Synthesis, Characterization, and X-Ray Crystal Structures of Bis[*N*-(3,3-diphenylallylidene)quinolin-8-amine-$\kappa N,\kappa N^8$]copper(1+) Tetraphenylborate(1−) ([Cu(dpa-qa)$_2$]BPh$_4$) and Bis[*N*,*N*′-bis(3,3-diphenylallylidene)-[1,1′-biphenyl]-2,2′-diamine-$\kappa N,\kappa N'$]copper(1+) Perchlorate ([Cu(bdpa-bda)$_2$]ClO$_4\cdot$3 H$_2$O)

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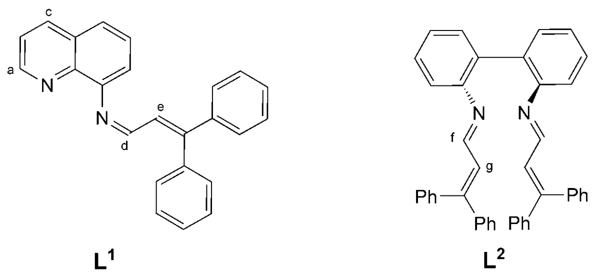
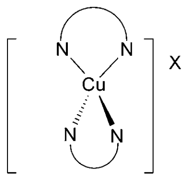
Two new ligands, *N*-(3,3-diphenylallylidene)quinolin-8-amine (dpa-qa; **L^1**) and *N*,*N*′-bis-(3,3-diphenylallylidene)[1,1′-biphenyl]-2,2′-diamine (bdpa-bda; **L^2**), and their corresponding copper(I) complexes, [Cu(dpa-qa)$_2$]BPh$_4$ (**1**) and [Cu(bdpa-bda)$_2$]ClO$_4\cdot$3 H$_2$O (**2**), were synthesized and characterized by C,H,N analyses, ^{1}H- and ^{13}C-NMR, IR, and UV/VIS spectroscopy. The crystal and molecular structures of **1** and **2** were determined by X-ray crystallography from single-crystal data. Complex **1** crystallizes in the orthorhombic space group *Pbca*, with $a=14.391(3)$ Å, $b=21.967(5)$ Å, $c=35.463(8)$ Å, $V=11211(4)$ Å^3, and $Z=8$. Complex **2** crystallizes in the monoclinic space group *C*2/*c*, with $a=30.746(10)$ Å, $b=18.244(6)$ Å, $c=27.835(9)$ Å, $\beta=109.794(7)^\circ$, $V=14691(8)$, and $Z=8$. The coordination polyhedron about the Cu$^{\rm I}$ center in the two complexes is best described as a distorted tetrahedron. A quasireversible redox behavior is observed for complex **1** and **2** ($E_{1/2}=0.58$ and 1.04 V).

1. Introduction. – There has been a growing interest in the synthesis and characterization of copper(I) complexes of π-acceptor ligands such as diimines, due to their potential application as photosensitizers [1–6]. Most of the studies have been on four-coordinated tetrahedral Cu$^{\rm I}$ complexes of the type [Cu(LL)$_2$]$^+$ or [Cu(LL)(P)$_2$]$^+$ where LL is a substituted phenanthroline and P is a phosphine [7–14]. Some of these complexes possess broad absorption bands in the VIS region with high extinction coefficients potentially useful for solar-energy harvesting [15–18]. The d^{10} configuration of Cu$^{\rm I}$ and π^* molecular orbitals of the ligands combine to produce metal-to-ligand charge-transfer (MLCT) states. The MLCT transitions can be tuned to lower energies by introducing a ligand with a low-lying π^* molecular orbital. The steric, electronic, and conformational interactions influence the redox potential of these complexes and modify their excited-states properties [15]. A thorough understanding of these effects will serve as the basis for a rational design of complexes with specific and predictable properties [3][19].

Our interest in the chemistry of copper(I) complexes with new synthetic ligands was stimulated by the question how the variations in the backbone of the ligands will influence their reactivity and the physicochemical and spectral properties of their copper(I)





	L	X
1	**L^1**	BPh_4
2	**L^2**	ClO_4

Fig. 1. *Ligands* **L^1** *and* **L^2**, *and Cu^I complexes* **1** *and* **2**

complexes as compared to those containing polypyridine ligands. Factors such as the delocalization of electron density provide a span of charged species from a single neutral precursor and low-energy MLCT pathways, which are important in electro- and photocatalysis.

In continuation of our work on the preparation of (diimine) copper(I) complexes with low-lying MLCT transitions [19], we now report the synthesis and characterization of two new ligands **L^1** and **L^2** with extended conjugation and their copper(I) complexes **1** and **2** (*Fig. 1*). The structures, spectral properties, and redox chemistry of these complexes are also discussed.

