Unusual Reactivity of a Luminescent Bis-μ-Sulfido Platinum(II) Dimer with Methylene Chloride. X-Ray Structural Characterization of $[Pt_2(\mu\text{-}S)_2(dppy)_4]$ and $[Pt(dppy)_2(S_2CH_2)]$ (dppy = 2-diphenylphosphinopyridine)

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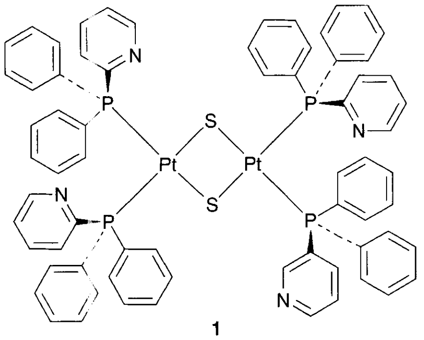
Reaction of $[Pt(dppy)_2Cl_2]$ with NaSH in the presence of triethylamine in MeCN produces a luminescent dimeric $[Pt_2(\mu\text{-}S)_2(dppy)_4]$ complex **1** which is characterized by X-ray crystallography; its unusual reactivity with CH_2Cl_2 to give novel monomeric $[Pt(dppy)_2(S_2CH_2)]$ **2**, identified by both NMR spectroscopy and X-ray crystallography, is described (dppy = 2-diphenylphosphinopyridine).

There has been considerable interest in the chemistry of soluble metal–sulfur complexes.[1] Recently, a tetranuclear d^{10} copper(I) cluster containing a μ_4-sulfido moiety has been shown by us to exhibit rich photophysical and photochemical properties.[2] This, together with our extensive efforts on the design of luminescent polynuclear d^8 and d^{10} metal complexes and the study of their photoreactivities with electron acceptors and halocarbons,[2–4] has prompted us to extend our studies to polynuclear d^8 metal–sulfur systems which are especially attractive in view of their ability to function as metalloligands in the synthesis of polynuclear heterometallic aggregates.[5] In addition, the ability of d^8 metal systems in the activation of carbon–halogen and carbon–hydrogen bonds has been well documented.[5,6] In this communication, we report on the synthesis, luminescent properties, and X-ray crystal structure of a dimeric $[Pt_2(\mu\text{-}S)_2(dppy)_4]$ complex **1**; its unusual reactivity with CH_2Cl_2 to give novel monomeric $[Pt(dppy)_2(S_2CH_2)]$ **2**, which has also been identified crystallographically, is also described (dppy = 2-diphenylphosphinopyridine).



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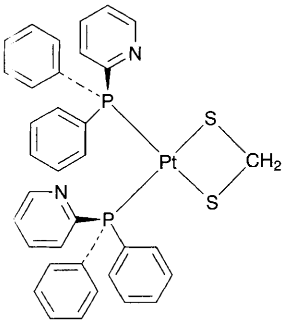

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Reaction of $[Pt(dppy)_2Cl_2]$ with NaSH in the presence of triethylamine in MeCN in an inert atmosphere of nitrogen gave the dimeric $[Pt_2(\mu\text{-}S)_2(dppy)_4]$ **1** as an orange solid. Recrystallization from benzene–diethyl ether gave reddish orange crystals of **1** in *ca.* 55% yield;† the identity of which has been confirmed by single-crystal X-ray diffraction‡ (Fig. 1). Complex **1** shows a flat square-planar geometry with the two platinum atoms bridged by two μ-sulfur ligands and the terminal dppy ligands P-coordinated to the platinum centre in a monodentate fashion. This differs substantially from other related dimeric platinum–sulfido complexes such as $[Pt_2(\mu\text{-}S)_2(PMe_2Ph)_4]$ which showed a hinged square-planar geometry with a dihedral angle of 121° (**1**, dihedral angle 0°). Dihedral angles lying in the range 131–141° have also been reported in other dimeric μ-alkylsulfido complexes of platinum. The Pt···Pt distance of 3.555(1) Å is significantly greater than the sum of the covalent radii, indicative of no formal metal–metal bond. The S···S separation of 3.005(2) Å is comparable to those observed in bidentate thioether and phosphine ligands and other related sulfido complexes which are known to function as metalloligands.[5,7]

