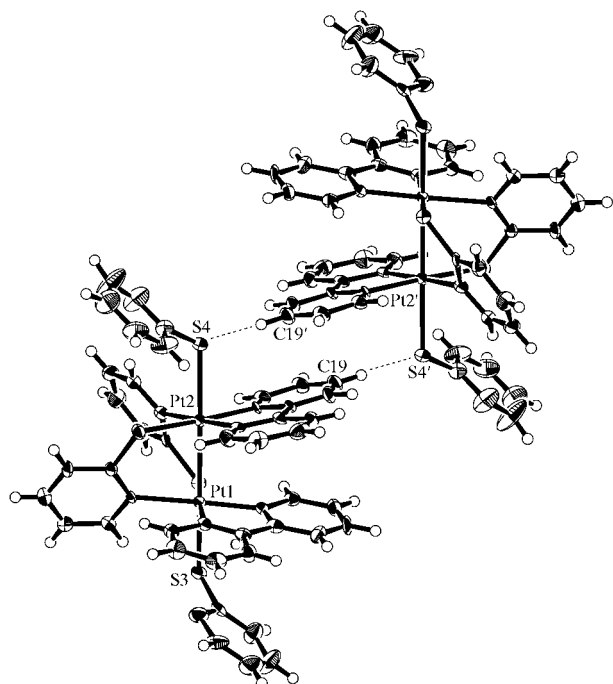
The molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level, except those for the solvated acetonitrile, which are drawn as ideal spheres of arbitrary radii. H atoms are also shown as small spheres of arbitrary radii. The disordered atoms of the acetonitrile molecule are shown as open circles. [Symmetry code: (i)  $-x, y, \frac{1}{2} - z$ .]

ppy-pyt ordering of ligands. The smaller Pt—S—C angle at the axial positions for (II) [103.7 (2)°] compared with those for (I) [109.7 (3)–112.1 (4)°] also supports these interactions.

For (I) and (II), the Pt—Pt distances of 2.6514 (5) and 2.6650 (2) Å, respectively, are normal for a Pt<sup>III</sup>—Pt<sup>III</sup> single bond but slightly longer than those for [Pt<sub>2</sub>Cl<sub>2</sub>(pyt)<sub>4</sub>] and its analogues held by four bridging pyt ligands: Pt—Pt = 2.532 (1) Å in *cis*-[Pt<sub>2</sub>Cl<sub>2</sub>(pyt)<sub>4</sub>], 2.539 (1) Å in *trans*-[Pt<sub>2</sub>I<sub>2</sub>(4-mpyt)<sub>4</sub>] (4-mpyt is the 4-methylpyridine-2-thiolate anion) and 2.566 (2) Å in *cis*-[Pt<sub>2</sub>(CN)<sub>2</sub>(pyt)<sub>4</sub>] (Umakoshi & Sasaki, 1993). In addition, it is interesting to note that the Pt—Pt distances for (I) and (II) are also slightly longer than that in [Pt<sub>2</sub>Cl<sub>2</sub>(ppy)<sub>2</sub>(pyt)<sub>2</sub>] [Pt—Pt = 2.615 (1) Å; Koshiyama *et al.*, 2004]. The coordination geometries of the equatorial planes for (I) and (II) are very similar to that for [Pt<sub>2</sub>Cl<sub>2</sub>(ppy)<sub>2</sub>(pyt)<sub>2</sub>]. Thus, the difference in the Pt—Pt distances could be attributed to the *trans* influence of the axial ligands, with the pyt ligand stronger than Cl<sup>-</sup>.

## Experimental

(Bu<sub>4</sub>N)[PtCl<sub>2</sub>(ppy)] was prepared according to the literature method of Mdeleleni *et al.* (1995). The preparation of the dinuclear Pt<sup>II</sup> complex [Pt<sub>2</sub>(ppy)<sub>2</sub>(pyt)<sub>2</sub>] was reported previously (Koshiyama *et al.*, 2004). The trivalent complex [Pt<sub>2</sub>(ppy)<sub>2</sub>(pyt)<sub>4</sub>] was prepared in two different ways. The brown powder of (I) was produced by stirring an acetonitrile–ethanol solution (8:2 *v/v*, 100 ml) of [Pt<sub>2</sub>(ppy)<sub>2</sub>(pyt)<sub>2</sub>] (92 mg, 0.1 mmol) and Hpyt (22 mg, 0.2 mmol) at room temperature for 2 d (yield 81 mg). The crude product contained *ca* 25% of unoxidized [Pt<sub>2</sub>(ppy)<sub>2</sub>(pyt)<sub>2</sub>], according to the <sup>1</sup>H NMR spectrum. Brown needle-shaped crystals of (I) were obtained by recrystalliza-



