Metal–Metal Interaction in a Binuclear Palladium(II) System. The ($d_{\sigma^*} \longrightarrow p_\sigma$) Transition and the X-Ray Crystal Structure of [$Pd_2(dppm)_2(CN)_4$] [dppm = bis(diphenylphosphino)methane]†

Hon-Kay Yip, Ting-Fong Lai and Chi-Ming Che *
Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong

The complex [$Pd_2(dppm)_2(CN)_4$] [dppm = bis(diphenylphosphino)methane] displays an intense absorption band at 272 nm ($\varepsilon_{max} = 5.2 \times 10^4$ dm^3 mol^{-1} cm^{-1}) attributed to the $d_{\sigma^*} \longrightarrow p_\sigma$ transition. Crystals of the complex are monoclinic, space group $P2_1/n$ (no. 14, non-standard) with $a = 11.476(2)$, $b = 17.565(2)$, $c = 13.964(2)$ Å, $\beta = 95.07(1)°$ and $Z = 2$. The measured intramolecular Pd···Pd distance is 3.276(1) Å.

In the past decade the spectroscopy, photochemistry and photophysics of binuclear d^8–d^8 metal complexes have been studied intensively.[1] These studies focused exclusively on compounds formed by metal ions such as Pt^{II},[1a] Rh^I and Ir^I.[1b] Surprisingly, corresponding work on binuclear palladium(II) complexes is sparse, being mainly confined to structural studies. The reported X-ray structural studies indicated relatively short intramolecular palladium–palladium separations; for example, the distances in [$Pd_2(PhNNNPh)_4$],[2] [$Pd_2(MeCS_2)_4$][3] and [$Pd_2(hmp)_4$] (hmp$^-$ is the anion of 2-hydroxy-6-methylpyridine)[4] have been determined to be 2.563(1), 2.738(1) and 2.546(1) Å respectively. Recently, Cotton *et al.*[5] studied the electronic structure of [$Pd_2(p\text{-}MeC_6H_4NCHNC_6H_4Me\text{-}p)_4$]. The SCH-X$\alpha$-SW calculation by these workers suggested there is no net metal–metal bonding in this complex. From previous work on [$Pt_2(dppm)_2(CN)_4$] **2**[6] [dppm = bis(diphenylphosphino)methane] we envisaged that the complex [$Pd_2(dppm)_2(CN)_4$] **1**, previously prepared by Shaw and co-workers,[7] may be a good candidate for spectroscopic studies of palladium(II)–palladium(II) interaction, such as those occurring in the solid form of the $M_2[Pd(CN)_4]$ complexes (M = monovalent cation). Herein is described the X-ray structure and UV/VIS absorption spectrum of **1**.

Experimental

Materials.—The dppm ligand was purchased from Strem Co. The complex [$Pd_2(dppm)_2(CN)_4$] **1** was prepared by the method of Shaw and co-workers.[7] The crystal used for X-ray crystallography was obtained by diffusing diethyl ether into a dimethylformamide solution of the compound.

Spectroscopy.—UV/VIS spectra were measured with a Shimadzu UV-240 spectrophotometer, IR spectra on a Perkin-Elmer model 577 spectrophotometer.

X-Ray Crystal Structure of [$Pd_2(dppm)_2(CN)_4$]·2HCONMe$_2$.—X-Ray diffraction data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation. The unit-cell dimensions were obtained from a least-squares fit of 25 reflections in the range of $19 < 2\theta < 28°$. Three check reflections monitored every 2 h showed no significant variation in intensity. The data were corrected for Lorentz, polarization and absorption effects. The empirical absorption correction was based on azimuthal (ψ) scans of eight reflections with $80 < \psi < 90°$. Crystallographic data are summarized in Table 1. Atomic scattering factors were taken from ref. 8. Calculations were carried out on a MICROVAX II computer using the Enraf-Nonius SDP programs.[9]

The position of the palladium atom was determined from a Patterson function and the rest of the non-hydrogen atoms were found in subsequent Fourier maps. Refinement was by full-matrix least squares; all non-hydrogen atoms in the metal complex were refined anisotropically, those in the solvent molecule isotropically. The hydrogen atoms of the metal complex placed at calculated positions and assigned isotropic thermal parameters were included in the structure-factor calculation but the hydrogen atoms of the solvent molecule were omitted. The final agreement factors are given in Table 1. Atomic coordinates of the non-hydrogen atoms are listed in Table 2, selected bond distances and angles in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Complex **1** was prepared by Shaw and co-workers[7] by the reaction of [$Pd(dppm)Cl_2$] with NaCN in methanol. As reported, its IR spectrum shows one intense ν(C≡N) at *ca.* 2130 cm^{-1}, in accordance with the *trans* geometry. The structure of this complex has been established by X-ray crystallography. Fig. 1 shows the ORTEP plot with atom numbering. The palladium(II) molecule, like its platinum(II) analogue **2**,[6] has a crystallographically imposed centre of symmetry. It consists of two palladium atoms bridged by two dppm groups and two cyanide ions bonded to each palladium atom. Each palladium atom exhibits square-planar co-ordination, with two *trans*-cyano groups and two *trans*-phosphorus atoms from dppm

