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Copper(I) complexes of 2-(benzen-1-yl)methyleneamino-3-aminomaleonitrile and triphenylphosphine ligands: synthesis, characterization, luminescence and catalytic properties

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Abstract Some mixed ligand copper(I) complexes of general formula [Cu(**L**)$(PPh_3)_3$]X (**X** = Cl (**1**), ClO_4 (**2**), BF_4 (**3**) or PF_6 (**4**); **L** = 2-(benzen-1-yl)methyleneamino-3-aminomaleonitrile) were prepared and characterized by physicochemical and spectroscopic methods. A single-crystal X-ray diffraction study of [Cu(**L**)$(PPh_3)_3$]ClO_4 (**2**) revealed that the copper atom is four coordinated in a distorted tetrahedral geometry. Electrochemical studies of complexes **1**–**4** show quasireversible redox behavior corresponding to the Cu(I)/Cu(II) couple. Room temperature luminescence is observed for all four complexes. These complexes proved to be effective catalysts for the Sonogashira coupling of terminal alkynes with aryl halides at 90 °C.

Introduction

Numerous mononuclear copper(I) complexes have been reported in the literature. Their structures depend on the nature of the ligands, metal-to-ligand ratio, reaction conditions and metal–ligand interactions [1–5]. Diaminomaleonitrile (DAMN) acts as a symmetric ligand. It is known as an unsaturated electron rich ligand, being a tetramer resulting from the polymerization of HCN under basic conditions [6]. The reaction of DAMN with aromatic aldehydes is interesting as in every case the 1 + 1 condensed Schiff base is obtained, even in presence of excess aldehyde [7]. These compounds are important as synthetic intermediates and also used in pharmacology [8], synthesis of conjugate linear polymers [9] and in thermostable optical materials [10]. However, the coordination chemistry of Schiff bases derived from DAMN is not well explored. Meanwhile, copper(I) complexes of phosphorous-containing ligands have been used to carry out a wide range of organic transformations such as allylic amination, hydrogenation, copolymerization, and cross-coupling reactions [11–14]. The steric crowding and π-acidic character imparted by these ligands are important prerequisites for stabilizing the copper(I) complexes and their redox, photophysical and catalytic behavior.

In this context, we report here the ligational behavior of 2-(benzen-1-yl) methyleneamino-3-aminomaleonitrile (**L**) with copper(I) in the presence of triphenylphosphine as a coligand. The catalytic and luminescence behavior of the complexes have been investigated. Complexes [Cu(**L**)$(PPh_3)_3$]X (**1**–**4**) have been prepared and characterized by physicochemical and spectroscopic techniques and additionally complex **2** by X-ray crystallography. The luminescence behavior and thermal stabilities of the complexes have been studied. The catalytic performance of the complexes for the Sonogashira coupling of terminal alkynes with aryl halides is also reported.

Experimental

Materials and methods

Benzaldehyde (Alfa Aesar), 2,3-diaminomaleonitrile (Aldrich, USA), triphenylphosphine (Aldrich, USA) were of reagent grade and used without further purification. CuCl [15], $Cu(CH_3CN)_4]ClO_4$ [16], $[Cu(CH_3CN)_4]BF_4$

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[16] and $[Cu(CH_3CN)_4]PF_6$ [17] were prepared according to the literature procedures.

Elemental analyses (C, H and N) were obtained on a Thermo Finnegan FLASH EA-1112 CHNS analyzer. IR spectra (KBr pellets) were recorded on a PerkinElmer-100 FTIR spectrometer, ^{1}H and ^{13}C NMR spectra of the samples dissolved in $CDCl_3$ were recorded on a Bruker 300 MHz instrument using TMS as an internal standard. Electronic spectra were recorded in dichloromethane (10^{-6} M) on a Shimadzu 3600 UV–Vis–NIR spectrophotometer. Mass spectra were measured on a GCMS Shimadzu-2010 instrument. Emission spectra were recorded using a PerkinElmer LS 55 spectrofluorometer equipped with quartz cuvettes of 1 cm^3 path length at room temperature. Thermal analysis was carried out on a PerkinElmer thermal analyzer in nitrogen atmosphere at a heating rate of 10 °C/min. Cyclic voltammetry measurements were taken with a CH-400A Electrochemical Analyzer. A Standard three electrode system, consisting of a Pt disk working electrode, Pt wire counter electrode and Ag/AgCl reference electrode was used. Tetrabutyl ammonium perchlorate (TBAP) was used as the supporting electrolyte, and all measurements were taken in CH_2Cl_2 solution at room temperature with a scan rate 100 mV s^{-1}.

Synthesis of L

2-[(Benzen-1-yl)methyleneamino]-3-aminomaleonitrile (**L**) was prepared by a modification of the method described in the literature [18]. To a solution of benzaldehyde (0.500 g, 4.71 mmol) in methanol (10 ml), a solution of 2,3-diaminomaleonitrile (0.509 g, 4.71 mmol) in methanol (10 ml) was added dropwise with constant stirring. The resulting mixture was refluxed at about 80 °C for 5 h until completion of the reaction (checked by TLC). The product 2-[(benzen-1-yl)methyleneamino]-3-aminomaleonitrile obtained was filtered off and purified by column chromatography (ether:dichloromethane) to afford a yellowish-brown solid.

Yield: 0.847 g (84%); Elemental analyses (C, H and N, wt%) Anal. Calc. for $C_{11}H_8N_4$: C, 67.3; H, 4.1, N, 28.5; found: C, 67.3; H, 4.09; N, 28.5%; IR (KBr, ν/cm^{-1}): 3404 s, 3298 w, 2237 w, 2204 s, 1605 s; ^{1}H NMR ($CDCl_3$; 300 MHz): δ 8.46 (s, 1H, HC=N), δ 7.46–7.96 (m, 5H, phenyl), δ 7.45 (s, 2H, NH_2); ^{13}C NMR ($CDCl_3$; 300 MHz): δ 156.61(HC=N), δ 128.99–128.88 (phenyl-C), δ 115.84 (CN), δ 114.85 (CN), δ 113.61 (HCNC=C), δ 104.65 (CNC=C).

