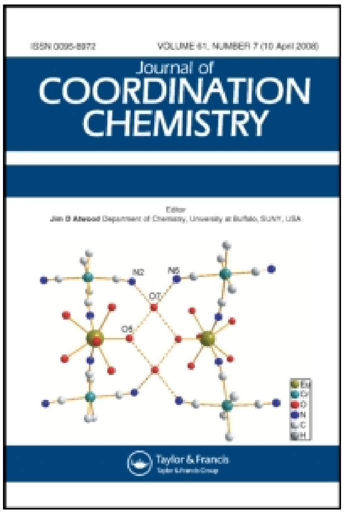

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Synthesis, characterization, and structures of copper(I) complexes with *N,N′-bis*[1-(4-chlorophenyl)ethylidene]ethane-1,2-diamine and *N,N′-bis*[1-(4-nitrophenyl)ethylidene]ethane-1,2-diamine

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Two ligands, *N,N′-bis*[1-(4-chlorophenyl)ethylidene]ethane-1,2-diamine (**L^1**) and *N,N′-bis*-[1-(4-nitrophenyl)ethylidene]ethane-1,2-diamine (**L^2**) and their corresponding copper(I) complexes, $[Cu(\mathbf{L}^1)_2]ClO_4$ (**1**) and $[Cu(\mathbf{L}^2)_2]ClO_4$ (**2**), have been synthesized and characterized by CHN analyses, ^{1}H-NMR, IR, and UV–Vis spectroscopy. The crystal structures of **L^1** and $[Cu(\mathbf{L}^1)_2]ClO_4$ (**1**) were determined from single crystal X-ray diffraction. **L^1** lies across a crystallographic inversion center and the C=N is approximately coplanar with the benzene ring and adopts *E* configuration. The coordination polyhedron about copper(I) in **1** is best described as a distorted tetrahedron. Quasireversible redox behavior is observed for the complexes.

Keywords: Acetophenone derivatives; Diimine ligands; Copper(I) complexes; Distorted tetrahedral structure

1. Introduction

Copper(I) complexes containing bidentate diimine ligands have been focus of much investigation. It has been pointed out and confirmed that four-electron donor diimines are or very efficient bidentate ligands and many copper(I) complexes containing diimine ligands are known with a variety of stereochemistry [1–4]. A key feature in the chemistry of $Cu(NN)_2^+$ complexes is the relatively stable framework and metal-to-ligand charge transfer transitions in the visible region. These features are the reasons for the reactivity and catalytic properties of such complexes that make them applicable for catalytic processes [5, 6], photosensitization of isomerization reactions [7, 8], light harvesting studies [9–11], and the design of supramolecular arrays [12–14]. Steric, electronic, and conformational effects of the coordinated diimines play important roles in modifying the properties of metal complexes. Diimine ligands derived from

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acetophenone derivatives seem to be good candidates, however, there are few reports on structural data and properties of copper(I) complexes of such ligands [15, 16]. In our ongoing study of copper(I) complexes [17–21], here we report the synthesis and characterization of two ligands with different electronic effects, *N*,*N*′-*bis*[1-(4-chlorophenyl)ethylidene]ethane-1,2-diamine ($\mathbf{L^1}$), and *N*,*N*′-*bis*[1-(4-nitrophenyl)-ethylidene]ethane-1,2-diamine ($\mathbf{L^2}$), and their corresponding copper(I) complexes, $[Cu(L^1)_2]ClO_4$ (**1**) and $[Cu(L^2)_2]ClO_4$ (**2**) (figure 1). The structures of *N*,*N*′-*bis*[1-(4-chlorophenyl)ethylidene]ethane-1,2-diamine ($\mathbf{L^1}$) and $[Cu(L^1)_2]ClO_4$ (**1**) and spectral properties and redox chemistry of these complexes are discussed.