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† Bis[μ-bis(diphenylphosphino)methane-κP:$\kappa P'$]-bis[dicyanopalladium(II)]–dimethylformamide (1/2).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

groups. The P–Pd–P angle of 175.40(6)° is close to that for a rectilinear geometry. The measured C(1)–Pd–C(2) angle of 167.8(3)°, however, deviates significantly from 180°, suggesting the presence of a weak interunit Pd ··· CN bonding interaction, as in the case of complex **2**.[6] The Pd–P(1) and Pd–P(2) distances of 2.326(2) and 2.347(2) Å are similar to the values of 2.333(7) and 2.326(3) Å found in *trans*-[Pd(PMe$_2$Ph)$_2$I$_2$][10] and *trans*-[Pd(Ph$_2$PC≡CBu^t)$_2$][11] respectively. The measured Pd–C distances of 2.034(8) and 2.007(8) Å are slightly shorter than those values found in [Pd(bipy)(CN)$_2$] [bipy = 2,2′-bipyridine, 2.12(1) Å].[12] They are, however, close to the Pt–C(CN) distances in **2** [2.009(4) and 1.997(4) Å].[6] An interesting structural feature of **1** is the intramolecular Pd ··· Pd distance of 3.276(1) Å, which is much longer than values found in other binuclear palladium(II) compounds.[2–6] However, this value

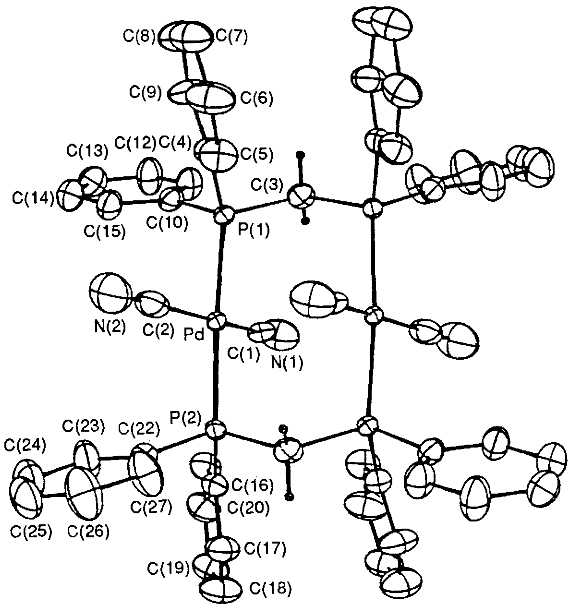

Fig. 1 ORTEP plot of [Pd$_2$(dppm)$_2$(CN)$_4$] showing the atom numbering scheme

Table 1 Crystallographic details for [Pd$_2$(dppm)$_2$(CN)$_4$]·2HCONMe$_2$

Formula	$C_{60}H_{58}N_6P_4Pd_2O_2$
M	1231.86
Crystal colour/shape	Colourless prism
Crystal dimensions (mm)	0.07 × 0.12 × 0.18
Crystal system	Monoclinic
Space group	$P2_1/n$ (no. 14, non-standard)
a/Å	11.476(2)
b/Å	17.565(2)
c/Å	13.964(2)
β/°	95.07(1)
U/Å^3	2804(1)
Z	2
F(000)	1256
D_c/g cm^{-3}	1.459
μ(Mo-Kα)/cm^{-1}	7.91
T/°C	20 ± 1
Collection range	$2\theta_{max} = 50°, \pm h, k, \pm l$
Scan mode and speed/° min^{-1}	ω–2θ, 0.916–5.493
Scan width (°)	0.60 + 0.34 tan θ
No. of reflections measured	9062
No. of independent reflections	5056
R (merging)	0.020
No. of reflections with $F_o > 3\sigma(F_o)$, m	3339
No. of parameters, p	309
R^a	0.052
R'^b	0.069
S^c	2.00
Residual extrema in final difference map (e Å^{-3})	1.09, −0.82

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R' = [w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, with $w = 4F_o^2/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$. [c] $S = [\Sigma w(|F_o| - |F_c|)^2/(m - p)]^{\frac{1}{2}}$.