Dissolution of **1** in dichloromethane followed by vapour diffusion of diethyl ether gave pale yellow crystals of $[Pt(dppy)_2(S_2CH_2)]$ **2**, which has been characterized both spectroscopically§ and crystallographically.‡ Fig. 2 shows a perspective drawing of **2** with atomic numbering. Complex **2** shows a slightly distorted square-planar geometry with an S–Pt–S angle of 76.23(5)°. A similar S–Pt–S angle of 74.7° has been reported for a related platinum dithiocarbamate complex, $[Pt(S_2CF)(PPh_3)_2]^+$.[8] To the best of our knowledge, this represents the first report on the isolation and the X-ray crystal structure of a saturated dithiolato four-membered platinacycle. Five- and six-membered platinacycles of dithiolate and diselenate are known.[9] A similar four-membered dithiolato

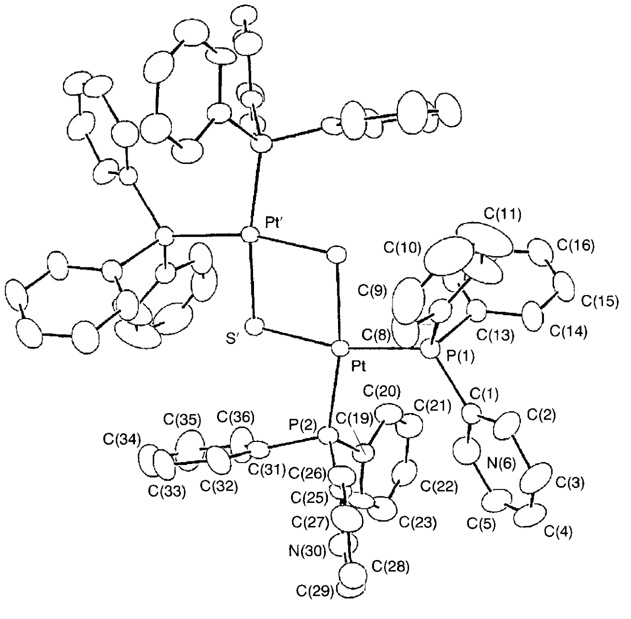

Fig. 1 Perspective drawing of compound **1** with the atomic numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 30% probability levels. Selected bond lengths (Å) and angles (°): Pt–S 2.333(1), Pt–P(1) 2.275(2), Pt–P(2) 2.279(1), Pt···Pt' 3.555(1), S···S' 3.005(2), S–Pt–P(1) 86.75(5), S–Pt–P(2) 170.05(7), P(1)–Pt–P(2) 102.98(6), S–Pt–S' 80.42(6), Pt–S–Pt' 99.58(6).

palladacycle $[Pd(PR_3)_2(S_2CHPR_3)]^+$ has been isolated from the reaction of $[Pd(PR_3)_3H]^+$ and CS_2.[10] The methylene protons in **2** have been unambiguously characterized by ^1H, ^{13}C and ^{13}C DEPT135 NMR spectroscopy (Fig. 3). The methylene group appears in the $^{13}C\{^1H\}$ NMR spectrum as a singlet at δ 38.0; this signal is negative in the DEPT spectrum, indicative of an even number of hydrogen atoms. The methylene protons appear as a triplet at δ 5.54 [^4J(P–H) = 1.8, ^3J(^{195}Pt–H) = 42.2 Hz] with platinum satellites in the ^1H NMR spectrum. Similar chemical shifts and ^3J(^{195}Pt–H) values have been observed in the ^{13}C and ^1H NMR spectra of other related systems.[9–11] The reaction of **1** with dichloromethane to give **2** is rather unusual. It is interesting that the activation of the C–X bond in dichloromethane or other halocarbons by other similar square-planar d^8 metal systems usually proceeds *via* an oxidative addition pathway.[5,12] It is likely that formation of **2** involves the attack of the nucleophilic sulfido bridges of **1** on dichloromethane which acts as the electrophile. A side product identified as $[Pt(dppy)_2Cl_2]$ has also been isolated in the reaction mixture [eqn. (1)].

$$[Pt_2(\mu\text{-}S)_2(dppy)_4] + CH_2Cl_2 \rightarrow [Pt(dppy)_2(S_2CH_2)] + [Pt(dppy)_2Cl_2] \quad (1)$$

The electronic absorption spectra of both **1** and **2** show low-energy absorption bands in the 350–425 nm region. Excitation of solid samples of both **1** and **2** at λ > 350 nm shows long-lived luminescence at *ca.* 630 nm at 77 K. The photophysical data are collected in Table 1. An emission lifetime of *ca.* 10 µs has been measured for a solid sample of **1** 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.* 350–425 nm and the emission at *ca.* 630 nm are only observable in the platinum sulfido complexes **1** and **2** and not in $[Pt(dppy)_2Cl_2]$, we suggest that the origin of these low-energy transitions is not derived from the dppy intraligand (IL) or the metal-to-ligand charge transfer [d(Pt) → π*(dppy) MLCT] transitions. With the good σ-donating capability of the sulfido moiety, it is likely that the low-energy emitting state should arise from states bearing a

