Luminescent and Coordinatively Unsaturated Heterobimetallic d^{10}–d^8 Complexes. Photoredox Properties and X-Ray Crystal Structure of $[AuPt(\mu\text{-dppm})_2(CN)_2]^+$ [dppm = bis(diphenylphosphino)methane]

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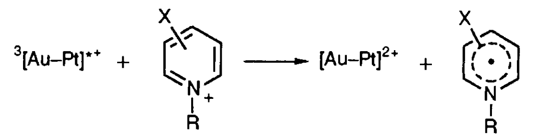
The X-ray structure and photoredox properties of $[AuPt(\mu\text{-dppm})_2(CN)_2]^+$ which has a long-lived (18 μs in acetonitrile at room temperature) and emissive excited state are described.

Despite intensive studies on the photochemistry and photophysics of homobimetallic d^8–d^8 and d^{10}–d^{10} complexes,[1,2] corresponding research on the heterobimetallic d^{10}–d^8 system[3,4] is still sparse. Recently Balch and coworkers reported the luminescence properties of $[AuIr(CO)Cl(\mu\text{-dppm})_2]PF_6$ [dppm = bis(diphenylphosphino)methane].[3a] However, the relatively short excited state lifetime of this complex (<50 ns at 298 K) renders it less attractive for photochemical work. Herein we describe the X-ray structure and spectroscopy of the heterobimetallic complex $[AuPt(\mu\text{-dppm})_2(CN)_2]^+$ **1** which exhibits intriguing photoredox properties.

The complex **1**·$[ClO_4]$ was obtained by the addition of $LiClO_4$ to a methanolic solution of the chloride salt, which was



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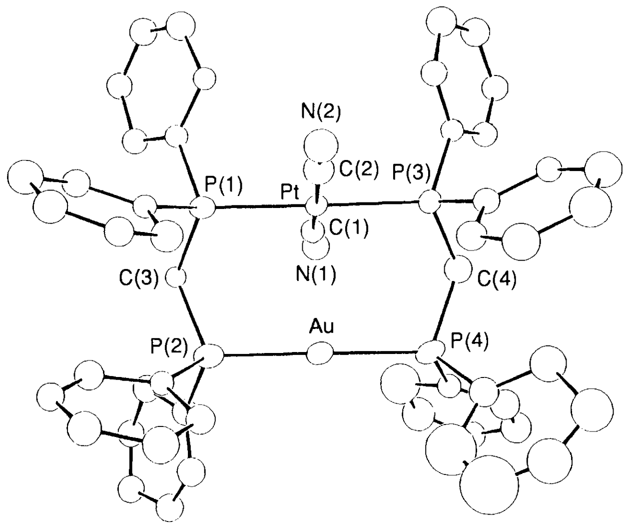

Fig. 1 ORTEP plot of [AuPt(μ-dppm)$_2$(CN)$_2$]$^+$ **1**. Selected bond distances (Å) and angles (°). Au–Pt 3.046(2), Au–P(2) 2.278(10), Au–P(4) 2.301(10), Pt–C(1) 2.09(3), Pt–C(2) 1.93(3), Pt–P(1) 2.314(9), Pt–P(3) 2.303(9) Å; P(2)–Au–P(4) 170.7(3), P(1)–Pt–P(3) 175.5(3), C(1)–Pt–C(2) 174.3(13), Au–Pt–C(1) 67.1(8), Au–Pt–C(2), 118.4(10).

