Photoluminescent Properties and Crystal Structure of a Metal-perturbed Donor–Acceptor Acetylene Complex

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Emission from the intraligand $^3(\pi\pi^*)$ and $^3(d_{\pi^*})(d_{\sigma^*})$ excited states has been observed in fluid solution and the solid state of $[Pt_2(dppm)_2Cl(L)]ClO_4$ [dppm = $Ph_2PCH_2PPh_2$, L = (4-chlorophenyl)(4-pyridyl)-acetylene], the structure of which has been determined by X-ray crystallography.

Luminescent donor–acceptor metal complexes have been receiving much attention in the context of intramolecular electron- and energy-transfer reactions.[1] Most of these complexes comprise a d^6-metal polypyridine fragment covalently linked to an organic donor/acceptor.[1] Since di- and polynuclear metal complexes are expected to facilitate multi-electron-transfer reactions, a study of donor–acceptor metal–metal bonded complexes may provide a new entry to new photocatalysts for energy-storage reactions. We have recently found that the reaction between $[Pt_2(dppm)_2Cl_2]$ [dppm = bis(diphenylphosphino)methane] and nitrogen bases gives a new class of dinuclear luminescent diplatinum(I) complexes having emissive $^3(d_\pi)(d_{\sigma^*})$ excited states.[2] Herein is described the crystal structure and luminescent properties of $[Pt_2(dppm)_2Cl(L)]^+$ [L = (4-chlorophenyl)(4-pyridyl)acetylene], which could be regarded as a metal-perturbed donor–acceptor acetylene molecule.

The ligand L was prepared by the literature method.[3] The reaction between $[Pt_2(dppm)_2Cl_2]$ (0.2 g) and L (0.06 g) in methanol (30 cm^3) at about 50 °C for 0.5 h gave $[Pt_2(dppm)_2Cl(L)]^+$, which was isolated as a yellow perchlorate salt upon addition of $LiClO_4$ (yield > 60%). It was recrystallised by diffusion of diethyl ether into an acetonitrile solution. Fig. 1 shows a perspective view of the complex cation.† Each platinum atom is in a pseudo-planar four-co-ordinated geometry. The intramolecular Pt–Pt distance of 2.618(1) Å is not unusual as similar values of 2.615(1) Å in $[Pt_2(dppm)_2(quin)_2]^{2+}$ (quin = quinoline)[2] and 2.627(2) Å in $[Pt_2(dppm)_2(tmpy)Cl]^+$ (tmpy = 2,4,6-trimethylpyridine)[2] have been reported. The dihedral angle between the phenyl rings of the ligand L is 61.1(1)° whereas the Pt–P bonds are nearly perpendicular to the pyridyl ring [dihedral angle between the plane through Pt(1), P(1) and P(2) and the pyridyl ring is 82.1(1)°].

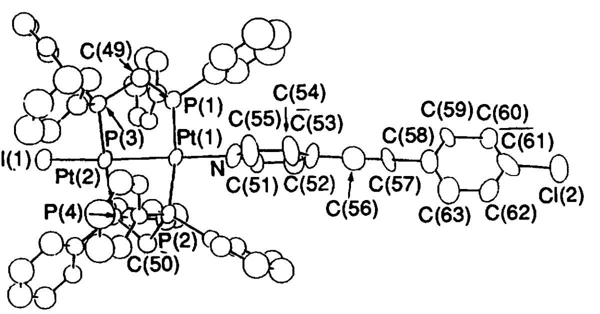

Fig. 1 A perspective view of the complex cation $[Pt_2(dppm)_2Cl(L)]^+$. Significant bond lengths (Å) and angles: Pt(1)–Pt(2) 2.618(1), Pt(1)–N 2.12(2), Pt(2)–Cl(1) 2.396(6), Pt(1)–P(1) 2.259(6), Pt(1)–P(2) 2.254(6), Pt(2)–P(3) 2.263(6), Pt(2)–P(4) 2.267(7) and C(56)–C(57) 1.22(3); Pt(2)–Pt(1)–N 177.6(4), P(1)–Pt(1)–P(2) 168.9(3), Pt(1)–Pt(2)–Cl(1) 173.5(2) and P(3)–Pt(2)–P(4) 175.1(3)

The UV/VIS absorption spectra of the ligand and metal complex in acetonitrile display similar vibronic structured bands ranging from 250 to 300 nm, which are assigned to the intraligand $\pi \longrightarrow \pi^*$ transition of L. For $[Pt_2(dppm)_2Cl(L)]^+$ there are also shoulders at 320 and 340 nm. With reference to previous studies,[2] these transitions are associated with metal–metal interaction and are assigned to the $d_{\pi^*} \longrightarrow d_{\sigma^*}$ transitions.

In its solid form and upon excitation at 350–400 nm the complex displays an intense red emission at 600–700 nm (λ_{max} = 645 nm) with a lifetime of ≈2.6 μs at room temperature. Similar findings have been reported for related complexes such as $[Pt_2(dppm)_2(py)_2][ClO_4]_2$ (py = pyridine) and $[Pt_2(dppm)_2(tmpy)Cl]ClO_4$.[2] The emitting state is assigned to the metal-localised $^3(d_\pi,d_{\sigma^*})$ excited state. Attempts were made to observe the intraligand emission of L from a solid sample of $[Pt_2(dppm)_2Cl(L)]ClO_4$. However, even on cooling the sample to 77 K, the emission spectrum still showed only a prominent peak at 645 nm suggesting that the intraligand emission is of much weaker intensity under these conditions.

