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Photophysical, electrochemical and electrochromic properties of copper-bis(4,4′-dimethyl-6,6′-diphenyl-2,2′-bipyridine) complexes

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Contents

Abstract

The synthesis, solution and solid state structural characterization, photophysical and electrochemical properties of two redox forms of an electrochromic copper-bis(4,4′-dimethyl-6,6′-diphenyl-2,2′-bipyridine) complex, $[Cu(\mathbf{3})_2]^n$ ($n = +1, +2$), are presented. Both complexes were characterized in the solid state by X-ray diffraction methods on single-crystals showing that both forms exist in a pseudo-tetrahedral coordination, and a comparison with other structures was made. Like most copper(I) complexes, the red $[Cu(\mathbf{3})_2]^+$ complex shows a rather weak emission ($\Phi_{em} = 2.7 \times 10^{-4}$, dichloromethane). The lifetime of the emitting MLCT state is 34 ± 1 ns, as observed with time resolved emission, and transient absorption (in deoxygenated dichloromethane). Typical emission and transient absorption spectra are presented. The transient absorption spectra indicate that the MLCT state absorbs stronger than the ground state, which is relatively uncommon for metal bipyridine complexes, i.e. no ground state bleaching is observed. The green $[(\mathbf{3})_2Cu]^{2+}$ complex does not show any observable emission or transient absorption, which is a common feature for Cu(II) complexes of this type. The electronic absorption spectra of the chemically and electrochemically produced copper(I/II) complexes

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are identical. The repeated electrochemical conversion of the Cu(I) center into Cu(II) and vice versa does not cause any decomposition. This is consistent with a fully reversible Cu(I)/Cu(II) redox couple in the corresponding cyclic voltammogram, ($E_{1/2}$ (Cu(I)/Cu(II)) = +0.68 V vs. SCE = +0.23 V vs. Fc/Fc$^+$). These observations indicate that no large structural reorganization occurs upon electrochemical timescales (sub second), and that the different ways of generating the complexes does not effect their final structure, apart from the small differences observed in the X-ray structures of both forms. These characteristics make these complexes rather well suited for their incorporation into an electrochromic display configuration.

Keywords: Inorganic photochemistry; Synthesis; X-ray structures; Emission; Transient absorption

1. Introduction

Chemical and physical properties of transition metal complexes may be controlled by electronic and steric factors, which may be introduced with the backbone of the organic ligands. In particular, using steric hindrance, one may promote the tetrahedral coordination mode by excluding octahedral and square-planar coordination geometries around the metal [1]. This aspect has been established for 2,2′-bipyridine [2,3] bearing two phenyl groups at 6 and 6′ positions as well as for phenanthroline [4,5] bearing two phenyl moieties at 2 and 9 positions, differently substituted 2,9-phenanthrolines [5–7] and heteroleptic phenanthroline [8] systems.

Copper complexes are well known for their exquisite colors, good stability, and together with the natural abundance of copper ore and the relative environmentally friendly nature of copper as compared with other metals, are attractive candidates for technical applications [9]. Organometallic copper complexes are interesting and colorful compounds that have good properties which may be used in photoinduced and ground state redox chemistry [10].

Whereas Cu(I), with the d^{10} electronic configuration, adopts preferentially the tetrahedral coordination geometry for Cu(II) (d^9) in contrast, penta- or hexa-coordination is usually observed [9]. Thus, one of the prevailing observations is that upon oxidation of Cu(I) to Cu(II), a large structural change occurs which often is accompanied by solvent coordination. Systems for which this process does not occur are very rare [9]. Both redox forms of the copper complexes of 2,9-diphenyl-1,10-phenanthroline have been reported [4] and the electrochemistry of this compound [7], of its bridged analog [11] and other 2,9 alkyl-substituted phenanthrolines [12] have received attention.

The electron rich Cu(I) species is able to transfer an electron to an acceptor ligand upon light excitation giving rise to a metal-to-ligand charge-transfer (MLCT) state. These types of states may be used in various photochemical applications such as solar energy conversion, electroluminescent devices and water photo-oxygenation systems.

Here we describe the synthesis, solution and solid-state structural characterization by single crystal X-ray diffraction analysis, photophysical properties as well as the redox properties of two stable copper species that conserve a nearly identical tetrahedral structure upon oxidation and reduction. Where appropriate, a comparison is made with reported copper complexes such as of 2,9-diphenyl-1,10-phenanthroline [4] and of 4,4′- 6,6′-tetramethyl-2,2′-bipyridine [13].

2. Experimental

2.1. Synthesis

2.1.1. 4,4′-dimethyl-2,2′ bipyridine (**1**)

In a 500 ml flask, 14 g of Pd | C was added and heated under vacuum to 100 °C to remove traces of water. To this, 430 ml of 4-picoline (distilled over KOH under argon) was introduced under argon. The black mixture thus obtained was refluxed for 9 days while stirring. The mixture was allowed to cool to 100 °C before benzene (150 ml) was added and the solid removed by filtration. (The Pd | C catalyst may be recovered after washing with 100 ml of hot toluene). Upon cooling the filtrate, the desired compound **1** precipitates leaving a yellowish solution. After filtration of the white solid, the filtrate was further cooled to 0 °C affording a further batch of compound **1**. The solids were combined, washed with EtOH and dried under vacuum affording 56 g of the pure compound **1** as a white crystalline powder in 14% yield. The purity of **1** was confirmed by elemental analysis. Both ^{1}H- and ^{13}C-NMR characterization was in agreement with reported data [14].