Synthesis of $[(CuL)(PPh_3)_3]Cl$ (1)

To a solution of CuCl (0.102 g, 1.02 mmol) in MeCN (10 ml), three equivalents of triphenylphosphine (0.802 g, 3.06 mmol) and one equivalent of **L** (0.200 g, 1.020 mmol) were added. The resulting reaction mixture was stirred for 2 h at room temperature under nitrogen. The volume of the solvent was reduced under vacuum, and the solid product was precipitated by diffusion of diethyl ether into the filtrate.

Yield: 0.905 g (82%); Elemental analyses (C, H, N, wt%) Anal. Calc. for $C_{65}H_{53}N_4P_3ClCu$: C, 72.1; H, 4.9, N, 5.1; found: C, 72.1; H, 4.9; N, 5.2%; IR (KBr, ν/cm^{-1}); 3413 s, 3303 w, 2237 w, 2195 s, 1622 s, 1483 s, 1435 s, 694 s, 518 s; UV–Vis (CH_2Cl_2) λ_{max} (nm) ($\varepsilon \times 10^6$, M^{-1} cm^{-1}): 283 (0.81), 334 (0.39), 442 (0.08); ^{1}H NMR ($CDCl_3$; 300 MHz): δ 8.19 (s, 1H, HC=N), δ 7.42–7.87 (m, 50H, phenyl), δ 7.39 (s, 2H, NH_2); ^{13}C NMR ($CDCl_3$; 300 MHz): δ 156.8 (HC=N), δ 134.75–128.96 (phenyl-C), δ 127.14 (Cu–CN), δ 115.88(CN), δ 113.57 (HCNC=C), δ 104.59 (CNC=C).

Synthesis of $[Cu(L)(PPh_3)_3]ClO_4$ (2)

Complex **2** was prepared by a similar procedure to that used for complex **1**, except that CuCl was replaced by $[Cu(CH_3CN)_4]ClO_4$ (0.334 g, 1.02 mmol).

Yield: 1.095 g (82%); Elemental analyses (C, H, N, wt%) Anal. Calc. for $C_{65}H_{53}O_4N_4P_3ClCu$: C, 68.1; H, 4.6; N, 4.89; found: C, 68.0; H, 4.63; N, 4.9%; IR (KBr, ν/cm^{-1}); 3415 s, 3306, 2237 w, 2197 s, 1610 s, 1481 s, 1436 s, 693 s, 519 s, 1094 b, 621 w; UV–Vis (CH_2Cl_2) λ_{max} (nm) ($\varepsilon \times 10^6$, M^{-1} cm^{-1}): 280 (0.69), 332 (0.32), 438 (0.06); ^{1}H NMR ($CDCl_3$; 300 MHz): δ 8.20 (s, 1H, HC=N), δ 7.42–7.88 (m, 50H, phenyl), δ 7.38 (s, 2H, NH_2); ^{13}C NMR ($CDCl_3$; 300 MHz): δ 156.59 (HC=N), δ 134.78–128.93 (phenyl-C), δ 127.13 (Cu–CN), δ 115.89 (CN), δ 113.55 (HCNC=C), δ 104.57 (CNC=C).

Synthesis of $[Cu(L)(PPh_3)_3]BF_4$ (3)

Complex **3** was prepared by a similar procedure to that used for complex **1**, except that CuCl was replaced by $[Cu(CH_3CN)_4]BF_4$ (0.321 g, 1.02 mmol).

Yield: 1.058 g (80%); Elemental analyses (C, H, N, wt%) Anal. Calc. for $C_{65}H_{53}F_4N_4P_3$ BCu: C, 68.8; H, 4.7; N, 4.9; found: C, 68.8; H, 4.6; N, 4.9%; IR (KBr, ν/cm^{-1}); 3413 s, 3304 w, 2237 w, 2195 s, 1620 s, 1482 s, 1435 s, 694 s, 517 s, 1084 s; UV–Vis (CH_2Cl_2) λ_{max} (nm) ($\varepsilon \times 10^6$, M^{-1} cm^{-1}): 283 (0.83), 334 (0.45), 432 (0.10); ^{1}H NMR ($CDCl_3$; 300 MHz): δ 8.18 (s, 1H, HC=N), δ 7.40–7.86 (m, 50H, phenyl), δ 7.38 (s, 2H, NH_2); ^{13}C NMR ($CDCl_3$; 300 MHz): δ156.7(HC=N), δ 134.79–128.92 (phenyl-C), δ 127.16 (Cu–CN), δ 115.89 (CN), δ 113.57 (HCNC=C), δ 104.58 (CNC=C).

Synthesis of $[Cu(L)(PPh_3)_3]PF_6$ (4)

Complex **4** was prepared by a similar procedure to that used for complex **1**, except that CuCl was replaced by $[Cu(CH_3CN)_4]PF_6$ (0.379 g, 1.02 mmol).