2. Experimental

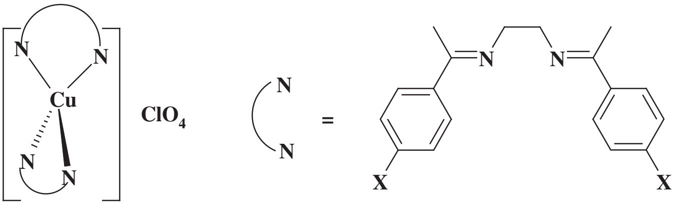
2.1. *General*

Elemental analyses were performed using a Heraeus CHN-O-RAPID elemental analyzer. Infrared spectra were recorded on a Bruker Tensor 27 instrument. Electronic absorption spectra were recorded on a JASCO V-570 spectrophotometer and reported as λ_{max} ($\log \varepsilon$). NMR spectra were obtained on a Bruker Avance DRX 250 (250 MHz) spectrometer. Proton chemical shifts are reported (ppm) relative to an internal standard of Me_4Si. All voltammograms were recorded with a three electrode system consisting of an Ag/AgCl reference electrode, a platinum wire counter electrode, and glassy carbon as a working electrode. A Metrohm multipurpose instrument model 693 VA processor with 694A VA stand was used. In all electrochemical experiments the test solution was purged with argon for at least 5 min.

All chemicals used were reagent grade and used as received. Solvents were purified by the methods given in [22]. $[Cu(CH_3CN)_4]ClO_4$ was freshly prepared according to the procedure provided in [23].

2.2. *Synthesis of* N,N′-bis*[1-(4-chlorophenyl)ethylidene]ethane-1,2-diamine* (L^1)

To a solution of 1-(4-chlorophenyl)ethanone (308 mg, 2 mmol) in 5 mL ethanol, a solution of ethane-1,2-diamine (60 mg, 1 mmol) in 5 mL ethanol was added, heated to reflux for 2 h. *N*,*N*′-*bis*[1-(4-chlorophenyl)ethylidene]ethane-1,2-diamine was obtained



Complex	X
1	Cl
2	NO_2

Figure 1. Chemical formulas of $\mathbf{L^1}$, $\mathbf{L^2}$, **1**, and **2**.

as a white microcrystalline precipitate, filtered off, washed with cold ethanol, and dried in air. Yield: 78%, m.p.: 96–97°C. IR (ν, cm^{-1}): 1618 ν(C=N). ^{1}H-NMR (250 MHz, CDCl$_3$): 2.15 (s, 6H, 2-CH$_3$); 3.78 (s, 4H, –CH$_2$CH$_2$–); 7.40 (d, $J = 8.5$ Hz, 4H, Ar–H); 7.62 (d, $J = 8.5$ Hz, 4H, Ar–H). Anal. Calcd for $C_{18}H_{18}Cl_2N_2$ (%): C, 64.87; H, 5.44; N, 8.41. Found (%): C, 64.90; H, 5.45; N, 8.39.

2.3. *Synthesis of N,N′-*bis*[1-(4-nitrophenyl)ethylidene]ethane-1,2-diamine (L^2)*

To a solution of 1-(4-nitrophenyl)ethanone (330 mg, 2 mmol) in ethanol (20 mL), a solution of ethane-1,2-diamine (60 mg, 1 mmol) in ethanol (5 mL) was added and heated to reflux for 1 h. The yellow microcrystalline precipitate was filtered off, washed with cold ethanol, and dried in air. Yield: 85%, m.p.: 112–113°C. IR (cm^{-1}, KBr): 1610 (C=N); ν(N=O) 1352 and 1545. ^{1}H-NMR (250 MHz, CDCl$_3$): 2.18 (s, 6H, 2-CH$_3$); 3.79 (s, 4H, –CH$_2$CH$_2$–); 7.45–7.52 (m, 8H, Ar–H). Anal. Calcd for $C_{18}H_{18}N_4O_4$ (%): C, 61.01; H, 5.12; N, 15.81. Found (%): C, 60.08; H, 5.13; N, 15.84.