2.1.2. 6,6′-phenyl-4,4′-dimethyl-2,2′ bipyridine (**3**)

In a dry 250 ml flask, 3.5 g (19 mmol) of compound **1** and dry toluene (70 ml) were introduced under argon and the mixture was stirred at 30 °C for 10 min. To the clear solution, 100 ml of a 1.8 M PhLi solution in cyclohexane–ether (70/30) was slowly added. After stirring at 30 °C for 72 h, the mixture was cooled to −15 °C and the excess PhLi was carefully quenched with water (100 ml). The mixture was extracted with CH_2Cl_2 (2 × 50 ml). To the organic phase, MnO_2 (20 g) was added and the mixture was stirred at 25 °C for 24 h before $MgSO_4$ (2 g) was added and the solid removed by filtration affording thus a sticky brownish mixture. Addition of cold EtOH (100 ml at 0 °C) afforded a yellowish suspension, which was filtered and further washed with cold EtOH (50 ml at 0 °C). After recrystallization of the solid thus obtained from hot toluene, the desired compound **3** (3 g, 47% yield) was obtained as a colourless crystalline solid.

The monosubstituted compound **2** was obtained in 23% yield (1.2 g) upon purification by chromatography (Al_2O_3, toluene–MeOH: 99.5/0.5) of the above mentioned mixture.

2.1.3. *Compound* **2**

$C_{18}H_{16}N_2$ (260.16): Calc. C 83.03, H 6.19, N 10.76; Found: C 82.95, H 6.19, N 10.51%. ^{1}H-NMR ($CDCl_3$, 300 MHz, 25 °C) δ 2.47 (s, 3H, CH_3), 2.49 (s, 3H, CH_3), 7.14 (d, 4.1 Hz, 2H, CH_{py}), 7.43 (3, 1H, CH_{ph}), 7.58 (s, 1H, CH_{py}), 8.13 (d, 6.8 Hz, 2H, CH_{ph}), 8.21 (s, 1H, CH_{py}), 8.45 (s, 1H, CH_{ph}), 8.54 (d, 5.1 Hz, 1H, CH_{ph}); ^{13}C-NMR ($CDCl_3$, 75.47 MHz, 25 °C) δ 21.2, 21.3, 120.3, 121.2, 122.1, 124.6, 126.9, 128.6, 128.7, 139.5, 147.9, 148.6, 148.7, 155.6, 156.4.

2.1.4. *Compound* **3**

$C_{24}H_{20}N_2$ (336.16): Calc. C 85.68, H 5.99, N 8.33; Found: C 85.59, H 5.96, N 8.18%. ^{1}H-NMR ($CDCl_3$, 300 MHz, 25 °C) δ 2.54 (s, 6H, CH_3), 7.43 (m, 2H, CH_{Ph}), 7.51 (m, 4H, CH_{Ph}), 7.60 (m, 2H, CH_{py}), 8.15 (m, 4H, CH_{ph}), 8.42 (s, 2H, CH_{py}); ^{13}C-NMR ($CDCl_3$, 50.3 MHz, 25 °C) δ 21.5, 120.5, 120.3, 127.0, 128.6, 128.8, 139.6, 148.5, 155.9, 156.3.

2.1.5. *[(**3**)$_2$Cu]BF$_4$*

In a 50 ml flask, compound **3** (60 mg, 0.178 mmol) dissolved in a degassed mixture of CH_2Cl_2 (9 ml) and MeCN (4 ml) was introduced under argon and at room temperature (r.t.). To the stirred mixture, anhydrous $[Cu(MeCN)_4]BF_4$ (28 mg, 0.089 mmol) was added and the reaction mixture was stirred at r.t. for 30 min. The solvents were removed and the red powder thus obtained was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH: 95/5) affording the pure complex [(**3**)$_2$Cu]BF$_4$ in 92% yield (67 mg).

$C_{48}H_{40}N_4Cu \cdot BF_4$(823.23). Calc. for: C 70.03, H 4.90, N 6.81 %, Found: C 70.25, H 4.90, N 6.53%; ^{1}H-NMR: ($CDCl_3$, 300 MHz; 25 °C): δ (ppm): 2.51 (s, 12H, CH_3); 6.85 (t, 7.5 Hz, 8H, CH_{ph}); 7.05 (t, 7.5 Hz, 4H, CH_{ph}); 7.26 (s, 4H, H_{pyr}); 7.44 (d, 7.5 Hz, 8H, CH_{ph}); 7.79 (s, 4H, H_{pyr}); ^{13}C-NMR: ($CDCl_3$, 75.47 MHz; 25 °C): δ (ppm): 21.22 (CH_3), 122.01 (C_{pyr}), 125.23 (C_{pyr}), 127.22, 127.33, 128.72 (C_{ph}),138.27 (C_{ph}), 149.65 (C_{pyr}),152.74 (C_{pyr}),156.22 (C_{pyr}).

