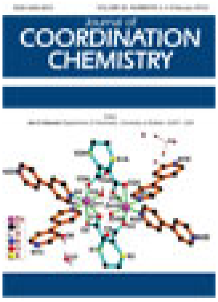

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Synthesis and structural characterization of heteroleptic Cu(I) complexes with α-diimines derived from pyridinyliminobenzoic acids

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The synthesis and molecular and electronic structure of heteroleptic univalent copper compounds [Cu(L)(PPh_3)X] are reported where X is a halide and L represents 3-pyridinylimino, 4-pyridinylimino or 3,5-dipyridinylimino-substituted benzoic acid, hereafter abbreviated as L1, L2, and L3, respectively. The crystal structures of two iodide and one bromide complexes are described. All compounds are hydrogen-bonded dimers. The electronic excitation spectra of the compounds are dominated by intraligand bands of ligands while characteristic MLCT transitions are observed at 430–480 nm. No emission is observed from the compounds either in the solid state or in solution; on the contrary a photodecomposition is observed resulting in triphenylphosphane ligand elimination and formation of halogen-bridged dimmers.

Keywords: Copper(I); α-Diimine; Triphenylphosphine; Crystal structure; Spectroscopic study

1. Introduction

Coordination compounds with α-diimines form one of the most populous groups not only because they can bind practically to any metal, but mainly due to their widely varying applications [1]. Substituted diimines offer additional challenges to the experimentalist since the presence of more than one coordination site may offer possibilities of realizing various coordination modes with concomitant alterations to the expected electronic and molecular structures and to the subsequent electronic and optical properties of the compounds [2]. Furthermore, the existence of active sites other than the diimine may give rise to intermolecular interactions which are of special interest in supramolecular structures. Vast numbers of coordination compounds have been reported which include, in the metal coordination sphere ligands such as 2,2′-bipyridine, 9,10-phenanthroline, various other polypyridyls [3], or the condensation

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products of amine-bearing molecules with diacetyl, benzyl, and other diketones. Several α-diimines produced from amino-substituted benzoic acids have also been studied and used as the free acids to coordinate late transition metals in heteroleptic coordination compounds [4–6] through their diimine site. Copper complexes with diimine and phosphine ligands are studied due to their interesting photophysical and photochemical properties [7] originating from the availability of low energy charge transfer excitations [8]. There have been few structures of complexes with the ligands discussed here reported with metals other than copper, $Pd(L1)Cl_2 \cdot DMSO$ [5], and $W(L1)(CO)_4 \cdot THF$ [6], while structures with divalent copper are reported for $[Cu(L1)_2](ClO_4)_2$, $[Cu(L1)_2(SO_4)] \cdot 3H_2O$ and the following polymeric ones where the ligand is present in its deprotonated form, denoted as L, $[Cu_2(L)_2Cl_2]_n \cdot 3H_2O$, and $[Cu_4(L)_2(L1)_2Cl_4] \cdot 2MeOH \cdot 2ClO_4$ [9].

In this study we examine molecular and electronic structure of univalent copper complexes of the three iminopyridine ligands presented in figure 1. The compounds are heteroleptic, the coordination sphere of the metal being completed by a triphenylphosphine, and a halide (Cl, Br, or I). The spectroscopic evidence for the compounds is discussed in view of the crystallographic information on three compounds.

2. Experimental

2.1. *Materials and methods*

The aminobenzoic acids were obtained from ACROS and used without purification. The solvents were of reagent grade and not subjected to any further drying process prior to their use. Elemental analyses for C, H, and N were performed on a Perkin-Elmer 240B elemental analyzer. Infrared spectra (IR) were recorded in KBr pellets on a Perkin-Elmer Spectrum One FTIR spectrometer with a resolution of $2\,cm^{-1}$ following collection of 16 scans from 4000 to $360\,cm^{-1}$. Solution NMR for ^1H and ^{13}C were measured at 300 and 75 MHz, respectively, in $CDCl_3$ solutions on a Bruker

