Synthesis, Photophysics and Electrochemistry of a Novel Luminescent Platinum(II) Sulfido Complex. Crystal Structure of $[Pt_2(\mu\text{-}S)(\mu\text{-dppm})(dppm)_2]^{2+}$ (dppm = $Ph_2PCH_2PPh_2$)

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The novel luminescent dimeric complex $[Pt_2(\mu\text{-}S)(\mu\text{-dppm})(dppm)_2]^{2+}$ has been isolated from the reaction of $PtCl_2$, dppm ($Ph_2PCH_2PPh_2$) and NaSH in the presence of triethylamine in MeCN; the crystal structure revealed dppm ligands displaying two different modes of co-ordination, bridging and chelating.

There has been considerable interest in the chemistry of soluble metal–sulfur complexes.[1] The ability of sulfur to bridge metals in various bonding modes with unusual stereochemistry has made this class of compounds attractive for studies, in particular, in the field of bioinorganic and catalytic research. Recently, a tetranuclear d^{10} copper(I) cluster containing a μ_4-sulfido moiety was shown by us to exhibit rich photo-physical and -chemical properties.[2] This together with our enormous efforts on the design of luminescent polynuclear d^8 and d^{10} metal complexes,[2–4] in particular the soluble polynuclear metal acetylides, have prompted us to extend our studies to the polynuclear d^8 metal–sulfur system. This system is especially attractive in view of its ability to function as a metalloligand in the synthesis of polynuclear heterometallic aggregates[5] as well as to activate carbon–halogen bonds.[5,6] Although there have been a number of reports on platinum sulfido complexes,[5,7] the photo-physical and -chemical properties of this class of compounds are relatively unexplored. In this communication we report the synthesis, luminescent properties and electrochemistry of a dimeric complex $[Pt_2(\mu\text{-}S)(\mu\text{-dppm})(dppm)_2]^{2+}$ (dppm = $Ph_2PCH_2PPh_2$), the crystal structure of which is also described.

Reaction of a mixture of $PtCl_2$ (100 mg), dppm (240 mg) and NaSH (34 mg) in the presence of triethylamine (45μl) in MeCN (10 cm^3) in a nitrogen atmosphere gave $[Pt_2(\mu\text{-}S)(\mu\text{-dppm})(dppm)_2]^{2+}$, isolated as the PF_6^- salt upon addition of $NaPF_6$. Subsequent recrystallization from acetonitrile–diethyl ether gave yellow crystals in *ca.* 40% yield,† the identity of which has been confirmed by single-crystal X-ray diffraction.‡ The methylene protons of the dppm ligands appear as two sets of multiplets at δ 3.44 and 4.46 in the ^1H NMR spectrum; the former has been assigned to the CH_2 of the bridging dppm ligand and the latter to the chelating phosphines on the basis of the integration ratios.

Fig. 1 depicts a perspective drawing of $[Pt_2(\mu\text{-}S)(\mu\text{-dppm})(dppm)_2]^{2+}$ with atomic numbering. It is interesting that the dppm ligands show different co-ordination modes, bridging and chelating, in the same molecule. The existence of different co-ordination modes of dppm in the same molecule is not uncommon; however, the modes that are commonly observed in coexistence are bridging and monodentate.[7c,d,g] An example is provided by $[Pt_2(\mu\text{-}S)(\mu\text{-dppm})(dppm\text{-}P)_2]$ formed from the reaction of $[Pt_2(\mu\text{-dppm})_3]$ with COS.[7c,d] The Pt • • • Pt distance of 4.108(2) Å in the present complex is significantly greater than the sum of the covalent radii, indicative of no formal metal–metal bond. The P(1)–Pt(1)–P(2) and P(5)–Pt(2)–P(6) angles of 72.4(2) and 71.8(2)° are far from square planar ones, possibly as a result of the steric requirement of the chelating dppm ligand. The Pt(1)–S–Pt(2) angle of 125.4(2)° is larger than that found in other similar systems such as $[Pt_2(\mu\text{-}S)_2(PMe_2Ph)_4]$ [mean Pt–S–Pt 85.5(4)°][5d] and $[Pt_2(\mu\text{-}S)(SCH_2Ph)_2(\mu\text{-dppm})_2]$ [Pt–S–Pt′ 84.9(2)°].[7b]

Table 1 Photophysical data for $[Pt_2(\mu\text{-}S)(\mu\text{-dppm})(dppm)_2][PF_6]_2$

