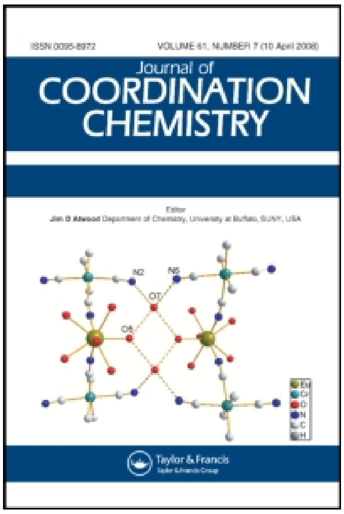


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and characterization of [Cu(mb$_2$en)$_2$]ClO$_4$ and [Cu(mb$_2$en)(PPh$_3$)$_2$]BPh$_4$: crystal structure of [Cu(mb$_2$en)$_2$]ClO$_4$

Saeed Dehghanpour[a]; Lida Fotouhi[a]; Mostafa Mohammadpour Amini[b]; Hamid Reza Khavasi[b]; KHadijeh Jahani[a]; Fatemeh Nouroozi[a]; Elham Zamanifar[a]
[a] Department of Chemistry, Alzahra University, Tehran 1993891176, Iran [b] Department of Chemistry, Shahid Beheshti University, Evin, Tehran 1983963113, Iran

To cite this Article Dehghanpour, Saeed , Fotouhi, Lida , Amini, Mostafa Mohammadpour , Khavasi, Hamid Reza , Jahani, KHadijeh , Nouroozi, Fatemeh and Zamanifar, Elham(2008) 'Synthesis and characterization of [Cu(mb$_2$en)$_2$]ClO$_4$ and [Cu(mb$_2$en)(PPh$_3$)$_2$]BPh$_4$: crystal structure of [Cu(mb$_2$en)$_2$]ClO$_4$', Journal of Coordination Chemistry, 61: 3, 455 — 463, First published on: 27 August 2007 (iFirst)

To link to this Article: DOI: 10.1080/00958970701360717
URL: http://dx.doi.org/10.1080/00958970701360717

Journal of Coordination Chemistry
Vol. 61, No. 3, 10 February 2008, 455–463

Taylor & Francis
Taylor & Francis Group

Synthesis and characterization of $[Cu(mb_2en)_2]ClO_4$ and $[Cu(mb_2en)(PPh_3)_2]BPh_4$: crystal structure of $[Cu(mb_2en)_2]ClO_4$

SAEED DEHGHANPOUR*†, LIDA FOTOUHI†, MOSTAFA MOHAMMADPOUR AMINI‡, HAMID REZA KHAVASI‡, KHADIJEH JAHANI†, FATEMEH NOUROOZI† and ELHAM ZAMANIFAR†

†Department of Chemistry, Alzahra University, Tehran 1993891176, Iran
‡Department of Chemistry, Shahid Beheshti University, Evin, Tehran 1983963113, Iran

(*Received 27 January 2007; in final form 25 April 2007*)

The ligand, *N*,*N′*-*bis*-(4-methoxy-benzylidene)-ethane-1,2-diamine (mb_2en), and its corresponding copper(I) complexes, $[Cu(mb_2en)_2]ClO_4$ (**1**), and $[Cu(mb_2en)(PPh_3)_2]BPh_4$ (**2**), have been synthesized and characterized by CHN analyses, ^1H and ^{13}C-NMR, IR, and UV-Vis spectroscopies. The crystal and molecular structure of $[Cu(mb_2en)_2]ClO_4$ (**1**), were determined by X-ray crystallography from a single-crystal. The coordination polyhedron about copper(I) is best described as a distorted tetrahedron. Quasi-irreversible redox behavior was observed for **1** and **2** ($E_{1/2} = 0.55$ and 0.95 V, respectively).