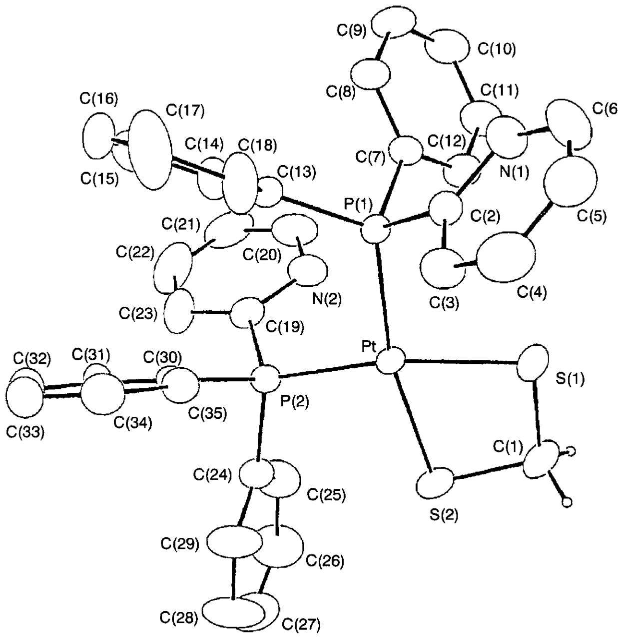

Fig. 2 Perspective drawing of compound **2** with the atomic numbering scheme. Of the hydrogen atoms, only the ones attached to the methylene carbon atom are shown; the others have been omitted for clarity. Thermal ellipsoids are shown at the 30% probability levels. Selected bond lengths (Å) and angles (°): Pt–S(1) 2.314(1), Pt–S(2) 2.310(1), Pt–P(1) 2.279(1), Pt–P(2) 2.277(1), S(1)–C(1) 1.814(7), S(2)–C(1) 1.831(7), S(1)–Pt–S(2) 76.23(5), S(1)–Pt–P(1) 90.72(6), S(1)–Pt–P(2) 168.02(5), S(2)–Pt–P(1) 166.94(6), S(2)–Pt–P(2) 92.38(5), P(1)–Pt–P(2) 100.65(5), Pt–S(1)–C(1) 90.3(2), Pt–S(2)–C(1) 90.0(3), S(1)–C(1)–S(2) 103.0(3).

