

## Synthesis, Characterization, and Crystal Structures of $[\text{Cu}(\text{ca}_2\text{en})_2]\text{ClO}_4$ , and $[\text{Cu}(\text{ca}_2\text{en})(\text{PPh}_3)_2]\text{ClO}_4$ Complexes

by Soraia Meghdadi<sup>a)</sup>, Mehdi Amirnasr<sup>\*a)</sup>, Kurt J. Schenk<sup>b)</sup>, and Saeed Dehghanpour<sup>c)</sup>

<sup>a)</sup> Department of Chemistry, Isfahan University of Technology, Isfahan 84156-83111, Iran

<sup>b)</sup> Institut de cristallographie de l'Université de Lausanne, BSP Dorigny, CH-1015 Lausanne

<sup>c)</sup> Department of Chemistry, Tarbiat Modarres University, P.O. Box 14155-4838 Tehran, Iran

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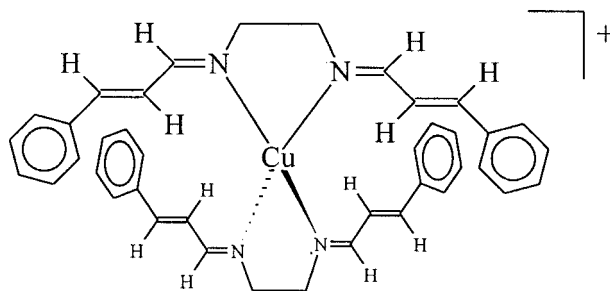
Synthesis, spectroscopy, and crystal structures of  $[\text{Cu}(\text{ca}_2\text{en})_2]\text{ClO}_4$  (**1**) and  $[\text{Cu}(\text{ca}_2\text{en})(\text{PPh}_3)_2]\text{ClO}_4$  (**2**) ( $\text{ca}_2\text{en} = N,N'$ -bis(*trans*-cinnamaldehyde)ethylenediimine) are reported. Compound **1** crystallizes in the orthorhombic space group *Pbca*, with  $a = 12.5647(7)$ ,  $b = 21.8203(11)$ ,  $c = 27.992(2)$  Å,  $V = 7674.3(7)$  Å<sup>3</sup>,  $Z = 8$ . Compound **2** crystallizes in the triclinic space group *P* $\bar{1}$ , with  $a = 13.0540(11)$ ,  $b = 14.2935(13)$ ,  $c = 14.9863(13)$  Å,  $\alpha = 84.130(2)$ ,  $\beta = 69.761(2)$ ,  $\gamma = 87.749(2)^\circ$ ,  $V = 2609.8(4)$  Å<sup>3</sup>,  $Z = 2$ . The coordination polyhedron about the Cu<sup>I</sup> center in the two complexes is best described as a distorted tetrahedron. The <sup>1</sup>H-NMR and electronic spectra of these complexes are also reported and discussed. The cyclic voltammetry of the complexes indicate a quasireversible redox behavior for complex **1** ( $E_{1/2} = 0.51$  V). However, complex **2** displays an irreversible oxidation wave at 0.91 V. A weak emission is observed for complex **2** in CHCl<sub>3</sub> at room temperature.

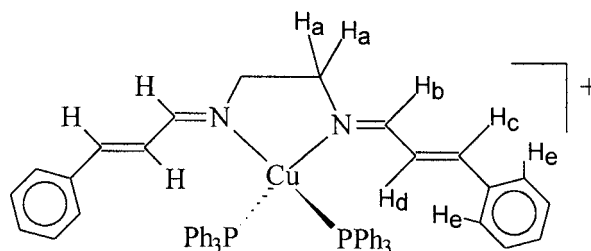
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**1. Introduction.** – The chemistry of many Cu<sup>I</sup>(phosphane) complexes have been investigated because of their luminescent properties [1–3] and their role as photosensitizers in isomerization reactions such as the conversion of norbornadiene to quadricyclane [4–6] or *cis*–*trans* isomerization of piperylene [7]. Several pseudotetrahedral Cu<sup>I</sup> complexes with diimine ligands such as phenanthroline and bipyridine are reported to be emissive at room temperature in solution. These complexes show an intense absorption band in the visible region, which has been assigned to metal-to-ligand charge-transfer (MLCT) [8–9]. The lifetimes of the MLCT excited state of these complexes is long enough to undergo bimolecular quenching [10–13] or show room-temperature emission [14–17].

Recent reports have indicated that, in addition to the effect from the steric properties of the diimine ligand, the lifetime of the MLCT excited state is influenced by the extent of  $\pi$ -delocalization in the diimine ligand [8]. Exploitation of these effects has served as the basis for synthetic tuning of excited-state properties, an area that has become an important focus of recent research efforts on approaches to solar-energy conversion [4][18]. One aspect of transition-metal chemistry that makes it attractive in this context is the geometrical and electronic-structural diversity that can be achieved by synthetic means.

