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Synthesis, Spectral Characterization, Redox Properties of [Cu(4-ampc)₂]BPh₄ and [Cu(4-ampc) (PPh₃)₂]BPh₄: Crystal Structure of [Cu(4-ampc)₂]BPh₄

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Synthesis, Spectral Characterization, Redox Properties of [Cu(4-ampc)₂]BPh₄ and [Cu(4-ampc)(PPh₃)₂]BPh₄: Crystal Structure of [Cu(4-ampc)₂]BPh₄

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The ligand, morpholin-4-yl-pyridin-2-ylmethylene-amine 4ampc, and its corresponding copper(I) complexes, [Cu(4ampc)₂]BPh₄ 1, and [Cu(4-ampc)(PPh₃)₂]BPh₄ 2, have been synthesized and characterized by CHN analyses, ¹H-NMR, IR, and UV-Vis spectroscopies. The crystal and molecular structures of [Cu(4-ampc)₂]BPh₄ 1 were determined by X-ray crystallography from a single-crystal. The coordination polyhedron about copper(I) is best described as a distorted tetrahedron. Quasireversible and irriversible redox behaviors were observed for 1 and 2, respectively.

Keywords copper(I) complexes, diimine ligand, 4-aminomorpholine, crystal structure, cyclic voltammogram

INTRODUCTION

The monovalent copper (d¹⁰) chemistry has drawn special attention because of its instability, unusual structural features, utility in solar energy and supramolecular devices, catalytic activity in photo-redox reactions, and the biological relevance of high potential copper complexes.^[1-10] Proper combination of the steric crowding and π -acidity in a well-designed ligand are the most important prerequisites for high stability of copper(I) complexes.^[11,12] Iminopyridine ligands to stabilize low valent metal-redox states seem to be a good candidate for such studies and these ligands are used for synthesis of Cu(I), Re(I), and Ru(II) complexes in such studies.^[13–16] However, the substituent on the iminopyridine ligands may modify the π -acidity and regulate the physical and chemical properties of the complexes.^[17-21]</sup>

In continuation of our work on the preparation of copper(I) diimine complexes with low-lying MLCT transitions,^[13,22,23] we report the synthesis and characterization of morpholin-4-

yl-pyridin-2-ylmethylene-amine and their copper(I) complexes (Figure 1). The spectral properties, redox chemistry, and structure of these complexes are also discussed.

EXPERIMENTAL

All chemicals used were reagent grade and used as received. Solvents used for the reactions were purified by literature methods.^[24] [Cu(MeCN)₄]BPh₄ was freshly prepared in acetonitrile according to the procedure,^[25] washed with cold acetonitrile, and dried under vacuum. Elemental analyses were performed by means of a Heraeus CHN-O-RAPID elemental analyzer (Alzahra University). IR spectra were recorded on a Shimadzu IR-460 instrument (Alzahra University). Electronic absorption spectra were recorded on a JASCOV-570 Spectrophotometer; λ_{max} (log ε) in nm. ¹H-NMR spectra were measured with Bruker ACP-200 spectrometer at 200 MHz; chemical shifts are reported in ppm relative to an internal standard of Me₄Si (Shahid Behesti University). Electrochemical data were obtained by cyclic voltammetry (CV) with a three-electrode cell consisting of an Ag/AgCl reference electrode, a Pt wire counter electrode, and the Pt as a working electrode. A Metrohm multipurpose instrument model 693 VA processor with 694A Va stand was used. CV measurements were performed in CH₂Cl₂ with 50 mM Bu₄NClO₄ (TBAP) as supporting electrolyte. In all electrochemical experiments, the solutions were purged with Ar gas for at least 5 min.