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† *Crystal data.* $C_{63}H_{52}Cl_3NO_4P_4Pt_2$, M = 1507.56, yellow, orthorhombic, space group $P2_12_12_1$, a = 15.131(2), b = 18.196(3), c = 21.393(3) Å, Z = 4, U = 5890.0(1.0) Å^3, D_c = 1.70 g cm^{-3}, T = 296 K, crystal dimensions 0.05 × 0.12 × 0.15 mm, μ(Mo-Kα) = 50.8 cm^{-1}. An empirical absorption correction based on azimuthal scans was applied, with transmission factors 0.793–0.998; Enraf-Nonius CAD-4 diffractometer, λ(Mo-Kα, graphite monochromator) = 0.7107 Å, $N(2\theta_{max}$ = 46°, ω–2θ mode) = 4562, $N_o[I > 3\sigma(I)]$ = 2898, number of variables in least-squares refinement on F = 444, $F(000)$ = 2944; h 0–16, k 0–20, l 0–23; R = 0.038, R' = 0.045. The weighting scheme used was $w = 4F_o^2/\sigma^2(F_o^2)$ where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.0045F_o^2)^2]$. Structure solution by Patterson and Fourier syntheses using the Enraf-Nonius SDP-1985 programs[4] on a MicroVAX II computer. Anisotropic thermal parameters except for the carbon atoms in dppm which were only refined isotropically; (x, y, z, U_{iso}) for hydrogen atoms at calculated positions were not refined. The maximum Δ/σ was 0.05 and the final Fourier difference map had maximum and minimum residual peaks of +0.74 and −0.59 e Å^{-3}. Three of the perchlorate oxygen atoms have higher thermal vibrations suggesting that they might rotate about the fourth Cl–O bond. The closest intermolecular contact is 3.2 Å between a perchlorate oxygen atom and a carbon atom in dppm. 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.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Photophysical properties of $[Pt_2(dppm)_2Cl(L)]^+$ and L

Compound	Solvent	Emission λ/nm	Quantum yield	Lifetime at 298 K (μs)	k_r/s^{-1}	k_{nr}/s^{-1}
$[Pt_2(dppm)_2Cl(L)]^+$	CH_2Cl_2	420	5.4×10^{-3}	0.15		
	CH_3CN	420	7.1×10^{-3}	0.21	1.2×10^4	4.8×10^5
L	CH_3CN	420	1.6×10^{-2}	3.31	4.7×10^3	3.0×10^5

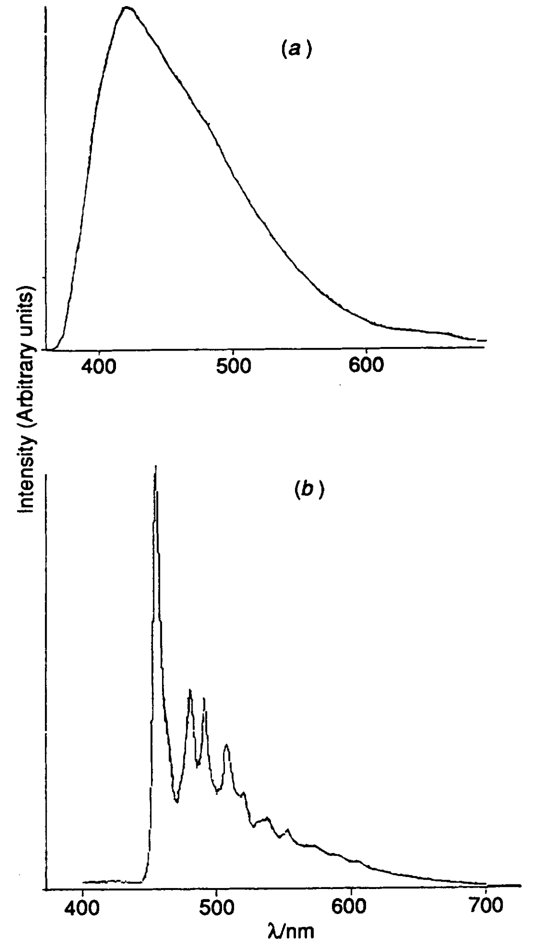

Fig. 2 Emission spectra of $[Pt_2(dppm)_2Cl(L)]ClO_4$: (*a*) in degassed acetonitrile at room temperature; (*b*) in *n*-butyronitrile glassy solution at 77 K. Excitation at 350 nm

In fluid solution the emission is different from that of the solid. Owing to the very rapid non-radiative decay of the $^3[(d_{\pi^*})(d_{\sigma^*})]$ excited state in fluid solution and even in glassy solution at 77 K, the emission of 645 nm was not observed in dichloromethane or acetonitrile solutions of $[Pt_2(dppm)_2Cl(L)]^+$. Instead, intraligonal emission of L which occurs at 420 nm was observed (Fig. 2). Although the free ligand also shows emission at similar energy the lifetime is significantly larger and the quantum yield is higher than for its complexed form (Table 1). The increase in k_{nr} from L to $[Pt_2(dppm)_2Cl(L)]^+$ may be explained by intramolecular energy transfer from the intraligand $^3(\pi\pi^*)$ state to the metal-localised $^3(d_{\pi^*}d_{\sigma^*})$ excited state. If this is the case, a rate constant of $\approx 10^6$ s^{-1} can be estimated for this intramolecular energy-transfer process.

Since the nature of ligand L is tunable, the present work provides an entry to donor–acceptor metal complexes whereby one can investigate energy- and electron-transfer reactions associated with a metal–metal bond.

Acknowledgements

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