2.1.6. *[(**3**)$_2$Cu](BF$_4$)$_2$*

In a 50 ml flask, compound **3** (60 mg, 0.178 mmol), dissolved in CH_2Cl_2 (9 ml), was introduced under argon and at r.t. To the stirred mixture, $[Cu(BF_4)_2] \cdot 6H_2O$ (30 mg, 0.087 mmol) was added and the mixture further stirred at r.t. for 30 min. The solvent was removed and the blue solid thus obtained was recrystallized from a $MeNO_2$–benzene mixture affording the pure complex [(**3**)$_2$Cu](BF$_4$)$_2$ in 92% yield (75 mg) as blue crystalline powder.

$C_{48}H_{40}N_4Cu \cdot 2BF_4$ (910.04). Calc. for: C 63.35, H 4.43, N 6.16, Found: C 63.13, H 4.45, N 5.99%.

2.2. *Crystal structure characterization*

X-ray diffraction data collection was carried out on a Kappa CCD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using graphite-monochromated Mo–K$_\alpha$ radiation. For all structures, diffraction data were corrected for absorption and analyzed using OPENMOLEN package. [15] All non-H atoms were refined anisotropically. Crystal data and details of measurements are reported in Table 1.

2.3. *Photophysical and electrochemical measurements*

Emission spectra were recorded on a SPEX Fluorolog I (1681) instrument equipped with an R928 photomultiplier (Products for Research). Emission spectra were measured on dilute solutions using a 490 nm (emission-path) cut-off filter. No corrections were applied to the emission spectra. For determination of the emission quantum yields (ϕ), using the 'optical dilute relative method' [16], $[Os(bpy)_3]$ in argon-degassed acetonitrile ($\Phi_{em} = 5 \times 10^{-3}$)[17] was used as a standard. Excitation wavelength was 480 nm, and the optical density of both the reference and the sample was adjusted to 0.1 (1 cm) at this wavelength.

Absorption spectra were recorded on a Hewlett–Packard 8453 diode array spectrophotometer, using 1 nm bandwidth.

Time resolved emission and transient absorption spectra were obtained with a gated Optical Multichannel Analyzer (OMA IV) of EG&G instruments similar to described earlier [18]. As excitation and white probe sources a tunable Coherent Infinity laser (1 ns pulses FWHM) and an EG&G Xe flash lamp (X 504) were used, respectively. The excitation beam is at a right angle to the probing beam. The probing path length is 1 cm. Samples were adjusted to an absorption of between 0.5 and 1 (1 cm) at the excitation wavelength. Laser-power was ca. 10 mJ per pulse (0.2 cm^2).

UV–vis spectroelectrochemistry was carried out with a home made OTTLE cell, similar as described elsewhere [19]. The working electrode potential of the OTTLE cell was controlled with a PA4 potentiostat (EKOM, Czech Republic). The spectroelectrochemical sample contained 5×10^{-3} M copper complex and 3×10^{-1} M tetrabutylammonium hexafluorophosphate as

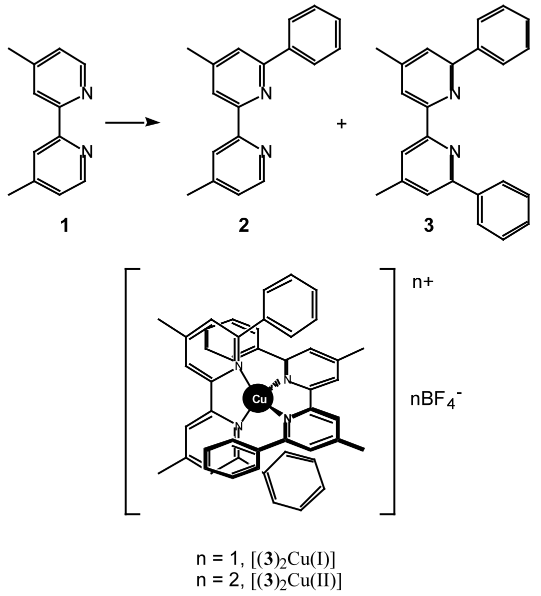
Table 1
X-ray data for compounds **3**, $[(\mathbf{3})_2Cu] \cdot BF_4$ and $[(\mathbf{3})_2Cu] \cdot (BF_4)_2$

	3	$[(\mathbf{3})_2Cu] \cdot BF_4$	$[(\mathbf{3})_2Cu] \cdot (BF_4)_2$
Formula	$C_{24}H_{20}N_2$	$C_{48}H_{40}BCuF_4N_4$	$C_{60}H_{52}B_2CuF_8N_4$
Molecular weight	336.44	823.23	1066.26
Crystal system	Monoclinic	Monoclinic	monoclinic
Space group	$P12_1/c1$	$P12_1/c1$	$C12/c1$
a(Å)	8.8800(5)	11.5370(4)	23.578(2)
b(Å)	10.6390(9)	13.9500(3)	15.751(1)
c(Å)	9.9190(7)	25.0480(9)	14.6720(7)
β (°)	107.795(4)	98.297(2)	106.392(2)
V (Å^3)	892.3(2)	3989.1(4)	5227(1)
Z	2	4	4
Color	Colorless	Red	green
Crystal dimension (mm)	0.20 × 0.16 × 0.16	0.20 × 0.10 × 0.10	0.20 × 0.16 × 0.12
D_{calc} (g cm^{-3})	1.25	1.37	1.35
F(000)	356	1704	2204
μ (mm^{-1})	0.073	0.606	0.490
Temperature (K)	173	173	173
Wavelength (Å)	0.71073	0.71073	0.71073
hkl limits	0.11/−13.13/−12.12	0/14.18/−17.32	0.30/−20.20/−17.16
Theta limits (°)	2.5/27.50	2.5/27.50	2.5/27.51
Number of data meas	5979	9454	19545
Number of data with $I > 3\sigma(I)$	1190	3899	3310
Number of variables	118	523	339
R	0.042	0.039	0.041
R_w	0.063	0.047	0.060
GOF	1.163	1.040	1.014

Radiation, Mo–K$_\alpha$ graphite monochromated; Diffractometer, KappaCCD; Scan mode, phi scans; Weighting scheme, $4F_o^2/(\sigma^2(F_o^2)+0.0064F_o^4)$.

supporting electrolyte. Thin-layer cyclic voltammograms were recorded during the electrolyses to localize the studied redox process.