Keywords: Copper(I) complexes; Diimine ligand; Crystal structure; Electrochemistry

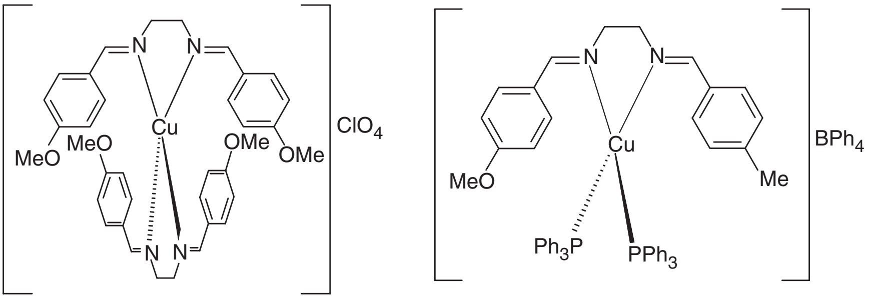
1. Introduction

Many advances in the chemistry of copper complexes have been achieved through the use of diimines ligands. These complexes draw special attention because of instability, unusual structural features, applications in solar energy and supramolecular devices, catalytic activity in photo-redox reactions and the biological relevance of high potential copper complexes [1–3]. Most of these investigations have been on four-coordinate tetrahedral Cu(I) complexes of the type $[Cu(LL)_2]^+$ or $[Cu(LL)(P)_2]^+$, where LL is a diimine and P is a phosphine, because of the interdependence of their coordination geometry and redox and photochemical behavior [4–6]. Effort has been devoted to design and synthesis of pre-organized ligands to control the geometric and steric properties of metal ions. Steric crowding and π-acidity in a well designed ligand are the most important prerequisites for stability of copper(I) complexes and their redox, photophysical and photochemical behavior [7–10].

---

*Corresponding author. Email: Dehganpour_farasha@yahoo.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970701360717



1 **2**

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

In continuation of our work on the preparation of copper(I) diimine complexes with low lying MLCT transitions [11–14], here we report the synthesis and characterization of a ligand and its copper(I) complexes (figure 1). The structures, spectral properties, and redox chemistry of these complexes are also investigated.

2. Experimental

2.1. *General*

Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with care.

Elemental analyses were performed by 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 in parts per million (ppm) relative to an internal standard of Me_4Si. All voltamograms were recorded with a three electrode system consisting of a Ag/AgCl reference electrode, a platinum wire counter electrode, and Pt 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 were reagent grade and used as received. Solvents used for the reactions were purified by literature methods [15]. $[Cu(CH_3CN)_4]ClO_4$ and $[Cu(CH_3CN)_4]BPh_4$ were freshly prepared according to literature procedures [16].

2.2. *Synthesis of* N,N′-bis-*(4-methoxy-benzylidene)-ethane-1,2-diamine, (L)*

To a solution of 4-methoxybenzaldehyde (272 mg, 2 mmol) in 20 mL ethanol was added a solution of ethylenediamine (60 mg, 1 mmol) in 10 mL ethanol with stirring for 2 h. The *N*,*N*′-dibenzylidene-ethane-1,2-diamine, (mb_2en) was obtained as a white microcrystalline precipitate. It was then filtered off, washed with cold ethanol, and dried in air. Yield: 90%. Anal. Calcd for $C_{18}H_{20}N_2O_2$ (%): C 72.95, H 6.80, N 9.45; found C 72.96, H 6.81, N 9.44. UV-Vis: λ(log ε) ($CHCl_3$): 275 (4.80). IR (cm^{-1}, KBr): ν(C=N) 1610. ^{1}H-NMR (ppm, $CDCl_3$): 3.75 (s, 4H, NCH_2CH_2N); 3.91 (s, 6H, 2-OCH_3); 7.40–7.65 (m, 8Ar–*H*); 8.07 (s, 2H, 2C*H*=N). $^{13}C\{^1H\}$-NMR(ppm, $CDCl_3$): 61.52 (–$N^{13}CH_2{}^{13}CH_2N$–), 81.65 (–$O^{13}CH_3$), 126.52, 128.63, 152.81, 162.51 (^{13}C=N).