**Figure 2**

The dimeric arrangement of (I). Atoms labelled with a prime are at the symmetry position ( $1 - x, 1 - y, -z$ ).

tion from an acetonitrile solution. The dark-red–purple powder of (II) was precipitated by the reaction of (Bu<sub>4</sub>N)[PtCl<sub>2</sub>(ppy)] (342 mg, 0.52 mmol) and Hpyt (58 mg, 0.52 mmol) in water (60 ml) at 343 K for 3 d (yield 77 mg, 26%). Recrystallization from acetonitrile gave dark-red prismatic crystals of (II). Both (I) and (II) exhibited essentially the same <sup>1</sup>H NMR spectra (DMSO-*d*<sub>6</sub>): δ 6.33 (*t*, 2H), 6.65 (*t*, 2H), 6.89 (*t*, 2H), 7.02 (*d*, 2H), 7.11 (*t*, 2H), 7.18 (*d*, 2H), 7.29 (*br*, 4H), 7.40 (*t*, 4H), 7.61 (*d*, 4H), 7.73 (*t*, 2H), 7.80 (*t*, 2H), 8.47 (*d*, 2H), 8.50 (*br*, 2H).

**Compound (I)**

*Crystal data*

[Pt<sub>2</sub>(C<sub>11</sub>H<sub>8</sub>N)<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>NS)<sub>4</sub>]  
*M<sub>r</sub>* = 1139.18  
 Triclinic, *P* $\bar{1}$   
*a* = 11.3534 (2) Å  
*b* = 12.3455 (2) Å  
*c* = 15.3328 (4) Å  
 $\alpha$  = 67.918 (9)°  
 $\beta$  = 84.242 (13)°  
 $\gamma$  = 69.034 (10)°  
*V* = 1858.1 (2) Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 2.036 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 5557 reflections  
 $\theta$  = 3.1–27.5°  
 $\mu$  = 7.76 mm<sup>-1</sup>  
*T* = 173.1 K  
 Needle, brown  
 0.22 × 0.04 × 0.04 mm

*Data collection*

Rigaku Mercury CCD diffractometer  
 $\omega$  scans  
 Absorption correction: numerical (NUMABS; Higashi, 1999)  
*T<sub>min</sub>* = 0.284, *T<sub>max</sub>* = 0.733  
 14 354 measured reflections  
 8029 independent reflections  
 6772 reflections with *F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)  
*R<sub>int</sub>* = 0.036  
 $\theta_{\text{max}}$  = 27.5°  
*h* = -14 → 13  
*k* = -16 → 16  
*l* = -19 → 18

*Refinement*

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.048  
*wR*(*F*<sup>2</sup>) = 0.085  
*S* = 1.17  
 8029 reflections  
 488 parameters  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0141P)^2 + 9.3496P]$   
 where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3  
 ( $\Delta\sigma$ )<sub>max</sub> = 0.001  
 $\Delta\rho_{\text{max}}$  = 0.90 e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}}$  = -1.52 e Å<sup>-3</sup>

**Table 1**  
 Selected geometric parameters (Å, °) for (I).

|            |            |             |            |
|------------|------------|-------------|------------|
| Pt1–Pt2    | 2.6514 (5) | Pt2–S2      | 2.306 (2)  |
| Pt1–S1     | 2.305 (2)  | Pt2–S4      | 2.466 (3)  |
| Pt1–S3     | 2.479 (3)  | Pt2–N2      | 2.066 (5)  |
| Pt1–N1     | 2.066 (5)  | Pt2–N4      | 2.184 (6)  |
| Pt1–N3     | 2.189 (6)  | Pt2–C12     | 2.004 (8)  |
| Pt1–C1     | 2.017 (8)  |             |            |
| S1–Pt1–Pt2 | 86.69 (6)  | Pt1–Pt2–C12 | 93.9 (3)   |
| Pt1–Pt2–S2 | 87.21 (6)  | Pt1–Pt2–S4  | 175.06 (4) |
| S3–Pt1–Pt2 | 167.57 (4) | S3–Pt1–S1   | 80.88 (7)  |
| N1–Pt1–Pt2 | 97.7 (2)   | N1–Pt1–S1   | 174.3 (2)  |
| Pt1–Pt2–N2 | 96.3 (2)   | N3–Pt1–S1   | 88.5 (1)   |
| N3–Pt1–Pt2 | 86.1 (2)   | C1–Pt1–S1   | 95.8 (2)   |
| Pt1–Pt2–N4 | 86.2 (2)   | Pt1–S3–C33  | 109.7 (3)  |
| C1–Pt1–Pt2 | 94.7 (3)   | Pt2–S4–C38  | 112.1 (4)  |

