

Dichloro(4,4'-dialkyl-2,2'-bipyridine- κ^2N,N')platinum(II), where alkyl is pentyl and heptyl

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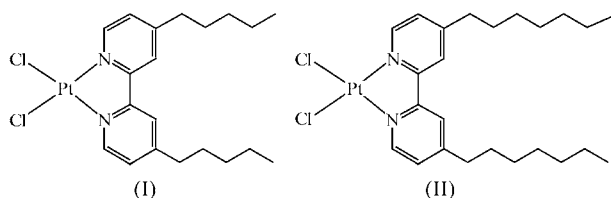
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Dichloro(4,4'-dipentyl-2,2'-bipyridine- κ^2N,N')platinum(II), [PtCl₂(C₂₀H₂₈N₂)], adopts a discrete π - π stacking structure, where the alkyl chains are located in a random manner. In contrast, dichloro(4,4'-diheptyl-2,2'-bipyridine- κ^2N,N')platinum(II), [PtCl₂(C₂₄H₃₆N₂)], forms a layer structure comprised of alkyl chain layers and paired coordination sites, as observed for analogous complexes with longer alkyl chains.

Comment

It is well known that long alkyl chains play an important role in controlling molecular arrangement. Such properties of long alkyl chains have been exploited in metal complexes in order to arrange them on the surface of matrices as monolayers or thin-layer films (Valenty *et al.*, 1979; Borgarello *et al.*, 1981). It is also known that square-planar Pt^{II} complexes are often stacked in the solid state so that they exhibit characteristic colours and intense luminescence (Houilding & Miskowski, 1991). Thus, the introduction of alkyl chains into Pt^{II} complexes would be expected to enhance and/or control their self-assembled properties. Such complexes are also expected



to exhibit amphiphilic properties, which are induced by the combination of a hydrophilic coordination site and the hydrophobic alkyl chains. In fact, we recently reported the Langmuir–Blodgett film of dicyano(5,5'-diundecyl-2,2'-bipyridine)platinum(II), which exhibits characteristic luminescence based on Pt \cdot ·Pt interactions with increasing surface pressure (Kobayashi *et al.*, 2004). We have also determined the

crystal structure of compound (III), the dichloroplatinum(II) complex with 4,4'-dinonyl-2,2'-bipyridine (dC₉bpy) (Kato & Ikemori, 2003). In (III), the molecules are arranged in an orderly fashion, forming an alternating layer structure of the alkyl-chain layers and paired coordination sites. Such a layer arrangement indicates that the discrimination between the hydrophobic and hydrophilic sites is clear. In order to investigate the effect of the alkyl chains on the arrangement of such Pt^{II} complexes, we have now synthesized a series of Pt^{II}

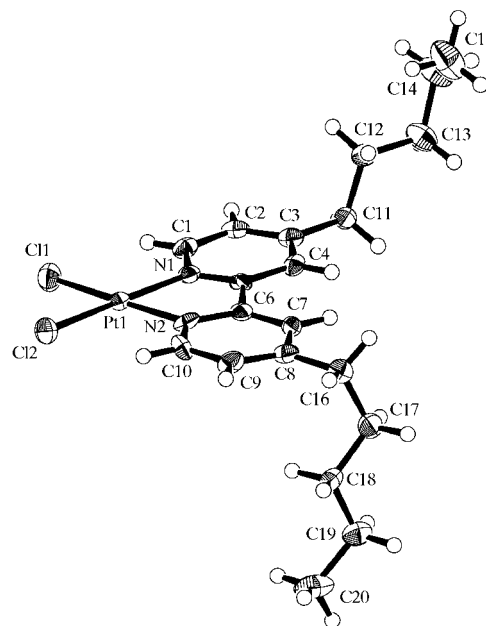


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are plotted at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

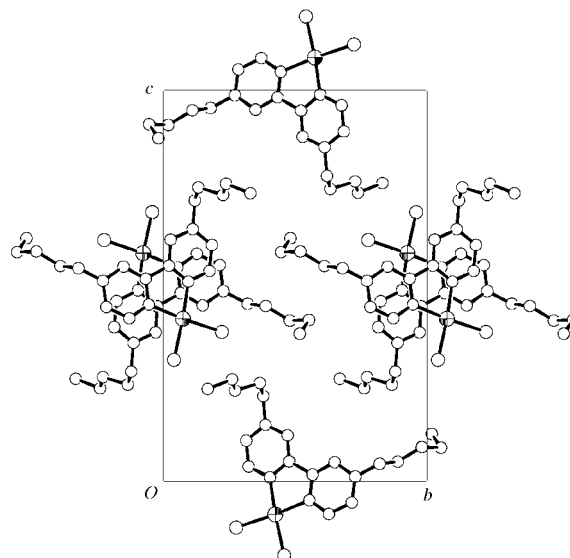


Figure 2
The packing structure of (I), viewed down the *a* axis. H atoms have been omitted for clarity.

complexes bearing alkyl chains of different lengths. In this paper, we report the crystal structures of two dichloro-platinum(II) complexes, (I) and (II), containing 4,4'-dipentyl-2,2'-bipyridine (dC₅bpy) and 4,4'-diheptyl-2,2'-bipyridine (dC₇bpy) ligands, respectively.