prepared by the method of Shaw and coworkers.[5] The structure of **1** is shown in Fig. 1.† The intramolecular Au–Pt distance of 3.046(2) Å is close to that of 3.034(1) Å in Au$_2$Pt[CH$_2$P(S)Ph$_2$]^6 despite the difference in bridging ligands. It is, however, shorter than the Pt–Pt separation [3.301(1) Å]^7 in [Pt$_2$(dppm)$_2$(CN)$_4$] **2** but slightly longer than the Au–Au separation [2.9268(3) Å]^8 in [Au$_2$(dppm)$_2$]$^{2+}$ **3**. Since **1**, **2** and **3** have the same bridging ligands, this may suggest that the order of bonding interaction is: Au$^{\text{I}}$–Au$^{\text{I}}$ > Au$^{\text{I}}$–Pt$^{\text{II}}$ > Pt$^{\text{II}}$–Pt$^{\text{II}}$. Interestingly, the measured Au–Pt–C(1) angle of 67.1(8) substantially deviates from 90°, indicating a weak intramolecular Au···CN interaction. Similar interunit Pt···CN interaction has been observed in **2** previously.[7] The ^{31}P NMR spectrum of **1**·[ClO$_4$] in acetonitrile at 298 K shows a singlet at δ 32.02 due to P–Au–P and a pseudo triplet at δ 6.86 due to P–Pt–P [$^1J_{\text{(Pt–P)}}$ 2344 Hz) suggesting that the structure of **1** is retained in solution.[5]

The electronic absorption spectrum of **1** in acetonitrile exhibits an intense absorption band at 320 nm ($\varepsilon_{\max}$ = 1.3 × 10^4 dm^3 mol^{-1} cm^{-1}, Fig. 2). Since both [Au(PR$_3$)$_2$]$^{+9}$ and [Pt(dppe)(CN)$_2$] [dppe = 1,2-bis(diphenylphosphino)ethane]^{10} do not have any significant absorption at wavelength greater than 300 nm, the 320 nm band is associated with metal–metal interaction. As in the cases of the d^8–d^8 and d^{10}–d^{10} systems,[1,2] this band is tentatively assigned to the spin-allowed ^{1}(p$_\sigma$ ← d$_{\sigma^*}$) transition, which is dipole-allowed (the d$_{\sigma^*}$ and p$_\sigma$ refer to the antisymmetric combination of the 5d$_{z^2}$ orbitals and symmetric combination of the 6p$_z$ orbitals of Pt$^{\text{II}}$ and Au$^{\text{I}}$$_1$ respectively). Similar^1 (p$_\sigma$ ← d$_{\sigma^*}$) transitions have also been reported in other related systems.[3] In **1**, there is also a weak and broad absorption around 380 nm ($\varepsilon_{\max}$ < 10^3 dm^3 mol^{-1} cm^{-1}).

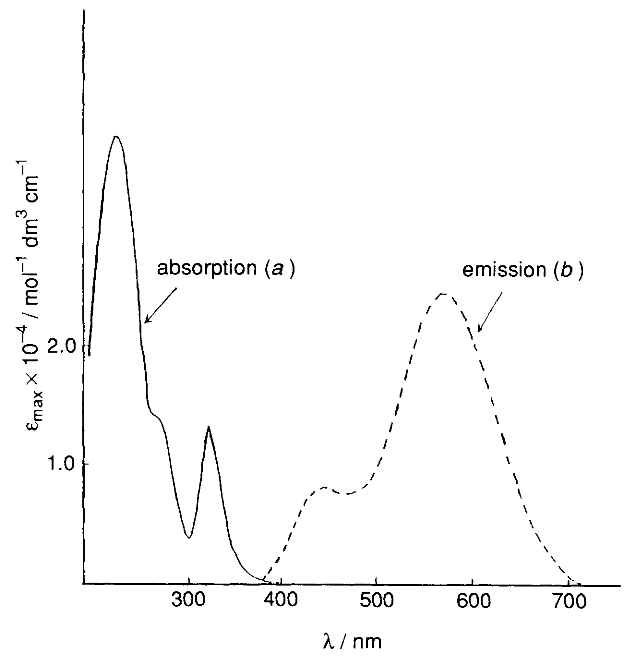

Fig. 2 (*a*) UV–VIS absorption and (*b*) emission (excitation of 350 nm) spectra of [AuPt(μ-dppm)$_2$(CN)$_2$]$^+$ in acetonitrile