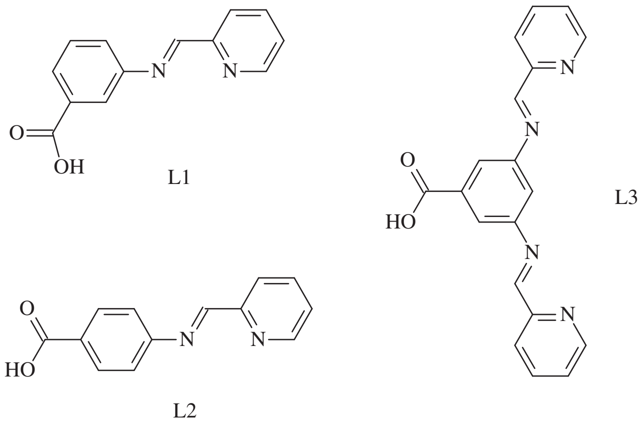

Figure 1. The asymmetric α-diimines used in this study.

300 spectrometer using TMS as internal standard. Electronic excitation spectra were recorded for $1 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$ solutions in methanol and dichloromethane in 1 cm cuvettes on a Perkin-Elmer Spectrum One spectrometer and were processed with the Peakfit program at the Aristotle University central computing facility. Fluorescence measurements were carried out for the above solutions as well as in the solid state in KBr pellets using a Perkin-Elmer F7000 fluorimeter. The crystal structures were determined using a Kuma KM4CCD κ geometry diffractometer. Data collection and cell refinement were carried out with *CrysAlis CCD* [10] and data reduction with *CrysAlis RED* [10]; *SHELX-97* programs [11] were used to solve and refine the structure. Molecular graphics were generated with ORTEP-III for Windows [12] and Mercury 1.4 software [13].

2.2. *Synthesis of the complexes*

The pyridinylimino-substituted benzoic acids were synthesized according to literature method [5] with slight variations, which include the use of ethanol and the avoidance of formic acid as catalyst. The products were identified by elemental analyses and IR spectra.

The copper complexes were prepared according to the following general scheme (figure 2). The appropriate cuprus halide (1 mmol) was dissolved in acetonitrile (10 mL) at 50°C and to this solution 1 mmol of solid triphenylphosphine was added under continuous stirring. After 10 min the formation of the white precipitate $[\mathrm{CuX(PPh_3)}]_n$ was complete [14]. To the resulting suspension, a suspension of the appropriate pyridinylimino benzoic acid (1 mmol) in dichloromethane (10 mL) was then added under continuous stirring. The dark red solution immediately formed from it was clear and gradually a red precipitate was deposited, which was filtered and washed with cold dichloromethane and diethylether. The filtrates were left at room temperature in the dark and the following days a few of them produced crystals suitable for crystal structure determination. The complexes were characterized spectrophotometrically (FTIR and UV-Vis) and by elemental analysis (theoretical values are shown in parentheses).

1a: C, 63.90% (63.37%); H, 3.71% (4.29%); N, 4.13% (4.77%); **2a**: C, 64.83% (63.37%); H, 4.48% (4.29%); N, 5.40% (4.77%); **3a**: C, 62.09% (62.74%); H, 4.28% (4.21%); N, 6.63% (5.31%); **1b**: C, 58.12% (58.92%); H, 3.82% (3.99%); N, 4.16% (4.43%); **2b**: C, 58.59% (58.92%); H, 3.83% (3.99%); N, 4.20% (4.43%); **3b**: C, 56.81% (57.85%); H, 3.84% (3.85%); N, 4.69% (4.91%); **1c**: C, 54.44% (54.84%); H, 3.59% (3.71%); N, 3.93% (4.13%); **2c**: C, 53.69% (54.84%); H, 3.64% (3.71%); N, 3.88% (4.13%); **3c**: C, 52.75% (53.45%); H, 3.49% (3.59%); N, 4.32% (4.53%).

$$\mathrm{CuX} \xrightarrow[\mathrm{MeCN}]{\mathrm{PPh_3}} [\mathrm{Cu((PPh_3)X}]_\mathrm{n} \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{L}} \underset{\text{1a-3c}}{[\mathrm{Cu(L)(PPh_3)X}]}$$

L= L1 (1), L2 (2), L3 (3)
X= Cl (a), Br (b), I (c)

Figure 2. General scheme of the synthetic procedure.