In the present work, we report the synthesis, characterization, and crystal structure of two Cu<sup>I</sup> complexes with diimine and phosphane ligands, **1** and **2**, respectively. The electrochemistry and spectral properties of these complexes are also reported and discussed.



$$[\text{Cu}(\text{ca}_2\text{en})_2]\text{ClO}_4 \quad (1)$$


$$[\text{Cu}(\text{ca}_2\text{en})(\text{PPh}_3)_2]\text{ClO}_4 \quad (2)$$

**2. Experimental.** – 2.1. *General. Caution!* Perchlorate salts of metal complexes with org. ligands are potentially explosive and should be handled with care.

All chemicals used were reagent grade and used as received. Solvents used for the reactions were purified by literature methods [19].  $[\text{Cu}(\text{MeCN})_4]\text{ClO}_4$  was freshly prepared in MeCN according to the procedure in [20], washed with cold MeCN, and dried under vacuum. Elemental analyses were performed by means of a *Heraeus CHN-O-RAPID* elemental analyzer. IR Spectra were recorded on a *Shimadzu IR-460* instrument. Electronic absorption spectra were recorded on a *JASCO V-570* spectrophotometer;  $\lambda_{\text{max}}$  ( $\log \epsilon$ ) in nm.  $^1\text{H-NMR}$  Spectra were measured with *Bruker ACP-200* spectrometer at 200 MHz; chemical shifts  $\delta$  are reported in ppm relative to an internal standard of Me<sub>4</sub>Si. 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  $\text{CH}_2\text{Cl}_2$  with 50 mM  $\text{Bu}_4\text{NClO}_4$  (TBAP) as supporting electrolyte. In all electrochemical experiments, the solns. were purged with Ar gas for at least 5 min.

Emission and excitation spectra were recorded with a *Spex Fluorolog 122* spectrofluorimeter. A Xe-arc lamp source and a single monochromator were employed for the excitation. A double monochromator and a *Hamamatsu R2658* photomultiplier tube were used for detection in single-photon-counting mode. All spectra were corrected for spectral-detection response and were obtained after subtraction of the background contribution of  $\text{CHCl}_3$  solvent.

2.2.1. *Preparation of the Ligand.* The ligand *N,N'*-bis[(*E*)-3-phenylprop-2-en-1-ylidene]ethylenediamine ('bis(*trans*-cinnamaldehyde)ethylenediimine',  $\text{ca}_2\text{en}$ ) was synthesized as reported in [21].  $^1\text{H-NMR}$  (200 MHz,  $\text{CDCl}_3$ ): 3.74 (*s*,  $\text{NCH}_2\text{CH}_2\text{N}$ ); 6.85 (*dd*,  $^3J = 16, 9$ , 2  $\text{CH}=\text{CHCH}$ ); 7.05 (*d*,  $^3J = 16$ , 2  $\text{PhCH}=\text{CH}$ ); 7.30–7.56 (*m*, 10 arom. H); 8.05 (*d*,  $^3J = 9$ , 2  $\text{CHCH}=\text{N}$ ).

2.2.2. *Preparation of  $[\text{Cu}(\text{ca}_2\text{en})_2]\text{ClO}_4$  (1).* To a stirring soln. of  $\text{ca}_2\text{en}$  (57.6 mg, 0.2 mmol) in 3 ml MeCN was added  $[\text{Cu}(\text{MeCN})_4]\text{ClO}_4$  (32.8 mg, 0.1 mmol), and the soln. was stirred for 20 min. The colorless soln.

turned deep orange. The volume of the solvent was reduced under vacuum to *ca.* 1 ml. The diffusion of Et<sub>2</sub>O vapor into the conc. soln. gave orange-red crystals suitable for X-ray studies. The crystals were filtered off and washed with Et<sub>2</sub>O/MeCN 9:1 (*v/v*), and dried under vacuum. Yield: 67 mg (90%). UV (CHCl<sub>3</sub>): 300 (4.97), 326 (4.79), 400 (3.73). IR (KBr): 1628 (C=N). <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>): 4.04 (*s*, 2 NCH<sub>2</sub>CH<sub>2</sub>N); 6.73 (*dd*, <sup>3</sup>*J* = 16, 9, 4 CH=CHCH); 7.17 (*d*, <sup>3</sup>*J*(H,H) = 16, 4 PhCH=CH); 7.34–7.40 (*m*, 4 Ph); 8.29 (*d*, <sup>3</sup>*J* = 9, 4 CHCH=N). Anal. calc. for C<sub>40</sub>H<sub>40</sub>ClCuN<sub>4</sub>O<sub>4</sub>: C 64.83, H 5.38, N 7.49; found: C 64.94, H 5.45, N 7.57.

