Synthesis, spectroscopic and electrochemical characterization of copper(I) complexes with functionalized pyrazino[2,3-*f*]-1,10-phenanthroline

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In memory of Professor Dr. Carlos Andrade Plaza

Abstract

The present work reports the synthesis and spectroscopic and electrochemical characterization of homoleptic copper(I) complexes with substituted pirazino [2,3-*f*]-1,10-phenanthroline, *RpplR'*, (R = H, Me, COOH or COOMe, and R' = H, Me) as ligand. The ligand ppl works as an acceptor of electronic density, which is delocalized mainly in the quinoxaline part of its structure. The UV–Vis spectra show that all the complexes display bands in the range 400–650 nm, which are MLCT in character. The λ_{max} and extinction coefficients of the MLCT band at 450 nm and the LC band do not change significantly when varying the R substituent. Nevertheless, the intensity of the shoulder around 500 nm does change; this absorption has been related to either a static or dynamic flattening distortion of the complex $D_{2d} \rightarrow D_2$ symmetry. The cyclic voltammetry of the complexes shows irreversible redox processes with E_p values that do not follow the tendency expected from the donor/acceptor character of the substituents on the ligand. All the complexes studied showed no emission both in acetonitrile and dichloromethane as solvent at room temperature and under argon atmosphere.

All the results are discussed in relation to the proposed flattened distortion of the ground state, as well as in relation to the donor/acceptor character of the substituents on the ligand, the steric effects on the symmetry of the metal center and the excited state distortion.

1. Introduction

Ru(II)–polypyridine complexes have been one of the most extensively investigated families in relation to their photochemical and photophysical properties. As a result, the comprehension of these properties allowed the complexes to be applied in molecular device technology and in solar energy-conversion [1a]. The most remarkable complex in this context has been the famous N3 black dye and its application in solar photo electrochemical cells [1b].

On the other hand, copper(I) complexes display a wide variety of excited states and especially rich photophysical and photochemical processes. Particularly, copper(I)–polypyridine complexes exhibit low-lying MLCT transitions that can participate, among others, in electron transfer processes [2]. Based on the possibility of a fine tuning of the absorption and emission properties, excited state lifetimes and a characteristic structural flexibility, the use of Cu(I)–phenanthroline type complexes was proposed as an alternative to the Ru(II)–polypyridine counterpart family [3]. However, this fine tuning is a complicate task since the properties mentioned above depend on several factors which not always work in the correct direction for all the given properties (*e.g.* $\phi_{emission}$ and $\tau_{1/2}$) [4]. In the case of

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copper(I)–polypyridine type complexes, the absorption characteristics of the MLCT band depends on the symmetry of the ground state, whereas the properties of the excited state strongly depend on the structural distortions following the change in the formal oxidation state after excitation. Different structural and chemical properties, and the coordination ability of the solvents, have been used to modulate the geometry distortions of the ground and excited state [2–6]. This line of research on the Cu–polypyridine family has been reviewed by Meyer et al. up to 1999 [7]. More recently, the dynamics of the distortion process on the photo excited MLCT state of the $[Cu(I)(dmp)_2]^+$, dmp = dimethylphenanthroline, has been investigated both experimentally and theoretically [8]. Using pulsed X-Ray, a transient five-coordinated MLCT state was proposed to have the coordination geometry of a distorted trigonal bipyramid [8a].

The plasticity of the coordination sphere in copper complexes has also been used to investigate specific changes in the microenvironments of electroactive and/or photoactive cores, by studying the size effect of the dendritic core in Cu(I)–polypyridine dendrimers [9].

Coppens et al. [10] with the aim to quantify the Cu coordination environment distortion, defined a distortion parameter ξ_{CD} and found an inverse correlation between the ξ_{CD} value for the ground-state geometry of $[Cu(bfp)_2]^+$ complex, bfp = 2,9-bis(trifluoromethyl)-1,10-phenanthroline, and its ^3MLCT excited-state lifetime. A more quantified relationship between structural changes and oxidation state has also been established [11]. Very recently, in order to further elucidate the role of the ligand structure in defining the photophysical properties of $[Cu(NN)_2]^+$ type complexes, Armaroli et al. [12], synthesized two novel phenanthroline ligands characterized by the presence of bulky aryl substituents in the 2,9-positions. The Cu(I) homoleptic complex with the most bulky substituent, shows an unusual absorption spectrum since the intensities of the characteristic band in the range 440–470 nm and the low lying shoulder (500–600 nm) are inverted, so the most prominent band is centered at 560 nm while that at 444 nm appears as a weak shoulder. This spectrum is similar to that of a Cu(I)–catenate complex, which presents a low symmetry, that is, a strongly distorted tetrahedral geometry.

In this context, the present work reports the synthesis, and the spectroscopic and electrochemical characterization of homoleptic copper(I) complexes with substituted pyrazino[2,3-*f*]-1,10-phenanthroline, RpplR′ (R = H, Me, COOMe, and R′ = H, Me) as ligand (Scheme 1).

