

Cyclopalladated and Cycloplatinated Complexes of 6-Phenyl-2,2'-bipyridine: Platinum-Platinum Interactions in the Solid State

Edwin C. Constable,^a Roland P. G. Henney,^a Troy A. Leese,^a and Derek A. Tocher^{*b}

^a University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

^b Department of Chemistry, University College London, 20 Gordon St., London WC1H 0AJ, U.K.

The crystal and molecular structures of the complexes [PdLCl] and [PtL(MeCN)][PF₆] (HL = 6-phenyl-2,2'-bipyridine) have been determined; in each case, the cyclometallated ligand behaves as a terdentate C,N,N-donor, analogous to 2,2':6',2''-terpyridine; in the case of the platinum complex metal-metal interactions are observed, giving rise to alternate long-short contacts [3.28(1), 4.59(1) Å] between cations.

Cyclometallated 2-phenylpyridine ligands may be regarded as C,N-donor analogues of the classical ligand 2,2'-bipyridine,¹ and such cyclometallated complexes have been shown to possess useful photophysical and photoelectrochemical properties.² We have shown that 6-(2'-thienyl)-2,2'-bipyridine³ and 6-phenyl-2,2'-bipyridine⁴ form cyclometallated complexes which are C,N,N-donor analogues of 2,2':6',2''-terpyridine, and have demonstrated further that molecular configurations and crystal packing are enhanced by π -stacking interactions between aromatic rings.

The complexes [MLCl] (M = Pd or Pt) are prepared by the reaction of [MCl₄]²⁻ with HL and exist in a single (yellow or orange) form. Solvolysis in acetonitrile results in the formation of the complexes [ML(MeCN)]⁺, but whereas [PdL(MeCN)][PF₆] is yellow, [PtL(MeCN)][PF₆] exists in purple-blue or orange forms depending upon the method of crystallisation. Rapid precipitation results in the deposition of a purple microcrystalline material, whereas recrystallisation yields orange needles. Solutions of both forms exhibit identical ¹H NMR spectra. In order to investigate further

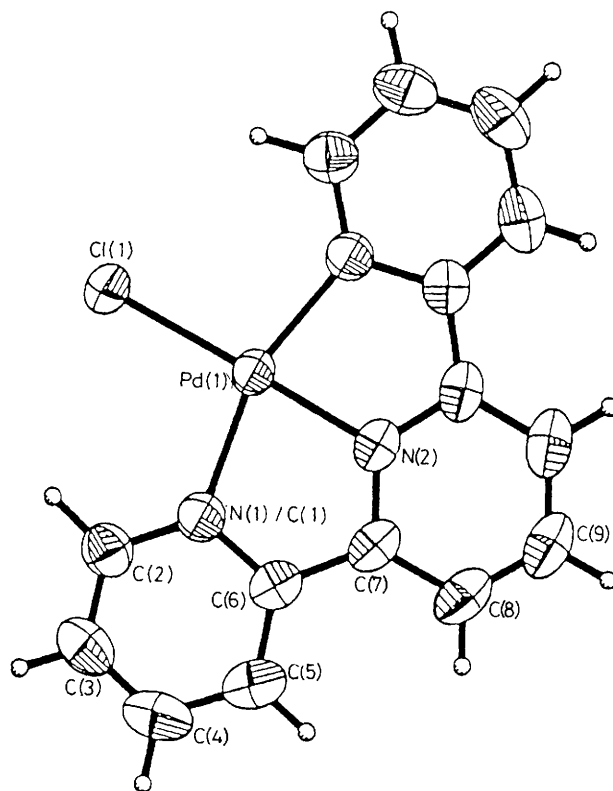
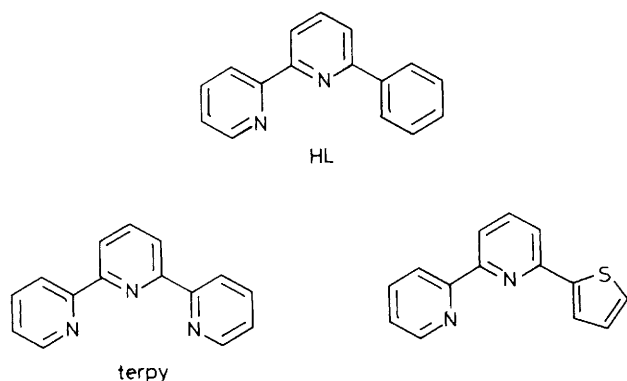