2.4. *Synthesis of* bis[N, N′-bis*[1-(4-chlorophenyl)ethylidene]ethane-1,2-diamine] copper(I) perchlorate (1)*

To a stirring solution of *N,N′-bis*[1-(4-chlorophenyl)ethylidene]ethane-1,2-diamine (66.6 mg, 0.2 mmol) in 3 mL acetonitrile, [Cu(MeCN)$_4$]ClO$_4$ (32.8 mg, 0.1 mmol) was added, and the solution was stirred for 20 min. The colorless solution turned deep orange. The volume of the solvent was reduced under reduced pressure to about 2 mL and diffusion of diethylether vapor into the concentrated solution gave red crystals suitable for X-ray studies. The crystals were filtered off and washed with diethylether : acetonitrile 9 : 1 (v/v) and dried under vacuum. Yield: 91%, m.p.: 196–198°C. IR (cm^{-1}, KBr): ν(C=N) 1589; ν(Cl–O) 1080. ^{1}H-NMR (250 MHz, CDCl$_3$): 2.25 (s, 6H, 2-CH$_3$); 3.81 (s, 4H, –CH$_2$CH$_2$–); 7.55 (d, $J = 8.1$ Hz, 4H, Ar–H); 7.82 (d, $J = 8.1$ Hz, 4H, Ar–H). Anal. Calcd for $C_{36}H_{36}Cl_5CuN_4O_4$ (%): C, 52.13; H, 4.37; N, 6.75. Found (%): C, 52.16; H, 4.35; N, 6.74.

2.5. *Synthesis of* bis[N, N′-bis*[1-(4-nitrophenyl)ethylidene]ethane-1,2-diamine] copper(I) perchlorate (2)*

Complex **2** was prepared by a procedure similar to **1** using 70.8 mg (0.2 mmol) of *N,N′-bis*[1-(4-nitrophenyl)ethylidene]ethane-1,2-diamine. Dark red crystals were collected by filtration and dried under vacuum. Yield: 94%, m.p.: 203–205°C. IR (cm^{-1}, KBr): ν(C=N) 1585; ν(N=O) 1351 and 1549; ν(Cl–O) 1090. ^{1}H-NMR (250 MHz, CDCl$_3$): 2.30 (s, 6H, 2-CH$_3$); 3.86 (s, 4H, –CH$_2$CH$_2$–); 7.53–7.61 (m, 8H, Ar–H). Anal. Calcd for $C_{36}H_{36}ClCuN_8O_{12}$ (%): C, 49.60; H, 4.16; N, 12.85. Found (%): C, 49.65; H, 4.15; N, 12.83.

2.6. *Crystal structure determination*

Diffraction data for **L^1** were collected on a Bruker PLATFORM/SMART 1000 CCD diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å).

An empirical absorption correction was applied using SADABS [24] and the structure solved by Patterson methods [25] and refined against F^2 with a full-matrix least-squares algorithm using the SHELXL-97 software package [26]. Diffraction data for **1** were collected on a Bruker SMART APEX2 CCD area detector using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Preliminary orientation matrices were obtained from the first frames using APEX2 [27]. An empirical absorption correction was applied using SADABS [24]. The structures were solved using direct methods and refined by the full-matrix least-squares method on F^2 data using SHELXTL [28]. All H-atoms were positioned geometrically and refined using a riding model with d(C–H) = 0.93 Å, $U_{\text{iso}} = 1.2U_{\text{eq}}$ (C).

3. Results and discussion

3.1. *Ligands and complexes*

N,*N*′-*bis*[1-(4-chlorophenyl)ethylidene]ethane-1,2-diamine (**L^1**) and *N*,*N*′-*bis*[1-(4-nitrophenyl)ethylidene]ethane-1,2-diamine (**L^2**) were prepared by condensation of 1-(4-chlorophenyl)ethanone and 1-(4-nitrophenyl)ethanone with ethylenediamine. Complexes **1** and **2** were synthesized by reaction of the ligands with $[Cu(CH_3CN)_4]ClO_4$ in acetonitrile. These complexes are soluble in chloroform, dichloromethane, THF, and acetone, and stable in air as solids and solution for 3 weeks.

