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Bow–step and Twist Conformations and Stacking Interactions in Palladium Bipyridine and Phenanthroline Complexes

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Crystal structures for $[Pd(L\text{–}L)_2][PF_6]_2$ (L–L = bipyridine, 1,10-phenanthroline or 3,4,7,8-tetramethyl-1,10-phenanthroline) were determined: a variety of ligand distortions and stacking interactions were found.

In the past there has been considerable speculation about the nature of the geometrical distortions from ideal square planarity in cations $[M(L\text{–}L)_2]^{n+}$ where M is a d^8 metal ion and L–L = 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen).[1,2] Steric interactions between H^6 and $H^{6'}$ of separate bipy, and between H^2 and H^9 of separate phen molecules are generally alleviated by distortions of the square-planar co-ordination around the metal and/or of the ligands.[2,3] For $[Pd(bipy)_2][NO_3]_2$ **1**[4] and $[Pd(phen)_2][ClO_4]_2$ **2**[5] reduction in steric interaction is achieved by tetrahedral distortion of Pd from square-planar geometry. Complexes of general formula $[Pd(L\text{–}L)_2][X]_2$ (L–L = bipy, phen or their substituted derivatives; X = PF_6 or BF_4) as well as the *in situ* system $[Pd(CH_3CO_2)_2]$ + L–L have aroused new interest owing to their catalytic properties in several reactions of significant practical importance.[6–9] For these processes several authors have proposed a palladium monochelated derivative as the catalytically active species.[6,10]

In order to establish the specific activity of the above catalysts, mixed-ligand complexes $[Pd(L\text{–}L)(bipy)][PF_6]_2$, L–L = phen or 3,4,7,8-tetramethyl-1,10-phenanthroline (tmphen), have been synthesised and characterized.[9,†] Attempts failed to obtain single crystals of the mixed-ligand complexes from dimethyl sulfoxide–methanol. For L–L = tmphen two different kinds of crystals were isolated and characterized by X-ray analysis as $[Pd(bipy)_2][PF_6]_2$ **3** and $[Pd(tmphen)_2][PF_6]_2\cdot 2bipy$ **5**, whereas for L–L = phen, crystals of $[Pd(phen)_2][PF_6]_2$ **4** were isolated and structurally characterized.[‡]

Crystals of **3** and **4** are built up of discrete PF_6^- anions and $[Pd(L\text{–}L)_2]^{2+}$ cations, while those of **5** also contain unco-ordinated bipy molecules. The ORTEP[12] drawings of the cations of **3**, **4** and **5** are shown in Fig. 1.

The $[Pd(bipy)_2]^{2+}$ cation [Fig. 1(*a*)] lies on a crystallographic symmetry centre with Pd–N distances very close to those reported for $[Pd(bipy)_2][NO_3]_2$.[4] The $[Pd(phen)_2]^{2+}$ cation [Fig. 1(*b*)] has crystallographic 2/*m* symmetry, with the mirror plane bisecting both ligands. The Pd–N bond length is close to those reported for $[Pd(phen)_2][ClO_4]_2$.[5] However, the geometry of both cations in **3** and **4** differs from those of the corresponding NO_3^- and ClO_4^- analogues, respectively. The co-ordination geometry of Pd in the cations **1** and **2** is tetrahedrally distorted from square planarity with dihedral angles, α, between the Pd–N(1)–N(2) and Pd–N(1′)–N(2′) planes of 24.1 and 18.7° respectively. Consequently, the almost planar ligands in **1** and **2** alleviate their steric interaction through a *twist* conformation as shown in Fig. 2(*a*). On the contrary, in both **3** and **4**, due to the strictly planar geometry about Pd imposed by the crystallographic symmetry, the crowding between the two ligands in the cations is instead relieved partly by the cation assuming a *step* conformation, and partly by a bowing of each of the two chelating ligands as shown in Fig. 2(*b*). The *step* conformation is characterized by the dihedral angle, β, between the co-ordination plane and the N–C–C–N plane, which is 21.6° in **3** and 16.2° in **4**. The dihedral angles between the two pyridyl rings and between the two chemically equivalent moieties of phen are a measure of the bowing, being 19.1 and 13.4°, respectively. The distortions in **3** and **4** are very similar to those found in $[M(bipy)_2][X]_2$ (X = 3,4,6-trinitrophenolate, M = Pd;[3] X = tetracyano-*p*-quinodimethane, M = Pt[13]). By reference essentially to the distortion of the ligand, some authors,[2] refer to this conformation as *bow*. However we suggest that *bow–step* is a more appropriate term to describe the overall shape of the cation. It should however be noted that the kind of conformation, *bow–step* or *twist*, does not influence the Pd–N bond lengths.