2. Results and Discussion. – *2.1. Spectral Data.* The IR spectra of the free ligands exhibit the characteristic band of the imine group, which appears at 1583 and 1598 cm^{-1} for **L^1** and **L^2** respectively. This band is shifted to lower frequencies in the IR spectra of the corresponding complexes due to the coordination of the imine N-atom [20], and appears at 1576 cm^{-1} in **1** and 1590 cm^{-1} in **2**. A strong band at *ca.* 1085 cm^{-1} in the IR spectrum of **2** is characteristic of the asymmetric Cl–O stretching mode of the perchlorate anion [21].

The electronic absorption spectra of the ligands **L^1** and **L^2** and the corresponding complexes **1** and **2** are presented in *Table 1*. Since no d-d transitions are expected for a d^{10} complex, the UV/VIS bands are assigned to MLCT or ligand-centered $\pi \rightarrow \pi^*$ transitions [22]. The absorption spectrum of $[Cu(dpa\text{-}qa)_2]BPh_4$, (**1**) in $CHCl_3$ features a band with a true maximum at 503 nm (*Fig. 2*), whereas $[Cu(bdpa\text{-}bda)_2]ClO_4$ (**2**) shows a clear shoulder at 428 nm. This observation is in agreement with a higher conjugation in the coordinated dpa-qa (**L^1**) relative to bdpa-bda (**L^2**), which conforms to the X-ray data (*vide infra*). In addition, the lower energy of the MLCT band is in accord with the observed lower redox potential of complex **1** relative to that of complex **2**. Interestingly, the position (λ_{max} 503 nm) and the intensity (ε 6357) of the MLCT absorption band of complex **1** are comparable to those reported for the most attractive complex of this series, [Cu(dmesp)(dpep)](PF_6) (λ_{max} 500 nm, ε 5300; dmesp = 2,9-dimesityl-1,10-phenanthroline, dpep = 2,9-diphenylethynyl-1,10-phenanthroline), [23]. The considerable red shift in the position of the first MLCT band of complex **1** as compared to that of other bis(diimine)copper(I) complexes is quite interesting and points to the possible application of this complex as a more efficient charge-transfer photosensitizer in the VIS region. Additional absorption bands are also observed in the spectra of **1** and **2** in $CHCl_3$ in the UV region (*Table 1*). The intensity of these bands are consistent with their assignment to ligand-centered $\pi \rightarrow \pi^*$ or/and charge-transfer transitions.

Table 1. *UV/VIS Data* ($CHCl_3$) *of Ligands* **L**^{1} *and* **L**^{2} *and of Complexes* **1** *and* **2**

	λ_{max}/nm (log ε/M^{-1}cm^{-1})		
L^1, dpa-qa	358 (17113),	314 (23217)	
L^2, bdpa-bda	350 (25027),	308 (45807)	
1, [Cu(dpa-qa)$_2$]BPh_4	503 (6357),	373 (53367)	
2, [Cu(bdpa-bda)$_2$]ClO_4	428 (1445),	372 (25819),	329 (63880)

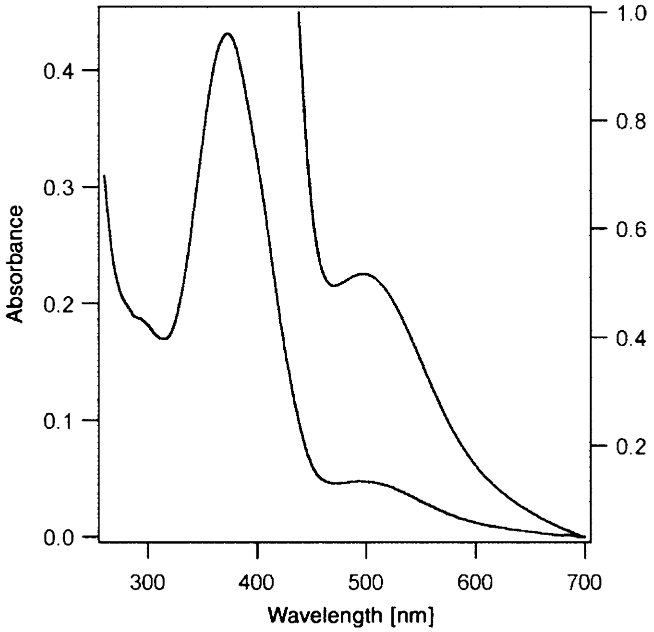


Fig. 2. *Electronic absorption spectrum* ($CHCl_3$, 298 K) *of [Cu(dpa-qa)$_2$]BPh_4* (**1**)

The ^{1}H-NMR spectrum of complex **1** shows that several of the aromatic protons are nonequivalent due to the presence of the asymmetric ligand dpa-qa (**L**^{1}) (*Fig. 3*). A total of 13 nonequivalent aromatic protons are observed due to the ligand and the