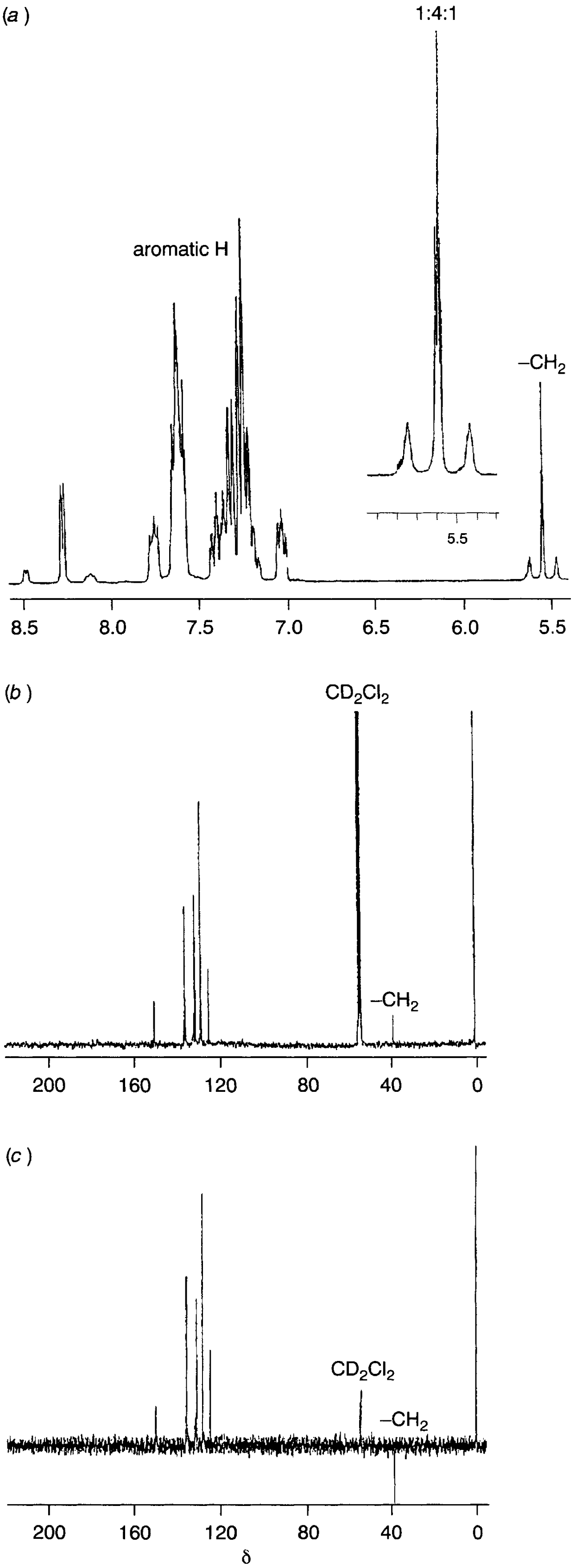

Fig. 3 Diagram showing the ^1H (*a*), $^{13}C\{^1H\}$ (*b*), and ^{13}C DEPT135 (*c*) NMR spectra of compound **2** in CD_2Cl_2

Table 1 Photophysical data for compounds **1** and **2**

Compound	Medium (T/K)	λ_{em}/nm	τ_o/μs
1	Solid (298)	430	0.30 ± 0.04
		645	10.0 ± 1.0
	Solid (77)	635	
	THF (298)	430	< 0.1
		550	0.06 ± 0.01
2	Solid (298)	460	
	Solid (77)	440, 630	
	$CHCl_3$ glass (77)	440(sh), 600	
	CH_2Cl_2 (298)	420	< 0.1

large amount of ligand-to-metal charge transfer (LMCT) character. Similar assignments have been suggested in a tetranuclear copper(I) sulfur cluster.[2]

It is envisaged that the present platinum sulfido system should show interesting thermal and photochemical reactivities with electrophiles. Work is in progress to investigate the reactivity of this class of compounds with various halocarbons and electrophiles such as Lewis acids and to explore its potential as a metalloligand in the synthesis of polynuclear heterometallic complexes.

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Footnotes

† **1**. UV–VIS (THF): λ/nm (ε/dm^3 mol^{-1} cm^{-1}) 350 (8000), 425 (3000); positive FAB–MS: ion cluster at m/z 1506 {M}$^+$.

‡ *Crystal data*: **1**, triclinic, space group $P\bar{1}$, a = 9.496(4), b = 12.726(2), c = 14.236(2) Å, α = 64.93(1), β = 81.09(2), γ = 74.11(2)°, V = 1497.3(1.0) Å^3, Z = 1, D_c = 1.672 g cm^{-3}, μ(Mo-Kα) = 49.3 cm^{-1}, F(000) = 740; R = 0.026 for 3373 reflections with $I \geqslant 3.0\sigma(I)$. **2**, triclinic, space group $P\bar{1}$, a = 10.303(1), b = 12.882(1), c = 14.113(2) Å, α = 101.33(2), β = 102.15(2), γ = 112.56(2)°, V = 1609.3(1.0) Å^3, Z = 2, D_c = 1.650 g cm^{-3}, μ(Mo-Kα) = 46.5 cm^{-1}, F(000) = 788; R = 0.027 for 4504 reflections with $I \geqslant 3.0\sigma(I)$. For both structures, Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å); ω–2θ scans. The structures were solved by Patterson and Fourier methods and subsequent refinement by full-matrix least squares analysis using the Enraf-Nonius SDP Programs on a Micro Vax II computer. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ **2**. UV–VIS (CH_2Cl_2): λ/nm (ε/dm^3 mol^{-1} cm^{-1}) 373 (405); positive FAB–MS: ion cluster at m/z 817 {M + H_2O}$^+$, 799 {M}$^+$; ^{1}H NMR (270 MHz, CD_2Cl_2, 298 K): δ 5.54 [t, 2H, ^4J(P–H) 1.8, ^3J(Pt–H) 42.2 Hz, –CH_2], 7.0–8.5 (m, 28H, dppy); $^{13}C\{^1H\}$ NMR (67.9 MHz, CD_2Cl_2, 298 K): δ 38.0 (–CH_2, negative in the DEPT spectrum), 124–150 (dppy, positive in the DEPT spectrum); ^{31}P NMR (109.4 MHz, CD_2Cl_2, 298 K): δ 20.8 [s, J(P–Pt) 2910 Hz].

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