Articles

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Spectroscopy and X-ray Crystal Structure of Luminescent $Pt_2(dppm)_2(CN)_4$ [dppm = Bis(diphenylphosphino)methane]

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The reaction of $Pt(CN)_2 \cdot xH_2O$ with dppm [bis(diphenylphosphino)methane] in refluxing dimethylformamide (DMF) yielded $Pt_2(dppm)_2(CN)_4$. The X-ray structure of this binuclear platinum(II) complex has been determined: $Pt_2(dppm)_2(CN)_4 \cdot 2DMF$, space group $P2_1/n$, $Z = 2$, $a = 11.561$ (1) Å, $b = 17.475$ (1) Å, $c = 13.981$ (5) Å, $\beta = 95.34$ (2)°. The $Pt_2(dppm)_2(CN)_4$ molecule adopts the trans,trans geometry and consists of two platinum atoms bridged by two dppm groups, with two trans cyanide ions bonded to each platinum atom. The measured Pt···Pt distance is 3.301 (1) Å, indicative of a weak Pt···Pt bonding interaction. The UV–vis absorption spectrum of methanolic solutions of $Pt_2(dppm)_2(CN)_4$ exhibits an intense band at 324 nm (ϵ_{max} 10 500) and a weak band at ca. 390 nm, assigned to the ${}^1A_{1g} \rightarrow {}^1B_{1u}$ and ${}^1A_{1g} \rightarrow {}^3B_{1u}$ transitions, respectively. Excitation of $Pt_2(dppm)_2(CN)_4$ at 324 nm in degassed methanol leads to an intense emission at 425 nm with a shoulder at ca. 530 nm. The room-temperature triplet lifetime has been found to be 0.23 μs in degassed methanol.

Introduction

Although numerous studies on the chemistry of binuclear complexes of Rh(I) containing the bridging ligands bis(diphenylphosphino)methane (dppm) and bis(diphenylarsino)methane (dam) have been reported,[2] the chemistry of the corresponding isoelectronic Pt(II) dimers[3] has remained relatively unexplored. Our interest in the study of the binuclear complexes of Pt(II) containing bis(diphenylphosphino)methane bridges was aroused by the similarity of the face-to-face square planes of the dimers with the other isoelectronic $[Rh_2(bridge)_4]^{2+}$ (bridge = 1,3-diisocyanopropane),[4] $[Rh_2(RNC)_4(dppm)_2]^{2+}$ (R = *t*-Bu, *n*-Bu, Ph),[2a,2f] $[Rh_2(n\text{-}BuNC)_4(dam)_2]^{2+}$,[2d,2f] $[Pt_2(pop)_4]^{4-}$ (pop = $P_2O_5H_2^{2-}$),[5] and $[Pt_2(pcp)_4]^{4-}$ (pcp = $CH_2(PH(O)OH)_2$)[6] complexes and the existence of intense luminescence from these systems. Moreover, the ability of dppm to form binuclear complexes and strong metal–phosphorus bonds[7] renders the bridging diphosphine ligand capable of locking together two metal centers in close proximity and hence promoting organometallic reactions involving two metal centers. As part of a research program on photochemical C–H bond activation utilizing binuclear metal complexes, we report here the spectroscopic and X-ray structural properties of a novel $[Pt_2(dppm)_2(CN)_4]$ complex.

Table I. Crystallographic Data for $Pt_2(dppm)_2(CN)_4 \cdot 2C_3H_7NO$

fw = 1409.24
$a = 11.561$ (1) Å
$b = 17.475$ (1) Å
$c = 13.981$ (5) Å
$\beta = 95.34$ (2)°
$V = 2812$ (1) Å^3
$Z = 2$
$T = 23 \pm 1$ °C

space group $P2_1/n$ [No. 14 (nonstandard)]
$\lambda = 0.71073$ Å
$\rho_{calcd} = 1.664$ g cm^{-3}
$\mu = 51.69$ cm^{-1}
transmission coeff = 0.905–0.999
$R(F_o) = 0.023$
$R_w(F_o) = 0.030$

Experimental Section

Materials. The dppm ligand was purchased from Strem Co. Ltd. $Pt(CN)_2 \cdot xH_2O$ was prepared by the literature method.[8] The organic solvents for spectroscopic work are analytical grade and were purified by standard procedures before use.