Fig. 1 shows the molecular structure of (I). The coordination geometry is planar, including the bipyridine moiety, with a deviation of 0.17 (1) Å for atom C8, but the two alkyl chains are located randomly out of the coordination plane. The complexes are stacked at the bipyridine moieties along the *a* axis, with an interplanar spacing of 3.27 (2) Å (Fig. 2). In this stack, the Pt···Pt distance is 5.1936 (5) Å. There is no particular orientation of the pentyl groups in the packing structure. For this complex, π–π stacking would be a main factor in controlling the packing structure. A similar stacking structure was reported for the analogous complex bearing *tert*-butyl groups, [PtCl₂(bu₂bpy)] (bu₂bpy is 4,4'-di-*tert*-butyl-2,2'-bipyridine; Achar & Catalano, 1997). The arrangement of the

pentyl groups in (I) could be one of several conformations. In fact, a different crystal form, a solvate, was deposited from the same solution as used for the crystallization of complex (I).

In contrast with the above, complex (II) exhibits a well ordered arrangement of the alkyl chains. As shown in Fig. 3, the heptyl groups are extended in the same direction and the complex molecules are arranged to form a layer structure (Fig. 4). There is an alternating arrangement of the alkyl layers and the metal-coordination parts. No particular interactions are observed between the alkyl chains and the Cl ligands. There is no C–H···Cl distance shorter than 2.95 Å, the sum of the van der Waals radii of H and Cl (Bondi, 1964). The molecular arrangement of (II) is essentially the same as that of (III). In proportion to the length of the alkyl chain, the width of the alkyl layers for the dC₇bpy complex is narrower than that for the dC₉bpy complex. This is reflected in the smaller value of the lattice parameter of the *a* axis [15.102 (8) Å, space group *P2₁/c*] for (II) compared with that of the corresponding *c* axis for (III) [17.652 (2) Å, *P2₁/a*], while the other lattice parameters are similar. The coordination sites are arranged in a face-to-face fashion, with an interplanar spacing of 3.40 (1) Å. The Pt···Pt distance is long enough to indicate no interaction between them [5.3416 (2) Å]. Thus, seven or more C atoms in the alkyl chains are necessary for the adoption of a layer arrangement.

Cocker & Bachman (2004) reported the crystal structures of Pt complexes containing a series of 4,4'-dialkyl-2,2'-bipyridines and a benzene-1,2-dithiolate ion. These complexes are roughly planar, including the extension of the alkyl chains, and are packed in an overlapping arrangement of the π–π stack of the coordination sites and the alkyl chains. These packing structures are different from the segregated and alternating layer structures of (II) and (III). Thus, the alternating layer structures of (II) and (III) would reflect good amphiphilic properties for dichloro-platinum(II) complexes. Further studies are in progress regarding related complexes bearing alkyl chains with even numbers of C atoms, in addition to those with odd numbers of C atoms.

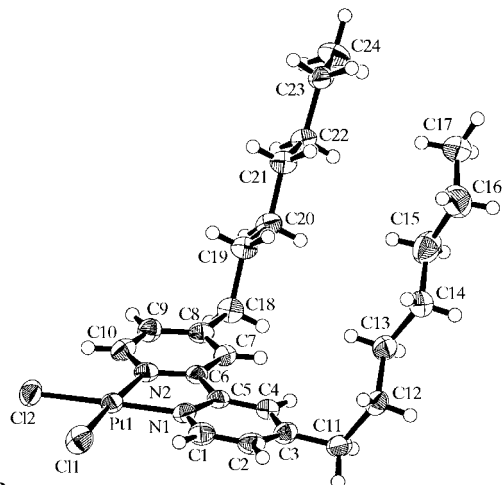


Figure 3
The molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are plotted at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

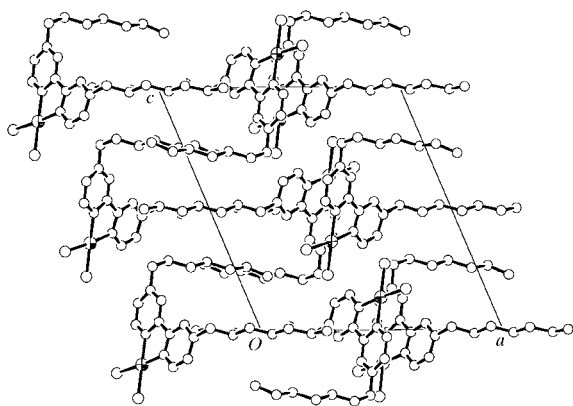


Figure 4
The packing structure of (II), viewed down the *b* axis. H atoms have been omitted for clarity.