2.3. *Synthesis of [Cu(mb$_2$en)$_2$]ClO$_4$ (1)*

To a stirring solution of mb$_2$en (59.2 mg, 0.2 mmol) in 3 mL MeCN was added $[Cu(MeCN)_4]ClO_4$ (32.8 mg, 0.1 mmol), 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 ca 1 mL; diffusion of Et_2O vapor into the concentrated solution gave orange-red crystals suitable for X-ray studies. The crystals were filtered off and washed with Et_2O/MeCN 9 : 1 (v/v), and dried under vacuum. Yield: 90%. Anal. Calcd for $C_{36}H_{40}ClCuN_4O_8$ (%): C 57.21, H 5.33, N 7.41; found: C 57.21.24, H 5.33, N 7.41. UV-Vis: λ(log ε) ($CHCl_3$): 305 (4.90), 326 (4.79), 375 (3.52). IR (cm^{-1}, KBr): ν(C=N) 1575. ^{1}H-NMR (ppm, $CDCl_3$): 3.89 (s, 8H, NCH_2CH_2N); 4.05 (s, 12H, 4-OCH_3); 7.35–7.40 (m, 12Ar–*H*); 8.30 (s, 4H, 4C*H*=N). $^{13}C\{^1H\}$-NMR (ppm, $CDCl_3$): 62.32 ($N^{13}CH_2{}^{13}CH_2N$), 82.15 (–$O^{13}CH_3$), 127.95, 128.79, 152.83, 167.41 (^{13}C=N).

2.4. *Synthesis of [Cu(mb$_2$en)(PPh$_3$)$_2$]BPh$_4$ (2)*

To a 3 mL MeCN solution of $[Cu(CH_3CN)_4]BPh_4$ (54.8 mg, 0.1 mmol), 2 equivalent of Ph_3P (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 $[Cu(CH_3CN)_2(PPh_3)_2]BPh_4$, was added to a colorless stirred solution of 23.6 mg (0.1 mmol) mb$_2$en in 3 mL MeCN. The solution rapidly turned yellow, and was stirred for 20 min at room temperature. The reaction medium was concentrated under reduced pressure, until the first crystals appeared in the liquid phase. Bright-yellow crystals suitable for X-ray analysis were obtained by diffusion of Et_2O vapor into the concentrated solution. Yield: 95%. Anal. Calcd for $C_{78}H_{70}BCuN_2O_2P_2$ (%): C 77.83, H 5.86, N 2.33; found: C 77.84, H 5.85, N 2.32. UV-Vis: λ(log ε) ($CHCl_3$): 301 (4.65), 310 (4.57). IR (cm^{-1}, KBr): ν(C=N) 1689. ^{1}H-NMR (ppm, $CDCl_3$): 3.83 (s, 4H, NCH_2CH_2N); 3.91(s, 6H, 2-OCH_3); 7.05–7.55 (m, 38 Ar–*H*); 8.45 (s, 2H, 2C*H*=N). $^{13}C\{^1H\}$-NMR (ppm, $CDCl_3$): 63.16, (–$N^{13}C^{13}CN$–), 82.21, 127.96, 128.96, 129.23, 129.47, 132.32, 136.28, 137.18, 154.41, 164.75 (^{13}C=N).

2.5. *Crystal structure determination*

Crystals of **1** suitable for X-ray crystallography were obtained as described above. Diffraction data for **1** were collected on a STOE-IPDSII diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Data were collected and integrated using the stoe X-AREA software package [17]. A numerical absorption correction was applied using X-RED and X-SHAPE software [18]. The structure was solved by direct methods (SHELXS-97 [19]). The structure refinement was performed by a full-matrix least-squares method against F^2 (SHELXL-97 [19]). All non-H-atoms were refined anisotropically, all H-atoms were inserted in the calculated positions.

3. Results and discussion

3.1. *General characterization*

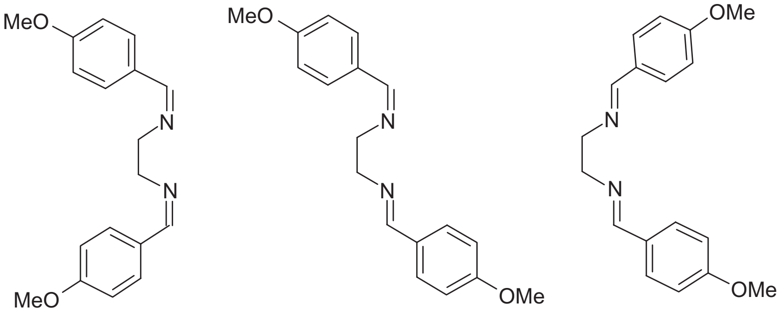
The IR spectra of the free ligands exhibit the characteristic imine band at $1610\,\mathrm{cm}^{-1}$. This band shifts to lower frequencies in the IR spectra of the corresponding complexes due to coordination of the imine nitrogen [20], at $1580\,\mathrm{cm}^{-1}$ in **1** and $1585\,\mathrm{cm}^{-1}$ in **2**. A strong band at $1085\,\mathrm{cm}^{-1}$ in the IR spectrum of **1** is characteristic of the asymmetric Cl–O stretching mode of the perchlorate anion [21].

