Photochemistry and photophysics of the tetrahedral silver(I) complex with diphosphine ligands: $[Ag(dppb)_2]PF_6$ (dppb = 1, 2-bis[diphenylphosphino]benzene)†

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The photophysical and photochemical properties of $[Ag(dppb)_2]PF_6$ (1) having a tetrahedral coordination geometry have been described.

Highly phosphorescent metal complexes have received much attention owing to their importance as light emitters for organic light emitting devices (OLED), biological sensors, and opto-electronic devices.[1] According to earlier studies,[2] phosphorescence from mononuclear metal complexes is confirmed to originate from the ^{3}MLCT or the locally excited triplet state of the ligand, ^{3}L. Extensive studies on metal complexes which exhibit strong phosphorescence at room temperature have been carried out for octahedral structures with central metals, Ru(II), Os(II), Rh(III), Pd(II), Pt(II), and Ir(III).[3]

A new trend in phosphorescent metal complex chemistry has focused on the coordination compounds containing a d^{10} metal center such as the monovalent coinage metals, Cu(I), Ag(I), and Au(I).[4] Among these complexes, tetrahedral $[Cu(N\hat{\ }N)_2]^+$ complexes (N^N = bisimine ligand), which are characterized by structural changes in the excited states, have been intensively investigated to elucidate the nature of the excited states.[5] Upon excitation, the tetrahedral Cu(I) complex forms the MLCT excited state, in which an electron is transferred from the central metal to the ligand. Then, the central Cu(I) atom is formally oxidized to Cu(II) (d^9) at the MLCT excited state, leading to flattening of the structure of the complex.

A number of studies have been accumulated for photophysics of tetrahedral Cu(I) complexes. However, the luminescence properties of mononuclear Ag(I) or Au(I) complexes with a tetrahedral configuration are less explored.[6] This paper describes the luminescence and photochemistry of the bis-chelate silver complex, $[Ag(dppb)_2]PF_6$ (**1**) with the diphosphine ligand. During this work, we found that (1) phosphorescence of the complex **1** is orange in 2-MeTHF (2-methyltetrahydrofuran) but blue in polymethylmethacrylate (PMMA) films and (2) a colorless CH_2Cl_2 solution of the complex **1** turns deep blue-purple upon UV irradiation. These findings are interpreted on the basis of absorption, emission, and ESR spectroscopy.

$[Ag(dppb)_2]PF_6$ (**1**) was prepared by the reaction of dppb with $AgPF_6$ in CH_2Cl_2. A single crystal of the complex **1** for X-ray crystallography‡ was obtained by addition of Et_2O on the surface of the CH_2Cl_2 solution. The structure of **1** determined by X-ray crystallography is shown in Fig. 1. The two dppb ligands are symmetrically bound to Ag(I) with a highly distorted tetrahedral coordination geometry: a dihedral angle between the planes defined by P(1)Ag(1)P(2) and P(1a)Ag(1)P(2a) is 83.00(4)°. The acute bite angle [P(1)–Ag(1)–P(2) 79.99(2)°] in **1** is smaller than that [P–Cu–P 84.72(3)°] found in $[Cu(dppb)_2]^+$.[7]

The Ag–P bond lengths [Ag(1)–P(1) 2.4621(7), Ag(1)–P(2) 2.5063(6) Å] in **1** are significantly shorter than those [Ag–P 2.601 ∼ 2.746 Å] in the tetrakis(triphenylphosphine) silver(I) complex,[8] $[Ag(PPh_3)_4]^+$, indicating that the chelate effect of the dppb ligand toward Ag(I) is much stronger than that of PPh_3. This observation is also confirmed by ^{31}P NMR in CD_2Cl_2. It is known that the Ag–P coupling in the room temperature spectrum of Ag–phosphine complexes is unresolved because of the rapid exchange equilibrium.[9] However, the spectrum of the complex **1** shows well resolved typical pairs of doublets, due to $^1J(^{31}P–^{107}Ag)$ = 231 Hz and $^1J(^{31}P–^{109}Ag)$ = 264 Hz even at 293 K. These results suggest that the dppb ligand markedly stabilizes the tetrahedral structure of **1**.