Cyclic voltammetry was performed using a PAR Model 283 potentiostat. Cyclic voltammograms were recorded with a conventional single-compartment three-electrode cell under an argon atmosphere. The electrode potentials are given relative to the standard ferrocene–ferrocenium couple ($E_{1/2}$(Fc/Fc$^+$) = +0.45 V vs. SCE in dichloromethane). However, cobaltocenium hexafluorophosphate was added as more convenient internal reference standard in this case ($E_{1/2}$(Cc/Cc$^+$) = −1.34 V vs. Fc/Fc$^+$). [20,21] The working electrode was a Pt disk (0.42 mm^2 apparent surface area) polished between scans with 0.25 μm diamond paste (Mecaprex Presi). The auxiliary and pseudoreference electrodes were coiled Pt and Ag wires, respectively. The voltammetric solutions were 10^{-3} M in the copper complex and 10^{-1} M in the supporting electrolyte. Freshly distilled spectroscopy grade solvents were used in all determinations.



Scheme 1.

3. Results

The ligand **3** (6,6′-diphenyl-4,4′-dimethyl-2,2′-bipyridine, see Scheme 1) was designed in order to study the role played by the two phenyl groups on the coordination geometry of both Cu(I) and Cu(II) complexes and consequently on their electrochemical as well as photophysical properties.

Synthesis: The synthesis of **3** was achieved by adaptation of the procedures developed for the preparation of 6,6′-diphenyl-2,2′-bipyridine [2] and 2,9-diphenyl-1,10-phenathroline. [22].

The staring material was 4,4′-dimethyl-2,2′-bipyridine **1** which was obtained by modification of the reported procedure consisting in a coupling reaction of 4-picoline in the presence of Pd/C (10%) as the catalyst [14] (Scheme 1). During the course of the reaction, we have noticed that the reaction yield was strongly dependent upon the reaction time, an almost linear correlation was observed. Thus, by performing the reaction at 170 °C for 9 days, compound **1** could be obtained on a 60 g scale in ca. 14% yield.

Upon treatment of **1** with an excess of PhLi (1.8 M solution in dry toluene) at 30 °C for 72 h., followed by quenching at −15 °C and subsequent oxidation using MnO_2, in addition to the desired disubstituted compound **3** (25–40%), the monosubstituted compound **2** (15–20%) was also obtained. The observed yields depend on the quality of PhLi used.

In order to correlate solid-state structural features as well as electrochemical and photophysical properties of the two complexes engaging the ligand **3** and the Cu(I) and Cu(II) centers, it appeared interesting to form both complexes using the same non-coordinating BF_4^- counterion. Thus, the ligand **3** was treated with $[Cu(CH_3CN)_4]BF_4$ in CH_2Cl_2–CH_3CN solvent mixture. The pure complex $[(\mathbf{3})_2Cu]BF_4$ was isolated after chromatography (SiO_2, CH_2Cl_2–MeOH) and recrystallization at 4 °C from a mixture of isopropyl ether–CH_2Cl_2 as red single-crystals in 92% yield. Dealing with the Cu(II) complex, treatment of **3** with $[Cu(BF_4)_2]\cdot 6H_2O$ in CH_2Cl_2–CH_3NO_2 solvent mixture afforded the desired $[(\mathbf{3})_2Cu](BF_4)_2$ complex again in 92% yield as blue single-crystals after recrystallization at r.t. from nitromethane–benzene mixture.

3.1. X-ray structures

The free ligand **3** was characterized in the solid state by X-ray diffraction on single-crystal (Table 1). Compound **3** crystallizes in the monoclinic system with $P2_1/c$ as the space group. The crystal is composed only of **3**, which presents a center of symmetry (Fig. 1). As expected and often observed, the two pyridine units (d_{C-N} of 1.345 and 1.351 Å) are almost co-planar (NCCC dihedral angle = −0.3°) and in *trans* configuration. The phenyl groups are not co-planar with respect to the pyridine units but tilted by 20.5°.

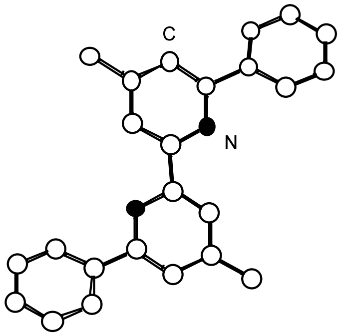


Fig. 1. Crystal structure of the free ligand **3** showing the *trans* configuration adopted by the two pyridine units. Hydrogen atoms have been omitted for clarity. For selected bond distances and angles see text.