$[Pt_2(dppm)_2(CN)_4] \cdot 2DMF$ (DMF = Dimethylformamide). A mixture of $Pt(CN)_2 \cdot xH_2O$ (0.2 g) and excess dppm ligand (1 g) in dimethylformamide (25 mL) was refluxed for 24 h. After refluxing, the solution was cooled to room temperature. A white solid precipitated from the solution; it was filtered out and washed with diethyl ether. The crude product was recrystallized from hot dimethylformamide.

Instruments. UV–vis spectra were measured with a Shimadzu UV-240 spectrophotometer. IR spectra (Nujol mull or KBr disk) were obtained on a Perkin-Elmer Model 577 spectrophotometer. Steady-state emission spectra (corrected) were recorded with Corning filters on a Hitachi 650-60 fluorescence spectrophotometer. The emission lifetimes were measured with a time-resolved laser system. The excitation source was the 355-nm output of a Quanta-Ray Q-switched DCR-3 pulsed Nd:YAG laser (10 Hz, G-resonator).

X-ray Crystal Structure of $[Pt_2(C_{25}H_{22}P_2)_2(CN)_4] \cdot 2C_3H_7NO$. X-ray diffraction data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The unit cell dimensions were obtained from a least-squares fit of 25 reflections in the range of $18° < 2\theta < 25°$. 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 nine reflections with $80° < \chi < 90°$. Crystallographic data are summarized in Table I. Atomic scattering factors are taken from ref 9a. Calculations were carried out on a MICROVAX II computer using the Enraf-Nonius SDP programs.[9b]

The position of the platinum atom was determined from a Patterson function, and the rest of the non-hydrogen atoms were found in subsequent Fourier maps. The hydrogen atoms of the metal complex were generated geometrically (C–H = 0.95 Å), while those of the solvent

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(2) For examples, see: (a) Balch, A. L. *J. Am. Chem. Soc.* **1976**, *98*, 8049. (b) Sanger, A. R. *J. Chem. Soc., Dalton Trans.* **1977**, 120. (c) Balch, A. L.; Tulyathan, B. *Inorg. Chem.* **1977**, *16*, 2840. (d) Balch, A. L.; Labadie, J. W.; Delker, G. *Inorg. Chem.* **1979**, *18*, 1224. (e) Mague, J. T.; DeVries, S. H. *Inorg. Chem.* **1980**, *19*, 3743. (f) Fordyce, W. A.; Crosby, G. A. *J. Am. Chem. Soc.* **1982**, *104*, 985.

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Table II. Fractional Atomic Coordinates and Thermal Parameters[a] for Non-Hydrogen Atoms in $[Pt_2(dppm)_2(CN)_4]\cdot 2C_3H_7NO$ with Esd's in Parentheses