The $[Pd(tmphen)_2]^{2+}$ cations [Fig. 1(*c*)] lie on a two-fold crystallographic axis and have a *twist* conformation with a dihedral angle α of 21.3°, the tmphen ligands atoms being coplanar within ±0.1 Å, discounting the methyl groups. The Pd–N bond lengths are significantly shorter than that found in **4**, in agreement with the greater electron-donor power of tmphen relative to phen.[14]

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† These compounds were prepared starting from the monochelated trifluoroacetate derivatives as reported in ref. 9.

‡ Crystal data. **3**, $C_{20}H_{16}F_{12}N_4P_2Pd$, M = 708.7, triclinic, space group $P\bar{1}$, a = 8.239(2), b = 8.577(2), c = 9.627(3) Å, α = 81.92(2), β = 73.64(2), γ = 63.41(2)°, U = 583.6(3) $Å^3$, Z = 1, D_c = 2.02 g cm^{-3}, μ = 10.3 cm^{-1}. **4**, $C_{24}H_{16}F_{12}N_4P_2Pd$, M = 756.8, monoclinic, space group $C2/m$, a = 14.558(2), b = 11.842(1), c = 7.327(1) Å, β = 95.64(1)°, U = 1257.1(3) $Å^3$, Z = 2, D_c = 2.00 g cm^{-3}, μ = 9.6 cm^{-1}. **5**, $C_{52}H_{48}F_{12}N_8P_2Pd$, M = 1181.3, monoclinic, space group $C2/c$, a = 7.819(3), b = 25.267(4), c = 24.861(8) Å, β = 92.40(2)°, U = 4907(3) $Å^3$, Z = 4, D_c = 1.60 g cm^{-3}, μ = 5.3 cm^{-1}. CAD4 diffractometer (Mo-Kα radiation, λ = 0.710 73 Å, graphite monochromator), $2\theta_{max}$ = 56° for **3** and **5** and 60° for **4**, 2982 (**3**), 2048 (**4**) and 6187 (**5**) measured reflections, 2623 (**3**), 1713 (**4**) and 4906 (**5**) with $I > 3\sigma(I)$ were regarded as observed; Lorentz polarization corrections and secondary extinction correction [coefficient $1.06(2) \times 10^{-6}$ (**3**), $2.7(3) \times 10^{-7}$ (**4**) and $3.7(6) \times 10^{-8}$ (**5**)] were applied. Solution by Patterson and Fourier methods and refined with the Molen package,[11] unit weights applied; R = 0.026, R' = 0.029 for **3**, R = 0.030, R' = 0.030 for **4**, R = 0.044, R' = 0.047 for **5**, all the non-hydrogen atoms refined anisotropically, hydrogen atom (in calculated positions) contribution included, anomalous dispersion applied for all the non-H atoms. No feature above 0.52 (**3**), 0.46 (**4**) and 0.35 (**5**) e $Å^{-3}$ on the final ΔF synthesis. No absorption correction was applied owing to the low value of μ and to the dimensions (not exceeding 0.3 mm) of the crystals used of all the three compounds.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