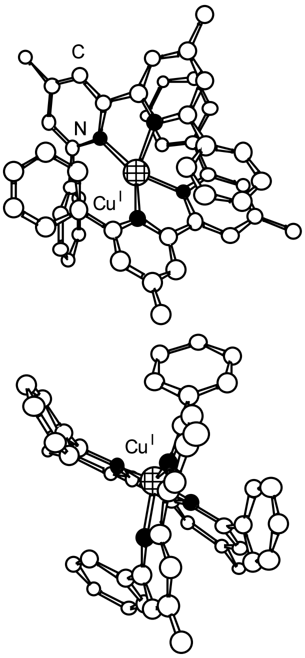


Fig. 2. Two views of the crystal structure of the Cu(I) complex $[(\mathbf{3})_2Cu]^+$ showing the pseudo-tetrahedral coordination geometry around the metal center. H atoms and BF_4^- counterion have been omitted for clarity. For selected bond distances and angles see text.

Both complexes were also characterized in the solid state by X-ray diffraction method on single-crystals (Table 1). Suitable crystals of $[(\mathbf{3})_2Cu]BF_4$ were obtained in 2–3 weeks time upon slow diffusion at 4 °C of isopropyl ether into a saturated CH_2Cl_2 solution of the complex. Similarly, good quality crystals of $[(\mathbf{3})_2Cu](BF_4)_2$ could be obtained again in 2–3 weeks time upon slow diffusion at 25 °C of benzene into a saturated solution of the complex in $MeNO_2$.

The red $[(\mathbf{3})_2Cu]BF_4$ complex crystallizes in the monoclinic system with $P2_1/c$ as the space group. The crystal is composed of only $[(\mathbf{3})_2Cu]BF_4$ complexes with four complexes in the unit cell (Fig. 2). As expected and often observed, the cationic part is composed of a Cu(I) ion coordinated to two ligands **3**. The coordination sphere around the metal cation is composed of four N atoms belonging to two ligands **3** with Cu–N distances varying between 1.98 and 2.14 Å. The coordination geometry around the metal center is pseudo tetrahedral with the NCuN angle varying between 81.7 and 140.2°. Both bipyridine units are in *cis* configuration with dihedral angles of 6.4 and 16.9° between the two pyridines. For each bipyridine unit, the two phenyl moieties are tilted (37.8°, −52.0°) and (−46.5°, −67.5°).

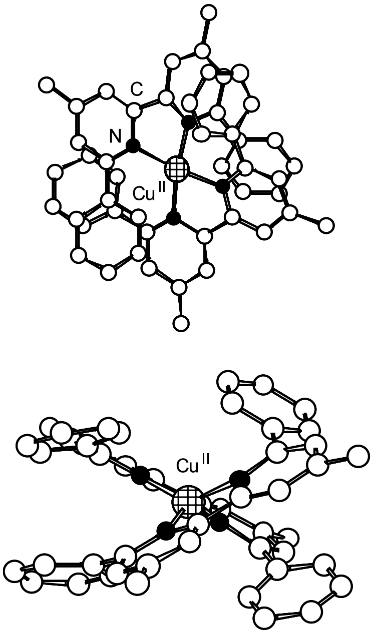


Fig. 3. Two views of the crystal structure of the Cu(II) complex $[(\mathbf{3})_2Cu]^{2+}$, showing the distorted tetrahedral coordination geometry around the metal center. H atoms, BF_4^- counterions and solvent molecules have been omitted for clarity. For selected bond distances and angles see text.

No specific interactions between the BF_4^- anions and the cationic complex are observed.

The $[(\mathbf{3})_2Cu](BF_4)_2$ blue–green complex crystallizes in the monoclinic system with $C2_1/c$ as the space group. The crystal in addition to $[(\mathbf{3})_2Cu](BF_4)_2$ complexes contains also benzene molecules (Fig. 3). Interestingly, the cationic part of the structure is composed of a Cu(II) metal ion also coordinated to two ligands **3**. The coordination sphere around the metal cation is again composed of four N atoms belonging to two ligands **3** with Cu–N distance varying between 1.96 and 2.00 Å. The Cu(II) complex is more symmetric compared with the above mentioned Cu(I) case. The coordination geometry around the metal center is also pseudo tetrahedral with NCuN angle varying between 82.0 and 138.3°. Again, both bipyridine units are in *cis* configuration with dihedral angles of 6.0° between the two pyridines. For each bipyridine units, the two phenyl substituents are tilted by -39.0 and $-50.0°$.

A structural comparison between the two complexes revealed the following relevant features. For the Cu(I) complex the angle between the two coordinated bipyridines is ca. 71°. This value is in the same range as those reported for other Cu(I)-bipyridine complexes reported in CCDC (mean value of 72°). However, in the case of the Cu(II) complex, the angle between the two bipyridines is ca. 59° which is 14° larger than the mean value of 45° obtained for other reported Cu(II)-bipyridine complexes. The above comparison shows a slight structural difference between the two complexes which is reflected in the difference (12°) between the angles formed by the two bipyridine units in each complex.

The remarkable structural conservation both in terms of coordination sphere and geometry between the two Cu(I) and Cu(II) complexes is reminiscent of the active site of plastocyanin, a bleu copper protein engaged in electron transfer processes, for which the coordination sphere around the metal remains unchanged during the redox process [23].