Crystal Structure Determination

Diffraction data for 1 were collected on a Bruker Smart AXS CCD diffractometer using graphite-monochromated MoK_{α} radiation ($\lambda = 0.71073$ Å) at Institute of Organic Chemistry in Heidelberg University. An empirical absorption correction was applied using SADABS^[26] based on the Laue symmetry of the reciprocal space. Structure was solved by direct methods and refined against F² with a full-matrix least-squares algorithm using the SHELXTL-PLUS (5.10) software package.^[27] Hydrogen atoms were treated using appropriate riding models. Crystallographic data (excluding structure factors) for the

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FIG. 1. Chemical formula of Cu(I) complexes 1 and 2.

structure **1** reported in this article have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 675854. A copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Synthesis of Morpholin-4-yl-Pyridin-2-Ylmethylene-Amine, 4-ampc

Although, this ligand synthesized before,^[28] here we report a simple method for synthesis of the ligand. To a solution of pyridine-2-carbaldehyde (107 mg, 1 mmol) in 5 mL diethylether was added a solution of 4-aminomorpholine (102 mg, 1 mmol) in 5 m: diethylether and stirred for 15 min. The ligand, morpholin-4-yl-pyridin-2-ylmethylene-amine, 4-ampc, was obtained as a vellow microcrystalline precipitate. It was then filtered off, washed with cold diethylether, and dried in air. Yield: 80%. IR data (KBr pellets, cm⁻¹): 1621 (C=N). ¹H-NMR (500 MHz, CDCl₃): ¹H-NMR (CDCl₃, ppm): $\delta = \delta = 3.11-3.21$ (m, 4H, -CH₂-N-CH₂-), 3.63-3.69 (m, 4H, -CH₂-O-CH₂-), 7.18 (d, 1H, $J_{H3,4} = 9.2$ Hz, H₄), 7.31 (dd, 1H, $J_{H3,4} = 9.2$, $J_{H3,2} =$ 11.5 Hz, H₃), 7.76 (t, 1H, $J_{H2,1} = 12.7$, $J_{H2,3} = 11.5$ Hz, H₂), $8.10 (d, 1H, J_{H1,2} = 12.7 Hz, H_1), 8.21 (s, 1H, H_5)$. Anal. Calcd. for C₁₀H₁₃N₃O (%): C, 62.81; H, 6.85; N, 21.97. Found: C, 62.83; H, 6.87; N, 21.95.

Synthesis of bis((Morpholin-4-yl-Pyridin-2-Ylmethylene-Amine)Copper(I) Tetraphenylborate, [Cu(4-ampc)₂]BPh₄, 1

To a stirring solution of morpholin-4-yl-pyridin-2ylmethylene-amine (19.1 mg, 0.1 mmol) in 5 mL acetonitrile was added [Cu(CH₃CN)₄]BPh₄ (27.4 mg, 0.05 mmol) in 5 mL acetonitrile and stirred for 10 min. The solution turned orange rapidly. The volume of the solvent was reduced under vacuum to about 4 mL. The diffusion of diethyl ether vapor into the concentrated solution gave orange crystals. The resulting crystals were filtered off and washed with a mixture of diethyletheracetonitrile (9:1 v/v) and dried under vacuum. Yield: 92%. IR data (KBr pellets, cm⁻¹): 1582 (C=N). ¹H NMR (CDCl₃; δ): δ = 3.15–3.30 (m, 8H, -CH₂-N-CH₂-), 3.68–3.71 (m, 8H, -CH₂-O-CH₂-), 6.86 (t. 8H, para H of BPh₄), 7.03 (m, 8H, meta H of BPh₄), 7.20 (d, 2H, J_{H3,4} = 9.5 Hz, H₄), 7.35 (dd, 2H, J_{H3,4} = 9.5, J_{H3,2} = 11.5 Hz, H₃), 7.53 (b. 8H, meta H of BPh₄), 7.72 (t, 2H, $J_{H2,1} = 7.9$, $J_{H2,3} = 11.5$ Hz, H₂), 8.16 (*d*, 2H, $J_{H1,2} = 7.9$ Hz, H₁), 8.30 (s, 2H, H₅). Anal. Calcd. for $C_{44}H_{46}BCuN_6O_2$ (%): C, 69.06; H, 6.06; N, 10.98. Found: C, 69.08; H, 6.07; N, 10.97.

