Dalton Communications

Synthesis and Crystal Structure of a Luminescent One-dimensional Phenylacetylide–Gold(I) Polymer with 2,6-Bis(diphenylphosphino)pyridine as Ligand

Shen-Jye Shieh,[a] **Xiao Hong,**[b] **Shie-Ming Peng***,[a] **and Chi-Ming Che***,[a,b]
[a] *Department of Chemistry, National Taiwan University, Taipei, Taiwan*
[b] *Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong*

The emissive one-dimensional gold(I) polymer [{$Au_2L(C{\equiv}CPh)_2$}$_\infty$][L = 2,6-bis(diphenylphosphino)pyridine] has been prepared and its crystal structure determined; $Au_2L(C{\equiv}CPh)_2$ is the repeating unit and the closest intermolecular $\mathrm{Au^{I}}\cdots\mathrm{Au^{I}}$ separation is 3.252(1) Å.

New organometallic polymers with intriguing electrooptical properties have been receiving our close attention. Recent studies by Puddephatt and co-workers[1] have shown a way to assemble linear-chain metal-containing polymers by reacting gold(I) acetylides with diphosphine and/or functional isocyanide ligands. However, the crystal structures of the gold(I) oligomers have not been determined. We therefore present herein the preparation and crystal structure of the one-dimensional gold(I) polymer [{$Au_2L(C{\equiv}CPh)_2$}$_\infty$][L = 2,6-bis(diphenylphosphino)pyridine], which is strongly emissive at room temperature.

The ligand L (ref. 2) and [{Au(C≡CPh)}$_\infty$][3] were prepared by literature methods. The reaction of L (0.14 g) with [{Au(C≡CPh)}$_\infty$] (0.10 g) in CH_2Cl_2 (40 cm^3) at room temperature for 30 min gave a yellow solution which was filtered. Upon diffusion of diethyl ether into the solution, bright yellow crystals of [{$Au_2L(C{\equiv}CPh)_2$}$_\infty$] were obtained in *ca.* 60% yield. This is an air-stable compound but has very low solubility in most common organic solvents. Satisfactory C, H and N analyses were obtained and its structure established by X-ray crystallography. Fig. 1 shows a perspective view of the molecule.† The structure features a one-dimensional polymer with the repeating unit $Au_2L(C{\equiv}CPh)_2$ held together by a weak

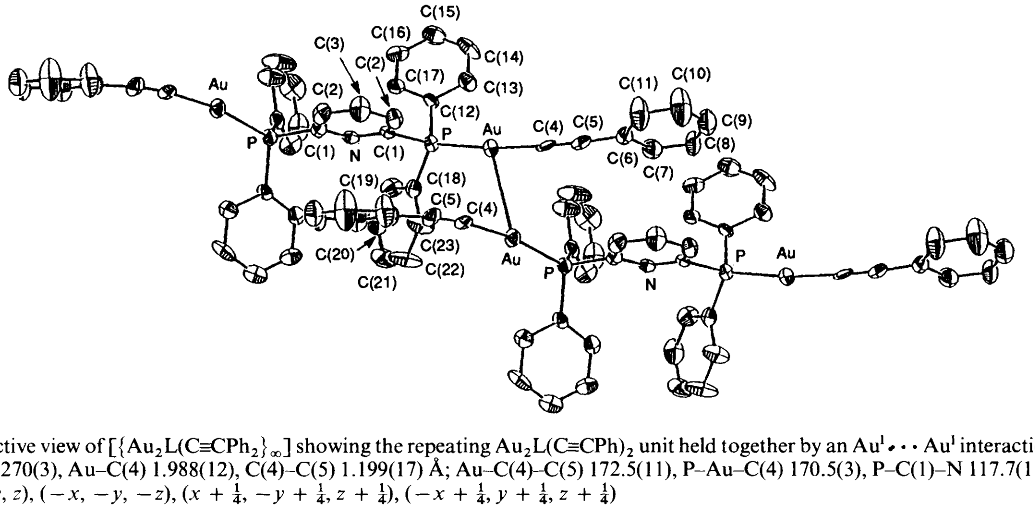

Fig. 1 A perspective view of [{$Au_2L(C{\equiv}CPh_2$}$_\infty$] showing the repeating $Au_2L(C{\equiv}CPh)_2$ unit held together by an $\mathrm{Au^{I}}\cdots\mathrm{Au^{I}}$ interaction; Au ··· Au 3.252(1), Au–P 2.270(3), Au–C(4) 1.988(12), C(4)–C(5) 1.199(17) Å; Au–C(4)–C(5) 172.5(11), P–Au–C(4) 170.5(3), P–C(1)–N 117.7(11)°. Symmetry coordinates: (x, y, z), $(-x, -y, -z)$, $(x + \frac{1}{4}, -y + \frac{1}{4}, z + \frac{1}{4})$, $(-x + \frac{1}{4}, y + \frac{1}{4}, z + \frac{1}{4})$

