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Note

Synthesis and optical properties of binuclear gold(I) complexes with bridging phosphine ligands: luminescence from intraligand and metal-centered excited states

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Abstract

The complexes Au_2Cl_2(P-P) with P-P = biphep (2,2′-bis(diphenylphosphino)-1,1′-biphenyl), binap (2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) and xantphos (9,9′-dimethyl-4,5-bis(diphenyl-phosphino)xanthene), were prepared and characterized by elemental analysis and ESI-MS. The solid compounds show a r.t. phosphorescence. While the binap complex emits from an intraligand (IL) triplet, the luminescence of the biphep complex originates from a metal-centered (MC) triplet which is presumably lowered by gold–gold interaction. The xantphos complex displays a dual phosphorescence. In this case, the emitting triplets are of the IL and MC type.

Keywords: Gold complexes; Phosphine complexes; Luminescence

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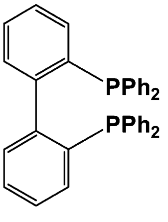
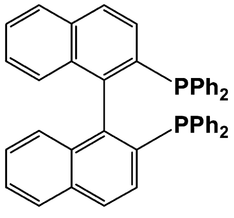
1. Introduction

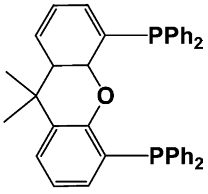
A variety of gold(I) compounds has been shown to be luminescent under ambient conditions [1–3]. Binuclear Au(I) complexes which contain bidentate phosphines as bridging ligands [4] constitute an important subclass of emissive gold(I) compounds. In this case the luminescence frequently originates from metal-centered (MC) excited states which are modified by gold–gold interaction. This applies in particular to complexes with alkyl substituents at phosphorus [5–8]. However, bidentate phosphines carry often chromophores including aromatic groups. Such phosphines have available intraligand (IL) states at relatively low energies [9,10]. The presence of MC and IL states at comparable energies complicates the emission behavior. On the other side, in favorable cases the IL emission is structured and resembles that of the free ligand. The IL emission can then be easily identified and may be even used as luminescent marker. Recently, new bidentate phosphines with aromatic substituents became available. While they were designed for applications in catalysis they might also contribute to gain more insight into the excited state properties of gold(I) phosphine complexes. We exlored this possibility and selected the bidentate phosphines 2,2′-bis(diphenylphosphino)-1,1′-biphenyl (biphep), 2,2′-bis(diphenylphosphino)-1,1′-bi-naphthyl (binap) and 9,9′-dimethyl-4,5-bis(diphenylphosphino)xanthene (xantphos) for the present study.



biphep



binap



xantphos

The complex Au_2Cl_2(biphep) has been previously sythesized by a complicated procedure [11]. However, it was expected that Au(I) complexes of biphep, binap and xantphos are accessible by simply reacting $Au(SMe_2)Cl$ with the corresponding diphosphine.

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2. Experimental

2.1. Materials

Solvents used for spectroscopic measurements were of spectrograde quality. The compounds Au(SMe$_2$)Cl, biphep, binap and xantphos were commercially available (Aldrich, Strem) and used without further purification.

The complexes Au$_2$Cl$_2$(P-P) were obtained by the following procedures.

2.1.1. Au$_2$Cl$_2$(biphep)

A mixture of Au(SMe$_2$)Cl (430 mg, 1.46 mmol) and biphep (390 mg, 0.73 mmol) in 40 ml CH$_3$CN/CH$_2$Cl$_2$ (1:1) was stirred under argon at r.t. for 1.5 h. A white material precipitated. It was collected by filtration, washed with ether and dried over silical gel, yield: 670 mg (68%). *Anal.* Calc. (Found): C, 43.79 (43.89); H, 2.86 (3.17); Cl, 7.18 (7.13%).

2.1.2. Au$_2$Cl$_2$(binap)

To a suspension of binap (160 mg, 0.25 mmol) in 20 ml CH$_3$CN/CH$_2$Cl$_2$ (1:1) under argon was added Au(SMe$_2$)Cl (150 mg, 0.5 mmol). A clear solution was formed under strirring. After 30 min a white material started to precipitate. Strirring at r.t. was continued for 2 h. The precipitate was collected by filtration, washed with ether and dried over silica gel, yield: 175 mg (64%). *Anal.* Calc. (Found): C, 48.59 (47.99); H, 2.97 (3.16); Cl 6.52 (6.30%).

2.1.3. Au$_2$Cl$_2$(xantphos)

A mixture of Au(SMe$_2$)Cl (300 mg, 1 mmol) and xantphos (290 mg, 0.5 mmol) in 30 ml CH$_3$CN/CH$_2$Cl$_2$ (1:1) was stirred under argon at r.t. for 1 h. A white precipitate was formed, collected by filtration, washed with ether and dried over silica gel, yield: 475 mg (91%). *Anal.* Calc. (Found): C, 44.89 (43.40); H, 3.09 (3.08%).