Fig. 2 shows the absorption spectra of dppb and **1** in 2-MeTHF as well as the phosphorescence spectra of **1** in 2-MeTHF (at 293 and 77 K) and PMMA film. The complex **1** in 2-MeTHF gives an absorption spectrum similar to that of

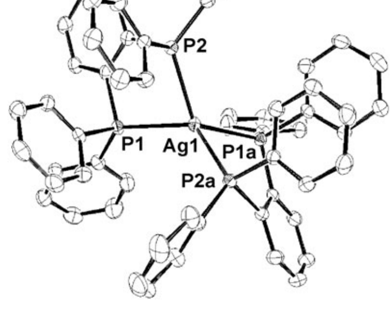

Fig. 1 Molecular structure of the cation in **1** (only one of the two molecules in the unit cell is shown here). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and counter anion, PF_6 are omitted for clarity.

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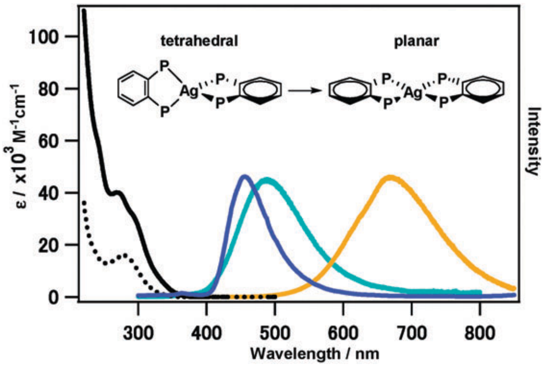

Fig. 2 Absorption spectra of dppb (dashed line) and **1** (solid line) in 2-MeTHF and emission spectra (λ_{exc} = 266 nm) of **1** in PMMA (light blue) and in 2-MeTHF (orange at 293 K, blue at 77 K). Intensities of emission spectra in solid state were adjusted arbitrarily for clarity. The inset shows photoinduced flattening distortion of **1**. The four phenyl groups in each ligand are omitted for clarity.

dppb: a broad absorption band (40 000 M^{-1} cm^{-1}) at λ_{max} = 267 nm with a shoulder at approximately 295 nm. However, the tail of the absorption of **1** extends to the long wavelength region (*ca.* 370 nm) more than that of dppb (Fig. S1 in ESI†).

Table 1 summarizes the absorption and phosphorescence peaks, phosphorescence lifetimes, and the yields. The complex **1** emits bright blue emission (λ_{max} = 456 nm, Φ_p = 0.42) in degassed 2-MeTHF at 77 K, whereas it gives orange luminescence (λ_{max} = 670 nm, Φ_p = 0.05) at room temperature (Fig. 2). On the basis of the 220 nm red shift of the emission peak and the low phosphorescence yield at ambient temperature, we assumed that these emissions occur from the MLCT state (the excitation spectrum in Fig. S2 in ESI†). So, the complex **1** undergoes a structure change in the excited state from the tetrahedral to the flattened structure, leading to a red shift of emission at room temperature (the inset in Fig. 2).[10,5,7c] Since it is difficult to change the structure in the excited state in 2-MeTHF glass at 77 K, the blue phosphorescence of complex **1** is concluded to occur from the tetrahedral structure. On the other hand, because of the low viscosity of the solvent at room temperature, the complex **1** readily changes its structure from the tetrahedral to the flattened one in the excited state, giving rise to orange phosphorescence. The structural changes are supposed to occur in the phosphorescent MLCT state in which charge-transfer occurs from the central Ag(I) atom to the dppb ligands. The flattened structure is more stable than the tetrahedral one in the MLCT excited state, and thus, the former gives luminescence in a longer wavelength region than the latter. A similar structure change in the MLCT excited state has been proposed for the bis-chelate Cu(I) complexes ($[Cu(N^\wedge N)_2]^+$ and $[Cu(P^\wedge P)_2]^+$).[5,7c]