2.2.3. *Preparation of [Cu(ca<sub>2</sub>en)(PPh<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> (2).* To a 3-ml MeCN soln. of [Cu(CH<sub>3</sub>CN)<sub>4</sub>]ClO<sub>4</sub> (32.8 mg, 0.1 mmol), 2 equiv. of Ph<sub>3</sub>P (52.2 mg, 0.2 mmol) were added, and the soln. was stirred for 15 min. The solvent was evaporated under vacuum at r.t. The dry product [Cu(CH<sub>3</sub>CN)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> was added to a colorless stirring soln. of 29 mg (0.1 mmol) ca<sub>2</sub>en in 3 ml MeCN. The soln. rapidly turned yellow, and it was stirred for 20 min at r.t. The reaction medium was concentrated under vacuum, until the first crystals appeared in the liquid phase. Bright-yellow crystals suitable for X-ray analysis were obtained by diffusion of Et<sub>2</sub>O vapor into the conc. soln. Yield: 93 mg (95%). UV (CHCl<sub>3</sub>): 302 (4.67), 316 (4.61). IR (KBr): 1625 (C=N). <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>): 3.77 (*s*, NCH<sub>2</sub>CH<sub>2</sub>N); 6.42 (*dd*, <sup>3</sup>*J* = 15, 9, 2 CH=CHCH); 6.67 (*d*, <sup>3</sup>*J* = 7, 2 H<sub>o</sub> of Ph); 7.10–7.40 (*m*, 2 PhCH=CH, 38 arom. H); 8.44 (*d*, <sup>3</sup>*J* = 9, 2 CHCH=N). Anal. calc. for C<sub>56</sub>H<sub>50</sub>ClCuN<sub>2</sub>O<sub>4</sub>P<sub>2</sub>: C 68.79, H 5.12, N 2.80; found: C 68.92, H 5.16, N 2.87.

2.3. *X-Ray Analysis.* Crystals of **1** and **2** suitable for X-ray crystallography were obtained as described above. A summary of the key crystallographic information is listed in *Table 1* for both complexes. The data were collected on a *Bruker SMART-1000-CCD* system with graphite-monochromated MoK<sub>α</sub> radiation ( $\lambda = 0.71073$  Å). Based on their habit (*Table 1*), absorption corrections were computed by means of the XPREP program [22]. With the SAINT package [23], the data were corrected for *Lorentz* and polarization effects. The structure was solved with the help of DIRDIF 96 [24], and refined by means of SHELXTL 5.05 [22]. All non-H-atoms of **1** and **2** were refined anisotropically. The H-atoms were placed at the expected positions, made to ride on their associated C-atoms and refined isotropically. Selected bond lengths and angles for both complexes are listed in *Table 2*.

**3. Results and Discussion.** – 3.1. *General Characterization.* It is well-known that Cu<sup>I</sup> compounds are diamagnetic and colorless, except where color arises from the anion or charge-transfer bands. The most common group of [Cu(L)<sub>*n*</sub>]X complexes (X = BF<sub>4</sub>, PF<sub>6</sub>, or ClO<sub>4</sub>) contain unsaturated ligands with empty  $\pi^*$  orbitals, which can act as electron acceptors [9]. These complexes absorb strongly in the visible and near-UV regions owing to the presence of one or more metal-ligand charge-transfer (MLCT) absorption bands.

The UV/VIS spectrum of [Cu(ca<sub>2</sub>en)<sub>2</sub>]ClO<sub>4</sub> (**1**) in CHCl<sub>3</sub> exhibits an absorption band at 400 nm ( $\epsilon = 5400$  M<sup>-1</sup> cm<sup>-1</sup>) at 298 K. The first MLCT band of [Cu(ca<sub>2</sub>en)-(PPh<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> (**2**) in CHCl<sub>3</sub> appears as a shoulder at 316 nm ( $\epsilon = 40500$  M<sup>-1</sup> cm<sup>-1</sup>), which is shifted considerably (*ca.* 84 nm) relative to that of complex **1**. A similar shift (90 nm) has been reported in going from [Cu(dmp)<sub>2</sub>]<sup>+</sup> ( $\lambda_{\text{MLCT}} = 454$  nm) to [Cu(dmp)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> ( $\lambda_{\text{MLCT}} = 365$  nm) [25]. The high molar absorptivity of this transition in **2** may stem from the overlap of the MLCT and the  $\pi, \pi^*$  transition of the coordinated *Schiff* base ligand.

The <sup>1</sup>H-NMR spectra of the free ligand, and the two complexes **1** and **2** are illustrated in *Fig. 1*, and the spectral data and peak assignments are presented in *Experimental* for each complex. These peaks are assigned based on the splitting of the resonance signals, spin coupling constants, and the literature, and clearly conform with the X-ray molecular structure. The <sup>1</sup>H resonances of the coordinated ca<sub>2</sub>en are commonly observed in complexes **1** and **2**. In complex **2**, however, the aromatic H-atoms of the coordinated Ph<sub>3</sub>P ligands overlap to some extent with those of the Ph H-atoms of ca<sub>2</sub>en. Aside from the aromatic H-atoms, which appear at 7.34–7.40 ppm in complex **1** and 7.10–7.40 ppm in **2**, the two imine protons (H<sub>d</sub>) appear as a *doublet* at *ca.* 8.29 ppm in **1** and at 8.44 in **2**. The ethylenic H-atoms appear as a *doublet of doublet*