Synthesis of (Morpholin-4-yl-Pyridin-2-Ylmethylene-Amine)bis(Triphenylphosphine)Copper(I) Tetraphenylborate, [Cu(4-ampc)(PPh₃)₂]BPh₄, 2

To a 3-mL acetonitrile solution of [Cu(CH₃CN)₄]BPh₄ (54.8 mg, 0.1 mmol), 2 equivalent of Ph₃P (52.2 mg, 0.2 mmol) were added, and the solution was stirred for 15 min. The solvent was evaporated under vacuum at room temperature. The dry product [Cu(CH₃CN)₂(PPh₃)₂]BPh₄ was added to a stirring solution of 19.1 mg (0.1 mmol) morpholin-4-yl-pyridin-2ylmethylene-amine, 4-ampc, in 3 mL acetonitrile. The solution rapidly turned yellow and it was stirred for 20 min at room temperature. The reaction medium was concentrated under vacuum, until the first crystals appeared in the liquid phase. Bright yellow crystals were obtained by diffusion of diethylether vapor into the concentrated solution. Yield: 80 mg (91%). IR data (KBr pellets, cm⁻¹): 1580 (C=N). ¹H NMR (CDCl₃; δ): δ = 3.13–3.29 (m, 4H, --CH₂--N--CH₂--), 3.59-3.65 (m, 4H, --CH₂--O--CH₂--), $6.82-7.52 (m_{2}, 53H, pyridine, Bph_{4}, PPh_{3}), 7.95 (d, 1H, J_{H2,1} =$ 8 Hz, H₁), 8.35 (s, 1H, H₅). Anal. Calcd. for C₇₀H₆₃BCuN₃OP₂ (%): C, 76.53; H, 5.78; N, 3.82. Found: C, 76.55; H, 5.77; N, 3.82.

RESULTS AND DISCUSSION

General Characterization

The IR spectra of the free ligand exhibit ν (C=N) at 1621 cm⁻¹. In complexes, the ν (C=N) appears at 1580–2 cm⁻¹ and is red shifted by 40 cm⁻¹. This has been attributed to the presence of d(Cu) $\rightarrow \pi^*$ (ligand) back-bonding.^[29,30]

The electronic spectra of the complexes were recorded in chloroform solution in the range 700-200 nm. The visible range of the spectrum is dominated by metal-to-ligand charge transfer (MLCT) transition, which is a characteristic feature of the copper(I) complexes when bonded with a conjugated organic chromophore.^[31,32] A similar situation is observed in Cu(NN)⁺₂ complexes.^[33] This is likely for a tetrahedrally distorted $Cu(NN)_2^+$ coordination sphere. A single crystal X-ray structural study supports this behavior (vide infra). The absorption spectrum of [Cu(4-ampc)₂]BPh₄ 1 in chloroform features a band with a true maximum at 485 nm. The [Cu(4ampc)(PPh₃)₂]BPh₄ **2** shows a clear shoulder at 390 nm, which is shifted considerably (ca. 95 nm) relative to complex 1. A similar shift has been reported in going from $[Cu(dmp)_2]^+ (\lambda_{MLCT})^+$ = 454 nm) to $[Cu(dmp)(PPh_3)_2]^+ (\lambda_{MLCT} = 365 nm).^{[34]} Addi$ tional absorption bands are also observed in the spectra of 1 and 2 in chloroform in the UV region. The intensity of these bands is consistent with its being ligand-centered $\pi \rightarrow \pi^*$ or/and charge-transfer transitions.