The structure change in the excited state is further confirmed by the luminescence measurement of **1** in the PMMA film. The phosphorescence peak (λ_{max} = 486 nm) in the blue region at room temperature is close to that in the solid state because of the highly rigid resin matrix: the complex **1** keeps the tetrahedral form in the PMMA film in the excited state. We observed that the phosphorescence peak of **1** in the film shifts to 520 nm on going from 293 to 373 K (Table 1). This observation is interpreted in terms of the fact that the rigidity of the film decreases at elevated temperatures. The change in the conformation from a tetrahedral to a flattened structure in the excited state takes place in the softened film, resulting in the red shift of the phosphorescence at 373 K.

In degassed CH_2Cl_2 and $CHCl_3$ solutions, we observed a dramatic decrease in intensity of orange phosphorescence of **1** (Table 1). Further, the color of the solution was changed from colorless to blue-purple upon UV irradiation. Fig. 3 shows the changes in the absorption spectra of the complex **1** in CH_2Cl_2 measured immediately after irradiation at 365 nm for 5 min with a portable UV lamp: the blue solid line was the spectrum measured at room temperature and the blue dotted one was at 195 K.

When the irradiation is stopped, the color disappears within a few seconds at 293 K. Thus, the lifetime of the blue-purple product is estimated as 4–5 s in CH_2Cl_2. In the 2-MeTHF solution of **1**, no color change is observed upon UV irradiation, suggesting that the photo-oxidation of **1** in CH_2Cl_2 and $CHCl_3$ is responsible for the formation of the blue-purple product.

Although the product is not isolated, a well-resolved ESR spectrum of the blue-purple product is obtained upon UV irradiation. Fig. 4 shows the ESR spectrum of the product in CH_2Cl_2 at 293 K. The spectrum, which exhibits hyperfine lines due to four P atoms (I = 1/2) with super-hyper lines due to a Ag atom (I = 1/2), is well interpreted on the assumption that one of the four P atoms has a coupling constant slightly smaller than that of the others: the three equivalent and one non-equivalent P atoms comprise the product. The ESR parameters were determined as g_{iso} = 2.019, $A_{iso}(Ag)$ = 2.17×10^{-3} cm^{-1}, $A_{iso}(P_{non\text{-}equivalent})$ = 1.52×10^{-2} cm^{-1}, and $A_{iso}(P_{equivalent})$ = 1.68×10^{-2} cm^{-1}. The value of $A_{iso}(P_{non\text{-}equivalent})$ is *ca.* 10% less than $A_{iso}(P_{equivalent})$. On the basis of these results, the blue-purple species from the complex **1** is considered to be the one-electron oxidation product, $\mathbf{1}^{\bullet +}$. The g_{iso} value 2.019 is close to that of a Ag(II) complex (g_{iso} = 2.024) with a square-planar coordination sphere, and $A_{iso}(Ag)$ in $\mathbf{1}^{\bullet +}$ is smaller than that of the Ag(II) complex (3.4×10^{-3} cm^{-1}).[11] Probably, the central Ag(I) atom in $\mathbf{1}^{\bullet +}$ is partly oxidized.

Table 1 Photophysical data of **1**

Medium (T/K)	λ_{max}/nm[a] ($\varepsilon \times 10^{-3}/M^{-1}\ cm^{-1}$)	λ_{max}/nm[b] (τ_0/μs)	Φ_p
2-MeTHF (293)	267 (40), 295 (sh)	670 (11)	0.05
2-MeTHF (77)	—	456 (—)	0.42
PMMA (293)[c]	270 (—)	486 (7.7)	—
PMMA (373)[c]	—	520 (—)	—
CH_2Cl_2	271 (38), 293 (sh)	670 (0.09)	$<10^{-3}$[d]

[a] Absorption maxima. [b] Emission maxima from corrected spectra, λ_{exc} = 266 nm. [c] Cast film (5.8 wt%). [d] Weak.