Table 1. *Crystal Data and Structure Refinement for 1 and 2*

Empirical formula	C <sub>40</sub> H <sub>40</sub> ClCuN <sub>4</sub> O <sub>4</sub>	C <sub>56</sub> H <sub>50</sub> ClCuN <sub>2</sub> O <sub>4</sub> P <sub>2</sub>
Habitus	{010}, {001} pinacoids, (100), (111)	{100}, {101} (121), (122)
Formula weight	739.75	975.91
Temp./K	293(2)	293(2)
Wavelength/Å	0.71073	0.71073
Crystal system	Orthorhombic	Triclinic
Space group	<i>Pbca</i>	<i>P</i> $\bar{1}$
<i>a</i> /Å	12.5647(7)	13.0540(11)
<i>b</i> /Å	21.8203(11)	14.2935(13)
<i>c</i> /Å	27.992(2)	14.9863(13)
$\alpha$ /°	90	84.130(2)
$\beta$ /°	90	69.761(2)
$\gamma$ /°	90	87.749(2)
<i>V</i> /Å <sup>3</sup>	7674.3(3)	2609.8(4)
<i>Z</i>	8	2
<i>D</i> <sub>calc.</sub> /g cm <sup>-3</sup>	1.281	1.242
$\mu$ /mm <sup>-1</sup>	0.683	0.576
<i>F</i> (000)	3088	1016
Crystal size/mm	0.16 × 0.36 × 0.54	0.4 × 0.2 × 0.1
$\theta$ /°	1.87 to 25.00	1.66 to 25.00
<i>h</i> / <i>k</i> / <i>l</i>	– 16,16/ – 28,28/ – 28,36	– 17,7/ – 16,18/ – 19,17
Reflections collected	41116	14743
Independent reflections	6753 [ <i>R</i> <sub>int</sub> = 0.0513]	9153 [ <i>R</i> <sub>int</sub> = 0.0331]
Absorption correction	Integration	Integration
Max. and min. transmission	0.9186 and 0.7442	0.9454 and 0.7895
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	6630/0/470	8975/26/590
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.085	1.274
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0466, <i>wR</i> <sub>2</sub> = 0.1391	<i>R</i> <sub>1</sub> = 0.0564, <i>wR</i> <sub>2</sub> = 0.1615
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0812, <i>wR</i> <sub>2</sub> = 0.1723	<i>R</i> <sub>1</sub> = 0.0823, <i>wR</i> <sub>2</sub> = 0.1878
Weights <sup>a</sup> )	[σ <sup>2</sup> ( <i>F</i> <sub>o</sub> <sup>2</sup> ) + (0.1 × <i>P</i> ) <sup>2</sup> ] <sup>-1</sup>	[σ <sup>2</sup> ( <i>F</i> <sub>o</sub> <sup>2</sup> ) + (0.1 × <i>P</i> ) <sup>2</sup> ] <sup>-1</sup>
Hole/e · Å <sup>-3</sup>	0.532 and – 0.252	0.580 and – 0.33

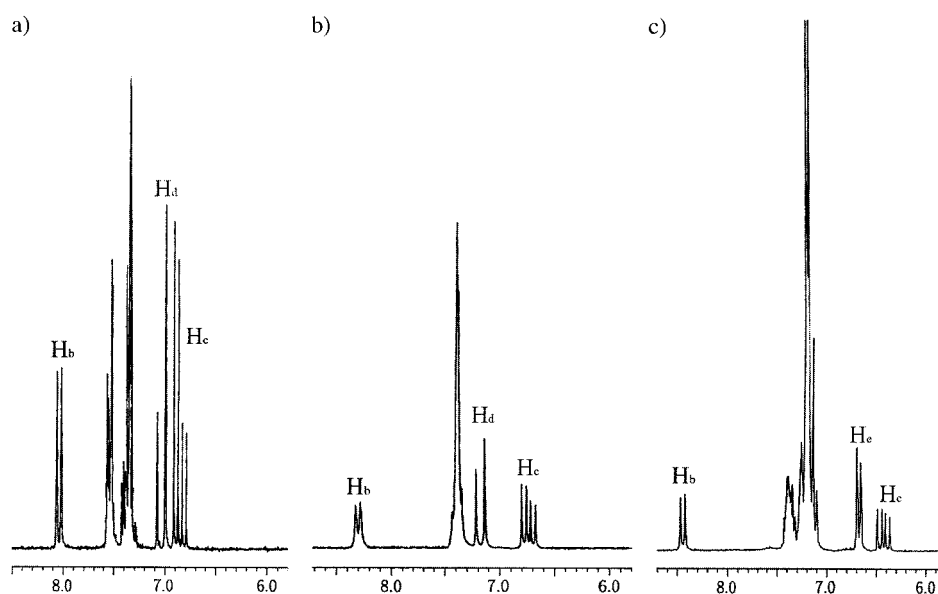
<sup>a</sup>)  $P = (\text{Max}(F_o^2, 0) + 2 \times F_c^2)/3$ .

