Structure and Photophysical Properties of [Pt^0(binap)$_2$] [binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl]

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A new luminescent tetrahedral platinum(0) complex [Pt(binap)$_2$] is structurally characterized by X-ray diffraction and its novel absorption and luminescence in the visible region are assigned as an MLCT transition.

There has been considerable interest in the photophysical and photochemical properties of d^{10} metal complexes.[1] Binuclear metal(0)–phosphine complexes (M = Pd, Pt), such as [Pd$^0_2$(dppm)$_3$] [dppm = bis(diphenylphosphino)methane], are known to exhibit an absorption band in the visible region, which is related to the large dσ–dσ* splitting by metal–metal interactions.[2] The photochemical behaviour of the palladium and platinum complexes have attracted much attention because of the long lifetimes of their excitation states ($\tau > 1$ μs).[3] The luminescent excited states and photoreactions of some mononuclear metal(0)–phosphine complexes have been reported previously,[3,4] but irradiation with UV light is necessary for their excitation. We now report on the first example of a luminescent mononuclear platinum(0)–phosphine complex, which shows an intense absorption band in the visible region, with use of the chiral diphosphine ligand, binap [binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl]. Palladium–binap complexes and their catalytic activities have been intensively studied,[5] but the use of platinum–binap complexes is much more limited.[6,7]

The complex [Pt^0(binap)$_2$] was prepared as follows. To a solution of [PtCl$_2${(*S*)-binap}][6] (0.13 mmol) and binap (0.13 mmol) in 15 ml of THF was added dropwise a solution of NaBH$_4$ (3.9 mmol) in 5 ml of H$_2$O. The wine-red solution was stirred for 30 min at room temp. The THF layer was collected and the volatiles were removed *in vacuo*. The residue was washed with water and dried *in vacuo*, affording [Pt^0{(*S*)-binap}$_2$] in 89% yield.† Recrystallization of the dark-red complex from diethyl ether gave single crystals of [Pt^0{(*S*)-binap)$_2$]·2/3C$_4$H$_{10}$O‡ which were used in the X-ray and spectroscopic studies. The enantiomer, [Pt^0{(*R*)-binap}$_2$], was also prepared. Although many crystal structures of metal complexes of binap have been reported,[8] this is the first example of a platinum(0) complex of this ligand.

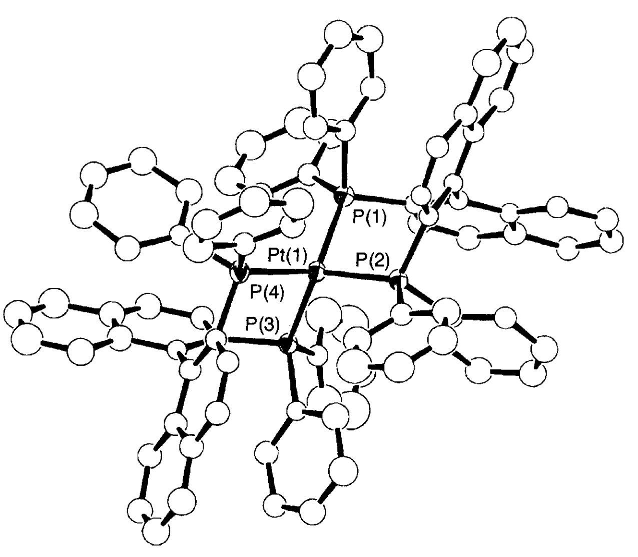

Fig. 1 An ORTEP drawing of [Pt{(*S*)-binap}$_2$]. One of the two molecules in the asymmetric unit is shown. Some bond lengths (Å) and angles (°); Pt(1)–P(1) 2.325(5), Pt(1)–P(2) 2.325(4), Pt(1)–P(3) 2.334(4), Pt(1)–P(4) 2.340(4), P(1)–Pt(1)–P(2) 91.6(1), P(1)–Pt(1)–P(3) 118.7(1), P(1)–Pt(1)–P(4) 121.2(2), P(2)–Pt(1)–P(3) 116.8(1), P(2)–Pt(1)–P(4) 118.8(2), P(3)–Pt(1)–P(4) 92.3(1).

In the crystal, two independent [Pt{(*S*)-binap}$_2$] molecules are found in the asymmetric unit.§ The two molecules essentially have the same structure except for the orientation of a phenyl ring on one of the four phosphorus atoms. Each molecule shows a large distortion from the idealized tetrahedral geometry, and adopts quasi-D_2 symmetry (Fig. 1). The average bite angle of the chelates is 92°. The average Pt–P bond distances (2.33 Å) are longer than those observed for normal four-coordinate platinum(0) complexes containing phosphines.[9] This fact may be connected with the large distortion around the tetrahedral metal centre. Best-plane calculations afford the average dihedral angle between the two naphthyl rings within binap to be 78°. The dihedral angle is similar to those reported for [Pt^{II}(C$_6$H$_4$OMe)$_2$(binap)] (77°).[7]

The complex shows a novel intense visible absorption band at λ_{max} = 530 nm ($\varepsilon = 1.4 \times 10^4$ dm^3 mol^{-1} cm^{-1}). The absorption intensity obeys the Lambert–Beer's law (2×10^{-4}–4.6×10^{-6} mol dm^{-3}). Moreover, the λ_{max} value agrees well with that observed on a solid sample prepared as a KBr pellet. These facts indicate that [Pt(binap)$_2$] retains its mononuclear structure in solution.