Yield: 1.118 g (81%); Elemental analyses (C, H, N, wt%) Anal. Calc. for $C_{65}H_{53}F_6N_4P_4Cu$: C, 65.5; H, 4.4; N, 4.7%; found: C, 65.4; H, 4.4; N, 4.8%; IR (KBr, ν/cm^{-1}); 3418 s, 3304 w, 2237 w, 2193 s, 1608 s, 1482 s, 1435 s, 694 s, 517 s, 841 s, 558 m; UV–Vis (CH_2Cl_2) λ_{max} (nm) ($\varepsilon \times 10^6$, M^{-1} cm^{-1}): 282 (0.64), 332 (0.35), 442 (0.08); ^{1}H NMR ($CDCl_3$; 300 MHz): δ 8.18 (s, 1H, HC=N), δ 7.40–7.88 (m, 50H, phenyl), δ 7.39 (s, 2H, NH_2); ^{13}C NMR ($CDCl_3$; 300 MHz): δ 156.8 (HC=N), δ 134.78–128.96 (phenyl-C), δ 127.16 (Cu–CN), δ 115.87(CN), δ 113.57 (HCNC=C), δ 104.58 (CNC=C).

Sonogashira coupling reactions

The coupling of phenylacetylene with aryl halides catalyzed by these copper(I) complexes was carried out according to the following procedure: The copper(I) catalyst (10 mol %) was added to the respective aryl halide (2 mmol), phenylacetylene (2 mmol), and K_2CO_3 (2 mmol) in toluene (10 ml), and the reaction mixture was stirred for 16 h at 90 °C under nitrogen. The reaction mixture was then cooled to room temperature, and the solution was filtered to remove the precipitated base. The filtrate was concentrated to dryness, and the crude product was purified by column chromatography using ether/chloroform (9:1). The purified product was then characterized by elemental analyses, IR, ^{1}H NMR and mass spectral studies.

X-ray crystallography

A single crystal of complex **2** suitable for X-ray analysis was obtained by slow evaporation of a saturated solution of the complex in methanol. The X-ray diffraction study was performed on a Bruker Apex-II CCD diffractometer with graphite-monochromatized MoKα radiation (0.71073 Å) with scan width of 0.30 at θ (0°, 90°, 180°). The X-ray generator was operated at 50 kV and 30 mA. Details of the crystal data, data collection and the refinement are given in Table 1. The structure was solved by direct methods using the SHELXS 93 program and refined using SHELXL-2014 software [19]. Molecular and packing diagrams were generated using ORTEP-3 [20] and Mercury [21].

Results and discussion

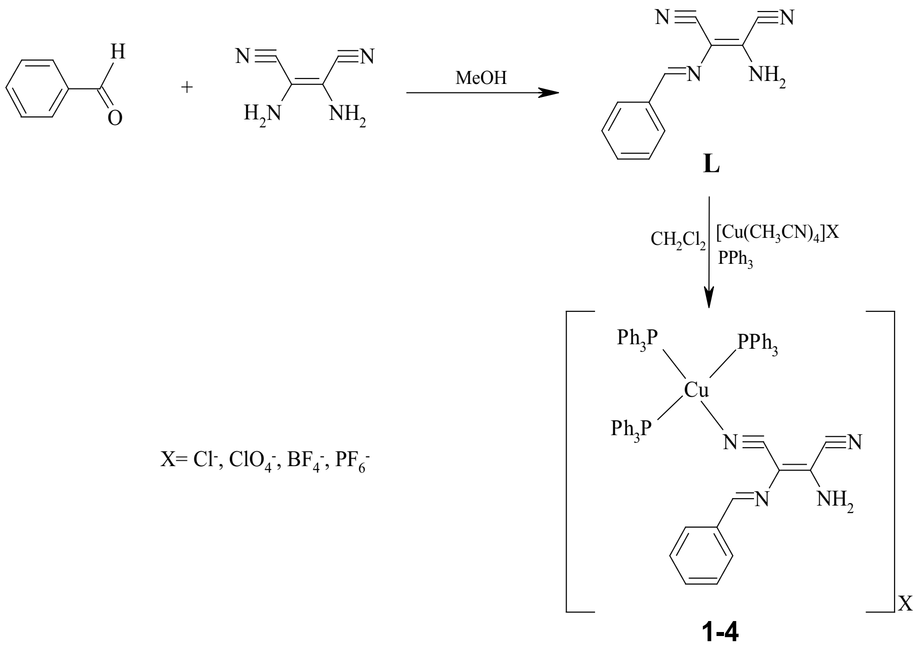
Synthesis and characterization

The synthetic route to complexes **1**–**4** is shown in Scheme 1. 2-[(Benzen-1-yl) methyleneamino]-3-aminomaleonitrile (**L**) was synthesized by the reaction of 2,3-diaminomaleonitrile with benzaldehyde according to the literature procedure. The obtained spectral data, elemental analysis and mass spectra confirm the formation of **L**. The mixed ligand copper(I) complexes [Cu(**L**)(PPh_3)$_3$]X were prepared by the reactions of **L** with CuCl, [Cu(CH_3CN)$_4$]ClO_4, [Cu(CH_3CN)$_4$]BF_4 or [Cu(CH_3CN)$_4$]PF_6 in the presence of triphenylphosphine. The complexes show good thermal stability and are stable to moisture, both in solution and in the solid phase. They are soluble in common organic solvents such as dichloromethane, chloroform, acetonitrile, tetrahedrofuran, methanol and ethanol. The complexes were characterized by elemental analysis, FTIR, UV–visible, ^{1}H and ^{13}C NMR spectra; in addition, the single-crystal X-ray structure of complex **2** was obtained. Molar conductivity values of 10^{-3} M solutions in CH_2Cl_2 of each of the complexes suggest that they are 1:1 electrolytes, indicating that the anions are not coordinated to the copper(I) center. At room temperature, all the complexes are diamagnetic, which is characteristic of copper(I).