(H<sub>b</sub>) at 6.73 ppm and as a *doublet* (H<sub>c</sub>) at 7.17 ppm in **1**, and at 6.42 and *ca.* 7.19 ppm in **2**. It is worth noting that the signals from H<sub>d</sub>-atoms in complex **2** overlap with those of the aromatic H-atoms. In contrast to complex **1**, the H<sub>e</sub>-atoms in complex **2** appear at 6.67 ppm due to the fact that these protons are located in the proximity of Ph rings of the bulky Ph<sub>3</sub>P ligands and in the region of the positive sign and, therefore, additionally shielded. The downfield shift of H<sub>b</sub>- and H<sub>d</sub>-atoms in **1** and **2** relative to the free ligand can be rationalized based on the positive charge delocalization onto the corresponding C-atoms through resonance resulting from the coordination of the ligand. The *singlet* at 4.04 ppm in **1** and at 3.77 ppm in **2** is assigned to the CH<sub>2</sub>CH<sub>2</sub> (H<sub>a</sub>) H-atoms.

The sharp NMR peaks are indicative of diamagnetic Cu<sup>I</sup> complexes. In principle, geometrical isomers are possible with respect to C=N bond as shown below. However, the appearance of a unique signal for each type of proton in CDCl<sub>3</sub> solution indicates that the symmetry of the molecules is retained in solution, and only one isomer is present.

Table 2. Selected Bond Lengths [Å] and Bond Angles [°] for **1** and **2**

<b>1</b>		<b>2</b>	
Cu–N(32)	2.048(3)	Cu–N(2)	2.108(3)
Cu–N(42)	2.033(3)	Cu–N(22)	2.096(3)
Cu–N(12)	2.083(3)	Cu–P(1)	2.2742(9)
Cu–N(22)	2.009(2)	Cu–P(2)	2.2753(10)
C(31)–N(32)	1.462(5)	C(1)–N(2)	1.469(5)
C(31)–C(41)	1.507(5)	C(1)–C(21)	1.513(7)
N(32)–Cu–N(42)	84.02(12)	N(22)–Cu–N(2)	82.65(13)
N(12)–Cu–N(22)	83.51(10)	P(1)–Cu–P(2)	123.31(3)
N(42)–Cu–N(12)	117.24(11)	N(22)–Cu–P(1)	107.95(9)
N(42)–Cu–N(22)	133.18(10)	N(22)–Cu–P(2)	112.04(9)
N(32)–Cu–N(12)	122.13(10)	N(2)–Cu–P(1)	111.10(10)
N(32)–Cu–N(22)	121.74(11)	N(2)–Cu–P(2)	112.38(10)
N(32)–C(31)–C(41)	107.7(3)	N(2)–C(1)–C(21)	108.6(3)
C(31)–N(32)–Cu	105.8(2)	C(1)–N(2)–Cu	108.5(2)
N(42)–C(41)–C(31)	109.8(3)	N(22)–C(21)–C(1)	109.1(4)
C(41)–N(42)–C(43)	108.8(3)	C(21)–N(22)–C(23)	117.3(3)

Fig. 1.  $^1\text{H-NMR}$  of the ligand  $\text{ca}_2\text{en}$  and  $\text{Cu}^{\text{I}}$  complexes **1** and **2**. a) Ligand; b)  $[\text{Cu}(\text{ca}_2\text{en})_2]\text{ClO}_4$ ; c)  $[\text{Cu}(\text{ca}_2\text{en})(\text{PPh}_3)_2]\text{ClO}_4$ .

3.2. X-Ray Structures of  $[\text{Cu}(\text{ca}_2\text{en})_2]\text{ClO}_4$  (**1**) and  $[\text{Cu}(\text{ca}_2\text{en})(\text{PPh}_3)_2]\text{ClO}_4$  (**2**). A view of the cation of complex **1**, including the atom-numbering scheme is illustrated in Fig. 2, and selected bond distances and angles are listed in Table 2. The coordination environment around the metal ion in this complex is pseudotetrahedral with large angular distortion, arising from the low intraligand N(32)–Cu–N(42), N(12)–Cu–N(22) chelate angles ( $84.02(12)^\circ$ ,  $83.51(10)^\circ$ ). These angles fixed by the bite size of the

