Synthesis, photophysics and thermal redox reactions of a $[\{Au(dppn)Cl\}_2]^{2+}$ dimer with an unsupported Au^{II}–Au^{II} bond

Vivian Wing-Wah Yam,* Sam Wing-Kin Choi and Kung-Kai Cheung

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong

A novel binuclear gold(II) complex containing a formal Au^{II}–Au^{II} bond is synthesized and characterized by X-ray crystallography; the compound is shown to possess rich photophysical and thermal redox properties.

Numerous gold clusters and gold(II) complexes exist and Au^{II}–Au^{II} bonds, which are formal single bonds, have been described.[1–4] Fackler and coworkers have studied a number of binuclear gold(II) complexes, containing the bis(ylide) ligand $[(CH_2)_2PPh_2]^-$.[1] In these complexes, the Au^{II}–Au^{II} distances are in the range 2.5–2.7 Å, which are much shorter than Au^I–Au^I interactions. Since the first discovery of $[\{Au(CH_2)_2PPh_2\}_2Au(C_6F_5)_3]$,[4] the first oligonuclear gold complex with an Au^I–Au^{III} bond unsupported by covalent bridges, there are only very few examples of complexes possessing a direct formal Au–Au bond unbridged by any other ligands. In this communication, a simple dimeric complex $[\{Au^{II}(dppn)Cl\}_2][PF_6]_2$ **1** [dppn = 1,8-bis(diphenylphosphino)naphthalene] with the monomeric units connected by a single unsupported Au^{II}–Au^{II} bond [Au–Au 2.6112(7) Å] will be described.

Reaction of $[Au_2(dppn)Cl_2]$ with $[Ag(MeCN)_4]PF_6$ and dppn in MeCN afforded **1**, isolated as air-stable dark purple crystals.† Complex **1** is stable in the solid state, whereas in dichloromethane and acetone solutions, it is stable only for a few weeks in the absence of light. X-Ray fluorescence studies confirmed the presence of Au, P and Cl, and the absence of Ag in complex **1**.

Fig. 1 shows the perspective drawing of the cation of **1**.‡ The molecule consists of two square planes about the two Au^{II} centres with a common Au^{II}–Au^{II} bond, with the two PF_6^- ions being non-coordinating. The Au(1)–Au(2) bond distance is 2.6112(7) Å, very similar to other reported Au^{II}–Au^{II} distances in dinuclear bis(ylide) gold(II) complexes.[1b,3f] However, it is slightly longer than the unsupported Au–Au bond of $[\{Au(CH_2)_2PPh_2\}_2Au(C_6F_5)_3]$ [2.572(1) Å],[4] but shorter than that in $[(C_6F_5)Au(CH_2PPh_2CH_2)_2Au\}_2Au(C_6F_5)_2][Au(C_6F_5)_4]$ [2.755(1) Å][2a] and $[\{(C_6H_2F_3\text{-}2,4,6)Au(CH_2PPh_2CH_2)_2Au\}_2Au(CH_2PPh_2CH_2)_2Au][ClO_4]_2$ [2.7368(7) Å].[2b] As the oxidation states of the Au centre in the latter two complexes are still uncertain, the Au^{II}–Au^{II} bond in **1** can be regarded as the first example of an unsupported Au^{II}–Au^{II} bond. The Au(2)–Au(1)–P(2) angle of 169.59(9)° and Cl(1)–Au(1)–P(1) angle of 173.3(1)°, are essentially close to linearity. The coordination planes of Au(1) and Au(2) are almost perpendicular to each other (dihedral angle 79.82°), which is comparable to the angles between adjacent planes in $[\{C_6H_2F_3\text{-}2,4,6)Au(CH_2PPh_2CH_2)_2Au\}_2Au(CH_2PPh_2CH_2)_2Au][ClO_4]_2$ [mean dihedral angles 83(1) and 74(1)°].[2b] The Au(2)–P(4) and Au(1)–P(1) distances which are *cis* to the Au–Au bond are 2.286(4) and 2.296(4) Å, respectively and those *trans* to the Au–Au bond are 2.385(4) and 2.387(3) Å for Au(1)–P(2) and Au(2)–P(3), respectively. All of them are longer than Au–P distances normally found in other gold(I) phosphine complexes.[5] This has also been observed in other gold(II) phosphine systems, such as 2.322(2) Å found in $[(C_6F_5)ClAu(dppa)AuCl(C_6F_5)]$ [dppa = bis(diphenylphosphino)amine].[3d] It is interesting that the Au–P distance *trans* to the Au–Au bond is longer than that *cis* to the Au–Au bond, indicating that the Au–Au bond is so strong that the *trans* effect of Au is larger than that of P. Besides, the Au–Cl distances [Au(1)–Cl(1) 2.332(4), Au(2)–Cl(2) 2.346(4) Å] are comparable to other Au^{II}–Cl bonds {2.341(3) Å in $[(C_6F_5)ClAu(dppa)AuCl(C_6F_5)]$,[3d] 2.359 Å in $[Au\{(CH_2)_2PEt_2\}Cl_2)]\}$.[3f]