A survey of the Cambridge Crystal Database (October 15 2001) was made. It indicated that: (i) among all structures published for Cu^I complexes (49 hits) with two 2,2′-bipyridine, 1,10-phenanthroline or (bis)quinoline ligands, for 76% of the cases the coordination sphere around the metal is composed of four N atoms. For 24% of structures, the metal center is surrounded by five or six coordination sites. On the other hand, with the same criteria, for Cu(II) complexes (142 hits), the majority of structures reported (ca. 95%) deals with coordination numbers of five or six. Interestingly, only for 5% (seven structures: BPYCUP [24], BPCUDT [25], BUWWOF [26], CEFCEV [27], SICCOW [28], RUQMOF [29] and BEDTIN [30]) of the reported cases, the coordination sphere around the metal cation is composed of four coordination sites. However, among the seven hits, two of them concern two interconnected bipyridines (SICCOW, RUQMOF), whereas for the other five hits, the differences are due to different counterions and/or interstitial solvent molecules.

3.2. Photophysical properties

The UV–vis absorption spectra of the $[(\mathbf{3})_2Cu]^+$ and $[(\mathbf{3})_2Cu]^{2+}$ complexes in dichloromethane are presented in Fig. 4, where the typical MLCT absorptions are distinct at 400, 540 nm for Cu(I) and 610 and 750 nm for Cu(II). The electronic transitions are characterized by rather low extinction coefficients (400 M^{-1} cm^{-1} at 600 nm (for both complexes) and 1900 M^{-1} cm^{-1} at 400 nm for $[(\mathbf{3})_2Cu]^+$). Both in spectral shape and in extinction, this compares well with the copper complexes of 2,9-diphenyl-1,10-phenanthroline [4].

Like most copper(I) species [13,31], the $[(\mathbf{3})_2Cu]^+$ complex shows a rather weak emission ($\Phi_{em} = 2.7 \times 10^{-4}$, deoxygenated CH_2Cl_2, using $[Os(bpy)_3]$ [$\Phi_{em} = 5 \times 10^{-3}$, deoxygenated CH_3CN] as a reference [17]). The lifetime of the emitting MLCT state is 34 ± 1 ns, as observed by time resolved emission, and transient absorption spectroscopy (in deoxygenated CH_2Cl_2). Typical emission and transient absorption spectra are shown (Figs. 5 and 6). The spectral shape of the nanosecond time resolved emission is independent of the delay time.

However, a very short lived (< 40 ps) ^{1}MLCT emission [13] was also observed.

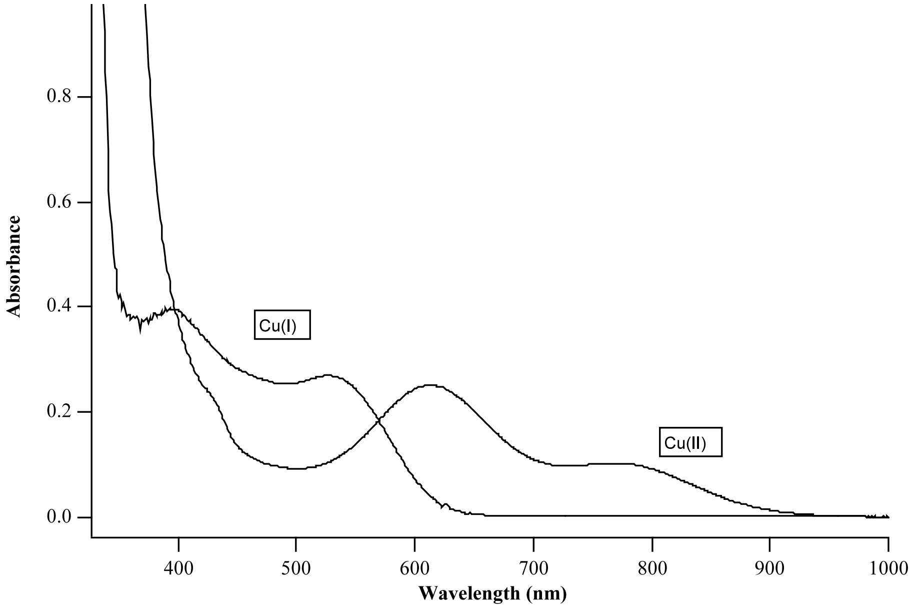


Fig. 4. UV–vis absorption spectra of the copper complexes $[(\mathbf{3})_2Cu]^+$ and $[(\mathbf{3})_2Cu]^{2+}$in CH_2Cl_2. Concentrations are 1.8×10^{-4} (Cu(I)) and 6.0×10^{-4} (Cu(II)).

The transient absorption spectra indicate that the MLCT state absorbs stronger than the ground state, which is rather uncommon for metal bipyridine complexes, i.e. no evident ground state bleaching is observed. The signal does not fully decay to zero-baseline above 550 nm due to slight decomposition of the compound. The $[(\mathbf{3})_2Cu]^{2+}$ complex does not show any observable emission or transient absorption, which is expected for Cu(II) complexes.

The lifetime of the excited state is of the $[(\mathbf{3})_2Cu]^+$ complex (34 ns) is about twice as long as that of the 4,4′-6,6′-tetramethyl-2,2′-bipyridine complex, but about two times shorter as the 80 ns lifetime of the of 2,9-dimethyl-4,7diphenyl-1,10-phenanthroline [13].