3.2. *Structures of the L^1 and 1*

A view of **L^1** and the cation of **1** along with the atom-numbering scheme are shown in figures 2 and 3, respectively. The crystallographic data are summarized in table 1, and selected bond distances and angles are given in table 2. **L^1** lies across a crystallographic inversion center and adopts an *E* configuration with respect to the C=N bond. The asymmetric unit is composed of one-half of the molecule. The C=N bond length (1.274(2) Å) is within normal ranges and comparable with values found in related structures (i.e. 1.268(2) Å for *N*,*N*′-*bis*(3-bromobenzylidene)ethane-1,2-diamine) [29, 30]. The imine groups are approximately coplanar with the benzene ring; the dihedral

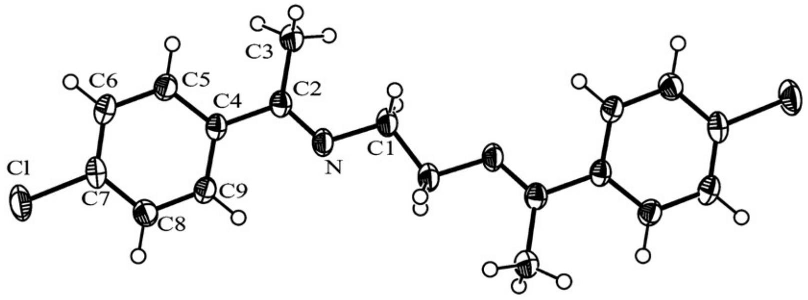


Figure 2. Structure of **L^1** showing the atom labeling scheme. Thermal ellipsoids are of 50% probability.

angle between benzene plane and the plane defined by N$-$C2$-$C4 is 18.64(2)°. The planar units are parallel, but extend in opposite directions from the methylene bridge.

The geometry about Cu^I in **1** is distorted by bite angles of the bulky chelating ligand. The intraligand N(4)–Cu(1)–N(3) and N(1)–Cu(1)–N(2) angles are 86.24(7)° and 86.48(7)°, respectively. These angles are fixed by the bite size of the ligand (2.846(2) Å for *d*(N(1)–N(2)) and 2.808(2) Å for *d*(N(3)–N(4)) in the range 82°–89° for ethylenediamine chelate compounds [17–20]. The N(4)–Cu(1)–N(1) and N(3)–Cu(1)–N(2) angles (142.92(7)° and 138.39(7)°, respectively) are larger than those for a tetrahedral complex.

The dihedral angle between the two chelate rings is 59.00(6)°. The average Cu–N bond distance (2.065 Å) is similar to that found in $[Cu(mb_2en)_2]^+$ (2.090 Å); and in other Cu^I pseudotetrahedral complexes (typical $Cu\text{–}N_{av} = 2.055$ Å) [17–21]. The average C=N bond length (1.285 Å) in the complex is only 0.011 Å longer relative to that in the ligand.

The average torsion angle between the Ph rings and imine moieties in **1** is 26.90°. This degree of coplanarity, which allows for increased π-conjugation in the ligand, is consistent with the observed C–C bond distances in the coordinated ligand: C(1)–C(7) 1.492(3) Å < C(7)–C(8) 1.516(3) Å [19].

While $\mathbf{L^1}$ is approximately planar, coordinated ligands twist along the C–C bond and act as bidentate ligands. Linking C9 is 0.325 Å above the MN2 plane defined by N1–Cu1–N2, while C10 is 0.361 Å below (corresponding values for N3–Cu–N4 are 0.380 Å for C9′ and 0.257 Å for C10′). The average dihedral angle between the benzene planes