2.2. Instrumentation

Absorption spectra were measured with a Shimadzu 2100 spectrophotometer. Emission spectra were recorded on a Hitachi 850 spectrofluorometer equipped with a Hamamatsu 928 photomultiplier for measurements up to 900 nm. The mass spectra were obtained using a TSQ 7000 Finnigan Thermoquest mass spectrometer.

3. Results

The complexes Au$_2$Cl$_2$(P-P) with P-P = biphep, binap and xantphos were prepared by the reaction of Au(SMe$_2$)Cl with P-P. They were obtained as white solids. Their composition were confirmed by elemental analysis. Au$_2$Cl$_2$(biphep) has been synthesized previously [11]. Au$_2$Cl$_2$(binap) and Au$_2$Cl$_2$(xantphos) were further characterized by ESI-MS. The +ESI spectrum of Au$_2$Cl$_2$(binap) in CH$_3$CN shows peaks at $m/z = 1051$, 1052, 1053, 1054 and 1055 which correspond to the loss of one chloride ligand. Additional peaks at $m/z = 819$, 820, 821 and 822 are caused by [Au(binap)]$^+$ which was generated as a further fragmentation product. Analogous results were obtained for Au$_2$Cl$_2$(xantphos) in CH$_3$CN. The +ESI-MS of [Au$_2$Cl$_2$(xantphos)] shows peaks at $m/z = 1007$, 1008, 1009, 1010, 1011 for [Au$_2$Cl$_2$(xantphos)]$^+$ and at 775, 776, 777 and 778 for [Au(xanthphos)]$^+$. In all cases the isotope distribution matches the calculated data.

The free biphep ligand in CH$_3$CN or ethanol exhibits a broad absorption at $\lambda_{max} = 270$ nm, a r.t. fluorescence at $\lambda_{max} = 384$ nm and a structureless phosphorescence at $\lambda_{max} = 490$ nm which appears only at low temperatures (ethanol, 77 K). The spectral data of binap have been previously reported [12]. The free xantphos ligand in ethanol displays an absorption at $\lambda_{max} = 259$ nm, and a lowtemperature phosphorescence at $\lambda_{max} = 475$ nm (ethanol, 77 K).

The electronic spectrum of Au$_2$Cl$_2$(biphep) in CH$_3$CN (Fig. 1) shows an absorption which increases towards shorter wavelength. Shoulders appear at $\lambda = 275$ nm ($\varepsilon = 10950$ M^{-1} cm^{-1}), 268 (14 300) and 262 (16 700). In solution the complex is not luminescent, but in the solid state at r.t. a greenyellow emission occurs (Fig. 1) at $\lambda_{max} = 580$ nm ($\lambda_{exc} = 275$ nm). The complex Au$_2$Cl$_2$(binap) exhibits absorptions (Fig. 2) at $\lambda_{max} = 337$ nm (3300) and 230 nm (85 300) and shoulders at 322 and 292 nm. Again, the complex is not luminescent in solution, but the solid compound shows a green r.t. emission (Fig. 2) with structural features at $\lambda = 502$, 535 and 570 nm ($\lambda_{exc} = 335$ nm). In the absorption spectrum of Au$_2$Cl$_2$(xantphos) in CH$_3$CN (Fig. 3) two shoulders at 276 nm (20 430) and 270 nm (21 300), and a maximum at 256 nm (24 040) are ob-

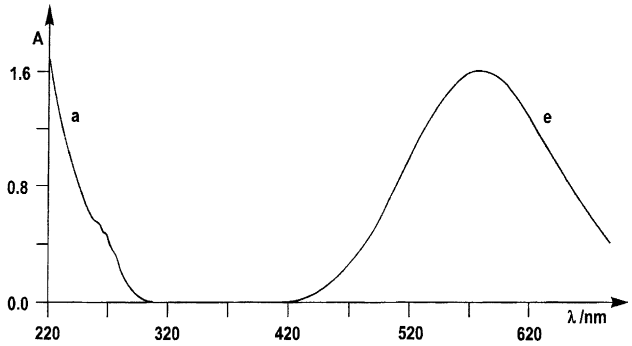


Fig. 1. Electronic absorption (a) and emission (e) spectrum of Au$_2$Cl$_2$(biphep) at room temperature. Absorption: 3.11×10^{-5} M in CH$_3$CN, 1-cm cell. Emission: solid, $\lambda_{exc} = 275$ nm, intensity in arbitrary units.