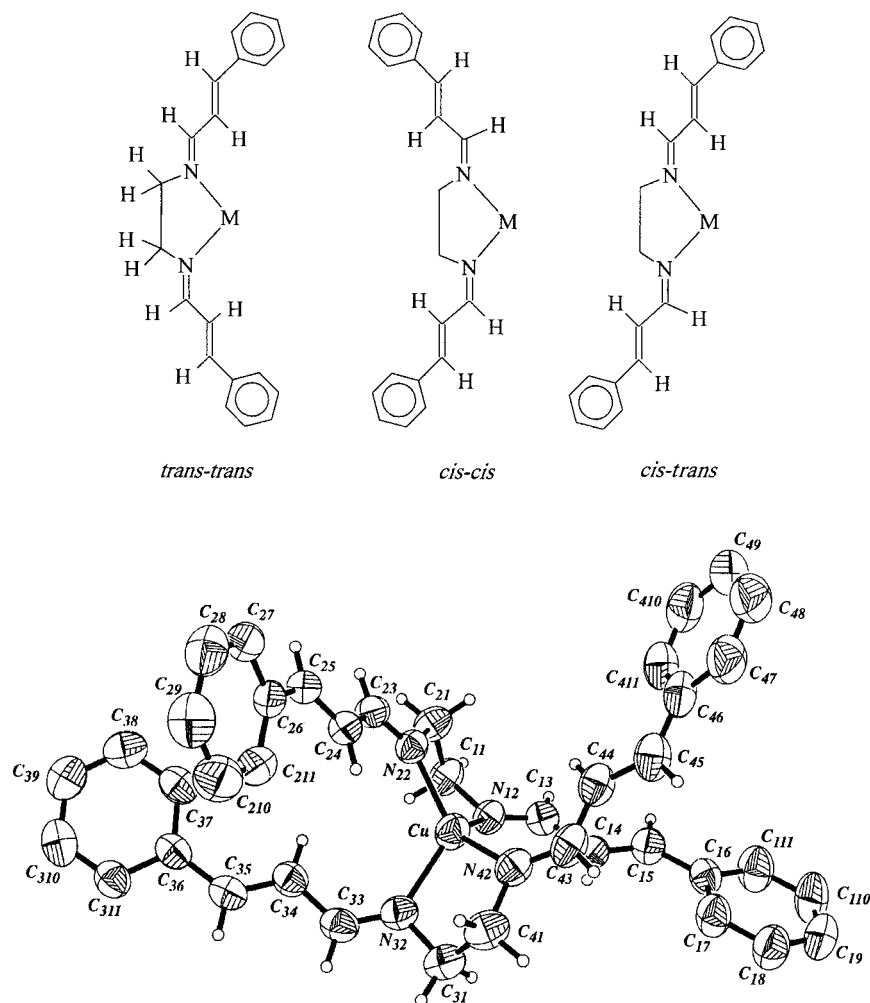


Fig. 2. ORTEP Diagram of  $[Cu(ca_2en)_2]^+$  cation showing 50% probability ellipsoids

ligand (2.726(4) Å for  $d(N(12)-N(22))$  and 2.731(4) Å for  $d(N(32)-N(42))$  are in the range of 82–89° found for ethylenediamine chelate compounds [26][27]. The  $N(22)-Cu-N(32)$  and  $N(22)-Cu-N(42)$  angles (121.74(11)° and 133.18(11)°, resp.) are larger than those of a tetrahedral complex. The Cu–N bond distances (2.048(3), 2.033(3), 2.083(3), and 2.009(2) Å) are similar to those found in  $[Cu(dpp)_2]^+$  cation (2.032(3), 2.082(3), 2.019(3), and 2.112(3) Å) at room temperature [28], and other Cu<sup>I</sup> pseudotetrahedral complexes (typical  $d(Cu-N_{av}) = 2.055$  Å) [29].

Despite the fact that the donor N-atoms are  $sp^2$ -hybridized, the chelate ring is significantly puckered in this complex, and some strain in the chelate ring is suggested by deviation from 120° angle about the N-atom,  $C(11)-N(12)-Cu$  (104.8(2)°),

C(21)–N(22)–Cu (110.1(2)°), C(31)–N(32)–Cu (105.8(2)°), C(41)–N(42)–Cu (109.4(2)°). Linking C-atom C(21) is 0.061 Å above the MN<sub>2</sub> plane defined by N(12)–Cu–N(22), while C(11) is 0.619 Å below. (Corresponding values for N(32)–Cu–N(42) are 0.038 Å for C(41) and 0.613 Å for C(31). The atoms C(41) and C(21) can be said to lie in the N–Cu–N planes). The dihedral angle between the two chelate rings (Cu–N–C–C–N) is 96.1°.

The Ph ring and the chain connecting the ring to the coordinated N-atom are roughly coplanar. The angle between the plane of the Ph ring (C(46) → C(411)) and the plane subtended by C(45)=C(44)–C(43)=N(42) is 22.1°. This degree of coplanarity, which allows for increased  $\pi$ -conjugation in the ligand, is consistent with the observed C–C bond distances in the coordinated ligand (C(43)–C(44), 1.428(5) Å < C(45)–C(46), 1.450(6) Å < C(31)–C(41), 1.507(5) Å). This result demonstrates that  $\pi$ -delocalization in the styryl moiety is diagnostic of an *endo* configuration with respect to the metal center in complexes of this type (*trans*–*trans* conformation, see above).