Table 1 Crystal data and structure refinements details for [Cu(**L**)(PPh_3)$_3$]ClO_4(**2**)

Empirical formula	$C_{65}H_{53}ClCuN_4O_4P_3$
Formula weight	1146.01
Crystal system	Monoclinic
Space group	*P*2(1)/*n*
a (Å)	12.2880 (7)
b (Å)	33.5542 (14)
c (Å)	13.9490 (7)
α (°)	90.00
β (°)	91.225
γ (°)	90.00
V (A^3)	5750.4 (5)
Z	4
Density (mg/m^3)	1.324
μ (M_0K_α) (mm^{-1})	0.562
F (000)	2376
Data collection	
Temperature (K)	123(2)
θ mini.-maxi. (°)	1.899–25.498
Data set [*h*, *k*, *l*]	−14/14, −40/40, −16/16
Total, unique data, R_{int}	[*R*(int) = 0.0769]
Observed data	>2\s(I)
Refinement	Full-matrix least-squares on F^2
No. of reflection, No. of parameters	67,934/10,696 (R_{int}) = 0.0558
Final *R* indices [$I > 2\sigma(I)$]	*R*1-0.0663, w*R*2-0.1760
R indices (all data)	*R*1-0.0961, w*R*2-0.1564
Goodness-of-fit	1.023

The IR frequencies of selected features in the spectra of the complexes are given in the experimental section. The IR spectrum of free **L** exhibits two characteristic bands of the nitrile υ(C≡N) group, at 2237 and 2204 cm^{-1}. The



Scheme 1 Synthetic route of **L** and its copper(I) complexes

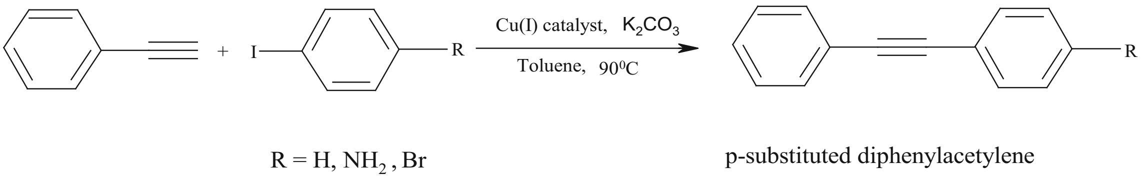
slight shifts of these bands toward lower frequency, at 2193–2197 cm^{-1} for complexes **1**–**4**, are ascribed to involvement of the nitrile group in coordination with the metal atom [22]. A strong band at 1605 cm^{-1} in the spectrum of the free ligand **L** corresponding to ν(HC=N) is shifted to higher frequency, appearing at 1608–1622 cm^{-1} in the spectra of the complexes; this suggests that the imine group is not coordinated. The spectrum of **L** shows broad bands at 3404 and 3298 cm^{-1} due to v_{sym} and v_{asym} vibrations of NH_2 which are also shifted to higher frequency in the spectra of the complexes, suggesting that the NH_2 groups are not involved in coordination. The presence of the PPh_3 ligand can be easily identified from the strong bands at around 1482, 1436, 694 and 518 cm^{-1}. The perchlorate complex **2** has a broad band at 1094 cm^{-1} (ν_3) and unsplit band at 621 cm^{-1} (ν_4), assigned to the non-coordinated ClO_4 ion in this complex [23]. For the tetrafluoroborate complex **3**, an intense band at 1084 cm^{-1} is attributed to the antisymmetric υ(B-F) stretching mode [24], while strong bands at 841 and 558 cm^{-1} for complex **4** are consistent with the PF_6^- anion in this complex [25].

The ^{1}H NMR spectral data of the complexes in $CDCl_3$ solution are given in the experimental section. The phenyl protons of the coordinated PPh_3 ligands overlap to some extent with those of the phenyl hydrogen atoms of **L** and are observed in the range of 7.40–7.88 ppm for all four complexes. The imine proton appears as a singlet at around δ 8.19 ppm. The upfield shift of the imine proton in the complexes relative to free **L** can be attributed to the shielding effect resulting from coordination of the nitrile group [26]. The NH_2 protons, which appear as a singlet at δ 7.45 ppm for free **L,** are shifted upfield to 7.38 ppm for the complexes, indicating noninvolvement of NH_2 in coordination.

The UV–Vis absorption spectra of the complexes were recorded in CH_2Cl_2 solution (10^{-6} M) at room temperature and are shown in Fig. 1. The free ligand **L** displayed two absorption bands at 274 and 338 nm, assigned to π–π* transitions. Complexes **1**–**4** show an intense absorption band at 280–344 nm, most likely originating from **L** and PPh_3. The red shifts in the π–π* absorptions of **1**–**4** compared to free **L** indicate conjugation of **L**, resulting in a smaller π–π* energy gap. In addition to the high energy absorption, complexes **1**–**4** displayed a low energy weak band at 448–456 nm corresponding to metal-to-ligand charge transfer from the $d\pi$ orbital of copper(I) to the unoccupied π orbitals of **L**, probably mixed with some intra-ligand charge transfer character [27].

X-ray crystal structure

The single-crystal X-ray analysis of $[Cu(\mathbf{L})(PPh_3)_3]ClO_4$ (**2**) reveals that this complex crystallizes in monoclinic space group $P2(1)/n$ and consists of discrete $[Cu(\mathbf{L})(PPh_3)_3]^+$ cations and perchlorate anions. The molecular structure of **2** along with the atom numbering scheme is illustrated in Fig. 2, and selected bond lengths and angles are given in Table 2. The monomeric complex **2** exhibits a distorted tetrahedral geometry around copper(I), provided by one nitrogen atom from **L** and three triphenylphosphine phosphorous atoms, giving P_3CuN coordination. The Cu–N bond distance in **2** (2.056 Å) is



Scheme 2 Sonogashira coupling of terminal alkynes with aryl halides catalyzed by **1-4**

