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Platinum(II) and copper(I) 1-(2-diphenylphosphino-1-naphthyl) isoquinoline complexes: Synthesis and phosphorescence at ambient conditions

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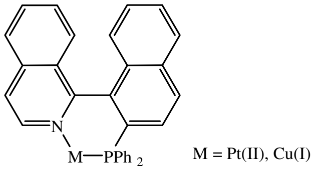
The compounds Pt(quinap)$(CN)_2$, Cu$(quinap)_2^+$ and $[Cu(quinap)I]_2$ with quinap = 1-(2-diphenylphosphino-1-naphthyl)isoquinoline were synthesized. Quinap is a bidentate ligand which contains a isoquinoline and an arylphosphine group with CT acceptor properties. Accordingly, the Pt(II) and Cu(I) quinap complexes are characterized by a phosphorescence originating from the lowest-energy MLCT triplets with some IL admixture.

1. Introduction

Applications of coordination compounds are often dependent on ligands with desired properties. Transition metal complexes which are phosphorescent at r.t. frequently rely on the presence of low-energy MLCT states [1–3]. Suitable ligands should provide low-energy empty π^* orbitals and a large ligand field (LF) strength in order to push up interfering LF states to higher energies. Moreover, it is also useful when ligands of this type are bidentate since this increases the stability and decreases the structural flexibility of the target complexes. The ligand 1-(2-diphenylphosphino-1-naphthyl)isoquinoline (quinap) largely combines these requested properties. The pyridine (or quinoline) moiety provides the CT acceptor function [1–3] while the arylphosphine is a strong-field ligand owing to its large σ-donor strength and π-accepting nature [4]. For the same reason, phosphines are able to stabilize metals in low oxidation states. Generally, such metals are reducing and therefore are strong CT donors which are required for complexes with low-energy MLCT states. For an initial confirmation of the expected behaviour we have previously reported the preparation and optical properties of $Re^I(quinap)(CO)_3Cl$ [5]. In addition to this octahedral d^6 complex, square-planar Pt(II) and tetrahedral Cu(I) complexes are prototypes of d^8 and d^{10} compounds with emitting MLCT triplets [1–3]. We explored this possibility and selected quinap complexes of Pt(II) and Cu(I) (Plate 1) for the present study in order to demonstrate the general benefit of this ligand for the design of MLCT triplet emitters.



2. Experimental

2.1. Materials

Solvents for preparations and spectroscopic measurements were of spectrograde quality. The compounds $Pt(CN)_2$, 1-(2-diphenylphosphino-1-naphthyl)isoquinoline (quinap) and CuI were commercially available from Strem Chemicals.

2.2. Pt(quinap)$(CN)_2$ × 2.5 H_2O

Finely powdered $Pt(CN)_2$ (200 mg, 0.82 mmol) and quinap (360 mg, 0.82 mmol) in 20 ml DMF were heated under reflux for 30 h. After cooling to r.t. the resulting suspension was filtered. Upon addition of 150 ml ether to the filtrate an off-white precipitate was formed. It was washed with ether and dried, yielding 120 mg (19%).

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Anal. Calc. for $Pt(CN)_2$quinap × 2.5 H_2O (755.64): C, 54.23; H, 3.77; N, 5.67. Found: C, 54.17; H, 3.72; N, 5.74.

2.3. *[Cu(quinap)I]$_2$*

CuI (91 mg, 0.48 mmol) was dissolved in 20 ml argon-saturated CH_3CN. Quinap (210 mg, 0.48 mmol) was added. The solution turned yellow and yellow crystals separated. After stirring for 1 h the precipitate was filtered off, washed with EtOH and ether, and dried yielding 200 mg (66%).

Anal. Calc. for $[Cu(quinap)I]_2$ (1259.88): C, 59.11; H, 3.52; N, 2.22. Found: C, 58.95; H, 3.64; N, 2.22.

2.4. *[Cu(quinap)$_2$]PF$_6$ × H$_2$O*

Quinap (264 mg, 0.6 mmol) was added to a solution of $[Cu(CH_3CN)_4]PF_6$ (112 mg, 0.3 mmol) in 20 ml CH_3CN. The mixture was refluxed for 30 min under stirring. After removing the solvent by vacuum evaporation the remaining residue was dissolved in CH_3OH. Solid impurities were filtered off. A mixture of ether/*n*-hexane (1:1) was added to the solution. The yellow precipitate was isolated by filtration, washed with *n*-hexane and dried over silica gel yielding 260 mg (78%).

Anal. Calc. for $[Cu(quinap)_2]PF_6 \times H_2O$ (1105.5): C, 67.36; H, 4.19; N, 2.53. Found: C, 67.59; H, 4.32; N, 2.49.