The cation of complex **2**, along with the atom-numbering scheme, is shown in Fig. 3, and selected bond distances and angles are listed in Table 2. As in complex **1**, the coordination environment around the metal ion in this complex is pseudotetrahedral with large angular distortion arising from the low intraligand N(2)–Cu–N(22) chelate angle, 82.65(13)°. Of the other five angles around Cu-atom, the N–Cu–P angles lie within  $\pm 3^\circ$  of those of a regular tetrahedron (Table 2), however, the P(1)–Cu–P(2) = 123.31(13)° angle has opened up due to the steric effects from the bulky Ph<sub>3</sub>P ligands. This angle is comparable to the angle observed in [Cu(dmp)(PPh<sub>3</sub>)<sub>2</sub>]NO<sub>3</sub> (122.7(1)°) [30]. The average Cu–N and Cu–P bond distances are 2.103(3) and 2.275(1) Å, respectively, and are comparable to those reported for [Cu(dmp)(PPh<sub>3</sub>)<sub>2</sub>]NO<sub>3</sub>

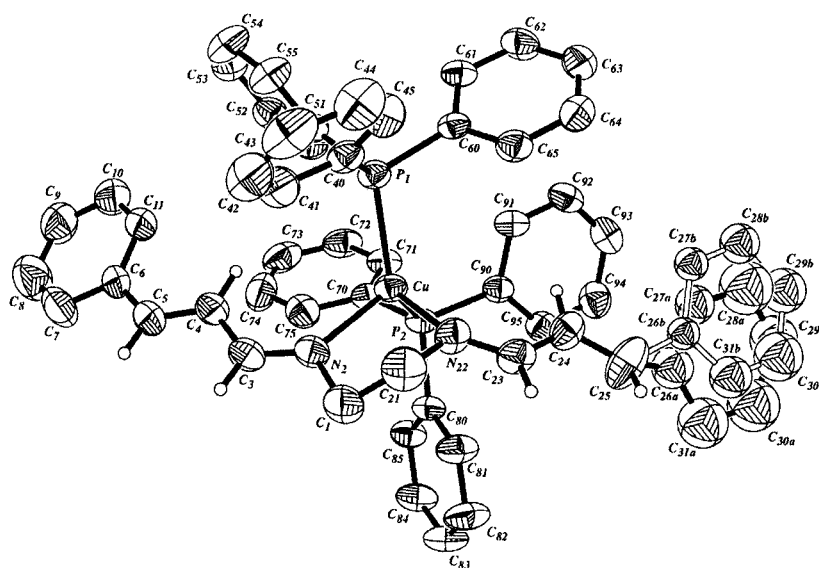


Fig. 3. ORTEP Diagram of [Cu(ca<sub>2</sub>en)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> cation showing 50% probability ellipsoids

(2.117(6) and 2.294(2) Å) [29]. In comparison with  $[\text{Cu}(\text{ca}_2\text{en})_2]^+$  (**1**), the  $\text{Cu}-\text{N}_{\text{av}}$  in  $[\text{Cu}(\text{ca}_2\text{en})(\text{PPh}_3)_2]^+$  (**2**) is slightly increased (*ca.* 0.06 Å) due to steric repulsions.

The chelate ring in complex **2** is also puckered with some strain caused by the deviation from 120° angle about the N-atom (C(1)–N(2)–Cu 108.5(2)°; C(3)–N(2)–Cu 133.5(3)°; C(21)–N(22)–Cu 107.4(3)°; C(23)–N(22)–Cu 132.5(3)°). Linking C-atom C(21) is 0.4134 Å above the  $\text{MN}_2$  plane defined by N(2)–Cu–N(22), while C(1) is 0.2823 Å below. The dihedral angle between the chelate ring (Cu–N–C–C–N) and the plane defined by P(1)–Cu–P(2) is 82.9° and agrees well with the 82.2° value for  $[\text{Cu}(\text{dmp})(\text{PPh}_3)_2]\text{NO}_3$  [30].

As in complex **1**, the Ph plane (C(6) → C(11)) and the chain connecting the ring to the coordinated N-atom are roughly coplanar. The angle between the plane of the Ph ring (C(6) → C(11)) and the plane spanned by C(5)=C(4)–C(3)=N(2) is 17.2°. The observed coplanarity, which allows for increased degree of  $\pi$ -conjugation in **2**, is consistent with the observed C–C bond distances in the coordinated ligand (C(3)–C(4), 1.433(6) Å < C(5)–C(6), 1.442(6) Å < C(1)–C(21), 1.513(7) Å).

The structural and electronic properties of complex **1** and **2**, and a comparison between the two is interesting. In spite of the bulky appearance of the  $\text{ca}_2\text{en}$  ligand the  $\text{Cu}-\text{N}_{\text{av}}$  bond distance in these complexes lies in the range observed for several other stable  $[\text{Cu}(\text{NN})_2]^+$  and  $[\text{Cu}(\text{NN})(\text{PPh}_3)_2]^+$  complexes [25–29]. The weaker interaction of  $\text{ca}_2\text{en}$  with Cu in complex **2** ( $\text{Cu}-\text{N}_{\text{av}}$  longer by *ca.* 0.06 Å) is compensated for by the strong  $\delta$ -donor  $\pi$ -acceptor  $\text{Ph}_3\text{P}$  ligand leading to a considerable blue shift (84 nm) in the MLCT position.