The ligand ppl (which can be seen as a "fusion" of a bipyridine and a quinoxaline moiety or a phenanthroline and a pyrazino moiety) has been formerly reported by our research group and others [13]. It works as an acceptor of electronic density, which is delocalized mainly on the quinoxaline ring of its structure [13]. This fact should improve the directionality of the electron transfer of the MLCT excited state in the copper complexes. The use of a substituent (R) in the quinoxaline moiety was in order to evaluate its effect on the ground and excited state properties; in the case of R = COOH, the group was envisioned as an anchoring group to a semiconductor oxide electrode, in a potential application of the complex as dye in a solar conversion cell. On the other hand, R′ = Me in the phenanthroline moiety of the ligand is used in order to evaluate comparatively the steric effect on the symmetry of the metal center and to avoid the possibility of exciplex quenching of the excited state [7].

2. Experimental

2.1. Materials

1,10-Phenantroline (hydrate), 2,9-dimethyl-1,10-phenantroline and NH_4PF_6 were p.a. Sigma–Aldrich. The rest of the solids were Merck p.a. chemicals; all of them were used as purchased. All solvents were Merck p.a.; when needed, they were purified and dried by standard methods [13]. The precursors 1,10-phenanthroline-5,6-dione and 2,9-dimethyl-1,10-phenanthroline-5,6-dione were synthesized following reported procedures. The corresponding elemental analysis and ^1H NMR spectra were in agreement with the published results [14].

2.2. Physical measurements

Elemental analyses were performed on a Fisons Instruments Analyzer, model EA 1108/CHNS-O with PC NCR system 3225. UV–Vis spectra were recorded on a Shimadzu, UV-3101 PC Spectrophotometer, IR Spectra on Bruker Vector-22FTIR spectrometer using KBr pellets and ^1H NMR Spectra on a Bruker AC/200 (200 MHz) or Bruker

D_{2d} or D_2 symmetry on Cu
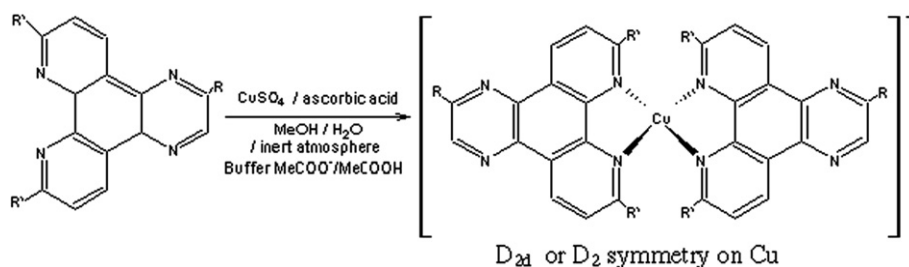
Scheme 1.

Aspect 400 MHz spectrometer, using CD_3CN or CD_3Cl as solvent and TMS as reference. ESR spectra were recorded in the X band (9.7 GHz) using a Bruker ECS 106 spectrometer with a rectangular cavity and 50 kHz field modulation.

Cyclic voltammetry experiments were carried out using a Bas CV-50W-2,3-MF-9093 equipment with a three-electrode arrangement with a platinum wire, a platinum coil and a Ag/AgCl electrode (in a tetra butyl ammonium chloride solution and adjusted to SCE) as working, auxiliary and reference electrodes, respectively. Experiments were carried out under argon atmosphere, with (TFBTBA) 0.1 M as supporting electrolyte and a scan speed of 200 mV s^{-1}. Emission measurements were carried out in an Aminco SLM-C spectrofluorimeter, at room temperature in Ar atmosphere.

2.3. Synthesis

2.3.1. Ligands

The synthesis of the pyrazino[2,3-*f*]-1,10-phenanthroline (ppl), 2-methylpyrazino[2,3-*f*]-1,10-phenanthroline (Meppl) and 2-carboxylic acid methyl ester pyrazino[2,3-*f*]-1,10-phenanthroline (COOMeppl) were carried out according to Ref. [13]. The pyrazino[2,3-*f*]-2,9-dimethyl-1,10-phenantroline (pplMe$_2$) was synthesized following the same procedure as for the ppl ligand but using 2,9-dimethyl-1,10-phenantroline as starting material. 2-Carboxylic acid pyrazino[2,3-*f*]-1,10-phenanthroline was synthesized as described in Ref. [13], but with the following modifications: after the green solution was poured over ice, the green solid obtained was filtered off and thoroughly washed with water. KOH (1 M) was added to a suspension of the green solid in water until complete dissolution. The solution was filtered and HCl (1:1) added to the supernatant. The white precipitate was filtered off, washed and dried in vacuum. Elemental analysis and ^{1}H NMR spectra for all the ligands were in agreement with the published results [13]. For pyrazino[2,3-*f*]-2,9-dimethyl-1,10-phenantroline (pplMe$_2$) the results are: Yield: 26.9% *Anal*. Calc. for $C_{16}H_{12}N_4$: C, 73.83; H, 4.65; N, 21.52. Found: C, 72.70; H, 4.67; N, 21.00%. IR (v_{max}/cm^{-1}): 750, 1391, 1362, 1362. ^{1}H NMR (CDCl$_3$ as solvent, δ in ppm, J in Hz): 7.64 (d, 2H, H$_2$, H$_{2''}$, $J_{2,3} = 8.32$), 9.35 (d, 2H, H$_3$, H$_3'$, $J_{3,2} = 8.32$), 8.90 (s, 2H, H$_4$, H$_4$), 2.98 (s, 6H; methyl).