3. Results and discussion

3.1. *IR and solution NMR spectra*

The most relevant data are reported in table 1. IR spectra of the complexes are indicative of coordination to metal through the diimine site as a lowering of the C=N stretching frequency by 40 wavenumbers relative to the corresponding band in the free ligand was observed [15]. The normal P–C stretching for copper(I)-coordinated phosphine at 500–550 cm^{-1} also indicates the phosphine coordination to metal [16]. The two carboxylate stretches in the copper complexes appear to be separated by more than 250 wavenumbers, indicating the participation in intermolecular interactions, probably hydrogen bonding which is very common in analogous compounds.

The ^1H and ^{13}C NMR spectra of the compounds were recorded in DMSO-d_6. As for many analogous compounds, the chemical shift of the carboxylate carbon in the complexes is not shifted relative to the corresponding one in the free ligand, indicating that the carboxylate region of the ligand is not participating in coordination to the metal center. The relative shift of the imino carbon is also small but consistent in the halide compounds with respect to the free ligands, giving a hint for diimine coordination of the ligands [5]. Furthermore, this shift is systematically drawn to higher frequencies from the deshielding effect of the halide coordinated to copper [17], providing evidence for coordination environment of copper as a CuN_2PX chromophore.

3.2. *Electronic excitation and emission spectra*

The electronic excitation spectra of the compounds are dominated by excitation bands which are primarily of the intraligand type [18]. However, there is ‘‘charge transfer’’ character in several bands occurring within these ligands since the molecular orbitals may be localized in either of the aromatic rings or may include carboxylate or imine sites making it almost certain that the initial and final energy levels of the excitations are discriminated appreciably [19]. Observaion of charge transfer bands between orbitals

Table 1. Relevant IR and NMR information of the compounds.

Compound	$\nu_{as}COO$	$\nu_{s}COO$	$\nu C{=}N$	C_{carb}	C_{im}	H_{im}
L1	1703	1293	1628	167.80	161.90	8.63
1a	1692	1436	1580	166.83	160.66	8.83
1b	1691	1435	1579	166.61	159.15	9.11
1c	1691	1435	1579	166.53	159.42	9.16
L2	1701	1272	1629	166.90	162.30	8.61
2a	1705	1435	1585	166.81	160.59	8.85
2b	1712	1436	1597	166.96	159.63	9.07
2c	1683	1434	1584	166.37	162.93	9.23
L3	1704	1294	1633	166.60	162.40	8.70
3a	1715	1434	1636	166.35	160.78	8.87
3b	1720	1434	1636	166.11	159.76	8.94
3c	1700	1435	1635	165.87	158.89	9.03

IR band maxima are given in wavenumbers and NMR shifts in ppm downfield from internal TMS standard. The carboxylate (carb) and imino (im) carbon atoms and hydrogen atoms are indicated.

located on two different ligands is possible because of the existence of other ligands with low-lying π^* energy levels to the coordination sphere of the metal.

There is a solvent effect when spectra are recorded in different solvents and therefore figure 3 gives spectra of group **1** recorded in dichloromethane, a solvent of low-polarity and low-coordinating ability. In general, the lower energy transition is blue-shifted in methanol by approximately 10 nm, but the spectra in the two solvents are similar. Such behavior is common for Cu(I) complexes and has been related to the nature of the shifting excitation band which is not expected to be a typical metal-to-ligand charge transfer (MLCT) band but one with ligand-to-ligand charge transfer (LLCT) character as well [20].

In all the spectra a very broad band with a low $\log \varepsilon$ value is observed with a maximum around 450 nm which can be assigned to an MLCT transition [21]. In general, at least three MLCT bands can be identified in this region. They are termed band I (above 500 nm), band II (maximum around 430–480 nm, the most prominent, attributed to $S_0 \rightarrow S_3$ transitions [22]), and band III (390–420 nm, often hidden by the onset of band II). A shoulder appearing in the spectra of the halide compounds relative to the corresponding perchlorates in the region 300–320 nm indicates a charge transfer between ligands since it appears to have characteristics of the heavy atom effect.