Figure 1. The crystal and molecular structure of [PdLCl] showing the numbering scheme adopted: Pd(1)–Cl(1) 2.317(1), Pd(1)–N(1) 2.067(3), Pd(1)–N(2) 1.960(4), Pd(1)–C(1) 2.067(3) Å; Cl(1)–Pd(1)–N(2) 180.0(1), Cl(1)–Pd(1)–N(1) 99.7(1), N(2)–Pd(1)–N(1) 80.3(1); Cl(1)–Pd(1)–C(1) 99.7(1), N(2)–Pd(1)–C(1) 80.3(1), N(1)–Pd(1)–C(1) 0.0(1)°.



these species we have determined the crystal and molecular structures of the complexes [PdLCl] and [PtL(MeCN)][PF₆] (HL = 6-phenyl-2,2'-bipyridine).

The molecular structure of [PdLCl] is shown in Figure 1,† and confirms the presence of the terdentate cyclometallated ligand in a distorted square planar arrangement about the palladium atom. The equivalence of the pyridyl and phenyl rings is notable, and the ligand is remarkably planar, with only a 1.1° angle between the planes of the central and terminal rings. The ligand shows a similar co-ordination mode to 2,2':6',2''-terpyridine with a short Pd–N contact [1.960(4) Å] to the central ring, and longer contacts [2.067(3) Å] to the terminal N(C) donors. The Pd–N(C) distances of 2.0 ± 0.07 Å are comparable with those previously reported for palladium(II)–pyridine complexes, although the longer distance is an average of the Pd–N and Pd–C distances. The bite angle N(2)–Pd(1)–N/C(1) of 80.3(1)° is typical of an α,α'-diimine ligand. The Pd–Cl distance of 2.317(1) Å is unremarkable. The ligand behaves as a true cyclometallating analogue of 2,2':6',2''-terpyridine. There are no metal–metal interactions in the solid phase.

The crystal and molecular structure of an individual cation of the orange form of [PtL(MeCN)][PF₆] (obtained by slow diffusion of ether into a dimethylformamide solution) is shown in Figure 2(a),† and reveals the approximately square planar geometry about the metal and the cyclometallated ligand. The cyclometallated ligand again resembles 2,2':6',2''-terpyridine with a short [1.912(12) Å] Pt–N bond length to the central ring and longer Pt–N [2.178(19) Å] and Pt–C [2.008(24) Å] contacts to the terminal rings. The cations form discrete dimeric units linked through short Pt–Pt contacts of 3.28(1) Å. This is reminiscent of, but considerably shorter than, the interaction observed in the homoleptic complex [Pt(ppy)₂] (Hppy = 2-phenylpyridine).⁶ The Pt–Pt vector is inclined at an angle of 80.5° to the stacked aromatic ligands (interplanar angle within the dimer 2.5°), and the two square planes within the dimer are twisted by an average value of 35.7° to each other. The complex also exhibits short interdimer contacts, to form a zig-zag chain of alternating Pt–Pt contacts (Pt–Pt ··· Pt 135.8°) along the *b* crystal axis [Figure 2(b)]. The shortest interdimer contact is between Pt(1b) and N(2a) [3.70(4) Å], and the interdimer Pt–Pt distance is 4.59(1) Å. The Pt–C [2.008(24)] and Pt–N [2.178(19)] distances closely resemble those reported for [Pt(ppy)₂] (2.006 and 2.133 Å respectively).⁶ We have been unable to obtain X-ray quality