Table 3 Selected bond distances (Å) and angles (°) in [Pd$_2$(dppm)$_2$(CN)$_4$]·2HCONMe$_2$

Pd–P(1)	2.326(2)	N(1)–C(1)	1.12(2)
Pd–P(2)	2.347(2)	N(2)–C(2)	1.11(1)
Pd–C(1)	2.034(8)	Pd ··· Pd′	3.276(1)
Pd–C(2)	2.007(8)		
P(1)–Pd–P(2)	175.40(6)	Pd–P(1)–C(3)	111.9(3)
P(1)–Pd–C(1)	85.0(2)	Pd–P(2)–C(3′)	108.56(8)
P(1)–Pd–C(2)	91.3(3)	Pd–C(1)–N(1)	173.1(7)
P(2)–Pd–C(1)	96.1(2)	Pd–C(2)–N(2)	173(1)
P(2)–Pd–C(2)	88.6(3)	P(1)–C(3)–P(2′)	116.6(3)
C(1)–Pd–C(2)	167.8(3)		

Symmetry code: ′ −x, −y, −z. Numbers in parentheses are e.s.d.s in the least significant digits.

Table 2 Fractional atomic coordinates for non-hydrogen atoms in [Pd$_2$(dppm)$_2$(CN)$_4$]·2HCONMe$_2$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	y	z	Atom	x	y	z
Pd	0.120 74(4)	0.033 68(3)	−0.038 09(4)	C(15)	0.420 1(6)	0.066 4(5)	0.092 7(5)
P(1)	0.191 3(1)	0.038 4(1)	0.123 1(1)	C(16)	0.065 4(6)	−0.045 6(4)	−0.277 9(4)
P(2)	0.034 5(1)	0.030 8(1)	−0.196 8(1)	C(17)	−0.000 0(7)	−0.048 5(5)	−0.367 9(5)
N(1)	0.158 9(7)	−0.143 0(4)	−0.012 2(5)	C(18)	0.023 3(8)	−0.105 0(5)	−0.432 9(5)
N(2)	0.163(1)	0.207 6(5)	−0.059 1(6)	C(19)	0.110 3(8)	−0.158 1(5)	−0.410 9(6)
C(1)	0.138 0(6)	−0.081 0(4)	−0.022 9(4)	C(20)	0.176 4(8)	−0.154 1(5)	−0.321 3(6)
C(2)	0.141 1(8)	0.146 6(5)	−0.051 6(5)	C(21)	0.153 7(6)	−0.098 4(4)	−0.255 7(5)
C(3)	0.124 8(5)	−0.034 9(4)	0.194 2(4)	C(22)	0.066 5(6)	0.114 7(4)	−0.267 3(5)
C(4)	0.182 9(6)	0.123 9(4)	0.194 9(5)	C(23)	0.175 3(7)	0.120 2(5)	−0.299 0(6)
C(5)	0.096 1(7)	0.177 9(5)	0.175 7(5)	C(24)	0.206 7(8)	0.182 2(6)	−0.352 6(7)
C(6)	0.087 5(9)	0.237 8(5)	0.238 1(6)	C(25)	0.129(1)	0.238 7(5)	−0.372 1(6)
C(7)	0.164 7(9)	0.247 3(5)	0.316 4(6)	C(26)	0.021(1)	0.235 0(6)	−0.339 4(8)
C(8)	0.252 7(9)	0.195 0(6)	0.334 9(6)	C(27)	−0.013 3(8)	0.172 3(5)	−0.287 8(6)
C(9)	0.262 4(8)	0.133 5(5)	0.274 8(6)	N(3)	0.621 5(8)	0.075 0(6)	0.478 8(6)
C(10)	0.347 0(5)	0.015 7(4)	0.133 5(5)	O	0.731(1)	0.067 2(7)	0.611 7(8)
C(11)	0.394 7(6)	−0.047 6(4)	0.179 6(6)	C(28)	0.659(2)	0.117(1)	0.561(1)
C(12)	0.512 4(7)	−0.061 4(5)	0.181 8(6)	C(29)	0.555(1)	0.104(1)	0.386(1)
C(13)	0.584 8(6)	−0.012 1(5)	0.140 6(6)	C(30)	0.675(2)	−0.000(1)	0.463(1)
C(14)	0.539 4(7)	0.052 6(5)	0.096 2(6)				