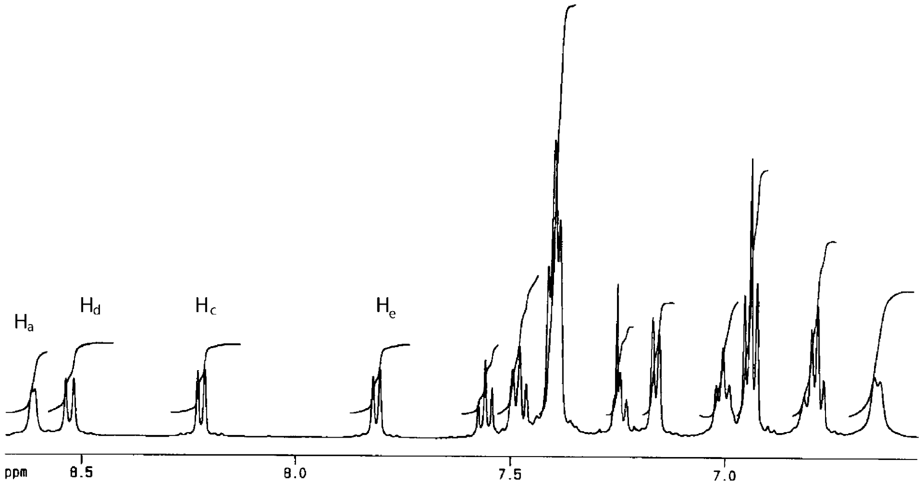


Fig. 3. *^{1}H-NMR Spectrum* ($CDCl_3$, 298 K) *of [Cu(dpa-qa)$_2$]BPh$_4$* (**1**)

Ph_4B^- ion. Since the electronic environment around most of the aromatic protons is similar, their signals appear in a narrow range of chemical shifts which is crowded due to the overlap of several signals. However, the presence of the expected number of aromatic protons of the complex is evident from the direct comparison of the intensity of the aromatic-proton signals with those of the clearly observable imine proton CH=N (=H_d) and aromatic protons H_a and H_c. The signal of CH=N (δ 8.53) in the complex is deshielded relative to the free ligand (δ 8.28) due to the deshielding effect resulting from the coordination of the ligand.

The ^{1}H-NMR spectrum of complex **2** shows a *d* at δ 7.89 due to the CH=N protons. The C=C*H*CH=N protons overlap with the aromatic protons of the phenyl rings, and they all appear in the δ 6.46–7.38 region.

The sharp NMR peaks are indicative of diamagnetic Cu^I complexes. In principle, geometrical isomers are possible with respect to the C=N bond as shown in *Fig. 4*. 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 is present.

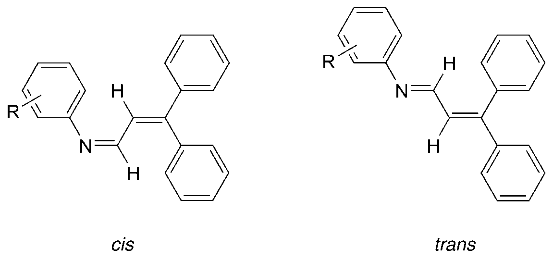


Fig. 4. *Possible geometrical isomers of the ligands*

2.2. X-Ray Structures of [Cu(dpa-qa)$_2$]BPh$_4$ (**1**) *and [Cu(bdpa-bda)$_2$]ClO$_4$·3 H$_2$O* (**2**). The crystallographic data are summarized in *Table 2*, and selected bond distances and angles are given in *Table 3*. A view of the cation of complex **1**, including the atom-numbering scheme is illustrated in *Fig. 5*. While a tetrahedral geometry might be expected for a four-coordinated copper(I) center, the coordination sphere around the metal ion in this complex is distorted by the restricting bite angles of the chelating ligand. The intraligand N(1)–Cu(1)–N(11) and N(27)–Cu(1)–N(37) angles are much less than 109.5°, being only 80.94(9)° and 81.19(9)°, respectively. On the contrary, the N(1)–Cu(1)–N(27) and N(1)–Cu(1)–N(37) angles (137.13(9)° and 130.50(9)°, resp.) are much larger than those of a tetrahedral complex. The average Cu–N bond distance (2.052 Å) is similar to that found in the $[\mathrm{Cu(dpdmp)_2}]^+$ cation (2.047 Å; dpdmp = 2,9-diphenyl-4,7-dimethyl-1,10-phenanthroline) at room temperature [20] and in other $\mathrm{Cu^I}$ pseudotetrahedral complexes (typical $\mathrm{Cu{-}N_{av}} = 2.055$ Å) [19][23].