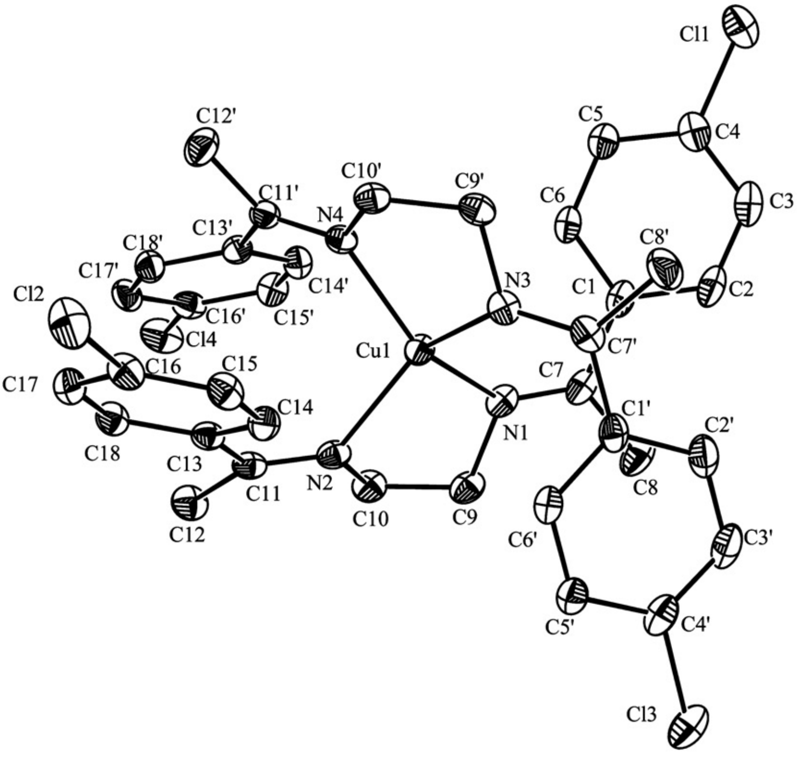


Figure 3. Structure of $[Cu(\mathbf{L^1})_2]^+$ of **1** in the crystal, showing the atom labeling scheme. Thermal ellipsoids are 50% probability. Hydrogen atoms are omitted for clarity.

Table 1. Crystal data and refinement details for **L^1** and **1**.

	L^1	**1**
Formula	$C_{18}H_{18}Cl_2N_2$	$C_{36}H_{36}Cl_5CuN_4O_4$
Formula weight	333.24	829.48
Temperature (K)	198(2)	120(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (No. 14)	*P21*/*n*
Unit cell dimensions (Å, °)		
a	4.2180(8)	8.2308(5)
b	10.211(2)	22.5207(13)
c	18.953(4)	19.6154(11)
β	91.312(2)	98.3030(10)
V (Å^3)	816.1(3)	3597.9(4)
Z	2	4
Density (g cm^{-3})	1.356	1.531
μ (mm^{-1})	0.395	1.024
F(000)	348	1704
Crystal size (mm^3)	0.42 × 0.30 × 0.26	0.50 × 0.45 × 0.30
θ range for data collection	2.15–27.46	1.81–28.00
Index ranges	$-5 \le h \le 5$, $-12 \le k \le 13$, $-24 \le l \le 24$	$-10 \le h \le 10$, $-29 \le k \le 29$, $-25 \le l \le 25$
Reflections collected	5985	36,685
Independent reflections [R_{int}]	1879 ($R_{int} = 0.0219$)	8661 ($R_{int} = 0.0258$)
Reflections with [$I > 2\sigma(I)$]	1584	7376
Maximum and minimum transmission	0.9042 and 0.6997	0.733 and 0.609
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1879/0/101	8661/0/455
Goodness-of-fit on F^2	1.065	1.001
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0408$, $wR_2 = 0.1038$	$R_1 = 0.0387$, $wR_2 = 0.0917$
R indices (all data)	$R_1 = 0.0493$, $wR_2 = 0.1114$	$R_1 = 0.0476$, $wR_2 = 0.1004$
Weighting scheme[a] x/y	0.06/0.24	0.05/4.9
Largest difference peak and hole (e Å^{-3})	0.361 and −0.276	0.690 and −0.450

[a] $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]^{-1}$, $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected bond lengths and angles of **L^1** and **1**.