Experimental

4,4'-Dipentyl-2,2'-bipyridine (dC₅bpy) and 4,4'-diheptyl-2,2'-bipyridine (dC₇bpy) were prepared by a similar method to that reported previously by Ellison & Iwamoto (1983), using 1-bromobutane for dC₅bpy and 1-bromohexane for dC₇bpy. The products were purified by silica-gel column chromatography (eluent: toluene–diethyl ether, 1:1). For dC₅bpy, ¹H NMR (CDCl₃): δ 0.90 (*t*, 6H, CH₃), 1.36 (*br*, 8H, CH₂), 1.70 (*m*, 4H, CH₂), 2.69 (*t*, 4H, CH₂), 7.14 (*d*, 2H, bpy), 8.24 (*s*, 2H, bpy), 8.57 (*d*, 2H, bpy); ESI–MS: *m/z* 296 ([*M* + H]⁺). For dC₇bpy, ¹H NMR (CDCl₃): δ 0.88 (*br*, 6H, CH₃), 1.31 (*br*, 16H, CH₂), 1.69 (*br*, 4H, CH₂), 2.69 (*t*, 4H, CH₂), 7.13 (*d*, 2H, bpy), 8.23 (*s*, 2H, bpy), 8.56 (*d*, 2H, bpy); ESI–MS: *m/z* 353 ([*M* + H]⁺).

The title Pt^{II} complexes were obtained by reaction of equimolar amounts of K₂[PtCl₄] and the respective ligand in an acidic aqueous solution at 343 K. After heating for 2 h, a yellow powder of (I) or (II) was deposited [yield: 30% for (I); 68% for (II)]. Recrystallization from dimethylformamide gave yellow needle-shaped crystals for (I) (m.p. 483–484 K) and yellow plate-shaped crystals for (II) (m.p.

421–424 K). For (I), ¹H NMR (CDCl₃): δ 0.93 (t, 3H, CH₃), 1.39 (br, 8H, CH₂), 1.75 (br, 4H, CH₂), 2.81 (t, 4H, CH₂), 7.20 (d, 2H, bpy), 7.90 (s, 2H, bpy), 9.20 (d, 2H, bpy). For (II), ¹H NMR (CDCl₃): δ 0.90 (t, 6H, CH₃), 1.30 (br, 8H, CH₂), 1.36 (br, 8H, CH₂), 1.75 (br, 4H, CH₂), 2.81 (t, 4H, CH₂), 7.20 (d, 2H, bpy), 7.90 (s, 2H, bpy), 9.19 (d, 2H, bpy).

Compound (I)

Crystal data

[PtCl₂(C₂₀H₂₈N₂)]
M_r = 562.45
 Monoclinic, *P*₂₁/*c*
a = 7.1791 (19) Å
b = 13.853 (4) Å
c = 20.609 (5) Å
 β = 94.3564 (9)°
V = 2043.6 (9) Å³
Z = 4
D_x = 1.828 Mg m⁻³
 Mo Kα radiation
 Cell parameters from 6090 reflections
 θ = 3.1–27.5°
 μ = 7.11 mm⁻¹
T = 173.1 K
 Needle, yellow
 0.45 × 0.10 × 0.10 mm

Data collection

Rigaku Mercury CCD area-detector diffractometer
 ω scans
 Absorption correction: numerical (NUMABS; Higashi, 1999)
T_{min} = 0.578, *T_{max}* = 0.868
 15324 measured reflections
 4537 independent reflections
 3263 reflections with *F*² > 2σ(*F*²)
R_{int} = 0.098
 θ_{max} = 27.5°
h = -9 → 8
k = -17 → 17
l = -26 → 26

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.067
wR(*F*²) = 0.180
S = 0.97
 4537 reflections
 227 parameters
 H-atom parameters constrained
w = 1/[σ²(*F_o*²) + (0.0864*P*)²]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} = 0.001
 Δρ_{max} = 2.30 e Å⁻³
 Δρ_{min} = -3.54 e Å⁻³

Table 1

Selected geometric parameters (Å, °) for (I).

| | | | |
|-------------|------------|------------|-----------|
| Pt1—Cl1 | 2.294 (3) | Pt1—N1 | 2.026 (8) |
| Pt1—Cl2 | 2.295 (2) | Pt1—N2 | 2.007 (9) |
| Cl1—Pt1—Cl2 | 89.50 (11) | Cl2—Pt1—N1 | 175.1 (2) |
| Cl1—Pt1—N1 | 95.1 (2) | Cl2—Pt1—N2 | 95.6 (2) |
| Cl1—Pt1—N2 | 174.7 (2) | N1—Pt1—N2 | 79.9 (3) |