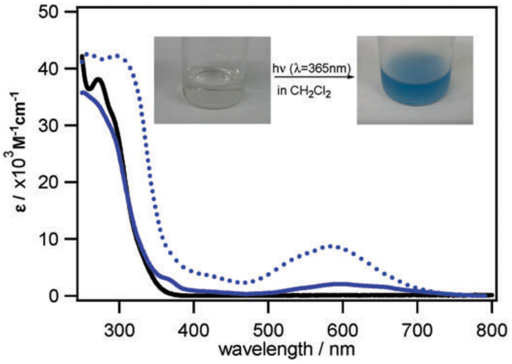

Fig. 3 The changes in the absorption spectra of **1** in CH_2Cl_2; before irradiation (black), after irradiation (λ_{ex} = 365 nm) at 293 K (blue), at 195 K (dashed blue). The inset picture shows the color change of **1** in CH_2Cl_2 upon UV irradiation.

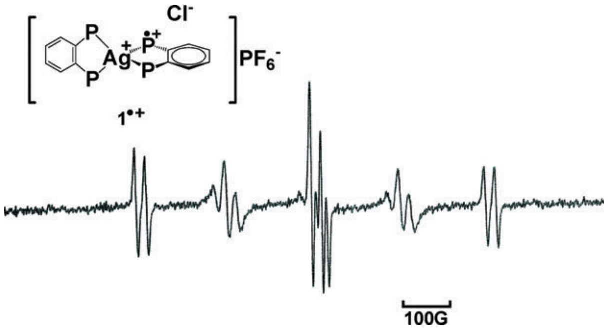

Fig. 4 EPR spectrum of $[Ag(dppb)_2]PF_6$ **1** in CH_2Cl_2 solution (0.012 M) under irradiation (150 W Xe lamp) at 293 K.

According to previous studies, the ESR parameters for the cation radicals of bis(diphenylphosphino) derivatives have been determined as $g_\perp$ = 2.002 ± 0.002, $g_\parallel$ = 2.006 ± 0.003, and $A_{iso}(P)$ = (3.2 ± 0.2) × 10^{-2} cm^{-1}.[12] Thus, the coupling constant of $A_{iso}(P)$ of $\mathbf{1}^{\bullet +}$ obtained in the present study is almost a half those of the cation radicals of bis(diphenylphosphino) derivatives. From the ESR studies, the unpaired electron in of $\mathbf{1}^{\bullet +}$ is supposed to be delocalized on both Ag and P atoms. It is noted that the absorption spectrum of $\mathbf{1}^{\bullet +}$ resembles those of the radical cation of triarylphosphine derivatives.[13]

Photo-induced one-electron oxidation of metal complexes as well as organic molecules in CH_2Cl_2 and $CHCl_3$ frequently occurs to give the cationic radical and the counter ion Cl^-.[14] In the present work, $\mathbf{1}^{\bullet +}$ was found to have three equivalent and one non-equivalent P atoms. It is suggested that the counter ion Cl^- is located around the non-equivalent P atom. A proposed structure of the blue-purple species, $\mathbf{1}^{\bullet +}$, is depicted in Fig. 4.

Notes and references

‡ *Crystal data*: $C_{60}H_{48}AgF_6P_5$, M = 1145.77, monoclinic, space group $C2/c$, a = 27.151(3) Å, b = 25.983(3) Å, c = 18.573(2) Å, β = 124.920(2)°, V = 10743(2) Å, T = 130(1) K, Z = 8, 15 648 unique observed reflections (R_{int} = 0.056) were used to refine 651 atomic parameters and gave a final $R_1[F > 2\sigma(F)]$ = 0.0541, wR_2 (all data) = 0.1194.

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