2.3.2. [Cu(RpplR′)$_2$] PF$_6$ type copper complexes

General method: The syntheses were carried out following the McMillin general procedure [15]. In a typical synthesis, two degassed solutions, one contains 0.64 mmol of the ligand in 20 ml of methanol and the other one containing 80 mg (0.32 mmol) of $CuSO_4 \cdot 5H_2O$ and 52 mg (0.32 mmol) of NH_4PF_6 dissolved in 10 ml of acetate/acetic acid buffer (0.05 M) were mixed. A green solution was obtained. The solution was degassed and the system maintained in Ar atmosphere. Excess of ascorbic acid (0.48 mmol) was added to the mixture and a reddish-violet solid suddenly precipitated. The solid was collected by vac-

uum filtration, washed with degassed water, methanol and finally with ethyl ether. The solid was then dried in vacuum and kept under nitrogen or argon. All the steps were carried out under an inert atmosphere.

Bis(pyrazino[2,3-*f*]-1,10-phenanthroline)copper(I) hexafluorophosphate, [Cu(I)(ppl)$_2$] PF$_6$ (**1**) Yield: 96.5%. *Anal*. Calc. for [Cu(I)(C$_{14}$H$_8$N$_4$)$_2$]PF$_6$: C, 49.92; H, 2.39; N, 16.64. Found: C, 49.96; H, 2.16; N, 16.96%. IR (v_{max}/cm^{-1}): 740, 841, 1391, 1467, 1581.

Bis(2-methylpyrazino[2,3-*f*]-1,10-phenanthroline) copper(I) hexafluorophosphate, [Cu(I)(Meppl)$_2$]PF$_6$ (**2**): Yield: 93.0%. *Anal*. Calc. for [Cu(I) (C$_{15}$H$_{10}$ N$_4$)$_2$]PF$_6$: C, 51.40; H, 2.87; N, 15.98. Found: C, 50.62; H, 2.80; N, 15.50%. IR (v_{max}/cm^{-1}), 735, 841, 1370, 1407, 1474, 1578.

Bis(pyrazino[2,3-*f*]-1,10-phenanthroline-2-carboxylic acid methyl ester)copper(I) hexafluorophosphate, [Cu(I)(MeCOOppl)$_2$] PF$_6$ (**3**): Yield: 96.5%. *Anal*. Calc. for [Cu(I)(C$_{16}$H$_{10}$N$_4$O$_2$)$_2$]PF$_6$: C, 48.64; H, 2.55; N, 14.18. Found: C, 48.59; H, 2.39; N, 14.40%. IR (v_{max}/cm^{-1}), 794, 841, 1366, 1726, 1745.

bis(Pyrazino[2,3-*f*]-2,9-dimethyl 1,10-phenanthroline)copper(I) hexafluorophosphate, [Cu(I)(pplMe$_2$)$_2$] PF$_6$ (**4**): Yield: 69.0%. *Anal*. Calc. for [Cu(I) (C$_{16}$H$_{12}$N$_4$)$_2$]PF$_6$: C, 52.71; H, 3.32; N, 15.37. Found: C, 52.62; H, 3.27; N, 15.25%. IR (v_{max}/cm^{-1}), 745, 840, 1363, 1389, 1584.

3. Results and discussion

Following McMillin's general procedure [15], it was possible to synthesize four new homoleptic complexes of Cu(I) with substituted pyrazino[2,3-*f*]-1,10-phenanthroline, RpplR′, as ligand. Elemental analysis results were in good agreement with the proposed formula for the complexes giving therefore evidence of their purity. The IR spectra of the complexes exhibit the characteristic bands of the corresponding free ligands, except for showing the effect of coordination to the metal. All the metal-complexes display a strong band at 841 cm^{-1} characteristic of the PF$_6^-$ ion.

The ^{1}H NMR spectra of the complexes display signals at the same region than that for the corresponding free ligands; nevertheless, since the signals are wide, no unambiguous assignment was possible. Initially we supposed that, although the species were manipulated under inert atmosphere, it was not possible to discard the presence of paramagnetic Cu(II) species as an explanation of the low resolution of the spectra; *nevertheless, a silent EPR*[1] for the complexes (not shown) indicated the definitive absence of Cu(II) species. This result was in agreement with the fact that on the NMR spectra, although the signals corresponding to the complexes are wide, the ones corresponding to the solvent were not. A fluxional process as the reason for the observed NMR behavior was postulated. To prove

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[1] EPR spectra conditions: Center field: 3250.500 G; sweep width: 1000.000 G; frequency: 9.750 GHz; receiver gain: 74 dB; modulation amplitude: 0.87 G; sweep time: 41.943 s.

this possibility, a VT NMR study was accomplished. Fig. 1 shows the results for the [Cu(I)(Meppl)] PF$_6$ compound.