Emission studies were carried out on the ligands for comparison, both in solution and in the solid state. Excitation wavelengths of 280, 305, 390, and 430 nm were used since the spectra of the ligands show absorption maxima at these points. No appreciable emission was obtained from the compounds in dichloromethane or in rigid matrix at low temperature (77 K). This can be attributed to the poor ability of the systems to limit distortion of the excited state geometry [23] as well as the inability to prevent external luminescence quenching. On the contrary, there was evidence for the photoreactivity of the excited state of the compounds provided during slow evaporation of solutions in the process of obtaining crystals for X-ray structural analysis. In several cases, after a

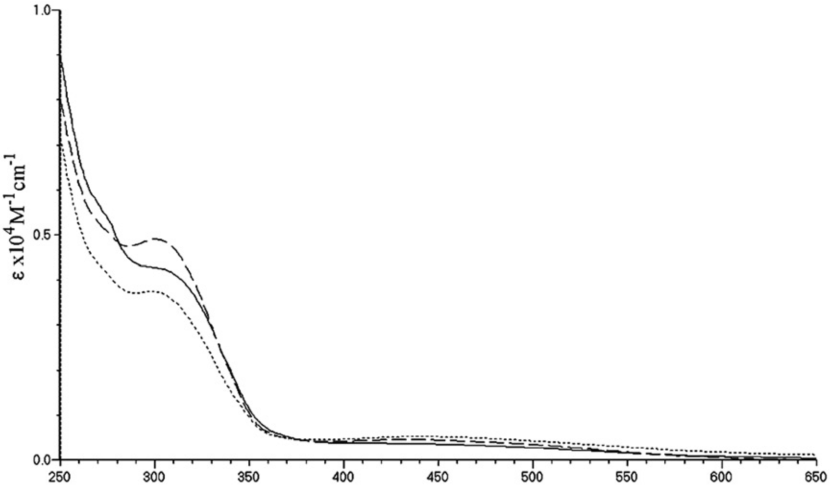

Figure 3. UV-Vis spectra in dichloromethane of group **1** complexes. Solid line chloro- (**1a**), dashed bromo- (**1b**), and dotted line iodo- (**1c**) compounds.

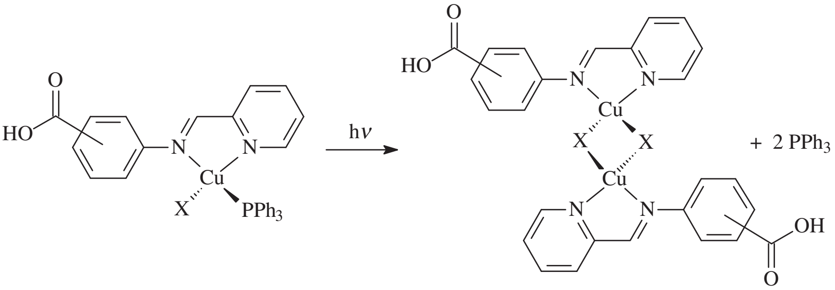

Figure 4. Outline of the observed photoreaction of the halide compounds studied.

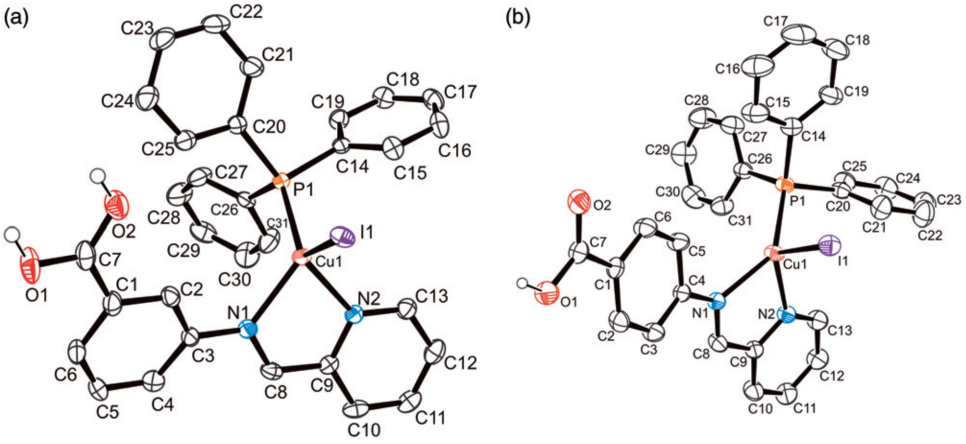

Figure 5. The molecular structure of **1c** (a) and **2c** (b). All hydrogen atoms except carboxylic H have been omitted for clarity. Displacement ellipsoids are drawn at 30% probability level. The solvent of **2c** is not shown.

period of a few days the turbulence was evident and upon filtration amounts of a white solid obtained. The solid was proved to be Ph_3PO and upon repetition of the experiment with carefully deaerated solutions, isolation of PPh_3 in small quantities was realized providing support for phosphine dissociation upon irradiation and formation of dimeric compounds with double halide bridges between the copper centers. The proposed reaction is presented in figure 4. Indeed, the dark red solids isolated at the end of the above experiments possess identical IR and visible spectra with samples prepared directly by the interaction of the ligands with copper(I) halides in 1 : 1 molar ratio in acetonitrile.