The very long lifetime of the copper(I) complex of 2,9-diphenyl-1,10-phenanthroline (310 ns) is clearly not attained [32].

3.3. Electrochemical properties

The electronic absorption spectra of the stable chemically generated copper complexes $[(\mathbf{3})_2Cu]^n$ ($n = +1, +2$) and the electrochemically generated species are identical. Furthermore, repeated electrochemical con-

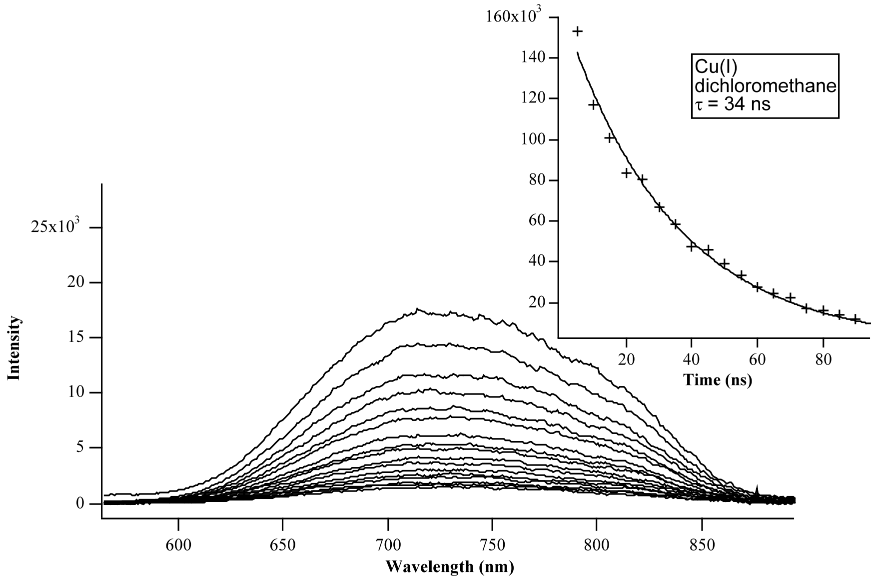


Fig. 5. Time-resolved emission spectra of the $[(\mathbf{3})_2Cu]^+$ complex in CH_2Cl_2, obtained upon laser excitation at 480 nm. Inset: Integrated time-resolved emission spectra of the $[(\mathbf{3})_2Cu]^+$ complex in CH_2Cl_2 vs. time, with a monoexponential fit. Incremental time delay is 5 ns.

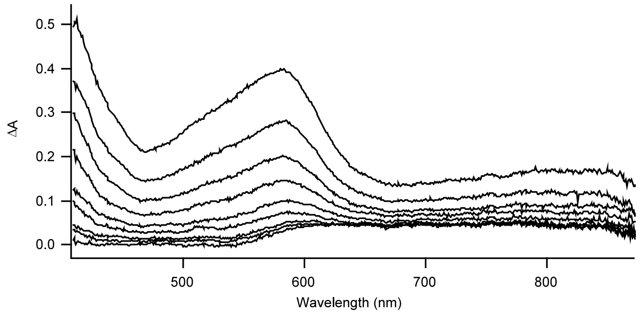


Fig. 6. Transient absorption spectra of the $[(\mathbf{3})_2Cu]^+$ complex in CH_2Cl_2. Excitation at 567 nm. Incremental time delay is 20 ns.

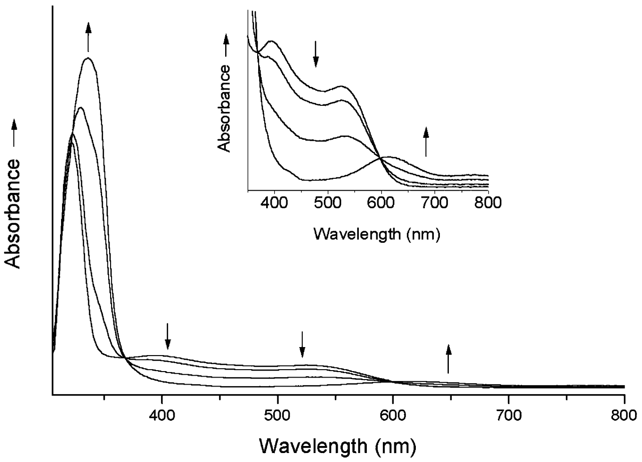


Fig. 7. UV–vis changes accompanying in situ oxidation of $[(\mathbf{3})_2Cu]^+$ into $[(\mathbf{3})_2Cu]^{2+}$ in CH_2Cl_2 (5×10^{-3} M) at r.t. within a spectro-electrochemical OTTLE cell.