The figure shows that at low temperature the signals sharpen, some of them resolve given support to the fluxionally hypothesis. Added to this fact (or maybe related with it) and considering that the RpplR′ ligands have an acceptor character, and that the experimental evidence indicates that even in the ground state (at room temperature) the Cu(I) geometry is distorted towards the Cu(II) preferred geometry, our interpretation is that it is possible to think that the complex presents a type of "internal paramagnetism" due to the presence of a more deshielded Cu(I) as consequence of the displacement of the electronic density towards the acceptor RpplR′ ligand.

Fig. 2 shows the electronic absorption spectra of the complexes. All of them display bands in the 400–650 nm range, which are of MLCT character.

According to the analysis of McMillin et al. [16] for similar complexes of Cu(NN)$_2$$^+$ type, the shoulder around 500 nm should be assigned to the band named as band I. The assignment of this electronic transition is still controversial [17], but it is related to either a static or dynamic flattening distortion ($D_{2d} \rightarrow D_2$ symmetry). The band centered around 450 nm, named as band II, is associated to an $e(xz, yz) \rightarrow e(\pi^*L)$ excitation on a D_{2d} symmetry or $b(yz) \rightarrow b_2(\pi^*L)$ on D_2 symmetry. The band named as band III, which appears around 380 nm in other polypyridine systems, seems to be, in our case, overlapped with a LC band in the proximity of 350 nm. The UV zone shows ligand centered $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ bands around 250, 300 and 350 nm. Table 1 summarizes the λ_m absorption data for band II.

As in the case of homoleptic and heteroleptic complexes of Ru (II) with Rppl as ligand, the λ_{max} of the MLCT band
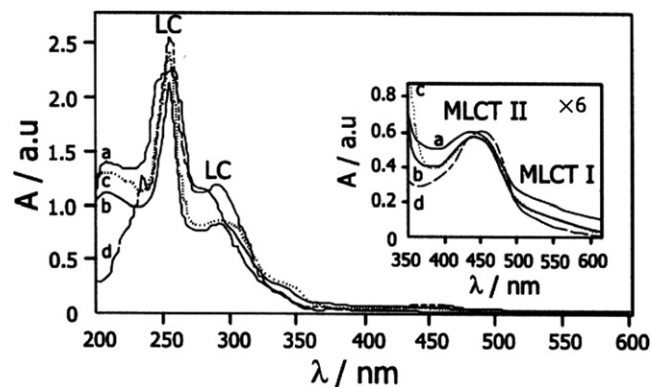

Fig. 2. Electronic absorption spectra of 1.7×10^{-5} M copper complexes solution in CH$_3$CN as solvent: [Cu(I) (ppl)] PF$_6$ (a), [Cu(I)(Meppl)] PF$_6$, (b), [Cu(I)(COOMeppl)]PF$_6$ (c), [Cu(I)(pplMe)]PF$_6$ (d); LC ligand centered, MLCT ligand to metal charge transfer.

Table 1
Absorption data for band II of [(RpplR′)$_2$ Cu]PF$_6$ complexes

Complex	λ_m (nm)[a]
R′ = –H, R = –H	439
R′ = –H, R = –CH$_3$	440
R′ = –H, R = –COOCH$_3$	443
R′ = –CH$_3$, R = –H	457

[a] CH$_3$CN as solvent.

around 450 nm and the LC bands in the copper complexes, do not change significantly with the R substituent [13]; the tendency of the small changes observed cannot be explained in terms of its donor/acceptor character. The changes are minor also at the shoulder around 350 nm, but the red or blue shift is in agreement with the acceptor or donor properties of the substituents respect to the ppl
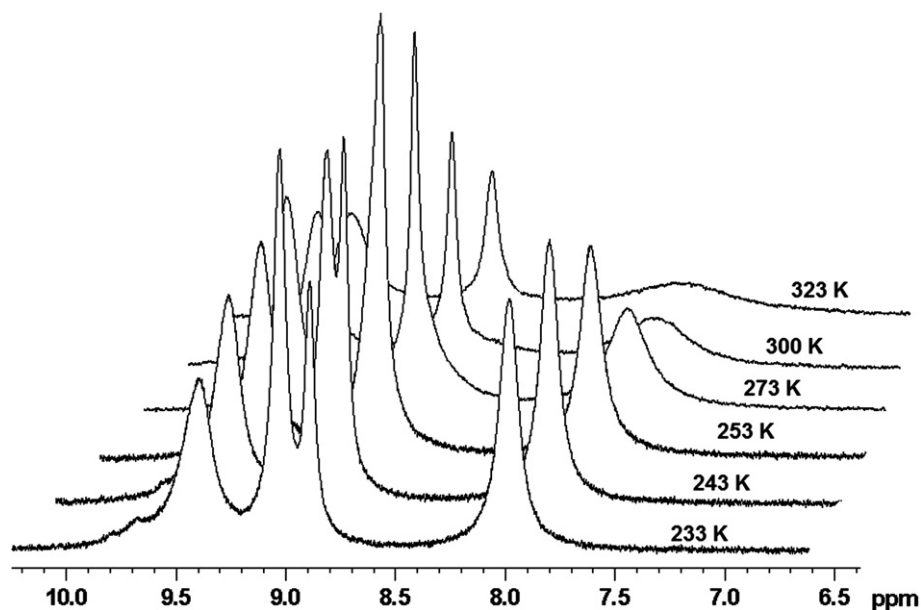