The UV–VIS absorption spectrum of **1** in dichloromethane exhibits an intense band at 304 nm (ε = 24 665 dm^3 mol^{-1} cm^{-1}), 354 (15900) and 520 (49650). From the previous spectroscopic work on d^{10} gold(I) phosphine compounds,[5f,6] the peaks at 304 and 354 nm probably arise from the $\pi \rightarrow \pi^*$ transition within the naphthyl ring and the $\sigma \rightarrow \pi^*$ (Np) transition, respectively. The peak at 520 nm and an absorption coefficient of the order of 10^4 indicate that the electronic transition corresponding to this absorption is both orbitally and spin-allowed. The transition is tentatively assigned as a transition involving considerable $d_\sigma \rightarrow d_{\sigma^*}$ character with some $d_\pi \rightarrow d_{\pi^*}$ character. Similar low-energy absorption bands have been reported in other gold(II) complexes.[1d] Upon absorption of light, electrons accommodated in the d_σ (HOMO) orbital will be excited to the d_{σ^*} (LUMO) orbital. As d_{σ^*} is antibonding in nature, the total bond order of the Au–Au bond will be zero and the bond will break. Because of this, the gold(II) complex is light sensitive and will decompose upon prolonged irradiation with visible light.

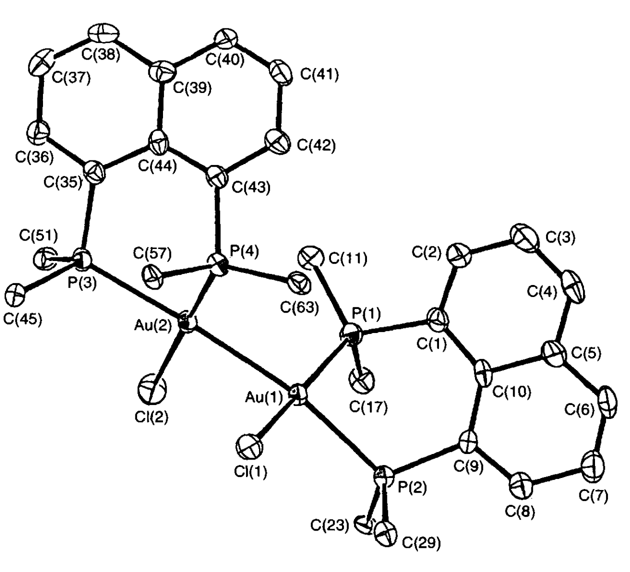

Fig. 1 Perspective view of $[\{Au^{II}(dppn)Cl\}_2][PF_6]_2$ **1** with atomic numbering scheme. Only the *ipso* carbons of the benzene rings are shown for clarity. Thermal ellipsoids are at the 40% probability level. Selected bond lengths (Å) and angles (°): Au(1)–Au(2) 2.6112(7), Au(1)–P(1) 2.296(4), Au(1)–P(2) 2.385(4), Au(1)–Cl(1) 2.332(4), Au(2)–P(3) 2.387(3), Au(2)–P(4) 2.286(4), Au(2)–Cl(2) 2.346(4); Au(2)–Au(1)–Cl(1) 81.12(9), Au(2)–Au(1)–P(1) 97.99(9), Au(2)–Au(1)–P(2) 169.59(9), Cl(1)–Au(1)–P(1) 173.3(1), Cl(1)–Au(1)–P(2) 95.4(1), P(1)–Au(1)–P(2) 86.6(1), Au(1)–Au(2)–Cl(2) 79.41(10), Au(1)–Au(2)–P(3) 174.02(9), Au(1)–Au(2)–P(4) 99.42(9), Cl(2)–Au(2)–P(3) 94.7(1), Cl(2)–Au(2)–P(4) 173.8(1), P(3)–Au(2)–P(4) 86.5(1).