 TABLE 1

 Crystal data and structure refinement for 1

Empirical formula	$C_{44}H_{46}BCuN_6O_2$	
Formula weight	765.22	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Z	4	
a = 11.8431(6) Å	$lpha=90^\circ$	
b = 17.6213(9) Å	$\beta = 106.120(1)^{\circ}$	
c = 18.9454(10) Å	$\gamma = 90^{\circ}$	
Volume	3798.3(3) Å ³	
Density (calculated)	1.34 g/cm^3	
Absorption coefficient	0.62 mm^{-1}	
Crystal shape	polyhedron	
Crystal size	$0.25 \times 0.11 \times 0.07 \text{ mm}^3$	
Crystal colour	Orange	
Theta range for data collection	1.8 to 28.4°	
Index ranges	$15 \le h \le 15, 23 \le k \le 23, 25 \le l \le 25$	
Reflections collected	39,850	
Independent reflections	9485 (R(int) = 0.0548)	
Observed reflections	7211 (I > 2σ (I))	
Absorption correction	Semiempirical from equivalents	
Max. and min. transmission	0.96 and 0.86	
Refinement method	Full matrix least squares on F ²	
Data/restraints/parameters	9485/99/482	
Goodness-of-fit on F ²	1.09	
Final R indices $(I > 2\sigma(I))$	R1 = 0.066, WR2 = 0.137	
Largest diff. peak and hole	1.27 and $-0.51 \text{ e}\text{\AA}^{-3}$	

The ¹H NMR spectra and peak assignments are presented in the experimental section. These peaks are assigned based on the splitting of the resonance signals, spin-coupling constants, and the literature and are clearly in accordance with the molecular structure determined by X-ray crystal structure analysis. The

TABLE 2 Selected bond length (Å) and bond angle (°) of 1

Cu1-N2	2.011(2)	Cu1-N28	2.068(2)
Cu1-N1	2.018(2)	N8-N11	1.374(3)
Cu1-N8	2.069(2)	C7-N8	1.281(3)
N21-Cu1-N1	132.20(9)	C6-N1-C2	117.5(2)
N21-Cu1-N28	81.68(9)	C6-N1-Cu1	130.3(2)
N1-Cu1-N28	119.14(9)	C2-N1-Cu1	112.19(18)
N21-Cu1-N8	126.90(9)	C7-N8-N11	120.9(2)
N1-Cu1-N8	81.10(9)	C7-N8-Cu1	111.91(19)
N28-Cu1-N8	121.24(9)	N11-N8-Cu1	126.90(16)
N8-N11-C1	118.2(2)	C12-N11-C16	114.0(2)
N8-N11-C16	112.0(2)	C13-O14-C15	108.1(2)

spectra of the ligand are clearly divided into two portions; the downfield part is due to pyridine and imine protons (1-5-H) and the upfield signals refer to alkyl protons. Aside from the aromatic H-atoms, which appear at 7.18–8.20 ppm in the ligand, the imine proton appears as a singlet at 8.21 ppm in the ligand. The multiplet peak at about 3.65 ppm in the ligand is assigned to the proton in vicinity of oxygen atom of morpholine ring. The other alkyl protons appear in 3.15 ppm as multiplet. The ¹H resonances of the coordinated ligand are commonly observed in complexes **1** and **2**. In complex **2**, however, the aromatic H atoms of the coordinated Ph₃P ligands and BPh₄ anion overlap to some extent with those of the phenyl H atoms of the ligand. The downfield shift of the iminic protons relative to the free ligands can be attributed to the deshielding effect resulting from the coordination of the ligands.^[30]

Crystal Structure of [Cu(4-ampc)₂]BPh₄, 1

The crystallographic data are summarized in Table 1 and selected bond distances and angles are given in Table 2. No classical H-bonding occurs in this crystal structure. A view of



FIG. 2. ORTEP view of the crystal structure of $[Cu(4-ampc)_2]BPh_4$ 1 showing the atom-labeling scheme. The thermal ellipsoids enclose 50% of the electronic density. Hydrogen atoms are omitted for clarity. The major component of the disordered cation (66%) was shown.