Since no d–d transitions are expected for a d^{10} complex, the UV-vis bands are assigned to metal to ligand charge transfer (MLCT) or ligand-centered $\pi \rightarrow \pi^*$ transitions [22].

The absorption spectrum of $[Cu(mb_2en)_2]ClO_4$ (**1**), in chloroform features a band with a true maximum at 375 nm whereas $[Cu(mb_2en)(PPh_3)_2]BPh_4$ (**2**) shows a clear shoulder at 310 nm. 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) [23]. The high molar absorbtivity of this transition in **2** may stem from overlap of the MLCT and the π, π^* transitions of the coordinated Schiff base. Additional absorption bands are also observed in the spectra of **1** and **2** in chloroform in the UV region. The intensity of these bands are consistent with being assigned as ligand-centered $\pi \rightarrow \pi^*$ or/and charge-transfer transitions.

The ^1H NMR spectra and peak assignment are presented in the experimental section for each complex. These peaks are assigned based on the splitting of the resonance signals, spin coupling constants, and data in the literature, and are clearly in accord with the molecular structure determined by X-ray crystal structure analysis. The ^1H resonances of the coordinated mb_2en are observed in **1** and **2**. In **2**, the aromatic H atoms of the coordinated Ph_3P ligands and BPh_4^- anion overlap to some extent with those of the phenyl H atoms of mb_2en. Aside from the aromatic H-atoms, which appear at 7.38–7.45 ppm in complex **1** and 7.05–7.55 ppm in **2**, the two imine protons appear as a singlet at ca 8.30 ppm in **1** and at 8.45 in **2**. The downfield shift of iminic protons relative to the free ligand ($\Delta\delta = 0.23$ and 0.38 for **1**, **2**) can be attributed to the deshielding effect resulting from coordination of the ligand. The singlets at 3.89 ppm in **1** and at 3.83 ppm in **2** are assigned to the CH_2CH_2 H-atoms. The singlets at 4.02 ppm in **1** and at 3.91 ppm in **2** are assigned to the $-OCH_3$ groups. The sharp NMR resonances are indicative of diamagnetic Cu(I) complexes. In principle, geometrical isomers are possible with respect to the C=N bond as shown in figure 2. However, the appearance of a unique signal for each type of proton in $CDCl_3$ solution indicates that the symmetry of the molecules is retained in solution and only one isomer or exchange is present within the NMR time scale.

The ^{13}C-NMR spectrum of the free ligand exhibits 7 signals. In the ^{13}C-NMR spectra of **1** and **2**, the carbon atoms adjacent to the donor nitrogen atoms show downfield shifts in their positions compared with the free ligand ($\Delta\delta = 4.9$ and 2.21 for **1**, **2**), clearly indicating coordination of the ligand and retention of the structure in chloroform solutions [14].



Cis–cis Cis–trans Trans–trans

Figure 2. Possible geometrical isomers of the ligand.

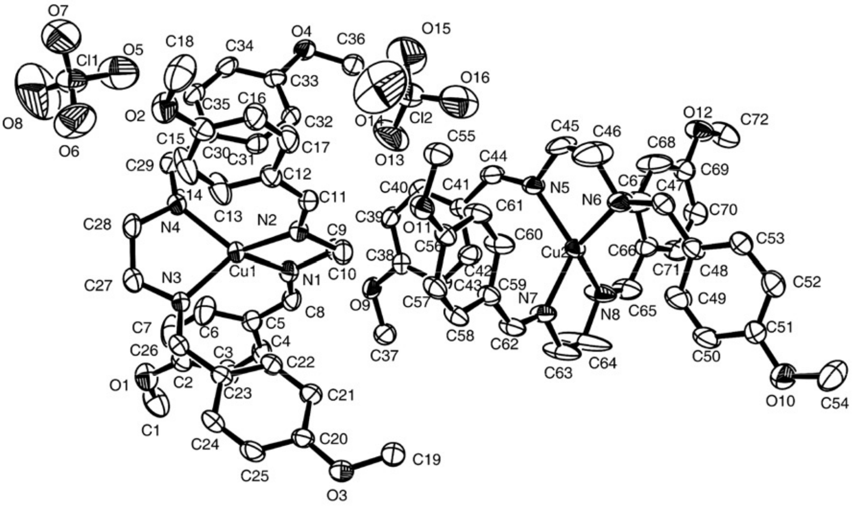


Figure 3. ORTEP view of the crystal structure of $[Cu(mb_2en)_2]ClO_4$ (**1**) showing the atom labeling scheme. The thermal ellipsoids enclose 50% of the electronic density. Hydrogen atoms are omitted for clarity.