**Table 2**  
 Hydrogen-bond geometry (Å, °) for (I).

| <i>D</i> –H··· <i>A</i>    | <i>D</i> –H | H··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> –H··· <i>A</i> |
|----------------------------|-------------|---------------|-----------------------|-------------------------|
| C19–H19···S4 <sup>i</sup>  | 0.93        | 2.76          | 3.60 (1)              | 150                     |
| C26–H26···N5 <sup>ii</sup> | 0.93        | 2.76          | 3.54 (1)              | 142                     |

Symmetry codes: (i) 1 – *x*, 1 – *y*, –*z*; (ii) –*x*, –*y*, 1 – *z*.

**Compound (II)**

*Crystal data*

[Pt<sub>2</sub>(C<sub>11</sub>H<sub>8</sub>N)<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>NS)<sub>4</sub>] $\cdot$ C<sub>2</sub>H<sub>3</sub>N  
*M<sub>r</sub>* = 1180.23  
 Monoclinic, *C*2/*c*  
*a* = 16.390 (1) Å  
*b* = 15.5766 (9) Å  
*c* = 17.534 (2) Å  
 $\beta$  = 118.199 (3)°  
*V* = 3945.3 (5) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.987 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 6621 reflections  
 $\theta$  = 3.6–27.5°  
 $\mu$  = 7.31 mm<sup>-1</sup>  
*T* = 173.1 K  
 Prism, dark red  
 0.40 × 0.20 × 0.18 mm

*Data collection*

Rigaku Mercury CCD diffractometer  
 $\omega$  scans  
 Absorption correction: numerical (NUMABS; Higashi 1999)  
*T<sub>min</sub>* = 0.148, *T<sub>max</sub>* = 0.268  
 15 006 measured reflections  
 4432 independent reflections  
 3887 reflections with *F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)  
*R<sub>int</sub>* = 0.028  
 $\theta_{\text{max}}$  = 27.5°  
*h* = -21 → 21  
*k* = -19 → 20  
*l* = -22 → 22

*Refinement*

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.031  
*wR*(*F*<sup>2</sup>) = 0.074  
*S* = 1.09  
 4432 reflections  
 255 parameters  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0329P)^2 + 33.7943P]$   
 where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3  
 ( $\Delta\sigma$ )<sub>max</sub> = 0.007  
 $\Delta\rho_{\text{max}}$  = 3.15 e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}}$  = -1.59 e Å<sup>-3</sup>

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

|                         |            |            |           |
|-------------------------|------------|------------|-----------|
| Pt1–Pt1 <sup>i</sup>    | 2.6650 (2) | Pt1–N1     | 2.072 (4) |
| Pt1–S1                  | 2.301 (1)  | Pt1–N2     | 2.180 (4) |
| Pt1–S2                  | 2.492 (2)  | Pt1–C1     | 2.011 (4) |
| S1–Pt1–Pt1 <sup>i</sup> | 87.20 (3)  | C1–Pt1–S1  | 96.0 (1)  |
| S2–Pt1–Pt1 <sup>i</sup> | 172.21 (4) | N1–Pt1–S2  | 94.4 (1)  |
| N1–Pt1–Pt1 <sup>i</sup> | 93.3 (1)   | N2–Pt1–S2  | 93.2 (1)  |
| N2–Pt1–Pt1 <sup>i</sup> | 87.3 (1)   | C1–Pt1–S2  | 84.6 (1)  |
| C1–Pt1–Pt1 <sup>i</sup> | 95.5 (1)   | Pt1–S2–C17 | 103.7 (2) |
| S2–Pt1–S1               | 85.05 (5)  | N2–Pt1–N1  | 95.7 (1)  |
| N1–Pt1–S1               | 176.3 (1)  | C1–Pt1–N1  | 80.3 (2)  |
| N2–Pt1–S1               | 88.0 (1)   | C1–Pt1–N2  | 175.2 (1) |

Symmetry code: (i) –*x*, *y*,  $\frac{1}{2}$  – *z*.