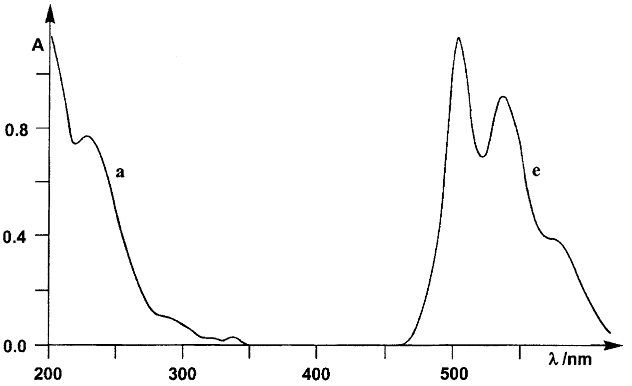


Fig. 2. Electronic absorption (a) and emission (e) spectrum of Au_2Cl_2(binap) at room temperature. Absorption: 8.97×10^{-6} M in CH_3CN, 1-cm cell. Emission: solid, $\lambda_{exc} = 335$ nm, intensity in arbitrary units.

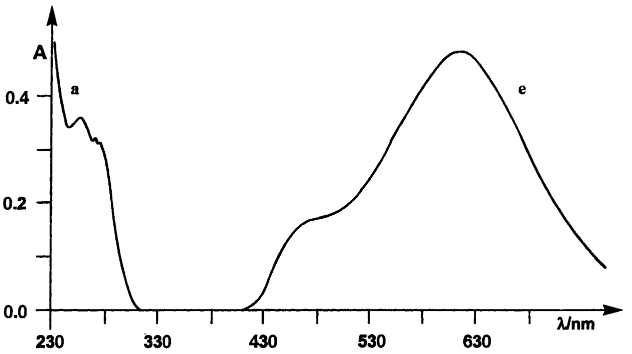
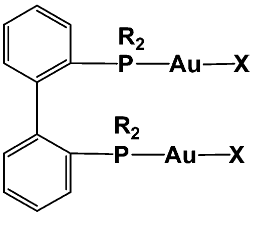


Fig. 3. Electronic absorption (a) and emission (e) spectrum of Au_2Cl_2(xantphos) at room temperature. Absorption: 1.51×10^{-5} M in CH_3CN, 1-cm cell. Emission: solid, $\lambda_{exc} = 300$ nm, intensity in arbitrary units.

served. While in solution the complex does not emit, solid Au_2Cl_2(xantphos) displays a r.t. luminescence (Fig. 3) which consists of two distinct bands. A maximum appears at $\lambda_{max} = 613$ nm and a shoulder at 480 nm ($\lambda_{exc} = 300$ nm). In all cases the excitation spectra match roughly the absorption spectra.

4. Discussion

Various complexes of the type Au_2Cl_2(2,2′-diphosphino-1,1′-biphenyl) including Au_2Cl_2(biphep) have been prepared and structurally characterized [11].



It is assumed that Au_2Cl_2(binap) and Au_2Cl_2(xantphos) have analogous structures. All three complexes are luminescent at r.t., but only in the solid state. These emissions certainly originate from triplet states owing to the heavy atom effect of gold [1–3]. In the case of Au_2Cl_2(binap) it is quite clear that the emitting state is of the IL (binap) type because the emission (Fig. 2) closely resembles the phosphorescence of the free binap ligand [12]. The IL assignment is facilitated by the appearance of a structured emission for the complex as well as for the free ligand.

Unfortunately, the phosphorescence of Au_2Cl_2(biphep) (Fig. 1) and of the free biphep ligand is not structured. However, the complex emits at distinctly longer wavelength ($\lambda_{max} = 580$ nm) than the ligand (490 nm). Accordingly, it is suggested that the phosphorescence of the complex does not come from an IL (biphep) state. It is assumed that the emission originates from a MC (ds, dp) excited state which is lowered in energy by gold–gold interaction [5–8]. Indeed it has been shown that the gold–gold distance of the closely related complex Au_2I_2(bis-2,2′-diethylphosphino-1,1′-biphenyl) amounts to 3.167 Å and is thus indicative of a weak metal–metal interaction [11]. In the case of Au_2Cl_2(binap) the steric requirements of the binap ligand could prevent such a close approach of both gold atoms. Accordingly, the MC state occurs at higher energies well above the emitting IL state.

The complex Au_2Cl_2(xantphos) shows two emissions (Fig. 3). The phosphorescence at 480 nm is assumed to originate from the xantphos IL state since the luminescence appears at an energy very close to that of the phosphorescence of the free xantphos ligand. The longer wavelength emission of the complex at $\lambda_{max} = 613$ nm is assumed to come from a MC triplet modified by gold–gold interaction.

In conclusion, solid complexes of the type Au_2Cl_2(P-P) which contain the bridging phosphines biphep, binap and xantphos show a room temperature phosphorescence which originates from MC and/or IL (P-P) triplets.

Acknowledgements

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