The complex **1**·[ClO$_4$] exhibits photoluminescence either in solid state or in fluid solutions. Room temperature excitation at 320 to 400 nm of a degassed acetonitrile solution of **1**·[ClO$_4$] gives two emissions with $\lambda_{\max}$ at 430 and 570 nm (Fig. 2), the latter one being more intense. Both emissions have similar excitation spectrum with two excitation maxima at 320 and 350 nm. The 430 nm emission which has a very short lifetime (<10 ns) at room temperature, is likely due to fluorescence. The 570 nm emission (quantum yield 0.02 in acetonitrile at 298 K) exhibits a simple first-order decay (k = 5.5 × 10^4 s^{-1}), has its lifetime of 18 μs, which is quite insensitive to the concentration of **1** (estimated self-quenching rate constant is less than 10^7 dm^3 mol^{-1} s^{-1}). The very long excited state lifetime suggests that the emission comes from a spin-triplet excited state (here abbreviated as ^{3}[Au–Pt]*+). ^{3}[Au–Pt]*+ is a powerful reductant and rapidly reacts with pyridinium acceptors according to eqn. (1). The E^0 of the redox couple, [Au–Pt]$^{2+}$ + e → ^{3}[Au–Pt]*+, determined by fitting the quenching rate constants and the redox potentials of alkylated pyridinium acceptors to Marcus' equation (the details are given in ref. 2*e* or 2*f*) is −1.8(1) V *vs.* standard calomel electrode indicating that **1** is a powerful photo-reductant.

The 570 nm emission of **1** is also quenched by some hydrocarbons and alcohols. The quenching rate constants (k_q) determined by the equation $\tau_o/\tau = 1 + k_q\tau_o$ [substrate] are 6.8 × 10^8, 1.77 × 10^5 and ≤10^4 dm^3 mol^{-1} cm^{-1} for 1,3-cyclohexadiene, cyclohexene, and cumene, respectively. These values apparently correlate to the order of C–H bond energy [kcal mol^{-1}; (1 cal = 4.184 J]: 1,3-cyclohexadiene (73 ± 5) < cyclohexene (82) < cumene (84.4), in accordance to a H-atom abstraction mechanism. The fact that quenching by cyclohexene exhibits a large kinetic isotope effect of >9 (k_q for

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† The molecular structure of **1**·[ClO$_4$] has been determined by an X-ray diffraction study. The crystal belongs to the orthorhombic system, space group, $P2_12_12_1$, a = 10.483(2), b = 18.825(3), c = 26.652(3) Å, V = 5259.6(13) Å^3, Z = 4. Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer using Mo-Kα radiation. A total of 3932 reflections were collected. Of the 3858 unique reflections, 2888 were considered observed having $I > 2\sigma(I)$. The positions of the Au and Pt atoms were taken from a Patterson Map. The remainder of the non-hydrogen atoms were located in differences Fourier maps. Final R = 0.058 and R_w = 0.064. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

C_6D_{10} is $<2 \times 10^4$ dm^3 mol^{-1} cm^{-1}) also suggests a linear transition state $\{^3[\text{Au–Pt}]^{*+} \cdots \text{H–R}\}$ for the photoreaction. The kinetic isotope effect found in this work is even greater than that found for the related photoreaction of $[Pt_2(P_2O_5H_2)_4]^{4-}$ with cyclohexene ($k_H/k_D = 5$),[11] which is known to proceed through a H-atom abstraction pathway.[1a] Quenching of $^3[\text{Au–Pt}]^{*+}$ by triphenylmethane has a k_q of 8.2 × 10^4 dm^3 mol^{-1} cm^{-1}, which is very much smaller than that of 6.8 × 10^8 dm^3 mol^{-1} cm^{-1} by 1,3-cyclohexadiene despite the similar C–H bond energies for these two substrates. As in the case of $[Pt_2(P_2O_5H_2)_4]^{4-}$,[1b] this is attributed to the steric effect of the phenyl groups which prohibit the approach of triphenylmethane to the metal complex. At room temperature, broad band ($\lambda > 300$ nm) irradiation (photoreactor from Applied Photophysics, 400 W mercury short arc lamp) of a degassed acetonitrile solution of **1**·[ClO$_4$] (10^{-3} mol dm^{-3}) and diphenylmethanol (0.1 mol dm^{-3}) for 8 h gave benzophenone. Similar photoreaction with 1,3-cyclohexadiene gave benzene (identified by GC–MS). In each case, the turnover of the organic product was low (less than 10) and **1** has been found to undergo some degradative reactions, the nature of which are under investigation.