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

	1	**2**
Empirical Formula	$C_{72}H_{56}BCuN_4$	$C_{84}H_{70}ClCuN_4O_7$
M_r	1051.56	1346.48
T/K	294(2)	297(2)
Wavelength/Å	0.71073	0.71073
Crystal system	orthorhombic	monoclinic
Space group	*Pbca*	*C*2/*c*
a/Å	14.391(3)	30.746(10)
b/Å	21.967(5)	18.244(6)
c/Å	35.463(8)	27.835(9)
α/°	90	90
β/°	90	109.794(7)
γ/°	90	90
V/Å^3	11211(4)	14691(8)
Z, $D_{\mathrm{calc.}}$/Mg·m^{-3}	8, 1.246	8, 1.212
μ/mm^{-1}	0.437	0.390
F(000)	4400	5584
Crystal size/mm	0.46 × 0.32 × 0.28	0.40 × 0.30 × 0.10
θ/°	1.79 to 23.26	1.41 to 23.25
$h/k/l$	−13, 15/−22, 24/−39, 39	−21, 34/−19, 20/−30, 30
Refl. collected	49114	34096
Independent refl.	8037	10516
R(int)	0.0500	0.0530
Completeness to θ (23.26°)/%	99.9	99.7
Observed intensities > 2σ	5863	6335
Max. and min. transmission	0.8873 and 0.8242	0.9620 and 0.8595
Data, restraints, parameters	8037, 0, 704	10516, 0, 874
Goodness-of-fit on F^2	1.028	1.003
Final R indices ($I > 2\sigma(I)$)[a])	$R_1 = 0.0394$, $wR_2 = 0.0908$	$R_1 = 0.0557$, $wR_2 = 0.1425$
R indices for all data[a])	$R_1 = 0.0645$, $wR_2 = 0.1037$	$R_1 = 0.1077$, $wR_2 = 0.1706$
Extinction coefficient	0.00042(7)	–
Largest difference peak and hole/e·Å^{-3}	0.210 and −0.289	0.554 and −0.550

[*] $R_1 = \Sigma\,||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$.

Table 3. *Selected Bond Lengths* [Å] *and Bond Angles* [°] *for* **1** *and* **2**

1		**2**	
Cu(1)–N(1)	1.992(2)	Cu(1)–N(1)	2.034(3)
Cu(1)–N(11)	2.117(2)	Cu(1)–N(14)	2.033(3)
Cu(1)–N(27)	1.994(2)	Cu(1)–N(58)	2.045(3)
Cu(1)–N(37)	2.105(2)	Cu(1)–N(45)	2.009(3)
N(11)–C(12)	1.291(3)	N(1)–C(15)	1.282(5)
N(11)–C(9)	1.412(3)	N(1)–C(2)	1.427(5)
N(1)–C(10)	1.370(3)	N(14)–C(13)	1.437(5)
N(1)–C(2)	1.325(3)	N(14)–C(30)	1.281(5)
C(12)–C(13)	1.433(3)	C(59)–C(60)	1.437(5)
C(13)–C(14)	1.345(3)	C(60)–C(61)	1.342(5)
C(14)–C(15)	1.381(4)	C(7)–C(8)	1.502(5)
C(14)–C(21)	1.479(3)	C(6)–C(5)	1.382(6)
N(1)–Cu(1)–N(11)	80.94(9)	N(1)–Cu(1)–N(14)	105.32(13)
N(1)–Cu(1)–N(27)	137.13(9)	N(1)–Cu(1)–N(45)	102.56(13)
N(1)–Cu(1)–N(37)	130.50(9)	N(1)–Cu(1)–N(58)	121.67(13)
N(11)–Cu(1)–N(37)	101.78(8)	N(45)–Cu(1)–N(58)	106.51(13)
N(27)–Cu(1)–N(37)	81.19(9)	N(45)–Cu(1)–N(14)	124.28(13)
Cu(1)–N(1)–C(2)	126.9(2)	Cu(1)–N(1)–C(2)	113.1(2)
Cu(1)–N(1)–C(10)	114.82(17)	Cu(1)–N(1)–C(15)	125.5(3)
Cu(1)–N(11)–C(9)	110.91(16)	Cu(1)–N(14)–C(13)	108.9(2)
Cu(1)–N(11)–C(12)	122.38(17)	Cu(1)–N(14)–C (30)	129.4(3)
C(2)–N(1)–C(10)	118.3(2)	C(13)–N(14)–C(30)	117.6(3)
C(9)–N(11)–C(12)	121.7(2)	C(2)–N(1)–C(15)	118.8(3)

The ligand adopts a *trans* configuration in complex **1**. The mean value for the dihedral angles of N=C−C=C is 9.56° (N(11)−C(12)−C(13)−C(14)) and 3.62° (N(37)−C(38)−C(39)−C(40)) indicating that this moiety is roughly planar. 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(14)−C(13) 1.345(3)Å < C(13)−C(12) 1.433(3)Å < typical single C−C bond, 1.507(5)Å [19].