Medium (*T*/K)	λ_{em}/nm	τ_0/μs
Solid (298)	625	4.0 ± 0.4
Solid (77)	625	
MeCN (298)	600	0.40 ± 0.04
CH_2Cl_2 (298)	450,600	

The electronic spectrum of $[Pt_2(\mu\text{-}S)(\mu\text{-dppm})(dppm)_2]^{2+}$ shows low-energy absorption in the 350–500 nm region. Excitation of a solid sample or fluid solution at $\lambda > 350$ nm results in long-lived luminescence at *ca.* 600–625 nm. The photophysical data are collected in Table 1. An emission lifetime of *ca.* 4 μs has been measured for a solid sample of $[Pt_2(\mu\text{-}S)(\mu\text{-dppm})(dppm)_2]^{2+}$ at room temperature. The long excited-state lifetime observed suggests that the emission is most likely associated with a spin-forbidden transition. Since both the low-energy absorption bands at *ca.* 350–500 nm and the emission at *ca.* 630 nm are only observable for the platinum sulfido complex and not for the monomeric $[Pt(dppm)_2]Cl_2$, we suggest that the origin of these low-energy transitions is not derived from the dppm intraligand nor the metal-to-ligand charge transfer $[d(Pt) \longrightarrow \pi^*(dppm)]$ transitions. An alternative possible assignment of a $d_{\sigma^*} \longrightarrow p_{\sigma}$ transition typical of the d^8–d^8 face-to-face dimeric system[9] is also unlikely given the large internuclear separation between the two Pt atoms. It is likely that, with the good σ-donating ability of the sulfido moiety, the low-energy emitting state should arise from states bearing a large amount of ligand-to-metal charge-transfer character. Similar assignments have been suggested for a tetranuclear copper(I) sulfur cluster.[2]

The cyclic voltammogram of $[Pt_2(\mu\text{-}S)(\mu\text{-dppm})(dppm)_2]^{2+}$ shows a quasi-reversible oxidation couple at *ca.* +0.65 V and an irreversible reduction peak at *ca.* −1.77 V *vs.* ferrocenium–ferrocene in MeCN (0.1 mol dm^{-3} $NBu^n{}_4PF_6$). Assuming the

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† Found: C, 47.2; H, 3.5; P, 13.9. Calc. for $[Pt_2(\mu\text{-}S)(\mu\text{-dppm})(dppm)_2][PF_6]_2\cdot H_2O$: C, 47.8; H, 3.6; P, 13.2%. UV/VIS (MeCN): λ/nm (ε/dm^3 mol^{-1} cm^{-1}) 259 (60 270), 291 (47 550), 409 (6650) and 438 (3930); IR (KBr, Nujol mull): 839 cm^{-1} [ν(P–F)]. ^1H NMR (270 MHz, CD_3CN, 298 K): δ 3.44 (m, 2 H, CH_2 of bridging dppm), 4.46 (m, 4 H, CH_2 of chelating dppm) and 7.0–7.7 (m, 60 H, Ph).

‡ Crystal data. $M = 1883.39$, triclinic, space group $P1$, crystal dimensions 0.15 × 0.20 × 0.35 mm, $a = 12.389(2)$, $b = 15.060(2)$, $c = 23.822(5)$ Å, $\alpha = 73.71(1)$, $\beta = 86.49(1)$, $\gamma = 87.70(1)°$, $U = 4256.9(1.0)$ Å^3, $Z = 2$, $D_c = 1.469$ g cm^{-3}, μ(Mo-Kα) = 35.5 cm^{-1}, $F(000) = 1852$, 452 parameters, $R = 0.072$ and $R' = 0.100$ for 5847 observed data with $I \geqslant 3.0\sigma(I)$ $[w = 4F_o^2/\sigma^2(F_o^2)]$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.065F_o^2)^2]$. Diffraction data were collected on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromatized Mo-Kα radiation (λ = 0.710 73 Å). The structure was solved by Patterson and Fourier methods and subsequent refinement by full-matrix least squares using the Enraf–Nonius SDP Programs[8] on a MicroVax II computer. 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.