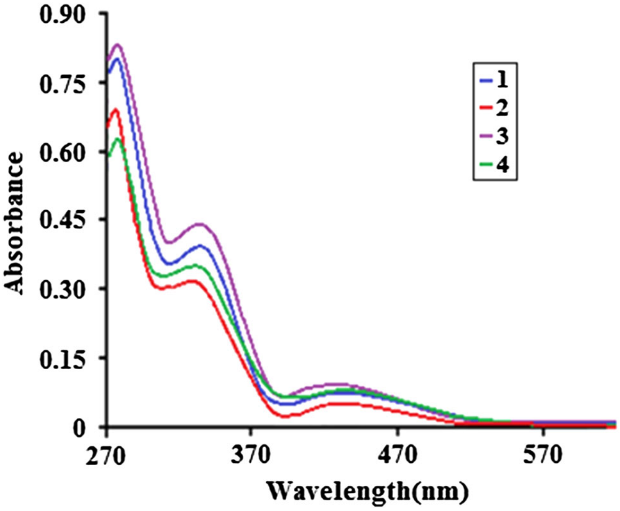


Fig. 1 UV–visible absorption spectra of **1–4**

comparable to those reported for other pseudo-tetrahedral complexes. All Cu–P bond lengths are as expected, i.e., close to the average value (2.324 Å) found in similar $[Cu(PPh_3)_3(CH_3CN)]X$ complexes [28]. The intra-ligand bond angles N(1)–Cu(1)–P(1), N(1)–Cu(1)–P(3) and N(1)–Cu(1)–P(2) are much less than tetrahedral, being 97.09(10)°, 104.37(10)° and 106.04(10)°, respectively. However, the bond angles P(2)–Cu(1)–P(1), P(1)–Cu(1)–P(3) and P(2)–Cu(1)–P(3) are 124.67(4)°, 112.46(4)° and 109.29(4)°, closer to the tetrahedral value. These geometrical parameters suggest that the copper(I) center in complex **2** has a highly distorted tetrahedral geometry. The distortion from ideal tetrahedral geometry in **2** is mainly due to the restricted bite angle of the chelating nitrile ligands, and steric hindrance of the phosphine ligands.

The crystal packing structure of **2** is given in Fig. 3. The complex forms intramolecular $\pi\ldots\pi$ interactions between the phenyl rings of PPh_3 and the ClO_4 anion. The ClO_4 anion is weakly interacting with phenyl-C–H groups, giving a loose supramolecular structure.

Cyclic voltammetry

In order to study their electron transfer properties, cyclic voltammetry studies of complexes **1–4** were carried out in 10^{-3} M CH_2Cl_2 solution in the potential range -1.5 to 1.5 V verses the SCE electrode. The electrochemical data are summarized in Table 3, and the cyclic voltammograms are shown in Fig. 4. In each case, there is a well-defined redox process on the positive potential side. A one electron oxidation peak corresponding to oxidation of copper(I) to copper(II) occurs in the potential range 0.512–0.578 (E_{pa}), while the reduction peak in the reverse scan falls within the range of 0.372–0.446 V (E_{pc}). The copper(I)/copper(II) redox process at around $E_{1/2} = 0.480$ V for all complexes is also supported by a comparison between cyclic voltammetry experiments involving the Fe(II)/Fe(III) redox couple (from ferrocene), at a potential range 100 mV s^{-1}. The current values found for the well-established one electron Fe(II)/Fe(III) redox process in the ferrocene/ferrocenium system are very similar to those observed for the Cu(I)/Cu(II) process at the same scan rate. The ratio of peak current (*Ipc/Ipa*) for complexes **1–4** is not equal to 1, and $\Delta E_p = (|E_{pa} - E_{pc}|)$ is >60 mV. These results confirm that the quasireversible redox behavior of these complexes is in good agreement with similar examples as reported in the literature [29].

Thermal studies and emission spectra

The thermal stabilities of the complexes were studied by thermogravimetric (TG) analysis between 25 and 800 °C under a nitrogen atmosphere. The perchlorate complex **1** is potentially explosive and hence not studied for safety reasons. The other complexes showed two decomposition stages. The first decomposition stage takes place in the region 165–425 (**1**), 170–422 (**3**), 165–428 °C (**4**), corresponding to mass losses of 72.80, 70.05 and 66.12, respectively [theoretical values 72.78 (**1**), 69.47 (**3**) and 65.99% (**4**)], attributed to decomposition of the triphenylphosphine ligands. The DTA curve gives exothermic peaks at 190, 196 and 192 for **1**, **3** and **4**, respectively. The second consists of a continuous weight loss from 425 to 655, 422 to 656 and 428 to 660 °C along with strong exothermic DTA peaks at 326, 320 and 324 °C, accompanied by mass losses of 18.25 (**1**), 17.40 (**3**), 16.56% (**4**). This process is attributed to decomposition of **L,** leaving CuCl, $CuBF_4$ and $CuPF_6$ as residues (theoretical mass loss 18.21, 17.36 and 16.51%).

Fig. 2 Molecular structure of $[Cu(\mathbf{L})(PPh_3)_3]ClO_4$ (**2**) showing 50% probability ellipsoids. The hydrogen atoms have been removed for clarity