Due to the geometrical restrictions in **1**, the C=C*H*CH=N protons, *i.e.*, the H-atoms at C(13) and C(39), lie in the vicinity of the metal atoms making the intramolecular interactions possible in the form of weak C−H···M H-bonds. This type of interaction is somewhat similar to the agostic interactions found in many organometallic complexes [24][25], though a C−H$^{\delta+}$···M$^{\delta-}$ charge-assisted H-bonding could be encountered here. As a matter of fact, the involvement of the metal centers in H-bonding is now well established and known as nontraditional H-bonds [26][27]. A recent survey by *Desiraju* and *Steiner* [28] gives the range 2.5–3.2 Å for the weak (C−)H···M H-bonds. Our structural data reveal that the (C−)H···M interactions ranging from 2.855 to 3.091 Å would meet the criteria and can be regarded as intramolecular weak H-bonds. Such an interaction may be responsible for the large values of the N(1)−Cu(1)−N(27) (137.13(9)°) and N(1)−Cu(1)−N(37) (130.50(9)°) angles relative to the smaller value for N(11)−Cu(1)−N(37) (101.78(8)°). The possibility of this type of interaction has also been reported by others for closely related structures [29][30].

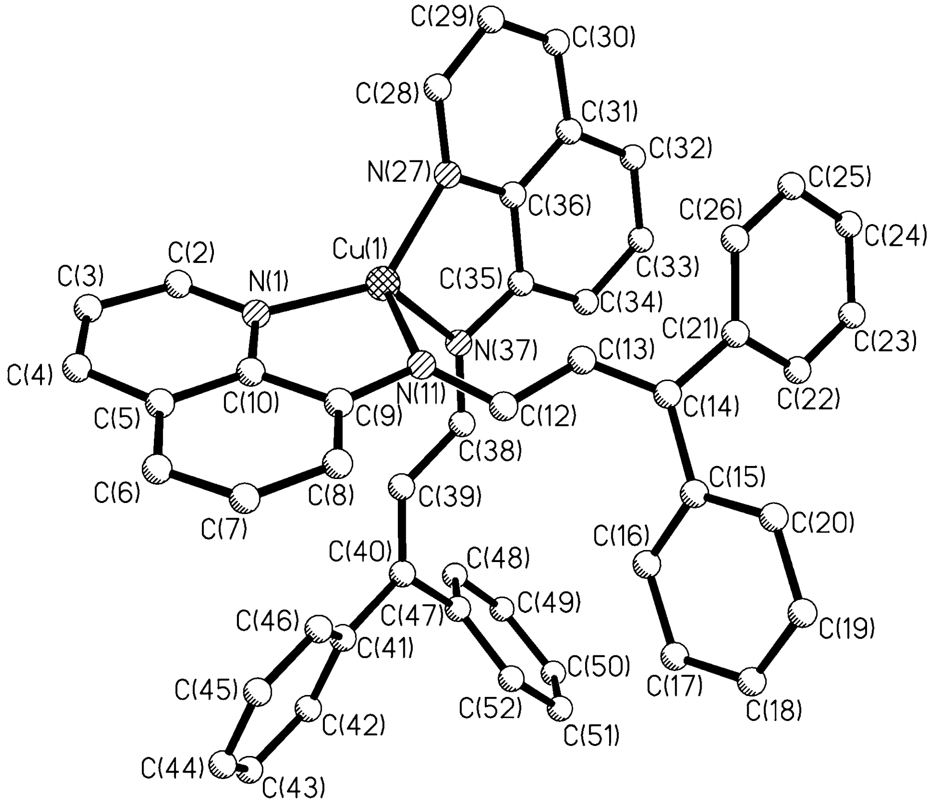


Fig. 5. *View of the structure of [Cu(dpa-qa)$_2$]$^+$ showing the atom labeling scheme*

The cation of complex **2**, along with the atom-numbering scheme, is shown in *Fig. 6*. As in complex **1**, the geometry about Cu^I in **2** is also distorted by the restricting bite angles of the bulky chelating ligand. The N(1)–Cu(1)–N(14) and N(45)–Cu(1)–N(58) angles are 105.32(13)° and 106.51(13)°, respectively. However, the N(1)–Cu(1)–N(58) and N(45)–Cu(1)–N(14) angles are 121.67(13)° and 124.28(13)°, respectively, and the dihedral angle between the two chelate rings is 73.38°. The dihedral angles between the two Ph rings of biphenyl is 68.94° (C(2)–C(13)) and 71.57° (C(46)–C(57)), resulting in a bite size of 3.233 Å for *d*(N(1)–N(14)) and 3.248 *d*(N(45)–N(58)) for the two chelating ligands. The average Cu–N bond distance (2.030 Å) is similar to that found in other [Cu^I(diimine)] pseudotetrahedral complexes [20] [23].