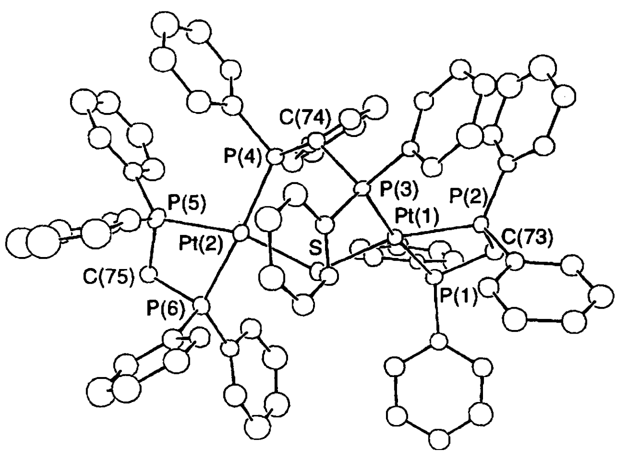

Fig. 1 Perspective drawing of the $[Pt_2(\mu\text{-}S)(\mu\text{-}dppm)(dppm)_2]^{2+}$ cation with atomic numbering. Hydrogen atoms and atomic numbering of the phenyl carbon atoms have been omitted for clarity. Thermal ellipsoids are shown at the 25% probability level. Selected bond lengths (Å) and angles (°): Pt(1)–S 2.315(7), Pt(2)–S 2.308(7), Pt(1)–P(1) 2.318(6), Pt(1)–P(2) 2.270(7), Pt(1)–P(3) 2.290(6), Pt(2)–P(4) 2.300(6), Pt(2)–P(5) 2.282(7), Pt(2)–P(6) 2.309(6), Pt(1)···Pt(2) 4.108(2), S–Pt(1)–P(1) 93.2(2), S–Pt(1)–P(2) 163.5(3), S–Pt(1)–P(3) 93.5(2), P(1)–Pt(1)–P(2) 72.4(2), P(1)–Pt(1)–P(3) 172.9(2), P(2)–Pt(1)–P(3) 101.3(2), S–Pt(2)–P(4) 93.8(2), S–Pt(2)–P(5) 160.6(2), S–Pt(2)–P(6) 90.1(2), P(4)–Pt(2)–P(5) 103.6(2), P(4)–Pt(2)–P(6) 172.9(2), P(5)–Pt(2)–P(6) 71.8(2), Pt(1)–S–Pt(2) 125.4(2), P(1)–C(73)–P(2) 96(1), P(3)–C(74)–P(4) 120(1), P(5)–C(75)–P(6) 93(1)

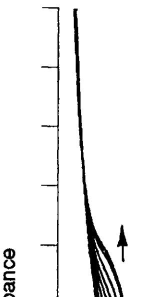

Fig. 2 The UV/VIS spectral traces for the reaction of $[Pt_2(\mu\text{-}S)(\mu\text{-}dppm)(dppm)_2]^{2+}$ and MeI in degassed MeCN upon steady-state photolysis at λ > 330 nm at time intervals of 0, 1, 2, 4, 6, 8, 11, 16, 21 and 30 min

oxidation and reduction couples to be metal-centred, excited-state reduction potentials $E_f[Pt_2(3+/2+^*)]$ of < −1.45 V (−1.07 V *vs.* saturated calomel electrode) and $E_f[Pt_2(2+^*/+)]$ of > +0.33 V (+0.71 V) *vs.* ferrocenium-ferrocene are estimated [$E_{0-0} \approx 2.1$ eV (*ca.* 3.36 × 10^{-19} J), where E_{0-0} is the zero–zero spectroscopic energy].

Preliminary work shows that $[Pt_2(\mu\text{-}S)(\mu\text{-}dppm)(dppm)_2]^{2+}$ reacts with halogenocarbons such as methyl iodide in MeCN upon irradiation with visible light. Fig. 2 depicts the spectral trace observed during the course of the reaction upon steady-state photolysis of a degassed MeCN solution of $[Pt_2(\mu\text{-}S)(\mu\text{-}dppm)(dppm)_2]^{2+}$ and MeI at λ > 330 nm. Clean isosbestic points at *ca.* 332 and 372 nm are observable with the 410 nm absorption decreasing concomitant with the increase in absorption at *ca.* 344 nm. The corresponding thermal reaction in the dark is extremely slow. It is envisaged that the present platinum sulfido system should show interesting thermal and photochemical reactivities with halogenocarbons. Work is in progress to investigate the detailed reactivity and mechanism of this class of compounds with various halogenocarbons and to isolate the reaction products.

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