Excitation of a dichloromethane solution of **1** at $\lambda > 350$ nm at room temperature results in weak emission. The emission spectrum shows a structureless band at 425 nm and a much weaker one at 585 nm, while the excitation spectrum shows bands at 276 and 335 nm if the emission wavelength is monitored at 425 nm, and a band at 530 nm appears if the emission wavelength is monitored at 585 nm. The higher energy emission band is likely to be derived from $\pi \longrightarrow \pi^*$ intraligand transition, as evidenced by the similarities of the excitation spectrum with the high-energy side of the UV–VIS absorption spectrum. In addition, from the excitation spectrum monitored at 585 nm, the band at 530 nm matches well with the UV–VIS absorption at 520 nm. If the excitation is performed at 530 nm, a single structureless band appears at 585 nm in the emission spectrum. Thus, the origin of the band at 585 nm is probably derived from the 520 nm absorption band.

Complex **1** is expected to exhibit rich redox behaviour. In this respect, the reactivities of **1** with electron donors such as benzyl alcohol has been studied. Fig. 2 shows the UV–VIS spectral changes of a dichloromethane solution of **1** (2×10^{-5} mol dm^{-3}) and benzyl alcohol (0.032 mol dm^{-3}) at 25 °C. It is noted that there is a gradual decrease in the 520 nm absorption, concomitant with a gradual rise in absorption intensity at *ca.* 350 nm, with an isosbestic point observed at 402 nm, indicative of a clean transformation from reactant to product. It is proposed that in the rate-determining step, one molecule of **1** collides with one molecule of benzyl alcohol, giving a second-order rate law. The bimolecular rate constant of the reaction, *k*, is estimated to be 3.02×10^{-3} dm^3 mol^{-1} s^{-1}. It is likely that the reaction is redox in nature, with the gold(II) dimer being reduced to $[Au(dppn)_2]^+$ (**2**) and the benzyl alcohol oxidized to benzaldehyde. This has been confirmed by the isolation of both **2** and benzaldehyde after the reaction; the X-ray crystal structure of **2** with a distorted tetrahedral structure has been determined.[7] It is interesting that a solid sample of **2**, unlike **1**, is strongly luminescent with $\lambda_{em} = 640$ nm upon visible-light excitation.

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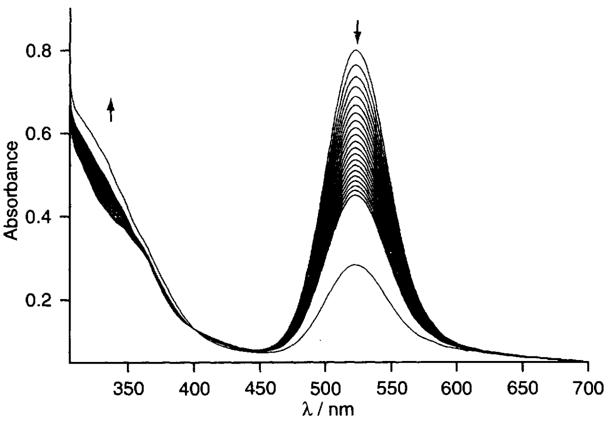

Fig 2 Spectral changes of $[\{Au^{II}(dppn)Cl\}_2]^{2+}$ (2×10^{-5} mol dm^{-3}) and benzyl alcohol (0.032 mol dm^{-3}) in dichloromethane. Spectra were recorded at 60 s intervals. The last trace was recorded after 24 h.

Footnotes

† ^{1}H NMR (CD_2Cl_2): δ 6.37—7.05 [dd, 8 H, Np], 7.25–8.09 [m, 40 H, PPh_2], 8.79 [dd,4 H, Np]. Positive FAB MS: *m/z* 1602 {M}$^+$. IR (Nujol) ν/cm^{-1} : 833 (s, P–F). Λ_M (Me_2CO) 265 Ω^{-1} cm^2 mol^{-1}. Anal. Calc. for $C_{68}H_{52}Au_2Cl_2F_{12}P_6 \cdot H_2O$: C, 46.23; H, 3.06; Cl, 4.02. Found: C, 45.98; H, 2.99; Cl, 4.04%.