L^1		**1**	
N–C1	1.464(2)	Cu1–N4	2.038(2)
N–C2	1.274(2)	Cu1–N1	2.066(2)
C2–C4	1.494(2)	Cu1–N3	2.070(2)
C2–C3	1.505(2)	Cu1–N2	2.087(2)
C1–N–C2	119.39(1)	N4–Cu1–N1	142.92(7)
N–C2–C3	124.67(1)	N4–Cu1–N3	86.24(7)
N–C2–C4	116.69(1)	N1–Cu1–N3	106.13(7)
		N4–Cu1–N2	107.49(6)
		N1–Cu1–N2	86.48(7)
		N3–Cu1–N2	138.39(7)

and the planes defined by N=C−C (imine moieties) is 27.67°, indicating that the coordinated ligand twists from planarity, possibly due to steric hindrance. In spite of steric hindrance, each coordinated ligand adopts *E* configuration with respect to the C=N bonds.

Table 3. UV–Vis spectral data of ligands and complexes.

Compound	λ_{max} in nm ($\log \varepsilon$ in $M^{-1} cm^{-1}$)
$\mathbf{L^1}$	245 (4.01), 289 (3.99), 331 (3.92)
$\mathbf{L^2}$	255 (4.36), 298 (4.15), 349 (3.95)
1	249 (4.21), 309 (4.15), 465 (3.61)
2	258 (4.39), 315 (4.07), 485 (3.53)

3.3. *Infrared spectra*

IR spectral assignments of the Schiff-base ligands and complexes are based on typical group frequencies. The strong absorption at 1618 cm^{-1} for $\mathbf{L^1}$ and 1610 cm^{-1} for $\mathbf{L^2}$ are assigned to the azomethine, ν(C=N) [31]; these bands shift to lower wavenumbers in the complexes, 1589 cm^{-1} for **1** and 1585 cm^{-1} for **2**, from coordination of the nitrogen to copper. The nitro ν(N–O) strong bands at 1352 and 1545 cm^{-1} for $\mathbf{L^2}$ [31] appear at 1351 and 1549 cm^{-1} in **2**. A strong band at about 1085 cm^{-1} in the IR spectra of the complexes is a characteristic of perchlorate [31].

3.4. *^{1}H NMR spectra*

The ^{1}H-NMR spectra show phenyl protons at 7.4–7.6 ppm in the ligands. The aryl proton signals of complexes are shifted to lower field than those in the free ligands. The methyl protons of $\mathbf{L^1}$ and $\mathbf{L^2}$ and complexes show a singlet at *ca* 2.2 ppm and the methylene protons a singlet at *ca* 3.8 ppm. The sharp NMR peaks are indicative of diamagnetic copper(I). The appearance of a unique signal for each type of proton in $CDCl_3$ solution indicates that the symmetry of the molecules (ligands and complexes) is retained in solution.

3.5. *Spectroscopic and electrochemical properties*

The absorption spectra of $\mathbf{L^1}$ and $\mathbf{L^2}$ have two bands in the 200 to 300 nm range (table 3) attributed to the intraligand π–π^* transition. In $CHCl_3$, the absorption spectra of complexes are similar to the ligands. In addition to the high energy absorption bands, **1** shows a broad low-energy band with $\lambda_{max} = 465$ nm region; this accounts for the red color of the complex, also observed for **2** ($\lambda_{max} = 485$ nm), due to the low-energy transition involving the low-lying unoccupied π^* orbital in diimine ligand and the electron-rich copper(I). The red shift of the first MLCT band of **2** as compared to **1** points to the high π-acidity of $\mathbf{L^2}$ relative to $\mathbf{L^1}$.

Redox properties of **1** and **2** were examined by cyclic voltammetry using a glassy carbon working electrode in CH_3CN solution and in the presence of TBAP as a supporting electrolyte. The potentials are expressed with reference to the silver–silver chloride electrode (RE). The ligands are electroinactive in the working potential region.