In spite of sterical hindrance in these complexes, each coordinated ligand adopts a *trans* configuration. The mean value for dihedral angles N=C–C=C is *ca.* 5.16° indicating the planarity of this moiety. However, the two N=C–C=C moieties in **2** are not coplanar.

The average dihedral angle between the two Ph rings of biphenyl in **2** is 70.26° and, in principle, the ligand bdpa-bda (**L^2**) can form a chiral bis(diimine)copper(I) complex.

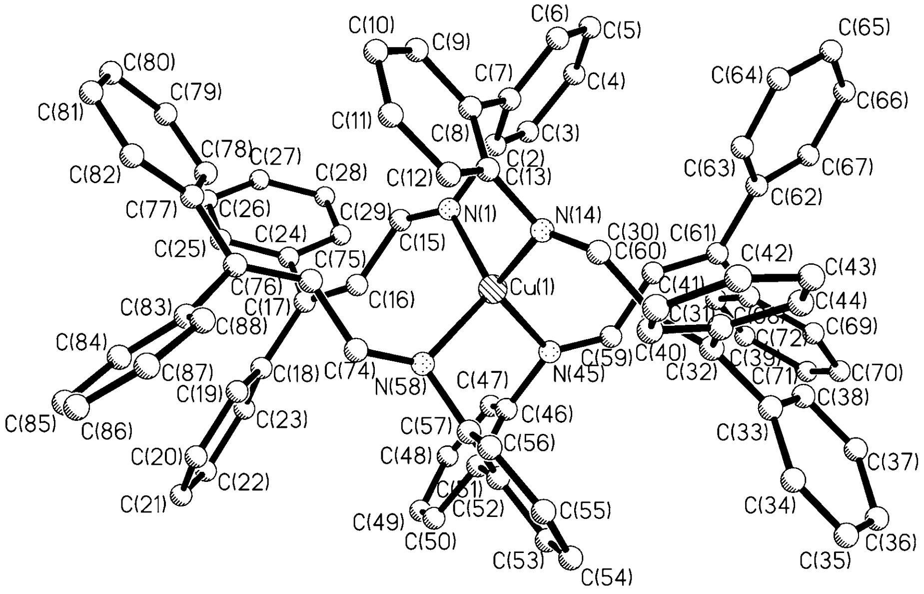


Fig. 6. *View of the structure of [Cu(bdpa-bda)$_2$]$^+$ showing the atom labeling scheme*

However, ^{13}C-NMR data, sharp ^{1}H-NMR signals in solution, and the X-ray analysis show that high diastereoselective complexation occurs in solution and in the solid state probably due to the steric hindrance in the complex [31][32].

The structural and electronic properties of complexes **1** and **2**, and a comparison between the two are interesting. In **1**, the angle between the planes C(9)–C(8)–N(11) and C(13)–C(12)–N(11) is 28.86°, and that between the planes C(39)–C(38)–N(37) and C(34)–C(35)–N(37) is 3.77°. However, the average dihedral angle between the two Ph rings of biphenyl in **2** is 70.26°, and the angle between the planes C(3)–C(2)–N(1) and C(16)–C(15)–N(1) is 52.46° and that between the planes C(75)–C(74)–N(58) and C(56)–C(57)–N(58) is 53.37°. A comparison between the angles in **1** and **2** indicates that there is a higher degree of conjugation in **1** relative to **2** leading to a considerable red shift (75 nm) in its MLCT position. Both structures do not show any ordering in their packing related to p-p interactions or H-bonds.

2.3. *Electrochemistry.* The electrochemistry of compounds **1** and **2** were investigated in CH_2Cl_2. The two ligands $\mathbf{L}^1$ and $\mathbf{L}^2$ are electroinactive in the working potential region. The complexes show a quasireversible $Cu^{II/I}$ couple with $E_{1/2}$ of 0.58 and 1.04 V, respectively. 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 varies from 120 to 180 mV for **1** and 120 to 180 mV for **2** as the scan rate is changed from 50 to 500 mV/s.

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 [23][33][34]. Although a higher degree of conjugation exists in dpa-qa relative to bdpa-bda (*vide supra*), the existence of bulkier ligands in **2** which prevent the inner-sphere reorganization to a flattened tetrahedral, more appropriate to Cu^{II} oxidation state, play a key role in shifting the oxidation potential to higher values for complex **2** relative to **1**.

3. Conclusions. – The Cu^{I} complexes show pseudotetrahedral symmetry, and ^1H-NMR data support the existence of Cu^{I} in **1** and **2**. The position of MLCT changes considerably and is red shifted by 75 nm, when the bdpa-bda ligand is replaced by dpa-qa. A major finding of the present work is that the chelating diimine ligand is in the *trans* configuration as indicated in structures **1** and **2**. Additional steric hindrance in complex **2** relative to **1** results in a more positive $Cu^{II/I}$ redox potential.