Fig. 1. NMR spectra as a function of the temperature of a [Cu(I)(Meppl)] PF$_6$, solution in CH$_3$CN as solvent.

ligand. Changes in the R′ substituents produce a more significant change in the λ_{max} of band II, although not in the way expected for the donor character of the methyl group.

The spectral characteristics of the complexes in Fig. 1, point to a certain degree of D_2 flattened symmetry distortion on the metal center [7,9,12]. If the intensity of the shoulder around 500 nm is taken as a measure of such distortion in the ground state, the observed order for the degree of distortion is [Cu(I)(ppl)$_2$]PF$_6$ > [Cu(I)(Meppl)$_2$] PF$_6 \cong$ [Cu(I)(COOMeppl)$_2$] PF$_6$ > [Cu(I)(pplMe$_2$)$_2$] PF$_6$.

The above mentioned similar tendency in the electronic absorption spectra of copper complexes and ruthenium complexes with ppl type ligands is less evident when the redox properties are analyzed, since the redox potential of the copper center on the complexes reported herein is affected by the electronic character of R and R′, although the corresponding Ru(II) complexes do not show this behavior [13]; Table 2 shows the electrochemical potentials for the series of complexes.

The redox potentials values do not show the expected correlation with the acceptor or donor electronic character of the substituents on the ligands, e.g. the Cu(I)/Cu(II) potential for [Cu(I)(Meppl)$_2$]PF$_6$ shows a more positive value than that for [Cu(I) (ppl)$_2$]PF$_6$ or, more surprising, the oxidation process for [Cu(I)(ppl(Me)$_2$)$_2$]PF$_6$ is energetically much more disfavored than the same process for [Cu(I)(COOMeppl)$_2$] PF$_6$. These results, as well as the irreversibility of the redox couples, are not unexpected taking into account the inner-sphere geometric change associated with the change in oxidation state. The relation of the irreversibility of the redox process with the distortion had also been observed electrochemically for some Cu(II) complexes [18]. Karpishin et al. [5a] reported that the absorption spectra of [Cu(II)(dpp)]$^{2+}$ ion, dpp = 2,9-diphenyl-1,10-phenanthroline, shows a low energy shoulder at 750 nm, assigned to a d–d transition and a 575 nm band, assigned to a LMCT. They concluded that [Cu(II)(dpp)]$^{2+}$ remains four-coordinated in solution as it was in the solid states indicated by the X-ray structure. In our case, the electronic absorption spectra of the Cu(II) complexes (not shown)[2] show a visible band centered at ~680 nm with a low extinction coefficient (≈ 70 cm^{-1} M^{-1}). Although it is difficult to establish the coordination symmetry around copper using visible absorption spectra, the characteristics of this band resembles the band for five or six-coordinated species of Cu(II), giving support to a distortion following the oxidation state change [19,20].

In order to model the solvent dependence of the redox potentials of [Cu(I)(dmp)$_2$](PF$_6$), Meyer et al. [7] consider solvent binding equilibrium, following the flattened distor-

Table 2
Electrochemical properties of [Cu(I)(RpplR)$_2$]PF$_6$ complexes, vs. SCE in CH$_3$CN as solvent

Compounds	E_{pa} (V)	E_{pc} (V)	$E_{\text{pc}_{(1)}}$ (V)
[Cu(I)(ppl)$_2$]PF$_6$	0.14	0.03	$\geqslant -1.5$
	0.10[a]	0.05[a]	
[Cu(I)(Meppl)$_2$]PF$_6$	0.18	0.07	$\geqslant -1.5$
[Cu(I)(COOMeppl)$_2$]PF$_6$	0.31	0.15	-1.1
[Cu(I)(ppl(Me)$_2$)$_2$]PF$_6$	0.59	0.40	$\geqslant -1.5$

[a] In DMSO as solvent; -1.5 is the cathodic limit of the solvent. E_{pa} is assigned to Cu(I)/Cu(II) oxidation. E_{pc} is the corresponding Cu(II)/Cu(I) back process. $E_{\text{pc}_{(1)}}$ corresponds to ligand reduction.

