Synthesis, Electronic Spectra and Solvent-Induced Reversible Dissociation of Diphosphine(hexafluoroacetylacetonato)copper(I) Complexes

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The complexes $Cu^{I}(P-P)(hfac)$ with P-P = 1,2-bis(diphenylphosphino)ethane (diphos), 1,3-bis-(diphenylphosphino)propane (prophos), 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (binap) and hfac = hexafluoroacetylacetonate were synthesized and spectroscopically characterized. In the solid state or in solutions of non-polar solvents these compounds are yellow owing to a long-wavelength (hfac⁻ \rightarrow P-P) ligand-to-ligand charge transfer absorption. In coordinating solvents such as CH₃CN the complexes undergo a reversible dissociation according to the equation:

 $\operatorname{Cu}(\operatorname{P-P})(\operatorname{hfac}) + n \operatorname{CH}_3\operatorname{CN} \rightleftharpoons [\operatorname{Cu}(\operatorname{P-P})(\operatorname{CH}_3\operatorname{CN})_n]^+ \operatorname{hfac}^-.$

While the complexes are not luminescent the ion pairs $[Cu(P-P)(CH_3CN)_n]^+hfac^-$ are emissive at 77 K. The cations and the anions show separate emissions as indicated by the excitation spectra.

Key words: Electronic Spectra, Luminescence, Copper Complexes, β -Diketonate Complexes

Introduction

Complexes of the type $Cu^{I}L_{n}(\beta$ -diketonate) with L = e. g. phosphine, diolefin and alkyne have attracted much interest because they are useful precursors for the chemical vapor deposition of copper metal [1-3]. Moreover, copper(I) compounds in general, including phosphine complexes, show a luminescence [4, 5]which might be utilized for various applications in optical devices. Most emissive Cu(I) complexes are either cations or polynuclear compounds. Since they are hardly volatile they cannot be used for copper deposition from the gas phase as required for diverse industrial processes. Their limited solubility in nonpolar solvents is a further disadvantage for certain technical procedures. It follows that neutral mononuclear complexes of the general composition $Cu^{I}(PR_{3})_{n}$ (β -diketonate) with n = 1 and 2 are valuable subjects for further explorations. Several such compounds have been prepared and structurally characterized [6-9]. Surprisingly, bidentate phosphines which may form more stable complexes have not been included in previous studies. We explored this possibility and selected compounds of the type Cu^I(P-P)(hfac) with P-P = 1,2-bis(diphenylphosphino)ethane (diphos),

1,3-bis(diphenylphosphino)propane (prophos), 2,2'bis(diphenylphosphino)-1,1'-binaphthyl (binap) and hfac = hexafluoroacetylacetonate for the present investigation. These complexes should be easily accessible and suitable targets for the examination of their optical properties. In this context it is of interest that neutral phosphine complexes of the type $Cu^{I}(P-P)BH_{4}$ have been shown to display an intraligand (IL) phosphorescence of the coordinated disphosphine at 77 K or even at r.t. [4, 10–13].

Experimental Section

Materials

All solvents used for spectroscopic measurements were of spectrograde quality. Cu(BTMSA)(hfac) (BTMSA = bis(trimethylsilyl)acetylene) (Aldrich), diphos (Acros), prophos (Acros) and binap (Strem) were commercially available and used without further purification. The complexes Cu(P-P)(hfac) were obtained by the following procedures.

Cu(prophos)(hfac)

A mixture of Cu(BTMSA)(hfac) (0.54 g, 1.22 mmol) and prophos (0.51 g, 1.24 mmol) in 15 ml of toluene was refluxed for 30 min. The mixture was then cooled to r.t. Upon addi-

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tion of hexane a red-brown oily precipitate was formed. It was removed by filtration. The volume of the filtrate was reduced by evaporation. Upon addition of ether and standing at r.t. red-orange crystals separated. They were collected by filtration and washed with ethanol and ether, and dried over silica gel.

Yield: 0.35 g (44%). Anal. calcd. C 56.27, H 3.98; found C 56.46, H 3.92.

Cu(diphos)(hfac)

A mixture of Cu(BTMSA)(hfac) (0.43 g, 1 mmol) and diphos (0.39 g, 1 mmol) in 20 ml of toluene was refluxed for 20 min. A yellow solution with a yellow solid was obtained. Precipitation was completed by addition of hexane. The yellow precipitate was collected by filtration, washed with hexane and dried over silica gel.

Yield: 0.47 g (72%). Anal. calcd. C 55.65, H 3.77; found C 56.16, H 4.03.

Cu(binap)(hfac)

A mixture of Cu(BTMSA)(hfac) (0.45 g, 1 mmol) and binap (0.63 g, 1 mmol) in 20 ml of toluene was refluxed for 1 h and then cooled to r.t. An orange precipitate formed. It was collected by filtration, washed with hexane and dried over silica gel.