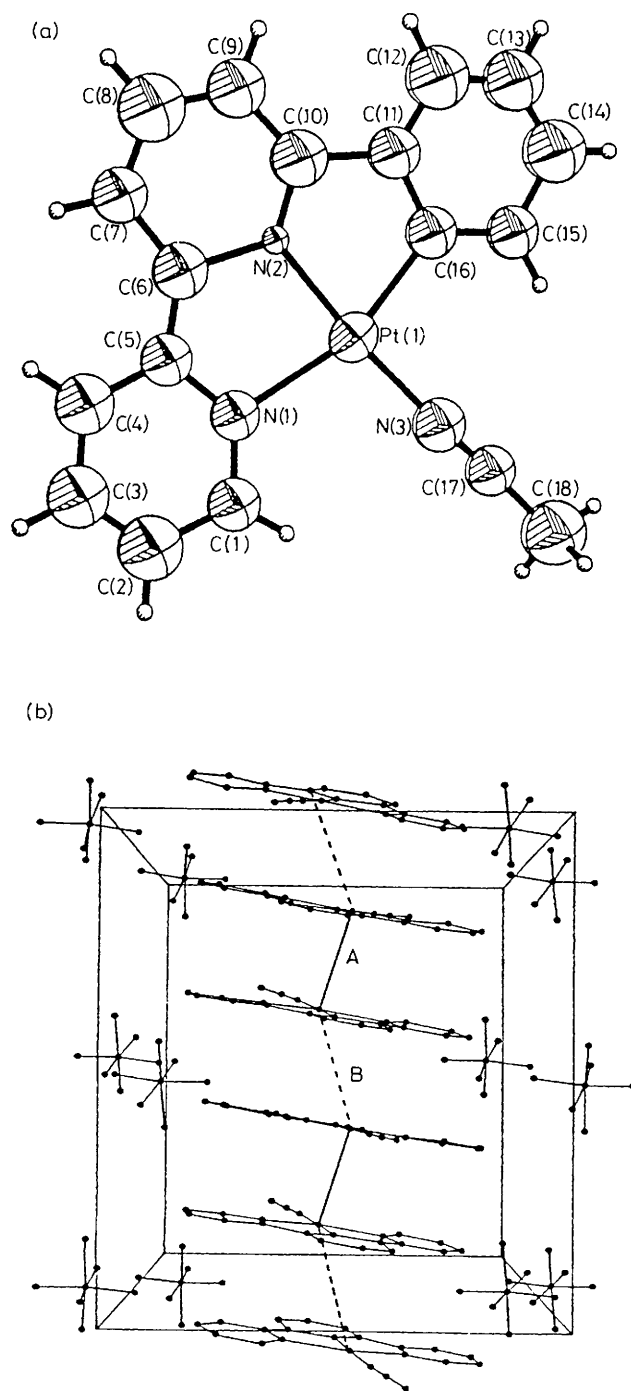


Figure 2. (a) The crystal and molecular structure of the cation in [PtL(MeCN)][PF₆] showing the numbering scheme adopted: Pt(1)–N(1) 2.178(19), Pt(1)–N(2) 1.912(12), Pt(1)–N(3) 1.940(22), Pt(1)–C(16) 2.008(24), Pt(1)–Pt(1') 3.28(1), Pt(1)–Pt(1A) 4.59(1) Å; N(1)–Pt(1)–N(2) 81.7(6), N(2)–Pt(1)–N(3) 175.0(7), N(2)–Pt(1)–C(16) 78.6(8), N(1)–Pt(1)–N(3) 103.3(8), N(1)–Pt(1)–C(16) 160.2(9), N(3)–Pt(1)–C(16) 96.5(10)°. (b) The packing of the cations in the crystal showing alternating long and short Pt–Pt contacts.