	x	y	z	$B_{eq}/Å^2$
Pt	0.12042 (1)	0.03417 (1)	−0.03847 (1)	2.136 (2)
P(1)	0.19141 (7)	0.03837 (5)	0.12194 (6)	2.29 (1)
P(2)	−0.03297 (7)	−0.03141 (5)	0.19523 (6)	2.26 (1)
N(1)	0.1700 (3)	−0.1417 (2)	−0.0144 (3)	4.41 (8)
N(2)	0.1444 (5)	0.2114 (3)	−0.0569 (3)	7.5 (1)
C(1)	0.1446 (3)	−0.0793 (2)	−0.0255 (2)	2.78 (7)
C(2)	0.1284 (4)	0.1480 (2)	−0.0492 (3)	3.80 (9)
C(3)	0.1249 (3)	−0.0355 (2)	0.1919 (2)	2.52 (6)
C(11)	0.1829 (3)	0.1247 (2)	0.1934 (3)	2.75 (6)
C(12)	0.0930 (3)	0.1773 (2)	0.1753 (3)	3.57 (8)
C(13)	0.0831 (4)	0.2375 (3)	0.2375 (4)	5.0 (1)
C(14)	0.1632 (5)	0.2469 (3)	0.3163 (3)	5.0 (1)
C(15)	0.2531 (4)	0.1973 (3)	0.3329 (3)	5.2 (1)
C(16)	0.2639 (4)	0.1357 (3)	0.2719 (3)	4.38 (9)
C(21)	0.3459 (3)	0.0164 (2)	0.1334 (3)	2.57 (6)
C(22)	0.3945 (3)	−0.0471 (2)	0.1812 (3)	3.41 (8)
C(23)	0.5127 (4)	−0.0600 (3)	0.1842 (4)	4.4 (1)
C(24)	0.5827 (3)	−0.0104 (3)	0.1401 (3)	4.20 (9)
C(25)	0.5358 (3)	0.0532 (2)	0.0938 (3)	3.81 (8)
C(26)	0.4180 (3)	0.0667 (2)	0.0895 (3)	3.37 (7)
C(31)	−0.0624 (3)	0.0454 (2)	0.2775 (2)	2.58 (6)
C(32)	−0.1534 (3)	0.0965 (2)	0.2577 (3)	3.24 (7)
C(33)	−0.1770 (4)	0.1514 (2)	0.3243 (3)	4.13 (9)
C(34)	−0.1097 (4)	0.1550 (3)	0.4121 (3)	4.6 (1)
C(35)	−0.0196 (4)	0.1044 (3)	0.4325 (3)	4.49 (9)
C(36)	0.0037 (4)	0.0491 (2)	0.3670 (3)	3.57 (8)
C(41)	−0.0630 (3)	−0.1157 (2)	0.2654 (2)	2.81 (7)
C(42)	−0.1734 (4)	−0.1221 (3)	0.2955 (3)	4.52 (9)
C(43)	−0.2042 (4)	−0.1841 (3)	0.3482 (3)	5.0 (1)
C(44)	−0.1255 (5)	−0.2407 (3)	0.3717 (4)	5.7 (1)
C(45)	−0.0162 (5)	−0.2348 (3)	0.3430 (4)	6.4 (1)
C(46)	0.0147 (4)	−0.1729 (3)	0.2908 (3)	4.6 (1)
N	0.6243 (4)	0.0669 (3)	0.4748 (3)	6.3 (1)
O	0.7317 (4)	0.0734 (4)	0.6135 (3)	10.6 (1)
C(51)	0.6621 (6)	0.1011 (5)	0.5492 (4)	8.8 (2)
C(52)	0.5526 (6)	0.0915 (5)	0.3944 (5)	9.2 (2)
C(53)	0.6802 (9)	−0.0093 (6)	0.4600 (7)	12.1 (3)

[a] $B_{eq} = {}^1/_3\sum_i\sum_j B_{ij}(a_i{}^*a_j{}^*)\mathbf{a}_i\cdot\mathbf{a}_j$.

Table III. Selected Interatomic Distances (Å) and Angles (deg) in $[Pt_2(dppm)(CN)_4]\cdot 2C_3H_7NO$

Pt–P(1)	2.317 (1)	C(2)–N(2)	1.130 (7)
Pt–P(2′)[a]	2.327 (1)	Pt···Pt′[a]	3.301 (1)
Pt–C(1)	2.009 (4)	C(1)···Pt′[a]	3.364 (4)
Pt–C(2)	1.997 (4)	C(2)···Pt′[a]	4.535 (4)
C(1)–N(1)	1.136 (5)		
P(1)–Pt–C(1)	84.9 (1)	Pt–P(1)–C(3)	111.5 (2)
P(1)–Pt–C(2)	91.5 (2)	C(3)–P(2)–Pt′[a]	108.8 (2)
P(1)–Pt–P(2′)[a]	175.00 (2)	P(1)–C(3)–P(2)	117.1 (2)
C(1)–Pt–C(2)	169.5 (2)	P(1)–Pt···Pt′[a]	85.96 (1)
C(1)–Pt–P(2′)[a]	96.2 (1)	P(2)–Pt′[a]···Pt	89.6 (1)
C(2)–Pt–P(2′)[a]	88.2 (2)	C(1)–Pt···Pt′[a]	74.2 (1)
Pt–C(1)–N(1)	172.7 (3)	C(2)–Pt···Pt′[a]	115.5 (1)
Pt–C(2)–N(2)	173.0 (4)		

[a] Symmetry code: $-x$, $-y$, $-z$.

molecule were located from a difference Fourier map. Refinement was by full-matrix least-squares; all non-hydrogen atoms were refined anisotropically, and all hydrogen atoms with assigned isotropic temperature factors were not refined. The final agreement factors are given in Table I. Atomic coordinates of non-hydrogen atoms are listed in Table II. Selected bond distances and angles are given in Table III. Tables of crystal and structure determination data, hydrogen atom parameters, anisotropic thermal parameters, complete bond distances and angles, and structure factors are available as supplementary material.