version of cation $[(\mathbf{3})_2Cu]^+$ into $[(\mathbf{3})_2Cu]^{2+}$ and vice versa does not cause any deviation and the electronic spectra are fully reproduced (see Fig. 7). The cyclic voltammograms of both complexes showed a perfectly reversible one-electron redox couple ($E_{1/2}$ (Cu(I)/Cu(II)) = +0.68 V vs. SCE = +0.23 V vs. Fc/Fc^+) with a peak-to-peak separation $\Delta E_p = 75$ mV identical to that for the cobaltocene–cobaltocenium internal reference. Importantly, the ΔE_p value of 75 mV is consistent with absence of any pronounced structural change during the Cu(I)/Cu(II) redox process. Thus, the energy needed for the slight reorganization of the pseudotetrahedral ligand geometry around the Cu(I) and Cu(II) redox centers, revealed by X-ray crystallography, is rather small and the diffusion-controlled electron transfer remains the rate-determining step. Thus the electrochemical conversion processes take place without structural reorganization within electrochemical timescales (sub second). The reorganization of the ligand geometry around the Cu(I) and Cu(II) centers as revealed by the X-ray crystallography is too small to be reflected in lower electron transfer rate on the sub-second voltammetric time scale. In other terms, the two different ways of generating both complexes (chemically or electrochemically) have no effect on the final structure of the complexes. Besides the Cu(I)/Cu(II) couple, a multi electron irreversible reduction of the Cu(I) complex was observed at $E_{p,c} = -2.44$ V versus Fc/Fc^+, independently the copper oxidation state of the starting material. This cathodic process, probably of an electrocatalytic origin, was not studied in detail.

Electrochemical data for different phenantroline copper complexes in dichloromethane have been reported. Thus, for the Cu(I) complex of 2,9-diphenyl-1,10-phenanthroline, +0.84 V versus Ag/AgCl (ca. 0.79 V vs. SCE) was found [7]. Values reported for of 2,9-dialkyl-1,10-phenanthrolines range between +0.68 and 0.50 versus Fc/Fc^+ [12]. These values are ca. 0.2 V lower in acetonitrile, which corresponds well to the +0.40 V versus Fc/Fc^+ which was found in acetonitrile for a bridged bis(bis-phenantroline)dicopper(I) system [11]. To the best of our knowledge, no spectroelectrochemistry has been reported for these compounds.

3.4. Electron paramagnetic resonance

The Cu(II) species is paramagnetic and in order to gain further structural information, it was studied by EPR spectroscopy (Fig. 8) at r.t. The X-band EPR spectrum of the $[(\mathbf{3})_2Cu]^{2+}$ complex is strongly anisotropic with a g-value of ca. 2.17 indicating a strongly anisotropic surrounding of the copper nucleus.

4. Conclusions

Using the 2,2′-bipyridine derivative **3** bearing two phenyl groups at the 6 and 6′ positions and thus introducing considerable steric hindrance, two novel complexes with Cu(I) and Cu(II) centers were prepared and structurally characterized in the solid state by X-ray diffraction on single-crystal. The structural study re-

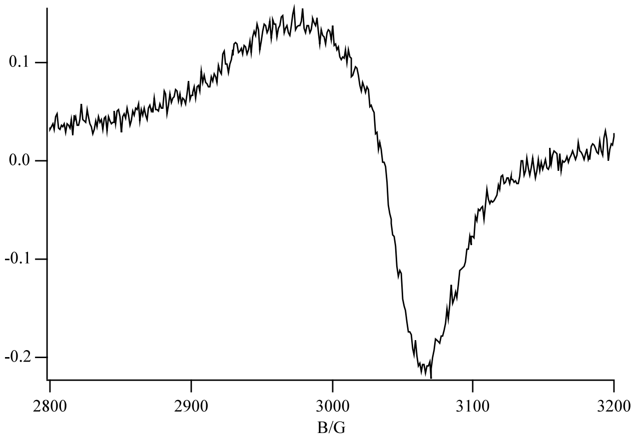


Fig. 8. EPR of $[(\mathbf{3})_2Cu(II)]$ in argon degassed CH_2Cl_2 obtained at r.t. with an X-band spectrometer.

vealed that in both cases, the metal cation was surrounded by four N atoms with distorted tetrahedral coordination geometry. Interestingly, a remarkable structural invariance was observed between the two complexes. In CH_2Cl_2, the chemically generated red Cu(I) complex shows a rather weak emission ($\Phi_{em} = 2.7 \times 10^{-4}$,) with a lifetime of the emitting MLCT state of ca. 34 ns. Since the MLCT state for the Cu(I) complex was found to absorb more strongly than the ground state, as demonstrated by transient absorption spectroscopy, no ground state bleaching is observed. As expected, the chemically generated green Cu(II) complex does not show any observable emission or transient absorption. Electrochemical studies using the cyclic voltammetry showed fully reversible reduction and oxidation processes ($E_{1/2}$ (Cu(I)/Cu(II)) = +0.68 V vs. SCE = +0.23 V vs. Fc/Fc$^+$). The absorption spectra of both chemically and electrochemically generated Cu(I) and Cu(II) complexes are identical, demonstrating that electrochemical conversion of the Cu(I) into Cu(II) complexes and vice versa does induce any decomposition. Furthermore, the limited structural reorganization during the Cu(I)/Cu(II) redox step gets support from the electrochemically reversible cyclic voltammetric response.

Concluding, the complexes $[(\mathbf{3})_2Cu]^n$ ($n = +1, +2$) are relatively stable systems that can be easily interconverted between their red Cu(I) and green Cu(II) states and represent interesting candidates for electrochromic materials, despite their low extinction coefficients. Our studies in solution showed that the $[(\mathbf{3})_2Cu]$ complexes have rather different absorption characteristics, good chemical stability as well as electrochemical interconvertibility. Furthermore, their emissive properties are influenced by the oxidation state of the metal center. These characteristics make these complexes rather well suited for their incorporation into an electrochromic display configuration, using ITO windows.

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