3.2. *Crystal structure of $[Cu(mb_2en)_2]ClO_4$ (1)*

Complex **1**, along with the atom-numbering scheme, is shown in figure 3, and selected bond distances and angles are listed in table 2. The compound **1** crystallizes with two molecules per asymmetric unit probably due to some small conformational differences (1A and 1B, table 2). While a tetrahedral geometry might be expected for a four-coordinate Cu(I) center, the coordination environment around the metal in this complex is pseudotetrahedral with large angular distortion arising from the low intraligand N(1)–Cu(1)–N(2) chelate angle, 84.3(2)° and N(3)–Cu(1)–N(4) chelate angle, 83.4(2)° in 1A, and N(5)–Cu(2)–N(6) chelate angle, 83.4(3)° and N(7)–Cu(2)–N(8) chelate angle, 82.1(2)° in 1B. However, the N(1)–Cu(1)–N(4), 125.8(2)° angle and the N(2)–Cu(1)–N(3), 126.6(2)° angle in 1A and N(5)–Cu(2)–N(8), 126.1(3)° angle and the N(6)–Cu(2)–N(7), 126.4(3)° angle in 1B are larger than

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	$C_{36}H_{40}ClCuN_4O_8$
Formula weight	755.72
Crystal structure	Triclinic
Space group	$P\bar{1}$
Z	4
a (Å)	12.7781(19)
b (Å)	12.750(2)
c (Å)	22.450(4)
α (°)	81.812(15)
β (°)	78.971(14)
γ (°)	89.780(13)
V (Å^3)	3552.4(11)
Calculated density (Mg m^{-3})	1.413
Absorption coefficient (mm^{-1})	0.747
T (K)	293(2)
F(000)	1576
Crystal size (mm^3)	0.5 × 05 × 0.2
No. of reflection used	11,251
No. of parameters	914
λ(Mo-Kα) (Å)	0.71073
$\theta_{\max}$ (°)	24.06
R_1	0.0909 [$I \geq 2\sigma(I)$]
wR_2	0.2425
Goodness-of-fit on F^2	1.120

Table 2. Selected bond length (Å) and bond angle (°) of **1**.

1A		**1B**	
Cu(1)–N(1)	2.066(6)	N(5)–Cu(2)	2.118(7)
Cu(1)–N(2)	2.125(6)	N(6)–Cu(2)	2.075(6)
Cu(1)–N(3)	2.062(6)	N(7)–Cu(2)	2.075(6)
Cu(1)–N(4)	2.108(6)	N(8)–Cu(2)	2.038(6)
N(1)–C(9)	1.493(9)	C(45)–N(5)	1.470(11)
N(1)–C(8)	1.256(9)	C(44)–N(5)	1.282(10)
N(2)–C(10)	1.469(9)	C(46)–N(6)	1.494(17)
N(2)–C(11)	1.275(9)	C(47)–N(6)	1.296(11)
N(1)–Cu(1)–N(2)	84.3(2)	N(8)–Cu(2)–N(7)	82.1(2)
N(2)–Cu(1)–N(3)	126.6(2)	N(7)–Cu(2)–N(6)	126.4(3)
N(2)–Cu(1)–N(4)	122.1(2)	N(8)–Cu(2)–N(6)	123.1(4)
Cu(1)–N(1)–C(8)	137.0(5)	Cu(2)–N(5)–C(44)	137.3(5)
Cu(1)–N(1)–C(9)	106.3(4)	Cu(2)–N(5)–C(45)	104.7(6)
C(8)–N(1)–C(9)	115.9(6)	C(44)–N(5)–C(45)	117.7(7)
N(1)–Cu(1)–N(4)	125.8(2)	N(8)–Cu(2)–N(5)	126.1(3)
N(3)–Cu(1)–N(4)	83.4(2)	N(6)–Cu(2)–N(5)	83.4(3)
Cu(1)–N(2)–C(10)	107.1(4)	Cu(2)–N(6)–C(46)	106.3(7)
Cu(1)–N(2)–C(11)	137.7(5)	Cu(2)–N(6)–C(47)	137.6(6)
C(10)–N(2)–C(11)	114.4(6)	C(47)–N(6)–C(46)	116.0(8)

those of a tetrahedral complex. The average Cu–N bond distances are 2.090 Å, comparable to those reported for $[Cu(dpdmp)_2]^+$ (2.047 Å; dpdmp = 2,9-diphenyl-4,7-dimethyl-1,10-phenanthroline) [24].