Results and Discussion

The $Pt_2(dppm)_2(CN)_4$ complex was initially prepared by Shaw and co-workers by reaction between $[Pt(\eta^1\text{-dppm})Cl_2]$ and NaCN in alcohol.[3a,d] No UV–vis spectroscopic data on this platinum complex were reported. In this work, we found that refluxing $Pt(CN)_2\cdot xH_2O$ and dppm in DMF gave $Pt_2(dppm)_2(CN)_4$, which precipitated from the solution as a white solid. It has a low solubility in most common organic solvents but can be recrystallized from hot DMF solution. Its IR spectrum shows one intense C≡N stretch at ca. 2130 cm^{-1}. The structure of this complex has been established by X-ray crystallography. Figure 1 shows an ORTEP drawing of $[Pt_2(dppm)_2(CN)_4]\cdot 2DMF$ with the atomic numbering scheme. The $Pt_2(dppm)_2(CN)_4$ molecule has a crystallographically imposed center of symmetry; it consists of two platinum atoms bridged by only two dppm groups, with two cyanide ions bonded to each platinum atom. The platinum atoms exhibit square-planar coordination, with two trans cyano groups and two trans phosphorous atoms from dppm groups. The P–Pt–P angles of 175.0 (2)° are close to that of rectilinear geometry whereas the C(1)–Pt–C(2) angles of 169.5 (2)° are somewhat distorted from the 180° geometry. The significant deviation of the Pt—C≡N angles of 172.7 (3)–173.0 (4)° from 180° indicates that the adjacent cyano groups tend to bend away from each other, possibly as a result of nonbonded repulsive interactions. This effect has also been observed in other cyanoplatinum(II) complexes such as $K_{1.75}[Pt(CN)_4]\cdot 1.5H_2O$ [176.4 (1)–179.1 (1)°].[10] The coordination planes of the Pt atoms are parallel to each other with the Pt–Pt vector approximately perpendicular to the P–Pt–P line [the Pt–Pt–P angles are 85.96 (2) and 89.64 (2)°]. However, the planes are displaced in the direction of the C–Pt–C line so that C(1) is much closer to the nonbonded Pt atom than C(2) [C(1)···Pt = 3.364 (4) and C(2)···Pt = 4.535 (4) Å; C(1)–Pt···Pt = 74.2 (1)°], thereby indicating the presence of a weak interunit Pt···CN bonding interaction. Such an intramolecular M···X interaction in the face-to-face *trans,trans*-$[M_2(L\text{-}L)_2(X)_4]$ (L-L = bridging ligand) system has previously been observed in $Pd_2(DMB)_2I_4$ (DMB = 1,8-diisocyano-*p*-menthane).[11] The respective average Pt–C and Pt–P distances of 2.003 (4) and 2.317 (1) Å are normal and comparable to those values found in $K_{1.75}[Pt(CN)_4]\cdot 1.5H_2O$ [Pt–C = 1.999 (4) Å][10] and $[Pt_2(pcp)_4]^{4-}$ [Pt–P = 2.328 (1) Å].[6]