‡ *Crystal data.* $[C_{68}H_{52}Au_2Cl_2F_{12}P_6] \cdot H_2O$; $M_r = 1765.84$, triclinic, space group $P\bar{1}$ (no. 2), $a = 16.638(3)$, $b = 16.841(3)$, $c = 13.696(3)$ Å, $\alpha = 109.91(4)$, $\beta = 96.70(2)$, $\gamma = 76.37(1)$°, $U = 3503(1)$ Å^3, $Z = 2$, $D_c = 1.674$ g cm^{-3}, μ(Mo-Kα) = 44.83 cm^{-1}, $F(000) = 1720$, $T = 298$ K, Rigaku AFC7R diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The centric space group was confirmed by the successful refinement of the structure solved by direct methods and difference Fourier method and refinement by full-matrix least squares using the software package TeXsan on a Silicon Graphic Indy computer, and anisotropic refinement on the 91 non-hydrogen atoms gave $R = 0.039$ and $wR = 0.050$ for 6327 reflections with $I > 3\sigma(I)$ with $w = 4F_o^2/\sigma^2(F^2)$, where $\sigma^2(F^2) = [\sigma^2(I) + (0.013F_o^2)^2]$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/53.

References

1 (*a*) C. King, D. D. Heinrich, G. Garzon, J. C. Wang and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, 1989, **111**, 2301; (*b*) H. H. Murray, J. P. Fackler, Jr., L. C. Porter, D. A. Briggs, M. A. Guerra and R. J. Lagow, *Inorg. Chem.*, 1987, **26**, 357; (*c*) J. D. Basil, H. H. Murray, J. P. Fackler, Jr., J. Tocher, A. M. Mazany, B. Trzcinska-Bancroft, H. Knachel, D. Dudis, T. J. Delord and D. O. Marler, *J. Am. Chem. Soc.*, 1985, **107**, 6908; (*d*) M. N. I. Khan, J. P. Fackler, Jr., C. King, J. C. Wang and S. Wang, *Inorg. Chem.*, 1988, **27**, 1672.

2 (*a*) R. Usón, A. Laguna, M. Laguna, J. Jiménez and P. G. Jones, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 198; (*b*) A. Laguna, M. Laguna, J. Jiménez, F. J. Lahoz and E. Olmos,, *Organometallics*, 1994, **13**, 253.

3 (*a*) M. C. Gimeno, J. Jiménez, P. G. Jones, A. Laguna and M. Laguna, *Organometallics*, 1994, **13**, 2508; (*b*) J. Vincente, M. T. Chicote and I. Saura-Llamas, *J. Chem. Soc., Dalton Trans.*, 1990, 1941; (*c*) M. A. Bennett, S. K. Bhargava, K. D. Griffiths and G. B. Robertson, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 260; (*d*) R. Usón, A. Laguna, M. Laguna, N. Fraile, P. G. Jones and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1986, 291; (*e*) H. Schmidbaur, A. Wohlleben, F. E. Wagner, D. F. van de Vondel and G. P. van der Kelen, *Chem. Ber.*, 1977, **110**, 2758; (*f*) H. Schmidbaur, J. R. Mandl, A. Frank and G. Huttner, *Chem. Ber.*, 1976, **109**, 466; (*g*) H. Schmidbaur and R. Franke, *Inorg. Chim. Acta*, 1975, **13**, 85.

4 R. Usón, A. Laguna, M. Laguna, M. T. Tarton and P. G. Jones, *J. Chem. Soc., Chem. Commun.*, 1988, 740.

5 See, for example, (*a*) V. W. W. Yam, T. F. Lai and C. M. Che, *J. Chem. Soc., Dalton Trans.*, 1990, 3747; (*b*) C. M. Che, H. L. Kwong, C. K. Poon and V. W. W. Yam, *J. Chem. Soc., Dalton Trans.*, 1990, 3215; (*c*) A. L. Balch, E. Y. Fung and M. M. Olmstead, *J. Am. Chem. Soc.*, 1990, **112**, 5181; (*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 and S. W. K. Choi, *J. Chem. Soc., Dalton Trans.*, 1994, 2057; (*f*) V. W. W. Yam, S. W. K. Choi and K. K. Cheung, *Organometallics*, 1996, in the press.

6 T. E. Müller, S. W. K. Choi, D. M. P. Mingos, D. Murphy, D. J. Williams and V. W. W. Yam, *J. Organomet. Chem.*, 1994, **484**, 209.

7 V. W. W. Yam, S. W. K. Choi and K. K. Cheung, unpublished work.

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