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Experimental Part

1. *General. Caution*! Perchlorate salts of metal complexes with organic 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 known methods [35]. $[Cu(MeCN)_4]ClO_4$ and $[Cu(MeCN)_4]BPh_4$ were freshly prepared according to [36][37]. Voltamograms: *Metrohm* multipurpose instrument, model *693 VA*, processor with *694A Va* stand; three-electrode system consisting of an Ag/AgCl reference electrode, a Pt-wire counter electrode, and the Au as a working electrode; the test soln. was purged with Ar for at least 5 min. UV/VIS Spectra: *Jasco-V-570* spectrophotometer; λ_{max} (log ε) in nm. IR Spectra: *Shimadzu-IR-460* instrument; in cm^{-1}. NMR Spectra: *Bruker-Avance-DRX500* (500 MHz) spectrometer, δ in ppm rel. to SiM_4 as internal standard. Elemental analyses were performed with a *Heraeus CHN-O-Rapid* elemental analyzer.

2. *Syntheses.* N-*(3,3-Diphenylallylidene)quinolin-8-amine* (dpa-qa; $\mathbf{L^1}$). To a soln. of 3,3-diphenylprop-2-enal (208 mg, 1 mmol) in EtOH (20 ml) was added a soln. of quinolin-8-amine (144 mg, 1 mmol) in EtOH (10 ml) and stirred for 2 h. The formed yellow microcrystalline precipitate was filtered off, washed with cold EtOH, and dried in air: 300 mg (90%) of $\mathbf{L^1}$. IR (KBr): 1583 (C=N). ^1H-NMR (500 MHz, $CDCl_3$): 7.08–7.59 (*m*, H_e, 15 arom. H); 8.11 (*dd*, 1 H, $^2J=8.2$, $^3J=1.4$, H_c); 8.28 (*d*, 1 H, $J=9.4$, H_d); 8.99 (*dd*, 1 H, $^2J=4$, $^3J=1.4$, H_a). ^{13}C-NMR (125 MHz, $CDCl_3$): 117.63; 121.47; 125.16; 126.72; 127.86; 128.19; 128.26; 128.38; 128.46; 128.90; 129.12; 130.58; 135.92; 138.35; 140.81; 142.72; 150.09; 150.33; 154.25; 162.35 (C=N). Anal. calc. for $C_{24}H_{18}N_2$: C 86.20, H 5.43, N 8.38; found: C 86.25, H 5.44, N 8.39.

N,N′-*Bis(3,3-diphenylallylidene)-[1,1′-biphenyl]-2,2′-diamine* (bdpa-bda; $\mathbf{L^2}$). To a soln. of 2,2′-dinitro-1,1′-biphenyl (4 g, 16 mmol) in EtOH (50 ml) was added 5% Pd/C (1 g), and the mixture was warmed up to 50°. A soln. of 80% hydrazine hydrate (15 ml) in EtOH (20 ml) was then added dropwise with vigorous stirring within 1 h. The mixture was refluxed for 2 h and then filtered. The filtrate was concentrated to *ca.* 5 ml. After the addition of H_2O (20 ml) and stirring for 5 min, the resulting white microcrystalline precipitate was filtered off, washed with H_2O and dried in air: 2.56 g (85%) of [1,1′-biphenyl]-2,2′-diamine. IR (KBr): 3350 (NH). ^1H-NMR (500 MHz, $CDCl_3$): 3.68 (*s*, 2 NH_2); 6.75–7.18 (*m*, 8 arom. H).

To a soln. of 3,3-diphenylprop-2-enal (208 mg, 1 mmol) in EtOH (20 ml) was added a soln. of [1,1′-biphenyl]-2,2′-diamine (92 mg, 0.5 mmol) in EtOH (5 ml) and stirred for 2 h. The obtained yellow microcrystalline precipitate was filtered off, washed with cold EtOH, and dried in air: 268 mg (94.4%) of **L**. IR (KBr): 1598 (C=N). ^1H-NMR (500 MHz, $CDCl_3$): 6.84 (*d*, $J=8.6$, 2 arom. H); 6.86 (*d*, $J=9.46$, 2 H_g); 6.96–7.33 (*m*, 26 arom. H); 7.50 (*d*, $J=9.46$, 2 H_f). ^{13}C-NMR (125 MHz, $CDCl_3$): 119.32; 125.42; 127.55; 128.04; 128.06; 128.15; 128.32; 128.96; 130.20; 131.21; 133.52; 137.95; 140.77; 151.20; 153.26; 160.82 (C=N). Anal. calc. for $C_{42}H_{32}N_2$: C 89.33, H 5.71, N 4.96; found: C 89.35, H 5.75, N 4.97.