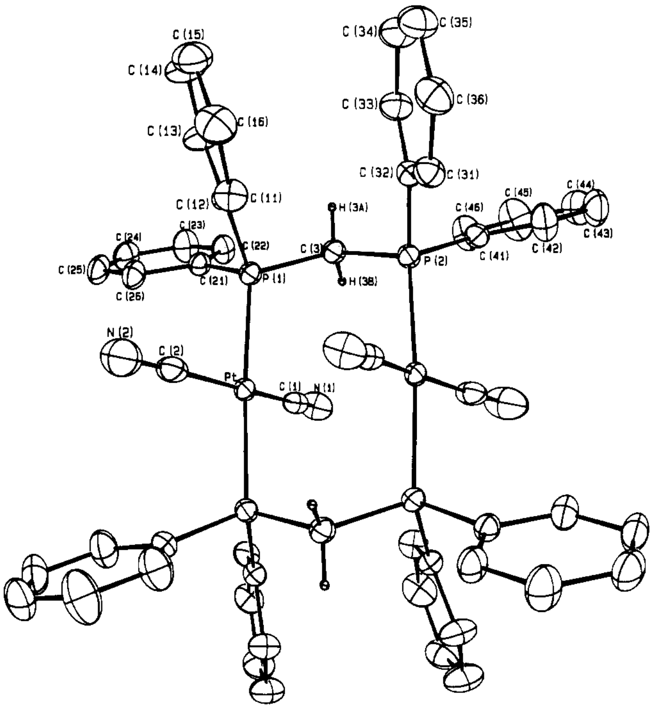

Figure 1. ORTEP drawing of $Pt_2(dppm)_2(CN)_4$ with atomic numbering scheme.

An important structural feature of the $Pt_2(dppm)_2(CN)_4$ molecule is the intramolecular Pt–Pt distance of 3.301 (1) Å, which indicates the presence of a weak Pt–Pt interaction. For square-

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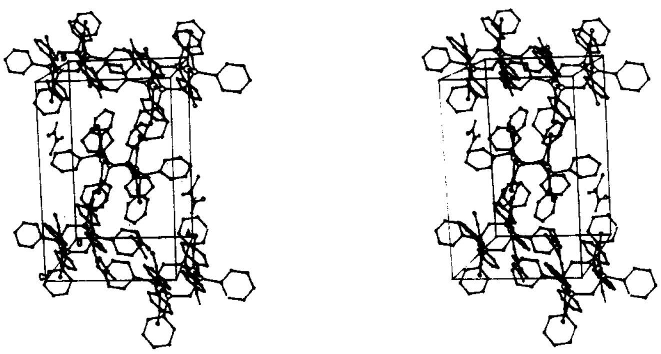

Figure 2. Crystal packing diagram for $Pt_2(dppm)_2(CN)_4{\cdot}2DMF$.

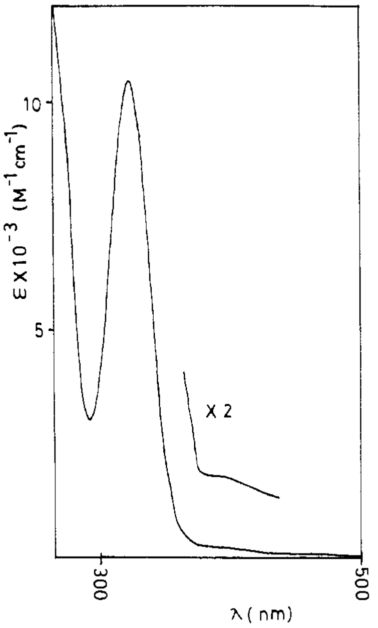

Figure 3. Room-temperature electronic absorption spectrum of $Pt_2(dppm)_2(CN)_4$ in methanol.

planar Pt(II) complexes consisting of monomeric units stacked to form a continuous chain of metal atoms, the intermolecular Pt–Pt distances lie in the range 3.09–3.50 Å.[12] Although the Pt–Pt distance of 3.301 (1) Å in $[Pt_2(dppm)_2(CN)_4]$ is somewhat longer than that for $[Pt_2(pop)_4]^{4-}$ [2.925 (1) Å],[13] it is comparable to the 3.381-Å value in the $K_2[Pt(CN)_4]{\cdot}3H_2O$ solid,[10] which exhibits unusual spectroscopic properties as a consequence of metal–metal interactions. In the present structure there is no close intermolecular Pt···Pt interaction (Figure 2).