tion after the Cu(I)/Cu(II) oxidation. This effect lowers the free energy, making the overall redox process (electron transfer process, distortion of the metal center and coordination of the solvent) more favorable. Therefore, the redox potential values must reflect the balance of the energies associated to all factors affecting the redox process. Consequently, the greater distortion of the Cu(I) site in [Cu(I)(ppl)$_2$]PF$_6$ ground state relative to [Cu(I)-(Meppl)$_2$]PF$_6$, as seen by absorption spectroscopy, reduces the positive ΔG value associated to the distortion process in the excited state, but not the negative ΔG of the solvent coordination. The effect of both facts favoring the oxidation process, could exceed the effect of the good donor character of the methyl in [Cu(I)(Meppl)$_2$]PF$_6$, explaining the less positive oxidation potential in the first complex. Otherwise, in the case of [Cu(I)(ppl(Me)$_2$)$_2$]PF$_6$ the distortion in the ground state of the Cu(I) center is partially hindered, as well as the distortion after the oxidation process. Consequently the good solvent coordination process and the donor character of the methyl group would not be compensated, explaining its more positive oxidation potential. On the other hand, as expected, the presence of an attractor group produces a change on the redox potentials disfavoring the copper oxidation process and favoring the reduction of the ligand, $E_{\text{pc}_{(1)}}$, (e.g.: free ppl < -1.5 V; pplCH$_3 < -1.5$ V and COOMeppl $= -1.1$ V). In the same solvent, the Cu(II)/Cu(I) processes for [Cu(I)(phen)$_2$]$^+$ and [Cu(I)(dmp)$_2$]$^+$ have a potential of 0.04 V and 0.68 V, respectively [21], as compared with E_{pa} (V) values 0.03 V and 0.4 V values for [Cu(I)(ppl)$_2$]$^+$ and [Cu(I)(ppl(Me)$_2$)$_2$]$^+$, respectively. Therefore, Cu(I) is more unstable with the ppl and ppl(Me)$_2$ ligand. This fact cannot be explained by the acceptor character of the ppl ligand; thus structural effects that would favor Cu(II) type geometry in the ground state should be responsible for this result.

The effect of the solvent on the redox potential values can be seen by comparing the values in two different solvents for the complex with ppl as ligand; as expected from the model described above, the oxidation is more favored in DMSO than in CH$_3$CN, in accordance with the greater coordination power of the latter solvent.

All complexes studied in this work showed no emission in acetonitrile at room temperature. Although starting