Yield: 0.74 g (83%). Anal. calcd. C 65.88, H 3.72; found C 66.05, H 3.63.

Instrumentation

Absorption spectra were measured with a Kontron Uvikon 932 double beam spectrophotometer. Emission spectra were recorded on a Hitachi 850 spectrofluorometer equipped with a Hamamatsu 928 photomultiplier. The luminescence spectra were corrected for monochromator and photomultiplier efficiency variations.

Results

The complexes Cu(P-P)(hfac) with P-P = diphos, prophos and binap were prepared by the reaction of Cu(BTMSA)(hfac) [14–16] with P-P in toluene according to the equation:

 $Cu(BTMSA)(hfac) + P-P \rightarrow Cu(P-P)(hfac) + BTMSA$

Table 1. Absorption maxima and extinction coefficients of Cu(P-P)(hfac) in dichlormethane at 298 K.

	$\lambda_{\rm max}$ / nm (ε / 1 mol ⁻¹ cm ⁻¹)
Cu(prophos)(hfac)	252 (13800), 288 (14700), \approx 400 (690)
Cu(diphos)(hfac)	253 (12500), 291 (12200), \approx 400 (670)
Cu(binap)(hfac)	275 (28100) sh, 290 (21400) sh, 329 (9100) sh,
	376 (4100)



Fig. 1. Electronic absorption spectra of Cu(P-P)(hfac) in dichlormethane at 298 K, 1 cm cell: (a) Cu(binap)(hfac), $c = 3 \cdot 10^{-5} \text{ mol } 1^{-1}$; (b) Cu(prophos)(hfac), $c = 7 \cdot 10^{-5} \text{ mol } 1^{-1}$; (c) Cu(diphos)(hfac), $c = 7 \cdot 10^{-5} \text{ mol } 1^{-1}$.

The compounds were obtained as orange or yellow solids. Their composition was confirmed by elemental analysis. The complexes dissolve in non-polar solvents such as CH_2Cl_2 to yield yellow solutions which are stable also in the presence of oxygen. The absorption spectra and maxima of Cu(P-P)(hfac) are presented in Fig. 1 and Table 1. The compounds are not luminescent as solids or in non-polar solvents.

When Cu(P-P)(hfac) complexes are dissolved in polar and coordinating solvents such as CH_3CN the yellow colour disappears and colourless solutions are obtained. This colour change is also observed if CH_3CN is added to the yellow solution of the complexes in CH_2Cl_2 . At constant complex concentrations and vari-

Table 2. Luminescence and excitation band maxima of Cu(P-P)(hfac) in acetonitrile at 77 K.

	Luminescence	Excitation
	$\lambda / \text{nm} (\lambda_{\text{exe}} = 300 \text{ nm})$	$\lambda_{\rm max}$ / nm
Cu(prophos)	405, 455, 484, 520 sh	306, 315 sh ($\lambda_{\rm em} = 450$ nm)
(hfac)		274 ($\lambda_{\rm em} = 400 \text{ nm}$)
Cu(diphos)	408, 452, 482, 520 sh	307, 317 sh ($\lambda_{\rm em} = 450 \text{ nm}$)
(hfac)		273 ($\lambda_{\rm em} = 400 \text{ nm}$)
Cu(binap)	457, 506, 544, 586 sh	314 ($\lambda_{\rm em} = 460 \text{ nm}$)
(hfac)		320, 353 ($\lambda_{\rm em} = 505 \text{ nm}$)



Fig. 2. Changes of the absorption spectrum of Cu-(diphos)(hfac) in variable CH_2Cl_2/CH_3CN mixtures: (a) CH_2Cl_2 ; (b) CH_2Cl_2/CH_3CN 16:1; (c) CH_2Cl_2/CH_3CN 16:2; (d) CH_2Cl_2/CH_3CN 16:5.

able CH₂Cl₂/CH₃CN mixtures spectral changes including an isosbestic point at 321 nm are observed (Fig. 2). These spectral variations are completely reversible. The evaporation of the solvent of a colourless solution of Cu(P-P)(hfac) in CH₃CN regenerates the yellow solid.

At r. t. the solutions of Cu(P-P)(hfac) in CH₃CN are not luminescent, but in a CH₃CN matrix at 77 K a strong emission appears (Figs. 3-4 and Table 2). The excitation spectra (Figs. 3-4 and Table 2) consist of separate excitation bands depending on the emission wavelength.

Discussion

Copper(I) arylphosphine complexes are characterized by two low-energy phosphine IL excited states [4, 10, 12, 13, 17]. Generally, the lower one is of σa_{π} type and involves the promotion of an electron from the Cu-P σ -bond to the π^* orbitals of the aromatic substituents. The $\pi\pi^*$ states of the aryl groups are located



Fig. 3. Electronic emission and excitation spectra of Cu(prophos)(hfac) in CH₃CN at 77 K. Emission (c): $\lambda_{exc} = 300$ nm. Excitation (a): $\lambda_{em} = 400$ nm; (b): $\lambda_{em} = 450$ nm.