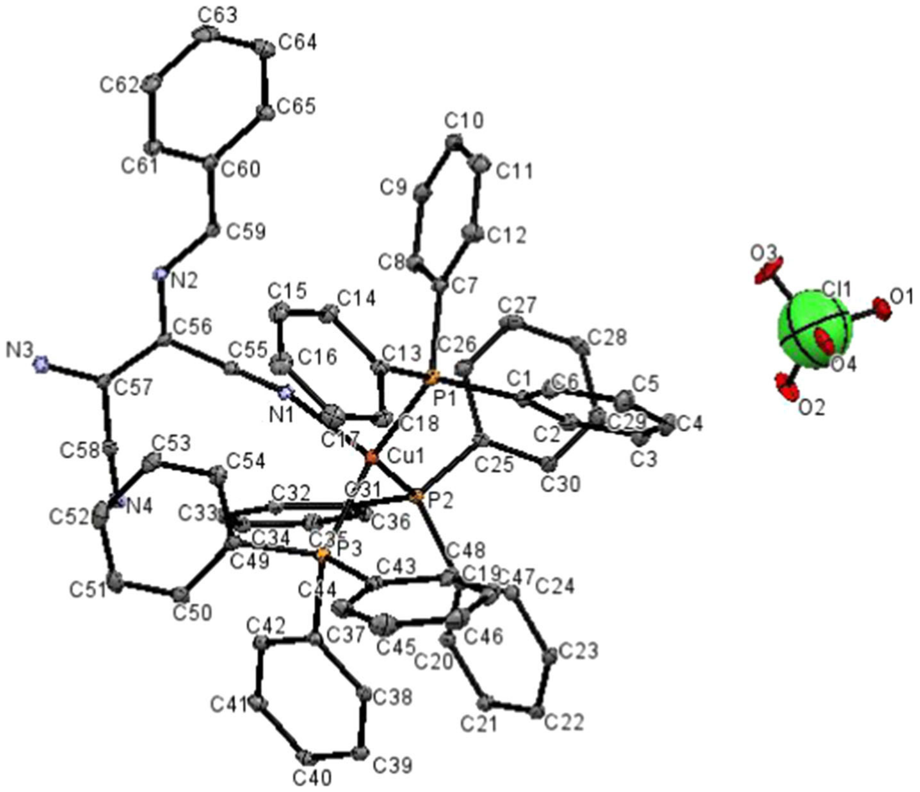


Table 2 Selected bond lengths (Å) and bond angles (°) for **2**

Cu(1)–N(1)	2.056(3)
Cu(1)–P(2)	2.304(11)
Cu(1)–P(1)	2.327(12)
Cu(1)–P(3)	2.342(12)
N(1)–Cu(1)–P(2)	106.04(10)
N(1)–Cu(1)–P(1)	97.09(10)
N(1)–Cu(1)–P(3)	104.37(10)
P(2)–Cu(1)–P(1)	124.67(4)
P(2)–Cu(1)–P(3)	109.29(4)
P(1)–Cu(1)–P(3)	112.46(4)

The emission properties of **L** and complexes **1**–**4** were studied at room temperature in CH_2Cl_2 solution (10^{-3} M). The emission spectra are shown in Fig. 5, and the data are summarized in Table 4. Free ligand **L** exhibits an emission in the violet–blue region centered at $\lambda_{max} = 426$ nm with an excitation at 324 nm assigned to a ligand centered π–π^* transition. In contrast, complexes **1**–**4** show marked differences in emission behavior in dichloromethane solution; their spectra show a broad emission band with λ_{max} at 462–475 nm, with excitation maxima at 341–346 nm. The complexes do not show significant emission when they are excited at their MLCT band maxima; hence, the emission can be attributed to $\pi \rightarrow \pi^*$ intra-ligand charge transfer. The enhancement of fluorescence efficiency in all of the complexes can be attributed to coordination of **L** and triphenylphosphine ligands to copper(I), which effectively increases the rigidity of the ligands and so reduces the loss of energy via radiationless decay [30]. The emission energies of the complexes are sensitive to the size of the counterion, following the sequence $PF_6^- > ClO_4^- > BF_4^- > Cl^-$. These results could be attributed to the different coordinating abilities of the anions, as well as the differences in solubility of the complexes [31].

The emission quantum yields (ϕ) of the complexes were determined using quinine sulfate as a reference, with known ϕ_R of 0.52 at 298 K, giving values of 0.077–0.093 (Table 4). The peak areas were integrated using software available on the instrument, and the quantum yields were calculated according to the following equation;

$$\frac{\phi_S}{\phi_R} = \frac{[A_S]}{[A_R]} \frac{[(\mathrm{Abs})_R]}{[(\mathrm{Abs})_S]} \frac{[\eta_S^2]}{[\eta_R^2]}$$

where ϕ_S and ϕ_R are the fluorescence quantum yields of the sample and reference, respectively. A_S and A_R are the areas under the fluorescence spectra of the sample and reference, respectively, $(\mathrm{Abs})_S$ and $(\mathrm{Abs})_R$ are the respective optical densities of the sample and the reference solution at the wavelength of excitation, and η_s and η_R are the values of refractive index for the solvent used for the sample and reference, respectively. The results obtained are in good agreement with values reported in the literature