† Crystal data for C₁₆H₁₁N₂PdCl: *M* = 373.14, monoclinic, space group *C2/c*, *a* = 10.578(2), *b* = 14.166(2), *c* = 9.016(1) Å, β = 99.03(1)°, *U* = 1334 Å³, *Z* = 4, *D_c* = 1.86 g cm⁻³, μ = 15.6 cm⁻¹, 2473 measured reflections, 1091 observed [*I* ≥ 1.5 σ(*I*)], 2θ_{max} = 50.0°, *R* = 0.0241, *R_w* = 0.0258 [Mo-*K*_α radiation, λ = 0.71073 Å, *T* = 292 K]. The data were collected on a Nicolet R3m/V diffractometer system using monochromated Mo-*K*_α radiation via the ω scan technique, similar to the methods described in ref. 4. The structure was solved by direct methods and refined by least-squares and difference-Fourier techniques.⁵ Attempts to refine the structure in the non-centrosymmetric space group *Cc*, in which the disorder of C(1) and N(1) is not mandatory, were unsuccessful. The final difference-Fourier map was featureless with no peaks above 0.4 e Å⁻³.

For C₁₇H₁₄N₃Pt·PF₆: *M* = 612.41, orthorhombic, space group *Pcnc*, *a* = 12.570(3), *b* = 13.853(2), *c* = 22.512(7) Å, *U* = 3920 Å³, *Z* = 8, *D_c* = 2.08 g cm⁻³, μ = 73.8 cm⁻¹, 3822 measured reflections, 1724 observed [*I* ≥ 3 σ(*I*)], 2θ_{max} = 50.0°, *R* = 0.0716, *R_w* = 0.0830 [Mo-*K*_α radiation, λ = 0.71073 Å, *T* = 292 K]. The final difference-Fourier map contained four peaks above 1 e Å⁻³ close to the platinum, but was otherwise featureless with no peaks above 0.4 e Å⁻³. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

crystals of the purple–blue form of the compound obtained by rapid precipitation.

We have confirmed the ability of HL to form cyclometallated complexes, in which the ligand behaves as a *C,N,N*-donor analogue of the classical ligand 2,2':6',2''-terpyridine;

this is in contrast to a previously reported ruthenium(II) complex in which only an *N,N*-bidentate mode was observed.⁴ The observation of long-range metal-metal interactions in the platinum complex, similar to those previously observed in [Pt(ppy)₂], suggests that this is a common feature in such cyclometallated complexes, and offers new methods for the design of one-dimensional materials with novel optical and electronic properties. The presence of metal-metal interactions in the platinum and not the palladium species presumably reflects the greater availability and overlap of the 5d and 6p orbitals compared to 4d and 5p.

We thank the S.E.R.C. for financial support and Johnson Matthey p.l.c. for the loan of precious metal salts.

Received, 30th November 1989; Com. 9/051271

References

- 1 E. C. Constable, *Adv. Inorg. Chem. Radiochem.*, 1989, in the press; *Polyhedron*, 1984, **3**, 1037; W. R. McWhinnie and J. D. Miller, *Adv. Inorg. Chem. Radiochem.*, 1969, **12**, 135.
 - 2 F. Barigelletti, D. Sandrini, M. Maestri, V. Balzani, A. von Zelewsky, L. Chassot, P. Jolliot, and U. Maeder, *Inorg. Chem.*, 1988, **27**, 3644; K. A. King and R. J. Watts, *J. Am. Chem. Soc.*, 1987, **109**, 1589, and references cited therein.
 - 3 E. C. Constable, R. P. G. Henney, and D. A. Tocher, *J. Chem. Soc., Chem. Commun.*, 1989, 913; E. C. Constable, R. P. G. Henney, and T. A. Leese, *J. Organomet. Chem.*, 1989, **361**, 277.
 - 4 E. C. Constable, R. P. G. Henney, T. A. Leese, and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 1990, 443.
 - 5 SHELXTL, G. M. Sheldrick, University of Göttingen, 1986.
 - 6 L. Chassot and A. von Zelewsky, *Helv. Chim. Acta*, 1983, **66**, 2443; L. Chassot, E. Mueller, and A. von Zelewsky, *Inorg. Chem.*, 1984, **23**, 4249.
-