Despite the fact that the donor N-atoms are sp^2-hybridized, the chelate ring is significantly puckered in this complex, and the deviations from 120° angle about the

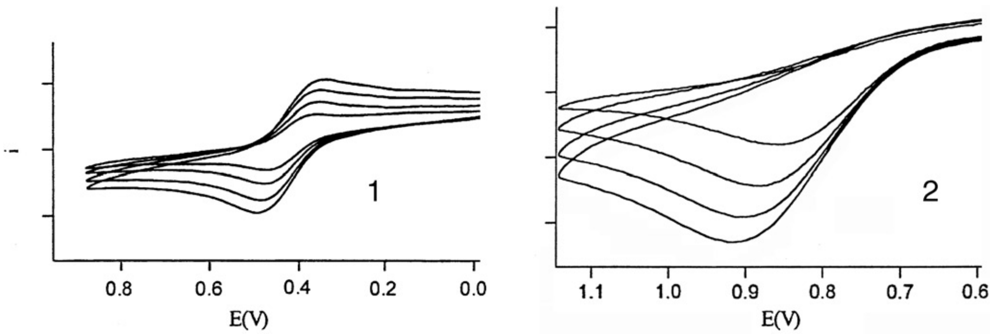


Figure 4. Cyclic voltammograms of $[Cu(mb_2en)_2]ClO_4$ (**1**) and $[Cu(mb_2en)(PPh_3)_2]BPh_4$ (**2**) in CH_2Cl_2 at 293 K. Scan rate: 50, 200, 350, 500 mV s^{-1}. (1) $c = 1 \times 10^{-3}$, (2) $c = 1.5 \times 10^{-3}$.

N-atom, Cu(1)–N(1)–C(8) (137.0(5)°), Cu(1)–N(1)–C(9) (106.3(4)°), C(8)–N(1)–C(9) (115.9(6)°) suggest strain in the chelate rings.

The Ph ring and the chain connecting the ring to the coordinated N-atom are roughly coplanar. The average angle between the plane of the Ph rings and the imine moieties is 173.95° and the ligand adopts a *trans*, *trans* configuration in these complexes (figure 2).

It is to be noted that the oxygen atoms of ClO_4^-, have a high thermal parameter due to data collection at room temperature. We tried refining these atoms in two positions with reduced occupancy but while this model converged satisfactorily, there was no decrease in the *R* value and therefore we consider that our original refinement is the best that can be achieved.

4. Electrochemistry

The electrochemical behavior of the complexes was examined using cyclic voltammetry in CH_2Cl_2. The ligand mb_2en is electroinactive in the working potential region. Complex **1** show a quasireversible $Cu^{II/I}$ couple with an $E_{1/2}$ of 0.43 V (figure 4). 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 105 to 165 mV, as the scan rate is changed from 50 to 500 mV s^{-1} [25]. The cyclic voltammogram of **2** in CH_2Cl_2 displays only one anodic peak ($E_{1/2} = 0.84$ 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^IN_4 chromophore is believed to increase with increasing π-acidity of the ligands and the resistance to tetrahedral distortion occurring in the corresponding $Cu^{II}N_4$ chromophore [26, 27]. Although, a higher degree of conjugation exists in **1** relative to **2**, the bulkier ligands in **2** preventing the inner-sphere reorganization to a flattened tetrahedron, more appropriate to Cu(II), play a key role in shifting the oxidation potential to higher values for **2** relative to **1**.

Supplementary material

Crystallographic data (excluding structure factors) for the structure **1** reported in this article have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 634974. 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; Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

The authors gratefully acknowledge the partial financial support from the research council of Alzahra University and the Office of the Vice-President for Research Affairs of Shahid Beheshti University.

References

[1] N. Armaroli. *Chem. Soc. Rev.*, **30**, 113 (2001).