Spectroscopy. The electronic absorption spectrum of a solution of $Pt_2(dppm)_2(CN)_4$ in methanol exhibits bands at 210 (ϵ_{max} 69 760), 228 (sh, 50 450), 275 (sh, 9690), and 324 nm (10 500) (Figure 3). A very weak band at ca. 390 nm has also been observed where a reliable extinction coefficient could not be obtained owing to the limited solubility of $[Pt_2(dppm)_2(CN)_4]$ in the solvent. The 324-nm band, which corresponds to a spin-allowed transition, arises from the weak Pt···Pt interaction because the monomeric $Pt(L)_2(CN)_2$ complexes (L = amine, alkyl isocyanide) show no appreciable absorptions at wavelengths greater than 300 nm.[15] With reference to previous spectroscopic work on binuclear d^8 systems,[2f,4c,14] the 324- and 390-bands are mostly to be derived from the $^1A_{1g} \rightarrow {}^1B_{1u}$ ($1b_{1u} \rightarrow 2a_{1g}$) and $^1A_{1g} \rightarrow {}^3B_{1u}$ ($1b_{1u} \rightarrow 2a_{1g}$) transitions, assuming a D_{2h} symmetry, where $1a_{1g}$ ($5d_{z^2}$) < $1b_{1u}$ ($5d_{z^2}$*) < $2a_{1g}$ ($6p_z$) < $2b_{1u}$ ($6p_z$*) for $Pt_2(dppm)_2(CN)_4$ (Figure 4). A similar scheme modified for D_{2h} symmetry has been used to explain the electronic spectra of the dppm-bridged Rh(I) dimers.[2f] The $1a_{1g}$ and $1b_{1u}$ orbitals are both occupied in the ground state. Interaction of the a_{1g} and b_{1u} orbital pairs, respectively, leads to weak Pt–Pt bonding, which is confirmed by the measured Pt–Pt distance of 3.301 (1) Å.

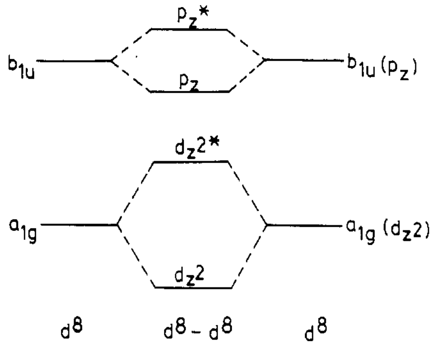

Figure 4. Orbital energy level diagram for interaction (face-to-face) of two d^8 square-planar units along the metal–metal axis.

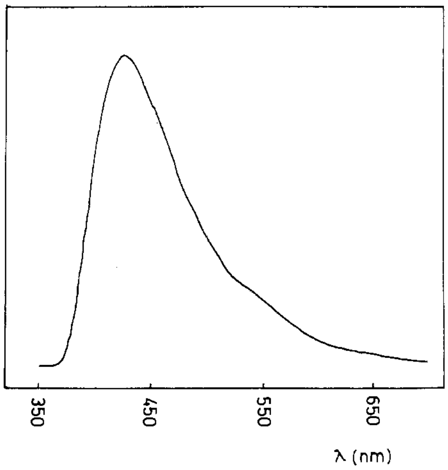

Figure 5. Room-temperature emission spectrum of $Pt_2(dppm)_2(CN)_4$ in methanol.

Excitation at 320 nm of a methanolic solution of $[Pt_2(dppm)_2(CN)_4]$ at room temperature results in an intense emission at 425 nm with a shoulder at ca. 530 nm under degassed conditions (Figure 5). The higher energy emission band is assigned as fluorescence ($^1B_{1u} \rightarrow {}^1A_{1g}$), while the shoulder at ca. 530 nm is likely derived from phosphorescence ($^3B_{1u} \rightarrow {}^1A_{1g}$). Similar assignments have been made to explain the emission spectra of $[Rh_2(RNC)_4(dppm)_2]^{2+}$.[2f] The phosphorescence lifetime in absolute methanol was found to be 0.23 μs (355-nm excitation) at room temperature. For the fluorescence, its lifetime is too short (less than 6 ns) to be determined with our instrument.

A direct comparison between $[Pt_2(dppm)_2(CN)_4]$ and $[Pt_2(pop)_4]^{4-}$ shows that the absorption and emission energies for the two systems are similar. In the $[Pt_2(dppm)_2(CN)_4]$ case, its triplet lifetime is about 40 times shorter than that for $[Pt_2(pop)_4]^{4-}$ ($\tau_0 \simeq 9.8$ μs),[5] thus rendering this system less attractive in photochemical work. However, the present study does suggest that the *trans,trans*-$[Pt_2(dppm)_2X_4]$ complexes are likely to have interesting luminescent properties and deserve our attention in the design of new photocatalysts based on binuclear $d^8 \cdots d^8$ complexes.

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Supplementary Material Available: Tables of crystal and structure determination data, hydrogen atom parameters, anisotropic thermal parameters and complete bond distances and angles (7 pages); a table of structure factors (28 pages). Ordering information is given on any current masthead page.

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