from a distorted ground state, the geometrical change to a more flattened coordination geometry in going to the Franck–Condon state, produced after light absorption (MLTC band), allows the exciplexes quenching process [22]; this explains the non emissive character of the complexes. In this context it was expected that this excited state distortion should be avoided by the steric effect produced by the dimethyl substitution in the 2 and 9 positions in the phenanthroline moiety of the ppl ligand, permitting in this way the $[Cu(I)(ppl(Me)_2)_2]PF_6$ complex to photoluminesce. Nevertheless, no emission was observed even in a less coordinant solvent such as dichloromethane. The excited state behaviour of $[Cu(I)(Meppl)_2]PF_6$ can be compared with the observed for $[Cu(I)(dmp)_2]^+$. In the latter, emission is observed, although with a low quantum yield even in rigid media at low temperature [23]. In spite of the fact that ligand delocalization arguments would predict longer lifetimes and a better excited emissive state [24], the absence of emission in $[Cu(I)(Meppl)_2]PF_6$ is not unreasonable because, as shown above, even in the ground state the geometry of the Cu(I) center in $[Cu(I)(Meppl)_2]PF_6$ is distorted toward the Cu(II) geometry. In general, the photophysical properties of the excited state of some metal polypyridinic type complexes [5b,24,25] reflect the mixture of a variety of electronic (basicity of the donor, electron delocalization) and structural factors (changes in metal-ligand distances, distortion on the metal geometry, change of the coordination number, fluxionally of the ligands). In contrast to ruthenium complexes, structural factors are predominant in the case of copper complexes, influencing even properties related to the ground state, as shown in this work.
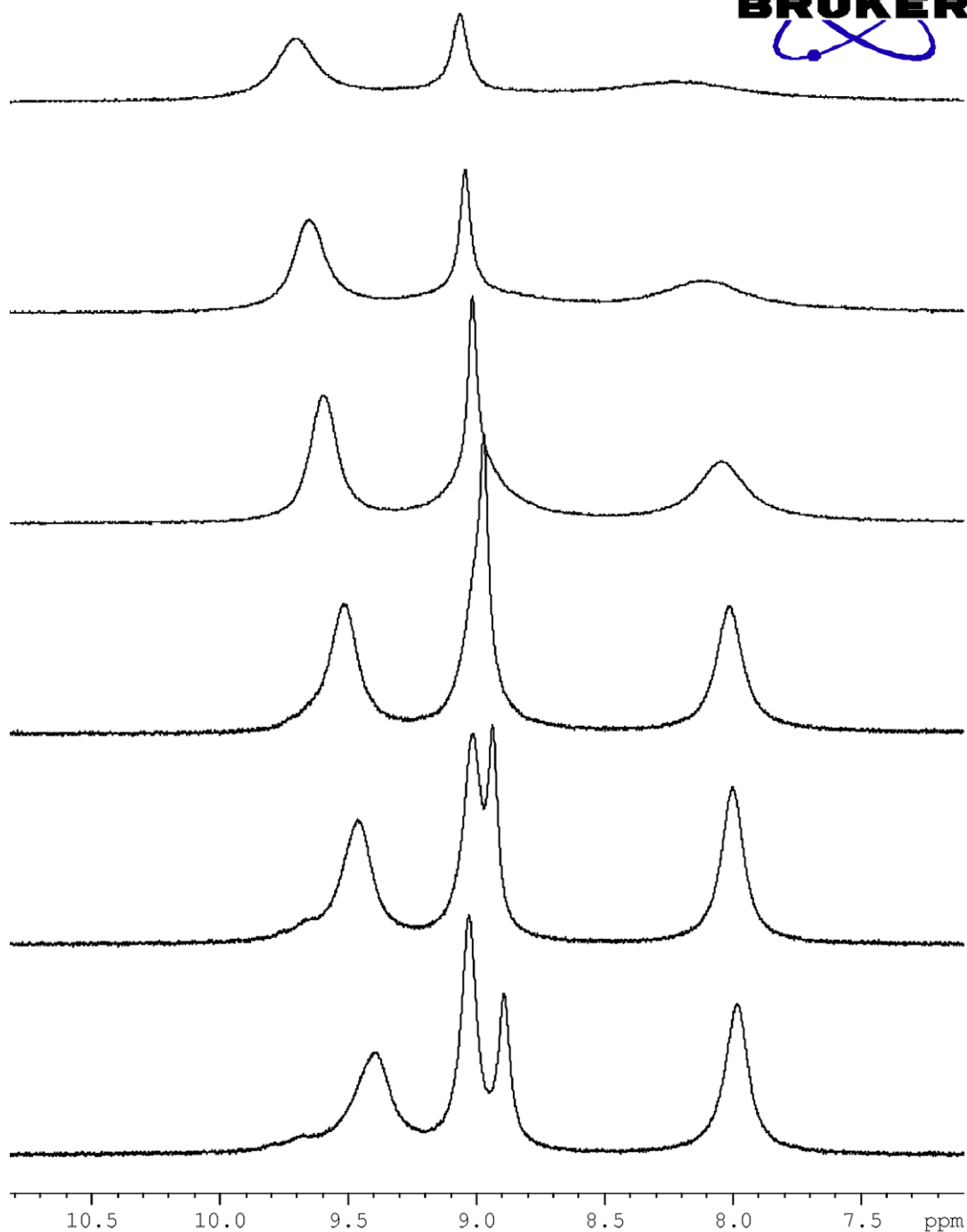
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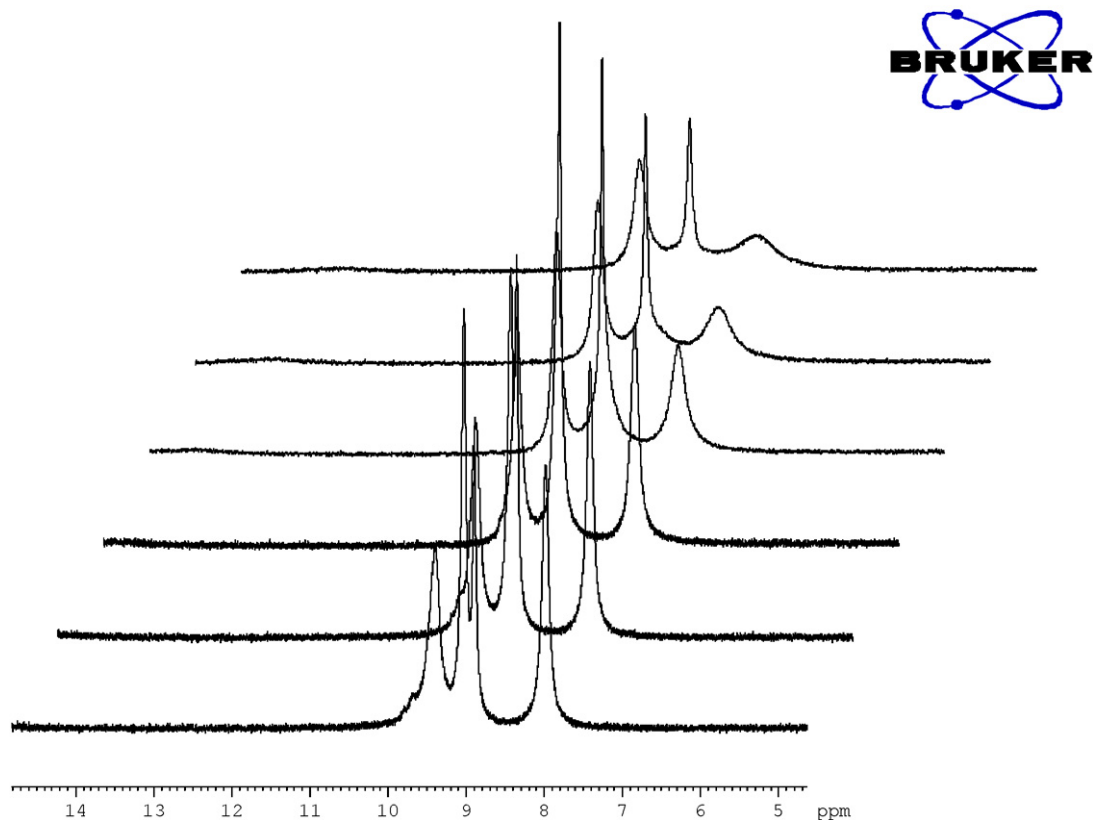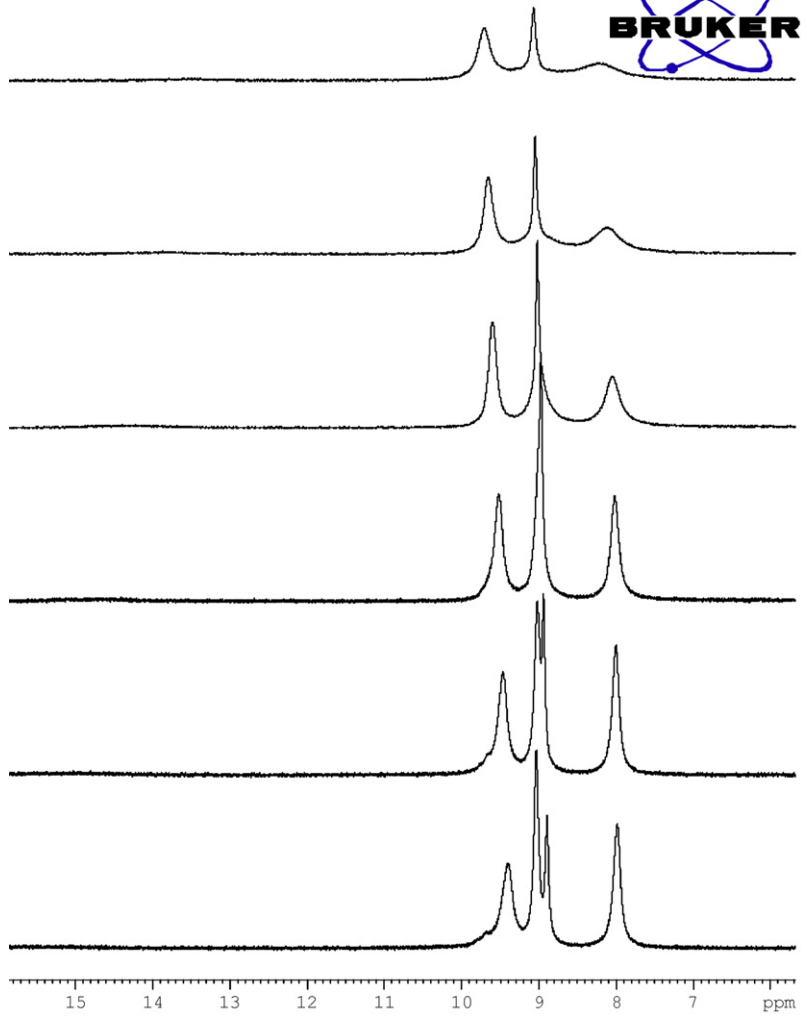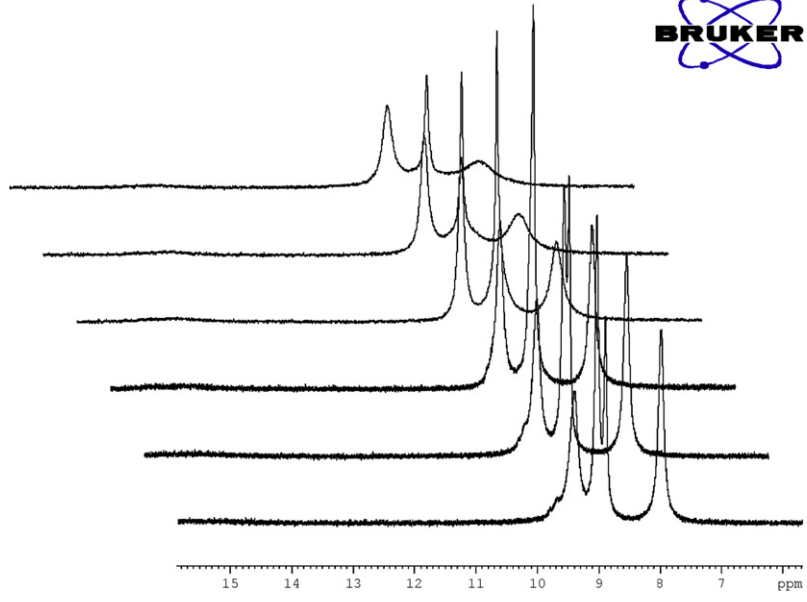
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