**Table 4**  
 Hydrogen-bond geometry (Å, °) for (II).

| <i>D</i> –H··· <i>A</i>   | <i>D</i> –H | H··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> –H··· <i>A</i> |
|---------------------------|-------------|---------------|-----------------------|-------------------------|
| C5–H5···N4                | 0.93        | 2.57          | 3.38 (3)              | 146                     |
| C14–H14···N3 <sup>i</sup> | 0.93        | 2.48          | 3.36 (1)              | 157                     |

Symmetry codes: (i)  $\frac{1}{2}$  – *x*,  $\frac{3}{2}$  – *y*, 1 – *z*.

For both (I) and (II), large ratios of *U*<sub>eq</sub>(max)/*U*<sub>eq</sub>(min) for C and N atoms were observed because of the fluctuation of the axial pyt ligands. The possibility of rotational disorder of the axial pyt ligands was rejected because of the steric factors of the packing. Other assignments of the N atoms would cause steric hindrance of the C–H moiety. The acetonitrile solvent molecule in (II) was found to be disordered, with the two components related by a twofold axis. The two possible sites share the terminal C23 atom, which lies on the

twofold axis. The non-H atoms of the solvent molecule were refined isotropically. The H atoms of the methyl group (C23) of the acetonitrile solvent molecule were positioned geometrically as two disordered sites having equal occupancies of 0.5 without further refinement. All other H atoms were treated as riding, with C–H = 0.93 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . For (I), the deepest hole of residual density was found 0.86 Å from atom Pt1. For (II), peaks of 3.15 and 2.24 e Å<sup>-3</sup> and a hole of -1.59 e Å<sup>-3</sup> were observed 0.78, 1.23 and 0.73 Å from atoms C5, N4 and Pt1, respectively.

For both compounds, data collection: *CrystalClear* (Molecular Structure Corporation & Rigaku, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MS, 2004). Program(s) used to solve structure: *DIRDIF99* (Beurskens *et al.*, 1992) for (I); *SHELXS97* (Sheldrick, 1997) for (II). For both compounds, program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *CrystalStructure*.

This work was supported by a Grant-in-Aid for Scientific Research, priority area 417 (grant No. 15033247), from MEXT, Japan, a Grant-in-Aid for Scientific Research (grant No. 15350034) from JSPS, Japan, and a Nara Women's University Intramural Grant for Project Research.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1216). Services for accessing these data are described at the back of the journal.

## References

- Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., García-Granda, S., Gould, R. O., Smits, J. M. M. & Smykalla, C. (1992). *The DIRDIF Program System*. Technical Report. Crystallography Laboratory, University of Nijmegen, The Netherlands.
- Chassot, L., Müller, E. & von Zelewsky, A. (1984). *Inorg. Chem.* **23**, 4249–4253.
- Higashi, T. (1999). *NUMABS*. Rigaku Corporation, Tokyo, Japan.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Koshiyama, T., Omura, A. & Kato, M. (2004). *Chem. Lett.* **33**, 1386–1387.
- Lippard, S. J. (1982). *Science*, **218**, 1075–1082.
- Mdleleni, M. M., Bridgewater, J. S., Watts, R. J. & Ford, P. C. (1995). *Inorg. Chem.* **34**, 2334–2342.
- Molecular Structure Corporation & Rigaku (2001). *CrystalClear*. Version 1.3. MSC, 9009 New Trails Drive, The Woodlands, TX 77381, USA, and Rigaku Corporation, Tokyo, Japan.
- Rigaku/MS (2004). *CrystalStructure*. Version 3.6.0. Rigaku/MS, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.
- Roundhill, D. M., Gray, H. B. & Che, C.-M. (1989). *Acc. Chem. Res.* **22**, 55–61.
- Sheldrick, G. M. (1997). *SHELXS97*. University of Göttingen, Germany.
- Umakoshi, K. & Sasaki, Y. (1993). *Adv. Inorg. Chem.* **40**, 187–239.
- Yamaguchi, T., Kubota, O. & Ito, T. (2004). *Chem. Lett.* **33**, 190–191.