The present work demonstrates a new luminescent heterobimetallic d^{10}–d^8 complex, having interesting photoredox properties as that encountered in the binuclear d^8–d^8 systems studied by Gray and coworkers over the past two decades. Given the fact that a wide variety of this class of compounds are available in the literature, it is not difficult to find a suitable heterobimetallic d^{10}–d^8 complex, which could serve as a good model system for studies of photochemical dehydrogenation of hydrocarbons by the Au–Pt colloid.[12]

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References

1 (*a*) D. M. Roundhill, H. B. Gray and C. M. Che, *Acc. Chem. Res.*, 1989, **22**, 55; (*b*) D. C. Smith and H. B. Gray, *Coord. Chem. Rev.*, 1990, **100**, 169.
2 (*a*) J. V. Caspar, *J. Am. Chem. Soc.*, 1985, **107**, 6718; (*b*) P. D. Harvey and H. B. Gray, *J. Am. Chem. Soc.*, 1988, **110**, 2145; (*c*) C. King, J. C. Wang, Md. N. I. Khan and J. P. Fackler, Jr., *Inorg. Chem.*, 1989, **28**, 2145; (*d*) C. M. Che, H. L. Kwong, V. W. W. Yam and K. C. Cho, *J. Chem. Soc., Chem. Commun.*, 1989, 885; (*e*) V. W. W. Yam, T. F. Lai and C. M. Che, *J. Chem. Soc., Dalton Trans.*, 1990, 3747; (*f*) C. M. Che, H. L. Kwong, C. K. Poon and V. W. W. Yam, *J. Chem. Soc., Dalton Trans.*, 1990, 3215.
3 (*a*) A. L. Balch, V. J. Catalano and M. M. Olmstead, *Inorg. Chem.*, 1990, **29**, 585; (*b*) A. L. Balch, J. K. Nagle, D. E. Oram and P. E. Reedy, Jr., *J. Am. Chem. Soc.*, 1988, **110**, 454; (*c*) A. L. Balch, V. J. Catalano and M. M. Olmstead, *J. Am. Chem. Soc.*, 1990, **112**, 2010.
4 S. Wang, G. Garzon, C. King, J.-C. Wang and J. P. Fackler, Jr., *Inorg. Chem.*, 1989, **28**, 4623.
5 F. S. M. Hassan, D. P. Markham, P. G. Pringle and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1985, 279.
6 H. H. Murray, D. A. Briggs, G. Garzon, R. G. Raptis, L. C. Porter and J. P. Fackler, Jr., *Organometallics*, 1987, **6**, 1992.
7 C. M. Che, V. W. W. Yam, W. T. Wong and T. F. Lai, *Inorg. Chem.*, 1989, **28**, 2908.
8 P. Y. Cheung and T. F. Lai, unpublished X-ray crystal structure of $[Au_2(dppm)_2](ClO_4)_2$.
9 H.-R. C. Jaw and W. R. Mason, *Inorg. Chem.*, 1989, **28**, 4370.
10 C. M. Che, unpublished result on the X-ray crystal structure and spectroscopy of $[Pt(dppe)(CN)_2]$.
11 H. L. Kwong, M. Phil. Thesis, University of Hong Kong, 1989.
12 A. Harriman, *J. Chem. Soc., Chem. Commun.*, 1990, 24.