2.5. *Instrumentation*

Absorption spectra were measured with an Uvikon 860 spectrophotometer. Emission spectra were recorded on a Hitachi 850 spectrofluorometer equipped with a Hamamatsu 928 photomultiplier up to 900 nm. The luminescence spectra were corrected for monochromator and photomultiplier efficiency variations.

3. Results

The compounds $Pt(quinap)(CN)_2$, $[Cu(quinap)_2]PF_6$ and $[Cu(quinap)I]_2$ were synthesized in analogy to previous preparations of related complexes of the type $Pt(1,2\text{-diimine})(CN)_2$ [6], $Pt(\text{diolefine})(CN)_2$ [7], $Pt(\text{bis-arylphosphine})(CN)_2$, [8], $[Cu(\text{bis-arylphosphine})_2]X$ [9] and $[Cu(\text{bis-arylphosphine})I]_2$ [9,10]. The syntheses were carried out according to the following equations:

$$Pt(CN)_2 + quinap \rightarrow Pt(quinap)(CN)_2 \quad (1)$$

$$[Cu(CH_3CN)_4]PF_6 + 2quinap \rightarrow [Cu(quinap)_2]PF_6 + 4CH_3CN \quad (2)$$

$$2CuI + 2quinap \rightarrow [Cu(quinap)I]_2 \quad (3)$$

The electronic spectrum of $Pt(quinap)(CN)_2$ in CH_2Cl_2 (Fig. 1) shows absorptions at λ_{max} = 441 (sh, ε = 50 M^{-1} cm^{-1}), 365 (sh, 2370), 345 (sh, 3950), 326 (sh, 5600) and 288 (sh, 14000) nm. The emission appears at 544 nm in CH_2Cl_2 and at λ_{max} = 588 nm in the solid state (Fig. 2). The emission spectrum in solution is not concentration dependent. The quantum yield amounts to approximately $\phi = 10^{-4}$ at λ_{exc} = 380 nm.

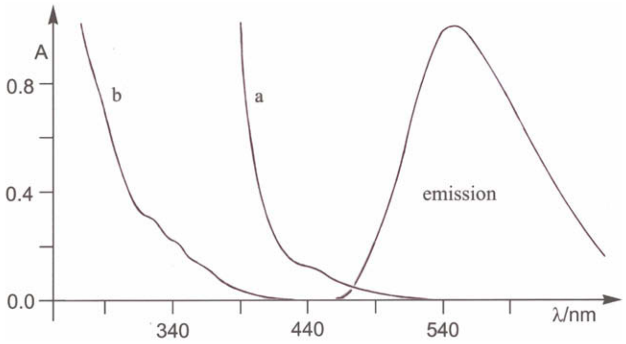

Fig. 1. Electronic spectra of $Pt(quinap)(CN)_2$ in CH_2Cl_2 at room temperature, 1-cm cell. Absorption: (a) 2.50×10^{-3} M, (b) 5.36×10^{-5} M. Emission: 5.36×10^{-5} M (under argon, λ_{exc} = 380 nm).

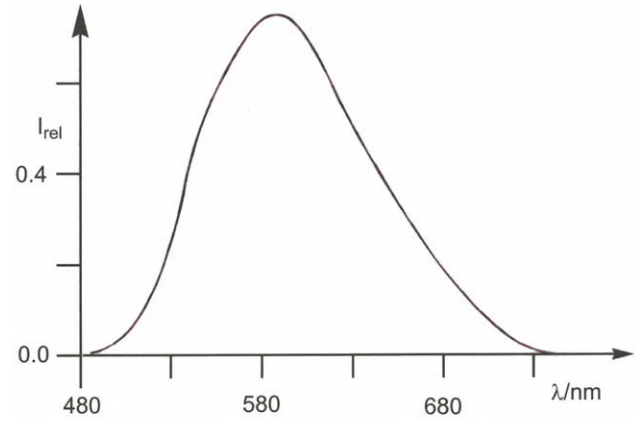

Fig. 2. Electronic emission spectrum (λ_{exc} = 350 nm) of solid $Pt(quinap)(CN)_2$ at room temperature, intensity in arbitrary units.

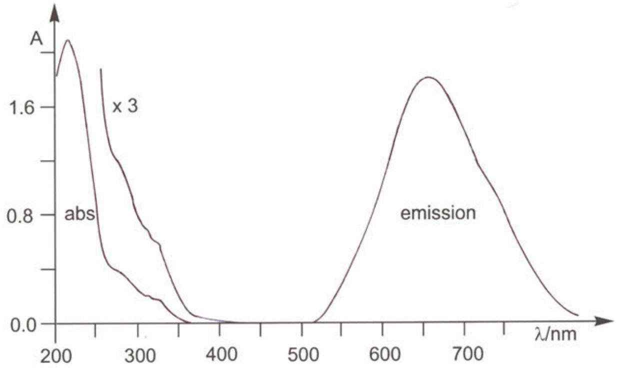

Fig. 3. Electronic absorption and emission spectrum of $[Cu(quinap)I]_2$ at room temperature. Absorption: 3.05×10^{-5} M in CH_3CN, 1-cm cell. Emission: solid, λ_{exc} = 275 nm, intensity in arbitrary units.