The lowest energy transitions in mononuclear metal(0)–phosphine complexes, such as [Pt^0(dppp)$_2$] [dppp = 1,3-bis(diphenylphosphino)propane], have been observed in the UV region and are assigned to the t$_2$(dσ) → t$_2$(Pσ*) transition.[4] An EHMO calculation, performed based on the crystal structure of [Pt(binap)$_2$], reveals that the HOMO (b$_2$ in D_2 group symmetry) is mainly made up of the d orbitals of the Pt atom, whereas the LUMO (b$_1$) of [Pt(binap)$_2$] has a great similarity to the LUMO of the ligand, binap, itself, although there is a small contribution of a d orbital of the Pt atom. The p orbitals of the C atoms in 1,1′-position of binap have the largest contribution to the LUMO of the platinum complex. By contrast, the LUMO of the dppp complex was calculated to be 0.7 eV higher in energy than that of the binap complex. Therefore, the lowest energy transition (b$_2$ → b$_1$), which is allowed in D_2 symmetry, in [Pt(binap)$_2$] should be assigned to an MLCT transition, and the π* orbitals on the chelate part (P–C–C–C–C–P) of the binap largely contribute the MLCT excited state.

[Pt(binap)$_2$] exhibits a red luminescence (λ_{max} = 730 nm, τ = 1.5 μs) in benzene solution upon irradiation with visible or

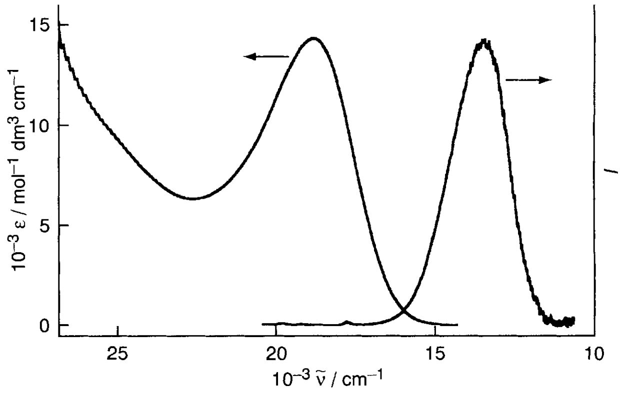

Fig. 2 Molar absorption coefficients (ε) and luminescence intensities (*I*) of [Pt(binap)$_2$] in C$_6$H$_6$ (λ_{exc} = 480 nm)

UV light ($\lambda_{exc} < 600$ nm) at room temp. (Fig. 2). The quantum yield of this luminescence ($\Phi = 0.024$, $\lambda_{exc} = 480$ nm) is comparable to that of tris(2,2′-bipyridine)ruthenium(II).[10] The luminescence is easily quenched by oxygen and its long lifetime indicates that the luminescence is originated from the ^{3}MLCT excited state.

In the present study, we have thus identified a new class of excited state in a low-valent d^{10} metal complex containing chiral phosphine ligands. We have already confirmed that the luminescence of [Pt(binap)$_2$] can be quenched by organic halides, such as chloropentane. This complex has potential applications in asymmetric photoreaction or photocatalysis. Further studies are now in progress.

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Footnotes

† ^{31}P NMR in C_6D_6; δ 21.3(s) with two ^{195}Pt satellites ($J_{Pt-P} = 3.74$ kHz).

‡ Anal. Calc. for [Pt(binap)$_2$]·3/2$C_4H_{10}O$: C, 72.76; H, 5.13. Found: C, 72.51; H, 5.49%.

§ *Crystal data*: $C_{88}H_{64}P_4Pt{\cdot}3/2C_4H_{10}O$, $M = 1551.64$, monoclinic, space group $P2_1$, $a = 11.885(1)$, $b = 22.777(5)$, $c = 28.008(1)$ Å, $\beta = 95.517(6)°$, $U = 7546(1)$ Å^3, $Z = 4$, $D_c = 1.37$ g cm^{-3}. A deep-red crystal of approximate dimensions 0.3 × 0.3 × 0.2 mm was used. Data were collected with Cu-Kα ($\lambda = 1.54178$ Å) radiation on a Rigaku AFC5S diffractometer using the ω-scan technique (8° min^{-1}). The 12215 reflections (11581 unique) were collected in the range $2\theta < 120°$. The structure was solved by Patterson method. The last least-square cycles was calculated with 201 atoms, 835 variables (anisotropic for Pt and P, isotropic for C and O atoms) and 7416 reflections [$I > 3\sigma(I)$]; $R = 0.046$ and $R_w = 0.038$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallogrpahic Data Centre. See Information for Authors, Issue No. 1.

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