Fig. 4. Electronic emission and excitation spectra of Cu(binap)(hfac) in CH₃CN at 77 K. Emission (c): $\lambda_{exc} = 300$ nm. Excitation (a): $\lambda_{em} = 460$ nm; (b): $\lambda_{em} = 505$ nm.

at higher energies. The σa_{π} IL as well as the $\pi \pi^*$ IL triplets of Cu^I(arylphosphine) complexes may be emissive, sometimes even at r.t. The phosphorescence from the σa_{π} IL state of coordinated phenylphosphines appears around 500 nm while the $\pi \pi^*$ triplets emit at shorter wavelength between 400 and 450 nm, depending on the specific ligand and the solvent.

In general, these arylphosphine complexes are colourless since the σa_{π} and $\pi \pi^*$ IL absorptions appear in the UV spectral region. Simple hfac complexes of redox-inert metals as well as Cu^I(CH₃CN)_nhfac are also colourless. These complexes are characterized by hfac IL absorptions at $\lambda_{max} \approx 300$ nm [18, 19].

In contrast, our complexes Cu(P-P)(hfac) as well as $Cu(PR_3)_n(hfac)$ with n = 1 and 2 [6-9] are orange to yellow. This colour is caused by a distinct absorption with a maximum at approximately 400 nm (Fig. 1 and Table 1). We suggest that this absorption belongs to a ligand-to-ligand charge transfer (LLCT) transition from the hfac ligand to the phosphine. Related LLCT transitions with phosphines and arsines as acceptor ligands have been identified in the spectra of other Cu(I) complexes [20, 21]. The CT donor ability of the hfac ligand is well known. Various hfac complexes with oxidizing metal centers display long-wavelength ligandto-metal charge transfer (LMCT) absorptions [18]. Moreover, photo electron spectroscopy and calculations have shown that the HOMO of Cu(PMe₃)(hfac) is essentially located at the hfac ligand [22]. Accordingly, it is quite reasonable to assign the longest-wavelength band of Cu(P-P)(hfac) in CH₂Cl₂ at $\lambda_{max} \approx 400$ nm to a LLCT transition.

What happens if Cu(P-P)(hfac) complexes are dissolved in CH₃CN? The disappearance of the yellow colour is certainly not a solvatochromic effect but is caused by a reversible chemical reaction as indicated by the concomitant spectral changes including an isosbestic point (Fig. 2). We suggest that our results are consistent with a ligand substitution:

$$Cu(P-P)(hfac) + nCH_3CN \rightarrow [Cu(P-P)(CH_3CN)_n]^+ hfac^-$$

(n = 1 or 2).

Previous observations have already shown that the hfac ligand of Cu(PMe₃)₂(hfac) is replaced upon addition of a phosphine excess [8]:

 $Cu(PMe_3)_2(hfac) + 2PMe_3 \rightarrow [Cu(PMe_3)_4]^+hfac^-.$

The release of hfac should be facilitated if the phosphine ligands of $Cu(PR_3)_2(hfac)$ are sterically demanding. In the case of $Cu(PCy_3)_2(hfac)$ with Cy = cyclohexyl it has been demonstrated that the steric overcrowding leads to a weakening and lengthening of the Cu-hfac bonds [9]. The bidentate P-P ligands apparently exert a similar effect. Moreover, the CH₃CN as a solvent does not only function as an entering ligand but it should also stabilize the ion pair $[Cu(P-P)(CH_3CN)_n]^+hfac^-$ owing to the high solvent polarity.

The loss of the yellow colour upon formation of the ion pair is now easily explained by the disappearance of the hfac \rightarrow P-P LLCT absorption. In addition, strong evidence for the ion pair formation in CH₃CN is based on luminescence measurement at 77 K. The presence of the hfac⁻ anion is indicated by its diagnostic green phosphorescence [18,23-25] (Figs. 3-4, Table 2) at $\lambda_{\text{max}} \approx 455$ nm. The excitation maxima at 306, 307 and 314 nm show that hfac⁻ exists as an isolated species. The other emission maxima of Cu(P-P)(hfac) in CH₃CN (Fig. 3, Table 2) with P-P = diphos, prophos are attributed to the IL (P-P) phosphorescence of $[Cu(P-P)(CH_3CN)_n]^+$. These emissions resemble those of $Cu^{I}(P-P)BH_4$ complexes [4, 10–13]. The long-wavelength emissions of $[Cu(binap)(CH_3CN)_n]^+$ $(\lambda_{\text{max}} = 506, 544 \text{ and } 586 \text{ nm}, \text{Fig. 4})$ is also clearly a phosphorescence of the binap ligand [26, 27]. Again, the corresponding excitation spectra cover the region of the P-P IL absorptions but do not include the hfac IL band.

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