The absorption spectrum of $[Cu(quinap)_2]PF_6$ in CH_3CN and $[Cu(quinap)I]_2$ (Fig. 3) in CH_3CN display bands at λ_{max} = 324 (sh, ε = 13800 M^{-1} cm^{-1}), 310 (sh, 16300), 272 (sh, 38000) and 218 (168000) nm and λ_{max} = 320 (sh, 19200), 310 (sh, 21800), 275 (sh, 39700) and 212 (68200) nm, respectively. The emission of $[Cu(quinap)_2]PF_6$ at λ_{max} = 650 nm and $[Cu(quinap)I]_2$ (Fig. 3) at λ_{max} = 659 nm appears only in the solid state.

4. Discussion

Square-planar complexes of the type $Pt(L–L)(CN)_2$ with L–L = neutral bidentate ligand such as 1,2-diimines or bis-arylphosphines can be prepared by various procedures. However, according to our own experience the best method simply involves the reaction of $Pt(CN)_2$ with L–L in a stoichiometric ratio [7,8]. This procedure was also successful for obtaining $Pt(quinap)(CN)_2$.

Tetrahedral cations of the type $[Cu^I(L–L)_2]^+$ with L–L = 1,2-diimines [11,12] or bis-arylphosphines [9] as well as the neutral dimers $[Cu^I(L–L)I]_2$, with L–L = bis-arylphosphines [9,10] have been also previously synthesized. These dimers are known to contain tetrahedral iodide-bridged $Cu^I(L–L)I_2$ fragments. The preparation of our target compounds $[Cu(quinap)_2]PF_6$ and $[Cu(quinap)I]_2$ was achieved by similar procedures.

The lowest-energy electronic transitions of Pt(II) complexes with 1,2-diimine and bis-arylphosphine ligands are frequently of the MLCT type [1–3,8]. Dependent on the particular ligand, IL excited states may be also involved [6,8]. The emission is a phosphorescence which in some cases appears only in the solid state. Generally, the solid compounds may consist of columnar structure with short Pt–Pt distances. These solids are frequently characterized by striking colours which are determined by metal-centered transitions [13]. They occur at much longer wavelength than those of the mononuclear components. Our target complex Pt(quinap)$(CN)_2$ does apparently not undergo such an aggregation in the solid state or in solution as indicated by the similarity of the electronic spectra in dilute solution and in the solid state. The quinap ligand seems to prevent a close approach of the complex molecules perpendicular to the square-planar geometry. The longest-wavelength absorption of Pt(quinap)$(CN)_2$ at $\lambda_{max} = 441$ nm (Fig. 1) is assigned to a spin-allowed mixed IL (quinap) and MLCT (Pt → quinap) transition. Shorter-wavelength bands may be of the IL type. The emission of Pt(quinap)$(CN)_2$ in solution at $\lambda_{max} = 544$ nm or in the solid state at $\lambda_{max} = 588$ nm (Fig. 2) is suggested to originate from the lowest-energy MLCT/IL triplet in analogy to other complexes of the general composition Pt(1,2-diimine)$(CN)_2$ [6] and Pt(bis-arylphosphine)$(CN)_2$ [8].

Tetrahedral $[Cu(1,2\text{-diimine})_2]^+$ complexes are well known to emit from MLCT triplets [14,15]. Frequently, this luminescence appears only when the complex is fixed in a rigid matrix. In solution, quenching is caused by large distortions from tetrahedral towards square-planar structures in the MLCT triplet. In contrast, various Cu(I) arylphosphine complexes are luminescent in solution at r.t. The origin of this emission has been controversially discussed [16] but quite recently calculations have shown that the emitting triplets are of the mixed parentage with partial MLCT character [17]. Again, rigid structures facilitate a phosphorescence in solution. Our target complexes $[Cu(quinap)_2]^+$ and $[Cu(quinap)I]_2$ are luminescent at r.t. but only in the solid state. Since the absorption and emission spectra of both complexes are very similar the emission properties are certainly determined by the Cu(quinap) moiety. It is suggested that in analogy to 1,2-diimine and arylphosphine complexes the quinap complexes of Cu(I) emit also from MLCT triplets.

5. Conclusion

Quinap combines the properties, in particular the CT acceptor ability, of 1,2-diimines and arylphosphines in one ligand. Accordingly, the new complexes Pt(quinap)$(CN)_2$, $Cu(quinap)_2^+$ and $[Cu(quinap)I]_2$ are characterized by lowest-energy MLCT triplets which are emissive at ambient conditions.

Acknowledgement

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