3.3. *Crystallographic information*

The crystal structures of the Cu(I) complexes **1b**, **1c**, and **2c** are shown in figures 5 and 6, and crystal data and refinement details are given in table 2. The Cu(I) center in all three complexes has a distorted tetrahedral geometry. The N–Cu–N and P–Cu–X planes are nearly perpendicular in **1c** and **1b** (dihedral angles of 89.83° and 88.68°,

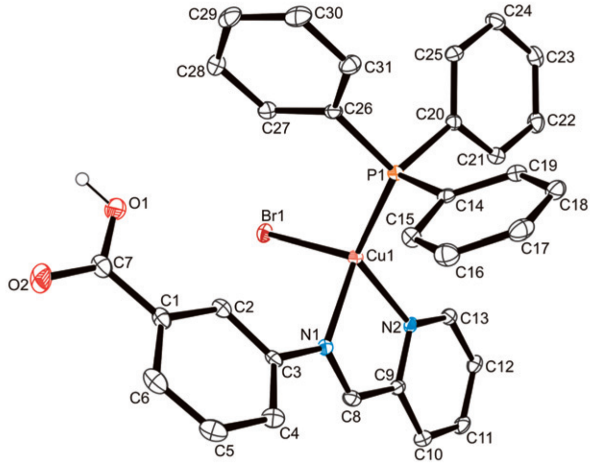

Figure 6. The molecular structure of **1b.** All hydrogen atoms except carboxylic H have been omitted for clarity. Displacement ellipsoids are drawn at 30% probability level.

Table 2. Crystal data and refinement details for **1b**, **1c**, and **2c**.

	1b	**1c**	**2c**
Empirical formula	$\{Cu(C_{13}H_{10}N_2O_2)$ $[P(C_6H_5)_3]Br\}$	$\{Cu(C_{13}H_{10}N_2O_2)$ $[P(C_6H_5)_3]I\}$	$\{Cu(C_{13}H_{10}N_2O_2)$ $[P(C_6H_5)_3]I\} \cdot CH_2Cl_2$
Formula weight	631.95	678.94	763.87
Temperature (K)	130	130	293
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
Unit cell dimensions (Å, °)			
a	18.9927(8)	8.2304(1)	9.4952(6)
b	8.4815(2)	19.4647(2)	10.0323(5)
c	19.1551(7)	17.6646(2)	18.3899(10)
α	90	90	93.209(4)
β	117.346(5)	95.469(1)	104.401(5)
γ	90	90	106.507(5)
Volume (Å^3)	2740.82(17)	2817.03(6)	1611.62(16)
Z, Z'	4, 1	4, 1	2, 1
Absorption coefficient (mm^{-1})	2.345	1.959	1.882
Reflections collected	14,396	53,639	41,758
Independent reflections	5857	5738	7819
Completeness up to θ (max) (%)	98.6	99.6	99.6
Data/restraints/parameters	5857/0/343	5738/0/345	7819/0/371
Goodness-of-fit on F^2	1.007	1.123	1.017
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0261$, $wR_1 = 0.0559$	$R_1 = 0.0204$, $wR_1 = 0.0415$	$R_1 = 0.0333$, $wR_1 = 0.0821$
R indices (all data)	$R_2 = 0.0443$, $wR_2 = 0.0642$	$R_2 = 0.0330$, $wR_2 = 0.0488$	$R_2 = 0.0757$, $wR_2 = 0.1020$
Largest difference peak and hole (e Å^{-3})	0.44 and −0.30	0.54 and −0.35	0.74 and −0.73

respectively) but strongly twisted in **2c** (dihedral angle of 72.02°). A similar observation has been made with Cu(I) complexes of the closely related ligands *o*-methyl substituted with respect to the pyridine [24]; in that case the 3-imino derivative in $[Cu(L)(MeCN)_2]^+$ revealed chelate ring planes of 88.19° while the 4-counterpart in $[Cu(L)_2]^+$ is only 81.5°.