*Bis[*N*-(3,3-diphenylallylidene)quinolin-8-amine-κ*N*,κ*N^8*]copper(1+) Tetraphenylborate(1−) ([*Cu^I*(dpa-qa)*$_2$*]BPh*$_4$; **1**). To a soln. of $\mathbf{L^1}$ (33.4 mg, 0.1 mmol) in MeCN (5 ml) was added $[Cu(MeCN)_4]BPh_4$ (27.4 mg, 0.05 mmol) in MeCN (5 ml), and stirring was continued for 10 min. The soln. turned dark red rapidly. Then soln. was concentrated to *ca.* 4 ml. The diffusion of Et_2O vapor into the conc. soln. gave dark-red crystals which were filtered off and washed with Et_2O/MeCN 9 : 1, and dried under vacuum: 90 mg (85%) of **1**. IR (KBr): 1576 (C=N). ^{1}H-NMR (500 MHz, $CDCl_3$): 6.64–7.56 (*m*, 50 arom. H); 7.82 (*d*, *J* = 9.46, 2 H_e); 8.22 (*d*, *J* = 8.28, 2 H_c); 8.53 (*d*, *J* = 9.46, 2 H_d); 8.61 (*d*, *J* = 3.46, 2 H_a). ^{13}C-NMR (125 MHz, $CDCl_3$): 117.16; 121.52; 123.69; 125.44 (*q*, *J*(B,C) = 2.75, C_o of BPh_4); 126.37; 127.83; 127.93; 128.04; 128.37; 128.55; 128.72; 129.59; 130.19; 130.43; 136.33; 137.34; 137.64; 139.57; 142.62; 143.36; 150.05; 157.98; 164.10 (*q*, *J*(B,C) = 49.75, C_{ipso} of BPh_4); 164.89 (C=N). Anal. calc. for $C_{72}H_{56}BCuN_4$: C 82.23, H 5.37, N 5.33; found: C 82.25, H 5.39, N 5.30.

*Bis[*N*,*N*'-bis(3,3-diphenylallylidene)-[1,1'-biphenyl]-2,2'-diamine-κ*N*,κ*N*']copper(1+) Perchlorate Water (1 : 1 : 3) ([*Cu^I*(bdpa-bda)*$_2$*]*$ClO_4 \cdot 3\ H_2O$; **2**). To a soln. of $\mathbf{L^2}$ (56.7 mg, 0.1 mmol) in MeCN (5 ml) was added $[Cu(MeCN)_4]ClO_4$ (16.4 mg, 0.05 mmol) in MeCN (3 ml), and stirring was continued for 10 min. The colorless soln. turned deep orange. Then the soln. was concentrated to *ca.* 1 ml. Slow evaporation of the solvent gave dark-red crystals suitable for X-ray studies. The crystals were filtered off, washed with a mixture of Et_2O/MeCN 9 : 1, and dried under vacuum: 55 mg (85%) of **2**. IR (KBr): 1590 (C=N), 1085 (Cl−O). ^{1}H-NMR (500 MHz, $CDCl_3$): 6.46–7.38 (*m*, 4 H_g, 56 arom. H); 7.89 (*d*, *J* = 9.69, 4 H_f). ^{13}C-NMR (125 MHz, $CDCl_3$): 121.04; 125.34; 127.29; 128.17; 128.28; 128.46; 129.14; 129.93; 129.98; 130.05; 132.06; 132.90; 136.72; 139.90; 150.03; 158.20; 163.48 (C=N). Anal. calc. for $C_{84}H_{70}ClCuN_4O_7$: C 74.93, H 5.24, N 4.16; found: C 75.10, H 5.31, N 4.10.

3. *X-Ray Analysis.* Crystals of **1** and **2** suitable for X-ray were obtained as described above. The crystals were mounted on glass fibers. Diffraction data were collected on a *Siemens-Smart-CCD* diffractometer by using graphite-monochromated MoK_α radiation (λ 0.71073 Å), a nominal crystal-to-detector distance of 4.40 cm, and 0.3° ω-scan frames. Crystal data and the details of the structure determinations are given in *Table 2*. The data were corrected for *Lorentz* and polarization effects, and an empirical absorption correction (SADABS [38]) was applied. The structure was solved by direct methods (SHELXS-86 [39]). The structure refinement was performed by a full-matrix least-squares method against F^2 (SHELXL-93 [40]). All non-H-atoms were refined anisotropically, all H-atoms were inserted in calculated positions. Compound **2** shows a relatively large index R_1 and wR_2 on all data which is due to the large amount of weak data that was not used in the refinement.

CCDC-278696 for **1** and -278697 for **2** contain the supplementary crystallographic data (excluding structure factors) for this paper. These data can be obtained free of charge from the *Cambridge Crystallographic Data Center via* http://www.ccdc.cam.ac.uk/data_request/cif.

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