The complexes undergo a quasi-reversible oxidation–reduction reaction ($E_{pa} = 0.51, E_{pc} = 0.62$ for **1** and $E_{pa} = 0.48, E_{pc} = 0.82$ for **2**) (figure 4). The quasi-reversible character is from the $\Delta E_p(E_{pa} - E_{pc})$ values under the conditions of measurement [32]. The ratio of the anodic and cathodic peak currents, (i_{pa}/i_{pc}), approaches 1 as the scan rate increases. The peak-to-peak separation increases as the

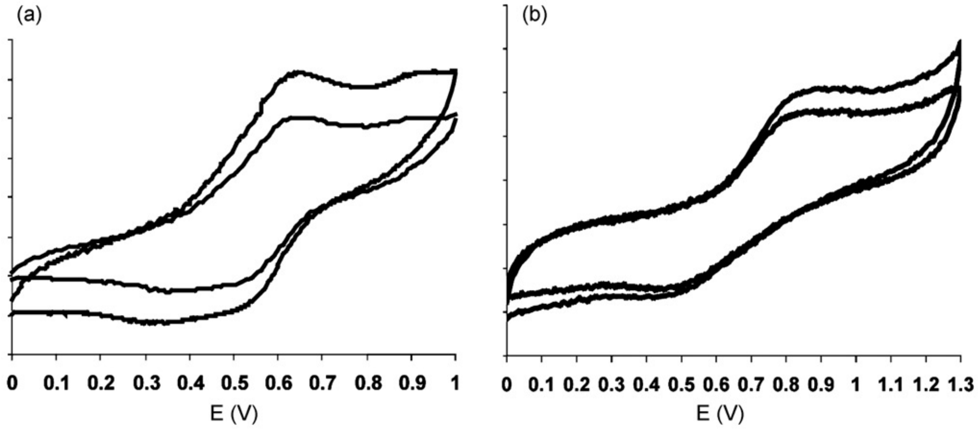


Figure 4. Cyclic voltammograms of $[Cu(\mathbf{L^1})_2]ClO_4$ (a) **1** and (b) $[Cu(\mathbf{L^2})_2]$ ClO_4 (**2**), in CH_3CN at 50 and $100\,mV\,s^{-1}$. (a) $c = 3 \times 10^{-3}$, (b) $c = 3.5 \times 10^{-3}$.

scan rate is changed from 50 to $300\,mV\,s^{-1}$. Similar redox behavior is observed for structurally related complexes [17–21].

The $Cu^{II/I}$ potential in a Cu^IN_4 chromophore is believed to increase with increase in the electron-donating or -withdrawing properties of the ligands and the resistance to tetrahedral distortion in the $Cu^{II}N_4$ chromophore [33]. Generally, assuming there are no extreme changes in the resistance to tetrahedral distortion that the ligands impart on the complex, this redox couple can be used to indicate the electron-donating or -withdrawing properties of the ligands by observing the shift in the $Cu^{2+/+}$ redox potentials. The lower redox potential is in accord with the observed lower energy of the MLCT band of **1** relative to that of **2** [34, 35].

4. Conclusion

From *N*,*N*′-*bis*[1-(4-chlorophenyl)ethylidene]ethane-1,2-diamine ($\mathbf{L^1}$) and *N*,*N*′-*bis*[1-(4-nitrophenyl)ethylidene]ethane-1,2-diamine ($\mathbf{L^2}$), two mononuclear copper(I) complexes $[Cu(L)_2]ClO_4$ (**1**–**2**) were synthesized. The crystal structure of **1** reveals a distorted tetrahedral configuration. ^{1}H-NMR data support the existence of Cu^I in **1** and **2**. The MLCT is red shifted by 20 nm in **2** over **1**. Comparison of the $[Cu(L)_2]^+$ complexes show a correlation between the spectroscopic and redox properties. Red shift of the MLCT absorption band is observed when the oxidation potential of the complex increases.

Supplementary material

Crystallographic data for $\mathbf{L^1}$ and **1** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos CCDC 710664 for $\mathbf{L^1}$ and 710665 for **1**. Copies of these data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk or by contacting, The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033).

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