the cation of complex **1**, including the atom numbering scheme, is illustrated in Figure 2. While a tetrahedral geometry might be expected for a four-coordinated copper(I) center, the coordination sphere around the metal ion in this complex is distorted by the restricting bite angles of the chelating ligand. The intraligand N1–Cu–N8 and N1–Cu–N8 angles are much less than 109.5°, being only 81.10(9)° and 81.68(9)°, respectively. On the contrary, the N21-Cu1-N1 and N21-Cu1-N8 angles (132.20(9)°, 126.90(9)°) are much larger than those of a tetrahedral complex (vide supra). The average Cu–N bond distance (2.042 Å) is similar to that found in the [Cu(dpdmp)₂]+ cation (2.047 Å) at room temperature^[32] and other Cu(I) pseudotetrahedral complexes (typical Cu–Nav = 2.055 Å).^[30] The average value for the dihedral angles of N1–C2–C7–N8 and N21–C22–C27–N28 is 2°, and comparison of the dihedral angles between the chelate rings and pyridine groups indicates the coplanarity of these moieties, resulting in a bite size of 2.66 Å of d(N–N) for the chelating ligand. The environment of the imine and pyridine nitrogen atoms is planar. The planarity is measured by three N atom bond angles (Σ N). For **1**, the average sum of these angles is 360° for N atoms. Despite the fact that the nitrogen atoms in **1** are sp² hybridized, some strain in the chelate ring is suggested by the deviation from the 120° angle about the nitrogen, Cu1–N1–C2 (112.19(18)°), C6–N1–Cu1 (130.3(2)°), N11–N8–Cu1 (126.90(16)°), C7–N8– Cu1 (111.91(19)°), C26–N21–Cu1 (130.6(2)°), C22–N21–Cu1 (111.72(18)°), C27–N28–N31 (121.4(3)°), and C27–N28–Cu1 (111.97(19)°). The morpholine rings in **1** adopt a chair conformation but one of the two morpholine rings is disordered over two positions, with the occupancy factors refined to 67:33.

Electrochemistry

The electrochemical behavior of the complexes was examined using cyclic voltammetry in CH₂Cl₂. The ligand 4-ampc is electroinactive in the working potential region. Complex 1 show a quasireversible $Cu^{II/I}$ couple with an E_p^c of 0.47 V (Figure 3). The ratio of the anodic and cathodic peak currents, (i_{pa}/i_{pc}) , approaches one as the scan rate increases and the peak-to-peak separation varies from 200 to 255 mV, as the scan rate is changed from 50 to 500 mV/s.^[35] The cyclic voltammogram of complex 2 in CH₂Cl₂ displays only one anodic peak ($E_p^c = 0.85$ V). The corresponding cathodic peak was not observed even under fast scan-rate conditions. This is probably due to an irreversible chemical reaction following the electron-transfer process. The Cu^{II/I} potential in a Cu^IN₄ chromophore is believed to increase with increasing the π -acidity of the ligands and the resistance to tetrahedral distortion occurring in the corresponding $Cu^{II}N_4$ chromophore.^[36–38] Although a higher degree of conjugation exists in 1 relative to 2, the existence of bulkier ligands in 2 that prevent the inner-sphere reorganization to a flattened tetrahedral, more appropriate to Cu^{II} oxidation state, plays a key role in shifting the oxidation potential to higher values for complex 2 relative to 1.



FIG. 3. Cyclic voltammograms of $[Cu(4-ampc)_2]BPh_4$ 1 and $[Cu(4-ampc)(PPh_3)_2]BPh_4$, 2 in CH₂Cl₂ at 293 K. Scan rate: 50 mVs⁻¹. (1) $c = 2 \times 10^{-3}$, (2) $c = 2.5 \times 10^{-3}$.

CONCLUSION

The Cu^I complexes show pseudotetrahedral symmetry, and ¹H-NMR data support the existence of Cu^I in **1** and **2**. The position of the MLCT changes considerably and is blue-shifted by 95 nm, when one of the 4-ampc ligands is replaced by two Ph₃P molecules. Additional steric hindrance in complex **2** relative to **1** results in a more positive Cu^{II/I} redox potential.

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