**3.3. Electrochemistry and Emission.** The electrochemical behavior of the complexes was examined by means of cyclic voltammetry in  $\text{CH}_2\text{Cl}_2$ . The ligand  $\text{ca}_2\text{en}$  is electroinactive in the working potential region. Complex **1** shows a quasireversible  $\text{Cu}^{\text{II/I}}$  couple with an  $E_{1/2}$  of 0.51 V (Fig. 4). The peak-to-peak separation varies from 120 to 180 mV, as the scan rate is changed from 50 to 500 mV/s [31]. The cyclic voltammogram of complex **2** in  $\text{CH}_2\text{Cl}_2$  displays only one anodic peak ( $E_{1/2}=0.91$  V). The corresponding cathodic peak was not observed, however, even under fast-scan-rate conditions (Fig. 4). This is probably due to an irreversible chemical reaction following

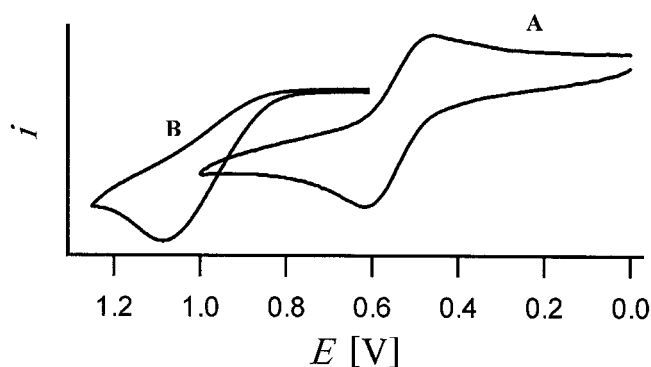


Fig. 4. Cyclic voltammograms of  $[\text{Cu}(\text{ca}_2\text{en})_2]\text{ClO}_4$  (A) and  $[\text{Cu}(\text{ca}_2\text{en})(\text{PPh}_3)_2]\text{ClO}_4$  (B) in  $\text{CH}_2\text{Cl}_2$  at 293 K. Scan rate: 50 mV/s. A)  $c = 1 \times 10^{-3}$  M, B)  $c = 1.5 \times 10^{-3}$  M.



the electron-transfer process. The shift to the higher potentials occur for complexes with bulkier ligands around Cu, because the ligand framework resists rearrangement to a more flattened structure that is appropriate for Cu<sup>II</sup> oxidation state [32][33].

The photophysical properties of **1** and **2** are strongly influenced by the steric requirements of the ligands. Complex **1** displays a very weak photoluminescence upon excitation (at 300, 320, 380, 400, and 420 nm) in CHCl<sub>3</sub> at room temperature, and a vibronically structured band is observed around 490 nm for complex **2** in CHCl<sub>3</sub> upon excitation at 300 nm (Fig. 5). Studies on Cu<sup>I</sup> complexes reveal that the emission intensity is enhanced as the Cu<sup>II</sup> center generated in the photoexcited state acquires a distorted tetrahedral geometry imposed by steric hindrance of the ligands [33–35]. It seems that the extra steric rigidity coming from the additional Ph<sub>3</sub>P groups in **2** is the origin of the observed emission in this complex. This is in accord with cyclic voltammetric results where Cu<sup>I</sup> is oxidized at a higher potential in complex **2** (0.91 V) relative to **1** (0.51 V).

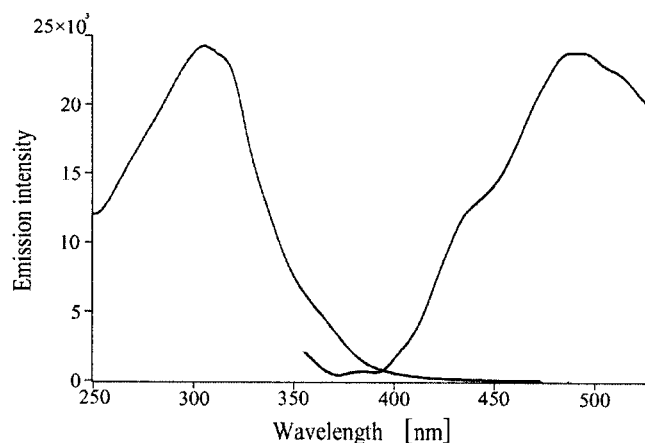


Fig. 5. Absorption and emission spectra of complex **2** in CHCl<sub>3</sub> at 298 K

**4. Conclusions.** – The Cu<sup>I</sup> complexes show pseudotetrahedral symmetry, and <sup>1</sup>H-NMR data support the existence of Cu<sup>I</sup> in **1** and **2**. The position of the MLCT changes considerably and is blue shifted by 84 nm, when one of the ca<sub>2</sub>en ligands is replaced by two Ph<sub>3</sub>P molecules. A major finding of the present work is that the chelating *Schiff* base ligand is in the *endo* configuration as indicated in structures **1** and **2**. Additional steric hindrance in complex **2** relative to **1** results in a more positive Cu<sup>II/I</sup> redox potential and the observation of room-temperature emission from the CHCl<sub>3</sub> solution of complex **2**.

*Supplementary Data.* Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre (CCDC) No. 168152 for **1** and 168153 for **2**. Copies of this information may be obtained, free of charge, from The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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