Compound (II)

Crystal data

[PtCl₂(C₂₄H₃₆N₂)]
M_r = 618.56
 Monoclinic, *P*₂₁/*c*
a = 15.102 (8) Å
b = 10.781 (6) Å
c = 16.525 (10) Å
 β = 112.570 (3)°
V = 2484 (2) Å³
Z = 4
D_x = 1.654 Mg m⁻³
 Mo Kα radiation
 Cell parameters from 7972 reflections
 θ = 3.1–27.5°
 μ = 5.85 mm⁻¹
T = 173.1 K
 Plate, yellow
 0.37 × 0.30 × 0.17 mm

Data collection

Rigaku Mercury CCD area-detector diffractometer
 ω scans
 Absorption correction: numerical (NUMABS; Higashi, 1999)
T_{min} = 0.182, *T_{max}* = 0.363
 18483 measured reflections
 5522 independent reflections
 4970 reflections with *F*² > 2σ(*F*²)
R_{int} = 0.027
 θ_{max} = 27.5°
h = -19 → 17
k = -14 → 14
l = -17 → 21

Table 2

Selected geometric parameters (Å, °) for (II).

| | | | |
|-------------|-------------|------------|-------------|
| Pt1—Cl1 | 2.2956 (15) | Pt1—N1 | 2.015 (3) |
| Pt1—Cl2 | 2.3019 (11) | Pt1—N2 | 2.014 (3) |
| Cl1—Pt1—Cl2 | 89.66 (5) | Cl2—Pt1—N1 | 174.64 (11) |
| Cl1—Pt1—N1 | 94.88 (12) | Cl2—Pt1—N2 | 95.14 (11) |
| Cl1—Pt1—N2 | 175.19 (12) | N1—Pt1—N2 | 80.31 (16) |

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.041
wR(*F*²) = 0.115
S = 1.12
 5522 reflections
 263 parameters
 H-atom parameters constrained
w = 1/[σ²(*F_o*²) + (0.0723*P*)² + 0.9111*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} = 0.001
 Δρ_{max} = 3.87 e Å⁻³
 Δρ_{min} = -1.83 e Å⁻³

H atoms were refined using a riding model, with C—H = 0.95, 0.98 and 0.99 Å for pyridyl, methyl and methylene groups, respectively, and with *U*_{iso}(H) = 1.2*U*_{eq}(C). For (I), the large ratio (3.7) of *U*_{eq}(max)/*U*_{eq}(min) for carbon is attributed to the fluctuation of the end of the pentyl groups. Several peaks of residual electron density (2.0–2.3 e Å⁻³) and the deepest hole of -3.5 e Å⁻³ were observed within 1.0 Å of atom Pt1 for (I). For (II), peaks of 3.9 and 3.4 e Å⁻³ and a hole of -1.8 e Å⁻³ were located 1.63, 1.78 and 0.73 Å from atoms C2, C24 and Pt1, respectively.

For both compounds, data collection: *CrystalClear* (Rigaku, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSK, 2004); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *CrystalStructure*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1249). Services for accessing these data are described at the back of the journal.

References

Achar, S. & Catalano, V. J. (1997). *Polyhedron*, **16**, 1555–1561.
 Altomare, A., Casciarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
 Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
 Borgarello, E., Kiwi, J., Pelizzetti, E., Visca, M. & Grätzel, M. (1981). *Nature*, **289**, 158–160.
 Cocker, T. M. & Bachman, R. E. (2004). *Mol. Cryst. Liq. Cryst.* **408**, 1–19.
 Ellison, D. K. & Iwamoto, R. T. (1983). *Tetrahedron Lett.* **24**, 31–32.
 Higashi, T. (1999). *NUMABS*. Rigaku Corporation, Tokyo, Japan.
 Houlding, V. H. & Miskowski, V. M. (1991). *Coord. Chem. Rev.* **111**, 145–152.
 Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 Kato, M. & Ikemori, M. (2003). *Acta Cryst.* **C59**, m25–m26.
 Kobayashi, K., Kishi, S., Kato, M., Ishizaka, S., Kitamura, N. & Yamagishi, A. (2004). *J. Phys. Chem. B*, **108**, 18665–18669.
 Rigaku (2001). *CrystalClear*. Version 1.3. Rigaku Corporation, 3-9-12 Akishima, Tokyo, Japan.
 Rigaku/MSK (2004). *CrystalStructure*. Version 3.7.0. Rigaku/MSK, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.
 Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
 Valenty, S. J., Behnken, D. E. & Gaines, G. L. Jr (1979). *Inorg. Chem.* **18**, 2160–2164.