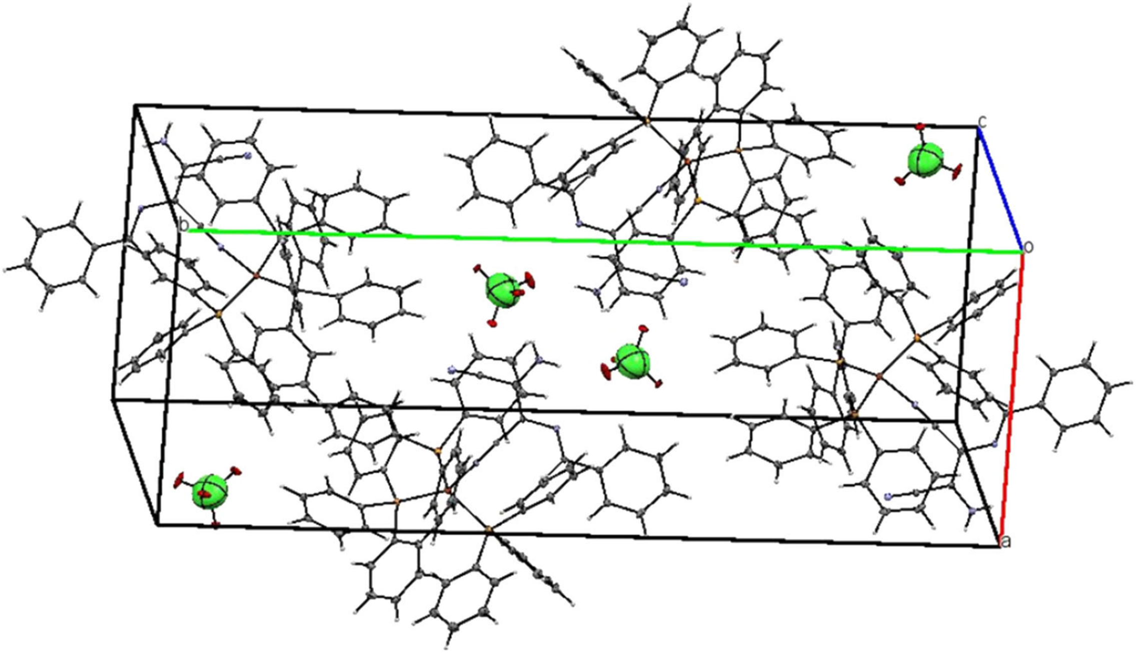


Fig. 3 The $\pi \ldots \pi$, C–H…π and hydrogen bonded ClO_4^- in $[Cu(\mathbf{L})(PPh_3)_3]ClO_4$ (**2**)

Table 3 Electrochemical data for copper(I) complexes (**1**–**4**)

Complex	E_{pa} (V)	E_{pc} (V)	ΔE_p (mV)	$E_{1/2}$ (V)
1	0.531	0.399	132	0.465
2	0.512	0.372	140	0.442
3	0.566	0.437	129	0.501
4	0.578	0.446	132	0.512

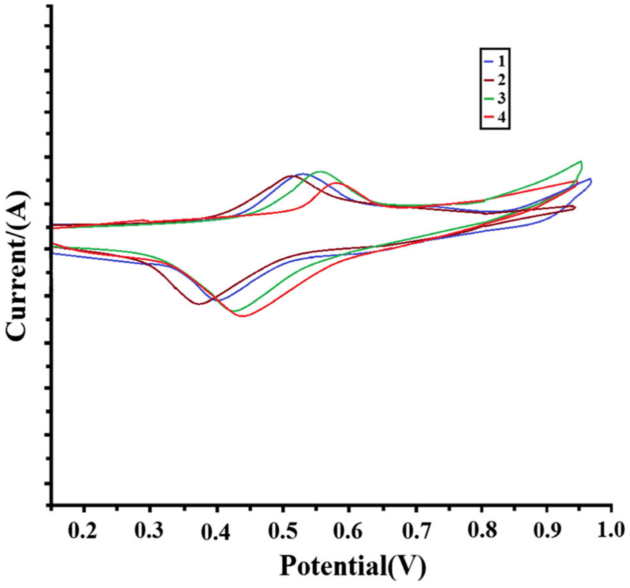


Fig. 4 Cyclic voltammogram of **1**–**4**

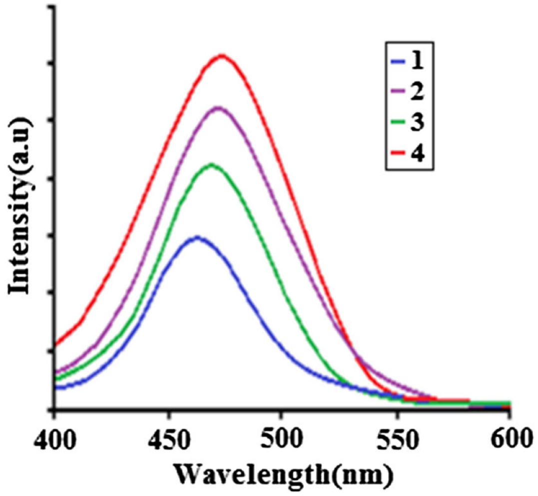


Fig. 5 Emission spectra of **1**–**4**

[32]. The lifetime data of the complexes were obtained upon excitation at 320 nm and are summarized in Table 4. The observed decay of each complex fits well to a single exponential. The average lifetimes of the complexes follow the same sequence described above with respect to increasing size of the counterion [33].

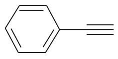
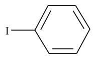
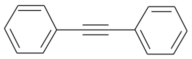
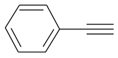
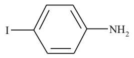
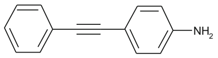
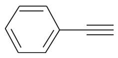
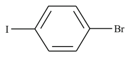
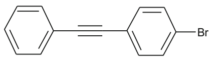
Catalytic activity

The Sonogashira Pd-catalyzed cross-coupling reaction is an important and powerful tool in organic synthesis. It involves coupling of aryl, alkyl, heteroaryl or vinyl halides with terminal acetylenes in the presence of a palladium

Table 4 Emission data of copper(I) complexes in CH_2Cl_2 (**1**–**4**)

Complex	λ_{ex} (nm)	λ_{em} (nm)	ϕ	τ (ns)	K_r ($s^{-1}/10^7$)	K_{nr} ($s^{-1}/10^9$)
L	324	426	0.069	2.32	2.974	0.4012
1	341	462	0.077	2.59	2.972	0.3563
2	342	473	0.087	2.72	3.198	0.3356
3	344	469	0.082	2.65	3.094	0.3463
4	346	475	0.093	2.83	3.286	0.3204