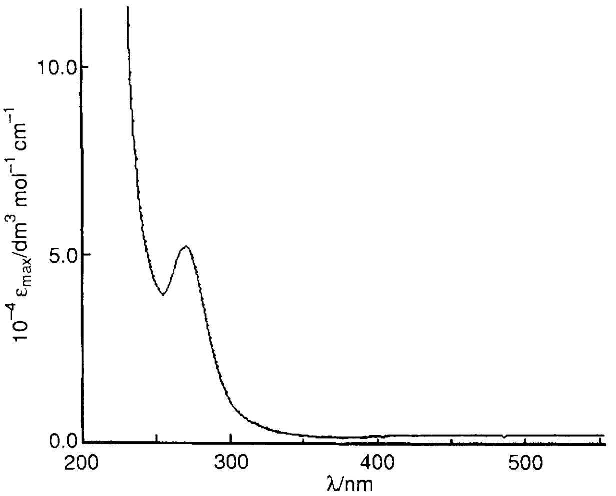

Fig. 2 UV/VIS absorption spectrum of $[Pd_2(dppm)_2(CN)_4]$ in dichloromethane

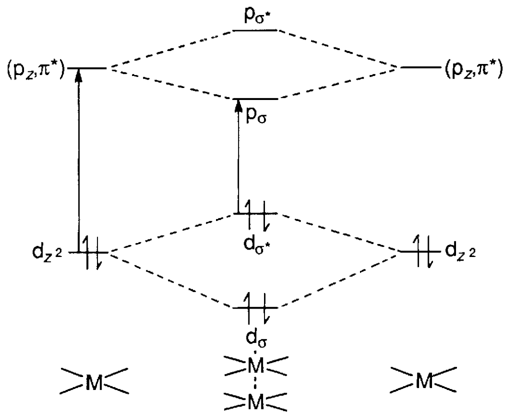

Fig. 3 A simplified molecular-orbital diagram of a binuclear d^8 system showing metal–metal interaction

is close to the intermolecular Pd···Pd separation in the $[Pd(bipy)(CN)_2]$ crystal.[12]

The electronic absorption spectrum of complex **1** is depicted in Fig. 2. The important feature of this spectrum is the intense absorption band at 272 nm with a measured ε_{max} of 5.2×10^4 $dm^3\ mol^{-1}\ cm^{-1}$. This kind of absorption band is absent from the UV/VIS spectra of most monomeric palladium(II) complexes such as *trans*-$[Pd(PBu_3)_2(CN)_2]$[13] and should arise from metal–metal interaction. With reference to previous work by Gray and co-workers[1] an intense low-energy absorption is a fingerprint for the spin-allowed $^1[(d_{\sigma^*})^2] \longrightarrow {}^1[(d_{\sigma^*})(p_\sigma)^1]$ transition in binuclear d^8 metal systems (Fig. 3). Thus, the absorption at 272 nm can be assigned to the spin-allowed $4d_{\sigma^*} \longrightarrow 5p_\sigma$ transition [p_σ is a hybrid of the $5p_z$(Pd) and π^*(dppm) orbitals]. Observation of this characteristic absorption band at a much lower energy transition than that of the metal-to-ligand charge-transfer (m.l.c.t.) at 244 nm [$Pd \longrightarrow \pi^*(PR_3, CN^-)$] in *trans*-$[Pd(PBu_3)_2(CN)_2]$[13] provides spectroscopic evidence for the presence of intramolecular metal–metal interaction in binuclear palladium(II) compounds. Whether this kind of interaction would lead to some net metal–metal bonding still remains uncertain. The relatively weak absorption around 359 nm (ε = 500 $dm^3\ mol^{-1}\ cm^{-1}$) is then accordingly assigned as the spin-forbidden $^1[(d_{\sigma^*})^2] \longrightarrow {}^3[(d_{\sigma^*})^1(p_\sigma)^1]$ transition. It is noted that there is a blue shift in the $nd_{\sigma^*} \longrightarrow (n + 1)p_\sigma$ transition energy from that of complex **2** (λ_{max} = 324 nm)[6] to that of **1** (λ_{max} = 272 nm). This can be explained by the fact that both the m.l.c.t. transition energy and the d–p energy separation for Pt are smaller than for Pd. Unlike **2**, complex **1** does not exhibit any room-temperature photoluminescence, either in the solid state or in solution.

Acknowledgements

We acknowledge support from the Croucher Foundation and the University of Hong Kong. H.-K. Y. is grateful for a studentship, administered by the Croucher Foundation.

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Received 19*th November* 1990; *Paper* 0/05207H