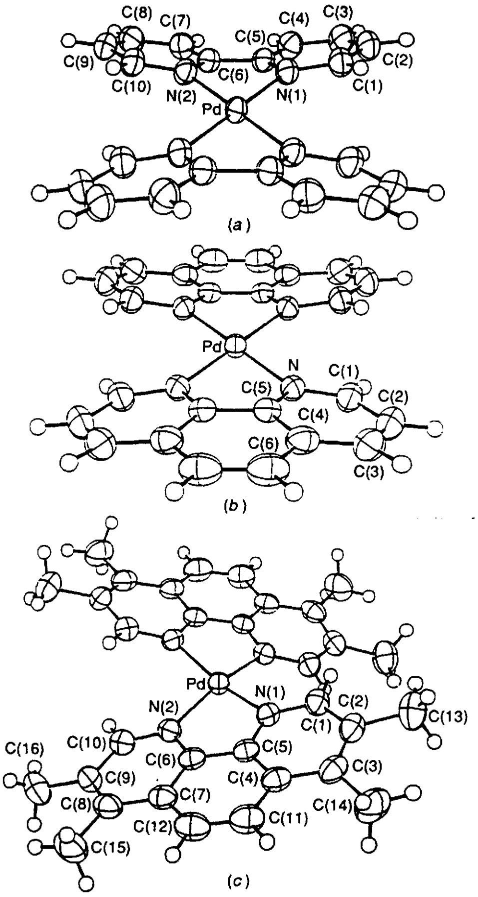

Fig. 1 (*a*) ORTEP drawing of the cation $[Pd(bipy)_2]^{2+}$; Pd–N(1) 2.039(2); Pd–N(2) 2.032(2) Å; N(1)–Pd–N(2) 78.92(9); N(1)–Pd–N(2′) 101.08(9)°. (*b*) ORTEP drawing of the cation $[Pd(phen)_2]^{2+}$; Pd–N 2.050(2) Å; N–Pd–N′ 80.41(7)°; N–Pd–N″ 99.59(7)°. (*c*) ORTEP drawing of the cation $[Pd(tmphen)_2]^{2+}$; Pd–N(1) 2.031(3); Pd–N(2) 2.039(3) Å; N(1)–Pd–N(2) 80.7(1); N(1)–Pd–N(1′) 100.3(1); N(2)–Pd–N(2′) 101.7(1); N(1)–Pd–N(2′) 166.3(1)°

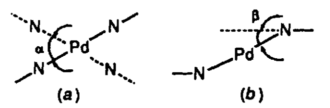

Fig. 2 Geometrical distortions of $[Pd(L\text{–}L)_2]^{2+}$ cations

The crystal packing of **3** does not show stacking, whereas in **4** the cations are arranged to stack in such a way that one phen ligand of each cation is facing a phen ligand of another (Fig. 3). The most interesting feature in the crystal packing of **5** is the presence of two unco-ordinated bipy molecules per cation. Each of these molecules, adopting the usual *trans* conformation (essentially planar, with a dihedral angle between the two pyridyl rings of 5.6°) is inserted between two tmphen ligands forming an alternating stacking of bipy molecules and tmphen ligands along the *a* axis (Fig. 4). From these results, the hypothesis that the stacking interaction is responsible for the stabilization of the *bow–step* conformation, as suggested by Okawa and co-workers[3] for $[Pd(bipy)_2][OC_6H_2(NO_2)\text{-}3,4,6]_2$, seems unlikely.

The presence of stacking in **4** and **5**, but not in **3**, supports the hypothesis, suggested by Cayley and Margerum,[15] that the stacking interaction depends on the number of the aromatic rings in the ligand and on the number of methyl substituent groups on the phenanthroline rings. Particularly, it should increase in the order bipy < phen < tmphen. It was also observed that the stacking interaction is responsible for high rate enhancements in substitution reactions involving $[Ni(L\text{–}L)(H_2O)_4]^{2+}$ complexes.[15] Therefore, stacking interactions may significantly contribute to the catalytic activity of $[M(L\text{–}L)]^{2+}$ species with suitable substrates having a delocalized structure, such as $PhNO_2$ or $Ph\text{–}CH{=}CH_2$.

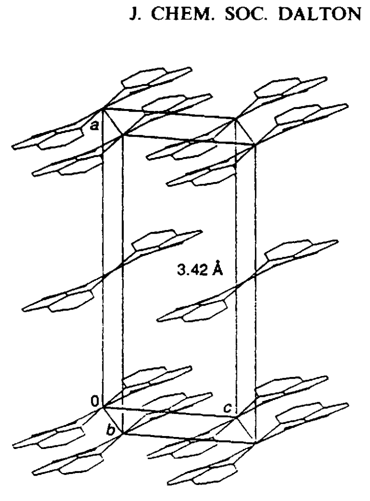

Fig. 3 Crystal packing of the cations $[Pd(phen)_2]^{2+}$ in **4**. The stacking distance is indicated

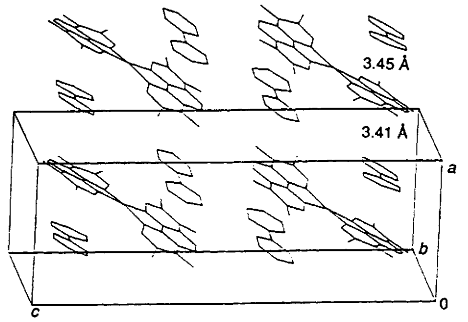

Fig. 4 Crystal packing of the cations $[Pd(tmphen)_2]^{2+}$ and bipy molecules in **5**. The stacking distances are indicated

Acknowledgements

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