Table 5 Sonogashira coupling reaction of terminal alkyne with aryl halides

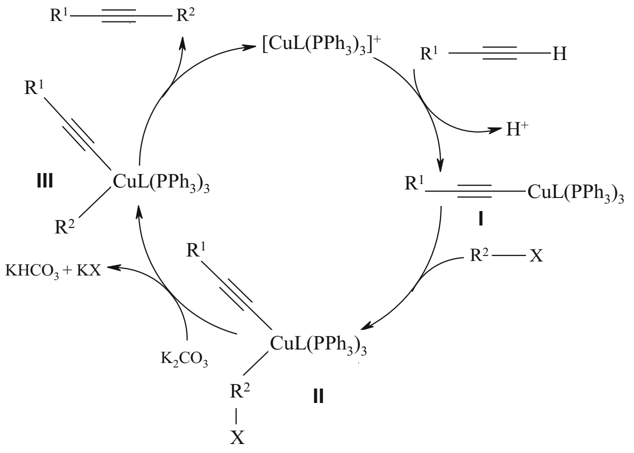
Entry	Phenylacetylene	Aryl halide	Product	Complex	% yield
1.				1	72
2.				2	77
3.				3	75
4.				4	79
5.				1	78
6.				2	84
7.				3	80
8.				4	86
9.				1	68
10.				2	72
11.				3	71
12.				4	76

Reaction conditions: phenylacetylene, 2.5 mmol; aryl halide, 2 mmol; copper(I) catalyst (10 mol %); K_2CO_3 (2 mmol); Toluene, 20 ml; temperature 90 °C; reaction time 16 h

Table 6 Microanalytical and spectral data of coupling product

Compound	C, H, N found (calculated)			IR (cm^{-1})	Mass	^{1}H NMR (δ ppm)
	C	H	N			
Diphenylacetylene	94.30 (94.34)	5.48 (5.66)	–	2152	*m/z* 178 $[C_6H_5C{\equiv}CC_6H_5]^+$, 77 $[C_6H_5]^+$	δ 7.40–7.55, (m, Ar–H)
4-Amino-diphenylacetylene	86.76 (87.01)	5.71 (5.74)	7.27 (7.22)	3411, 3292, 2151	*m/z* 193 $[C_6H_5C{\equiv}CC_6H_4NH_2]^+$, 178 $[C_6H_5C{\equiv}CC_6H_5]^+$, 77 $[C_6H_5]^+$	δ 7.40–7.62, (m, Ar–H) δ 3.84, (s, 2H, NH_2)
4-Bromo-diphenylacetylene	65.12 (65.40)	3.55 (3.53)	–	2152	*m/z* 257 $[C_6H_5C{\equiv}CC_6H_4Br]^+$, 178 $[C_6H_5C{\equiv}CC_6H_5]^+$, 77 $[C_6H_5]^+$	δ 7.41–7.58, (m, Ar–H)

complex such as $PdCl_2(PPh_3)_2$ or $Pd(PPh_3)_4$. Although Pd-catalyzed coupling [34] has become the most important method for laboratory scale synthesis, copper mediated coupling [35] is also well established and attractive due to low cost, non-toxicity and environmentally friendly nature. However, most of the copper catalyzed couplings reported so far are not well defined; the catalysts are generated in situ based on copper salt, ligands and additives. Also, they generally require prolonged reaction times, high temperature and a large amount of copper reagent. Therefore, it is necessary to develop well-defined and versatile catalysts that are active under mild conditions. In order to study the scope of copper(I) complexes **1**–**4** as catalysts for Sonogashira coupling, reactions of phenylacetylene with aryl halides were carried out using K_2CO_3 as a base in toluene at 90 °C (Scheme 2), with the results outlined in Table 5. The isolated products were characterized by elemental analyses, IR, ^{1}H NMR and mass spectra (Table 6). We found that these coupling reactions proceeded very smoothly to afford the corresponding coupling products in excellent yields. The catalytic efficiency was comparable with previously reported copper(I) complexes [36, 37] and all of the reactions proceeded smoothly at relatively low temperature for 16 h, attaining coupling yields of up to



Scheme 3 Probable mechanistic route for Sonogashira coupling of terminal alkynes with aryl halides using **1**–**4**

68–86% (Table 5). No significant increase in yield was obtained when the reaction time was increased further. For all four complexes, the coupling of phenylacetylene with iodobenzene reached yields up to 72–79%. With iodoaniline containing a *para*-electron donating group, the yield was 78–86%, whereas with 1-bromo-4-iodoaniline yields were 68–76%. These results confirm that various functional groups such as amino and bromo substituents were tolerated on the aryl halide component, while significant electronic effects were observed for substituted aryl halides containing an electron donating NH_2 group at the *para* position [38]. The copper(I) complexes with different counterions showed different activities; specifically, the complex with a PF_6^- counterion returned higher catalytic activities than the complexes with Cl^-, ClO_4^- and BF_4^- counter anions, with yields of up to 78–86%. The solubility of the complex is an important factor for high product yields.

The probable mechanism for the coupling reaction with the present complexes is illustrated in Scheme 3. In the first step, the copper(I) complex activates the C–H bond of the terminal alkyne to generate a copper acetylide (species I), which then undergoes oxidative addition of the aryl halide to give species II. Species II is again activated in the presence of base to give species III followed by reductive elimination to give diphenylacetylene and regenerate the copper(I) catalyst.

Conclusion

Mixed ligand copper(I) complexes were prepared from 2-(benzen-1-yl)methyleneamino-3-aminomaleonitrile and triphenylphosphine. The X-ray crystal structure of $[Cu(L)(PPh_3)_3]ClO_4$ shows a distorted tetrahedral geometry around copper(I). Quasireversible redox behavior was observed for all four complexes corresponding to the Cu(I)/Cu(II) couple. These complexes are effective catalysts for the Sonogashira coupling of terminal alkynes with aryl halides at low temperature. Further, the different counter anions in the complexes have a marked effect on the yields of the coupling products.

Supplementary data

CCDC 1434712 contains the supplementary crystallographic data for $[Cu(\mathbf{L})(PPh_3)_3]ClO_4$ (**2**). Supplementary data associated with this article can be found in the online version.

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