[2] S. Sakaki, T. Kuroki, T. Hamada. *J. Chem. Soc. Dalton Trans.*, **6**, 840 (2002).

[3] C.A. Luchaco-Cullis, H. Mizutani, K.E. Murphy, A.H. Hoveyda. *Angew Chem. Int. Ed.*, **40**, 1456 (2001).

[4] F. Franceschi, M. Guardigli, E. Solari, C. Floriani, A. Chiesivilla, C. Rizzoli. *Inorg. Chem.*, **36**(18), 4099 (1997).

[5] M. Riklin, D. Tran, X.H. Bu, L.E. Laverman, P.C. Ford. *J. Chem. Soc. Dalton Trans.*, **12**, 1813 (2001).

[6] S. Chowdhury, G.K. Patra, M.G.B. Drew, N. Chattopadhyay, D. Datta. *J. Chem. Soc. Dalton Trans.*, **3**, 235 (2000).

[7] M.T. Miller, T.B. Karpishin. *Inorg. Chem.*, **38**, 5246 (1999).

[8] A. Livoreil, J.P. Sauvage, N. Armaroli, V. Balzani, L. Flamigni, J.B. Ventura. *J. Am. Chem. Soc.*, **119**, 12114 (1997).

[9] M. Ruthkosky, C.A. Kelly, F.N. Castellano, G.J. Meyer. *Coord. Chem. Rev.*, **171**, 309 (1998).

[10] C. Kutal. *Coord. Chem. Rev.*, **99**, 213 (1990).

[11] S. Dehghanpour, A.H. Mahmoudkhani, M. Amirnasr. *Struct. Chem.*, **17**, 255 (2006).

[12] R. Hadjikhani, S. Dehghanpour, A. Mahmoudi, F. Mojahed. *Z. Anorg. Allg. Chem.*, **632**, 723 (2006).

[13] S. Meghdadi, M. Amirnasr, K.J. Schenk, S. Dehghanpour. *Helv. Chim. Acta*, **85**, 2807 (2002).

[14] M. Amirnasr, G. Kickelbick, S. Dehghanpour. *Helv. Chim. Acta*, **89**, 274 (2006).

[15] D.D. Perrin, W.L. Armarego, D.R. Perrin. *Purification of Laboratory Chemicals*, 2nd Edn, Pergamon, New York (1990).

[16] S. Dehghanpour, R. Kempe, S. Balireddi, L. Fotouhi, F. Tabasi, S. Salek. *Z. Anorg. Allg. Chem.*, **14**, 2321 (2006).

[17] Stoe & Cie. *X–RED, vesion 1.28b, Program for Data Reduction and Absorption Correction, Stoe & Cie GmbH*, Darmatadt, Germany (2005).

[18] Stoe & Cie. *X–SHAPE, vesion 2.05: Program for Crystal Optimization for Numerical Absorption Correction, Stoe & Cie GmbH*, Darmatadt, Germany (2004).

[19] G.M. Sheldrick. *SHELX97. Program for Crystal Structure Solution and Refinement*, University of Göttingen, Germany (1997).

[20] S. Dehghanpour, N. Bouslimani, R. Welter, F. Mojahed. *Polyhedron*, **26**, 154 (2007).

[21] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Complexes*, 4th Edn, Wiley, New York (1992).

[22] A.A. DelPaggio, D.R. McMillin. *Inorg. Chem.*, **22**, 691 (1983).

[23] R.A. Rader, D.R. McMillin, M.T. Buckner, T.G. Matthews, D.J. Casadonte, R.K. Lengel, S.B. Whittaker, L.M. Darmon, F.E. Lytle. *J. Am. Chem. Soc.*, **103**, 5906 (1981).

[24] C.T. Cunnighum, J.J. Moore, K.L.H. Cunningham, P.E. Fanwick, D.R. McMillin. *Inorg. Chem.*, **39**, 3638 (2000).
[25] A.J. Bard, L.R. Faulkner. *Electrochemical Methods, Fundamentals and Applications*, John Wiley & Sons, New York (1980).
[26] M.T. Miller, P.K. Gantzel, T.B. Karpishin. *Inorg. Chem.*, **38**, 3414 (1999).
[27] M.K. Eggleston, D.K. Crites, D.R. McMillin. *J. Phys. Chem. A*, **102**, 5506 (1998).