---

† Crystal data. $C_{45}H_{33}Au_2NP_2$, $M = 1043.63$, orthorhombic, space group *Fdd*2, $a = 10.754(3)$, $b = 40.453(10)$, $c = 17.218(8)$ Å, $U = 7491(4)$ Å^3, $Z = 8$, $D_c = 1.851$ g cm^{-3}, crystal dimensions 0.10 × 0.25 × 0.40 mm, $\mu = 79.18$ cm^{-1}, $F(000) = 3983$, number of parameters 227, number of unique reflections 1698, number of reflections with $I > 2\sigma(I)$ 1559, $R[= \Sigma|F_o - F_c|/|F_o|] = 0.027$, $R'\{= [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{\frac{1}{2}}\} = 0.020$, goodness of fit $\{= [\Sigma w(|F_o| - |F_c|)^2/(n - p)]^{\frac{1}{2}}\} = 1.98$, weighting scheme $w = 1/\sigma^2(F_o)$. Raw intensities were collected on a Nonius CAD4 fully automated four-circle diffractometer (graphite-monochromatized Mo-Kα radiation, $\lambda = 0.7107$ Å) using the ω–2θ scan mode. Data reduction and structure refinement were performed using the NRCC-SDP-VAX packages available from S. M. Peng upon request. The absolute structure was checked. The structure was solved by the Patterson method and refined by least-squares analysis. 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.*, 1994, Issue 1, pp. xxiii–xxviii.

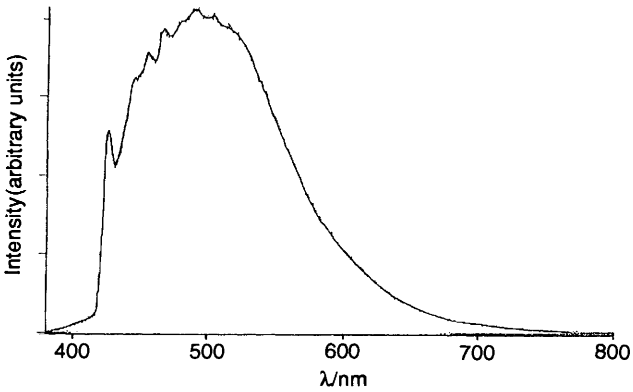

Fig. 2 Solid-state emission spectrum of $[\{Au_2L(C{\equiv}CPh)_2\}_\infty]$ measured at 77 K. Excitation at 350 nm

gold–gold interaction. For each $Au_2L(C{\equiv}CPh)_2$ unit, the two P and the N atoms of L and the two Au^I atoms are in a zigzag chain and a two-fold axis passes through the pyridine ring. The closest intermolecular $Au^I\cdots Au^I$ separation is 3.252(1) Å, which is slightly longer than the related value of 3.153(2) Å in $[Au_2(dppe)(C{\equiv}CPh)_2]$ [dppe = 1,2-bis(diphenylphosphino)ethane].[4] This distance, however, falls in the normal range of *ca.* 2.75–3.40 Å for weak intermolecular interactions between Au^I centres.[5] The ν(C≡CPh) absorption occurs at 2111 cm^{-1}, suggesting no intermolecular interaction between Au^I and the co-ordinated phenylacetylide.

The $[\{Au_2L(C{\equiv}CPh)_2\}_\infty]$ complex is a strongly emissive material in the solid state at room temperature. The emission (λ_{max} 500 nm) displayed in Fig. 2, is at a lower energy than the intraligand phosphorescence of the co-ordinated phenylacetylide (λ_{max} 400–450 nm)[4] but is at a higher energy than the solid-state emission of $[Au_2(dppe)(C{\equiv}CPh)_2]$ (λ_{max} 550 nm).[4] If the emission occurs from a $^3[d_{\delta^*}p_{\sigma^*}]$ or $^3[d_{\sigma^*}p_{\sigma^*}]$ excited state,[4,6] then the difference in the solid-state emission energies between $[\{Au_2L(C{\equiv}CPh)_2\}_\infty]$ and $[Au_2(dppe)(C{\equiv}CPh)_2]$ could be rationalized by the longer intermolecular metal–metal separation in the former.

Acknowledgements

We acknowledge support from the National Science Council of Taiwan and the Research Grants Council of Hong Kong.

References

1 G. Jia, N. C. Payne, J. J. Vittal and R. J. Puddephatt, *Organometallics*, 1993, **12**, 4771; G. Jia, R. J. Puddephatt, J. J. Vittal and N. C. Payne, *Organometallics*, 1993, **12**, 263; G. Jia, R. J. Puddephatt, J. D. Scott and J. J. Vittal, *Organometallics*, 1993, **12**, 3565.
2 G. R. Newkome and D. C. Hagen, *J. Org. Chem.*, 1978, **43**, 947.
3 G. E. Coates and C. Parkin, *J. Chem. Soc.*, 1962, 3220.
4 D. Li, X. Hong, C. M. Che, W. C. Lo and S. M. Peng, *J. Chem. Soc., Dalton Trans.*, 1993, 2929.
5 R. J. Puddephatt, in *Comprehensive Organometallic Chemistry*, eds. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon Press, Oxford, 1982, vol. 2, p. 756; G. K. Anderson, *Adv. Organomet. Chem.*, 1982, **20**, 39; R. J. Puddephatt, in *The Chemistry of Gold*, Elsevier, Amsterdam, 1978.
6 C. M. Che, H. K. Yip, W. C. Lo and S. M. Peng, *Polyhedron*, 1994, **13**, 887.

Received 1*st July* 1994; *Communication* 4/03989K