Table 3. Selected bond lengths (Å) and angles (°) for **1b**, **1c**, and **2c**.

Compound **1b**			
Cu1–Br1	2.4640(3)	Cu1–N2	2.1193(18)
Cu1–N1	2.0936(17)	Cu1–P1	2.2005(6)
N2–Cu1–N1	79.39(7)	N1–Cu1–Br1	102.77(5)
N1–Cu1–P1	119.41(5)	N2–Cu1–Br1	104.99(5)
N2–Cu1–P1	125.91(5)	P1–Cu1–Br1	116.994(19)
Compound **1c**			
Cu1–I1	2.5778(3)	Cu1–N2	2.0862(17)
Cu1–N1	2.0906(18)	Cu1–P1	2.1932(6)
N2–Cu1–N1	80.05(7)	N1–Cu1–I1	110.92(5)
N1–Cu1–P1	114.63(5)	N2–Cu1–I1	109.60(5)
N2–Cu1–P1	120.29(5)	P1–Cu1–I1	115.899(18)
Compound **2c**			
Cu1–I1	2.6217(5)	Cu1–N2	2.127(3)
Cu1–N1	2.089(2)	Cu1–P1	2.2086(9)
N2–Cu1–N1	78.95(10)	N1–Cu1–I1	100.82(7)
N1–Cu1–P1	140.25(8)	N2–Cu1–I1	117.84(8)
N2–Cu1–P1	111.47(8)	P1–Cu1–I1	106.52(3)

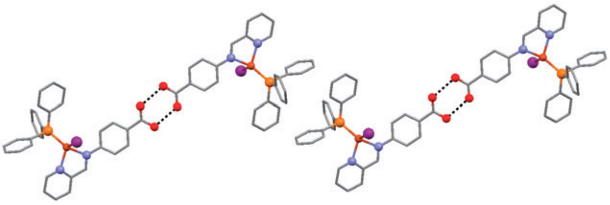

Figure 7. Six-fold phenyl embrace between PPh_3 ligands in **2c** connecting the carboxylic acid dimers. Hydrogen atoms are omitted for clarity. O, N, P, Br, and Cu atoms are shown as spheres of arbitrary radii.

The Cu–N (pyridyl) bond is longer than the Cu–N (imine) bond in **1b** and **2c** but in **1c** the two bonds are equal within experimental error (table 3). Similar variations were observed in the corresponding $[Cu(L)(PPh_3)_2]$ cations with slightly smaller Cu–N bond distances than the ones realized in this study [25]. The Cu–P bond lengths for all three complexes are similar. The five-membered chelate rings are planar and the N–Cu–N angles show only small variation (78.95–80.05°). The organic ligands L1 and L2 are twisted about the C–N bond between the benzoic acid fragment and the imine group by 31.82°, 19.64°, and 11.61° in **1b**, **1c**, and **2c**, respectively. In the heteroleptic compounds $[Cu(L)(PPh_3)_2]^+$, L1 was observed to be almost flat while L2 revealed a twist angle of 40.80° around the C–N bond between the carboxyphenyl and imine groups [25]. The complex molecules are connected *via* a pair of O–H $\cdots$ O hydrogen bonds into a typical carboxylic acid dimer. Moreover, in **2c** the triphenylphosphine groups of inversion center-related molecules are engaged in the so-called six-fold phenyl embrace (figure 7) [13].

4. Conclusion

The title pyridinylimino benzoates react with copper(I) halides and triphenylphosphine and produce complexes where coordination to copper occurs through their diimine site while their carboxylate groups are involved in a typical dimerization through double hydrogen bond formation. The chelate rings formed are coplanar while the iminopyridine rings are twisted relative to the benzoate ones. Visible spectra of the complexes are characterized by broad MLCT bands, however the excited states are not emissive but photoreactive as they lead to triphenylphosphine elimination and formation of dimers with double halide bridges between copper centers.

Supplementary material

CCDC Nos 786095–786097 contain the supplementary crystallographic data for this article. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033).

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