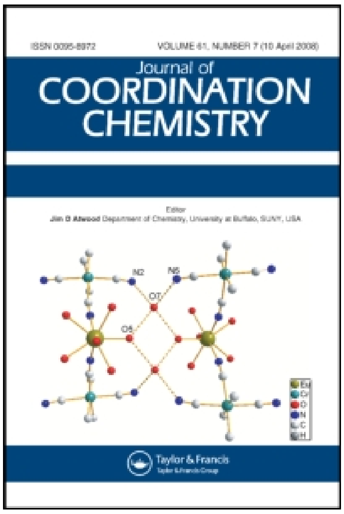

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BONDING PROPERTIES OF CU(II)-N CHROMOPHORES: SPECTROSCOPY AND ELECTRONIC STRUCTURES OF MIXED LIGAND DIETHYLENETRIAMINE (DIEN) COPPER(II) COMPLEXES, AND MOLECULAR STRUCTURES OF CU(DIEN) (4-METHYLIMIDAZOLE) $(CLO_4)^2$ AND CU(DIEN) (3-METHYLPYRIDINE) $(BF_4)_2$

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BONDING PROPERTIES OF CU(II)-N CHROMOPHORES: SPECTROSCOPY AND ELECTRONIC STRUCTURES OF MIXED LIGAND DIETHYLENETRIAMINE (DIEN) COPPER(II) COMPLEXES, AND MOLECULAR STRUCTURES OF CU(DIEN) (4-METHYLIMIDAZOLE) $(ClO_4)_2$ AND CU(DIEN) (3-METHYLPYRIDINE) $(BF_4)_2$

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Diethylenetriaminecopper(II) complexes of the [Cu(dien)L(anion)$_2$] type, where dien = diethylenetriamine, L = imidazole, 2-methylimidazole, 4-methylimidazole (4MImH), pyridine, 3-methylpyridine (3Mpy), 4-methylpyridine, 4-acetylpyridine, and NH_3, and anion = BF_4^- or ClO_4^-, have been synthesized and characterized. The crystal and molecular structures of [Cu(dien) (4MImH) $(ClO_4)_2$] (**1**) and [Cu(dien) (3Mpy) $(BF_4)_2$] (**2**) have been determined by three-dimensional X-ray diffraction methods. Complex **1** is monoclinic, $P2_1/n$, with a = 8.496(2), b = 17.290(4), c = 11.655(2)Å, β = 95.31(2)°, Z = 4, R = 0.052, and R_w = 0.077; complex **2** is monoclinic, $P2_1/c$, with a = 8.127(3), b = 14.204(5), c = 15.317(6)Å, β = 92.75(3)°, Z = 4, R = 0.066, and R_w = 0.077. Both complexes consist of square planar CuN_4 units formed by dien and a unidentate *N*-donor ligand, and two anions on a long axis. The bond lengths Cu-N(4MImH), 1.967(5)Å, and Cu-N(2°), 1.995(5)Å, of dien for complex **1** are shorter than the terminal Cu-N bond lengths of dien, 2.023±0.001Å. The corresponding bond lengths Cu-N(3Mpy), 1.996(7)Å, and Cu-N(2°), 2.011(7)Å, for complex **2** are not significantly shorter than the terminal Cu-N bonds of 2.018±0.005Å. The dihedral angles between the CuN_4 coordination plane and the heterocyclic nucleus are 41.2° for **1** and 57.7° for **2**. Similar structures with a CuN_4 coordination plane are proposed for other complexes based on spectroscopic data. Electronic structures are deduced from Gaussian analyses of their ligands field spectra. Bonding properties of the unidentate heterocyclic ligands are elucidated, suggesting some π-interactions for pyridine and 4-acetylpyridine, but not for 3-methylpyridine, 4-methylpyridine and imidazoles.

KEYWORDS: copper(II), diethylenetriamine, X-ray structure, electronic specta, Gaussian analysis.

INTRODUCTION

In the course of our investigation of the bonding properties of Cu(II)-N chromophores,$^{1-3}$ diethylenetriamine is one of the ligands useful for assignment of d orbitals. To date, X-ray structures of diethylenetriamine copper(II) complexes

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indicate that this ligand mainly assumes a planar terdentate bonding mode.[4–12] It is then possible for unidentate nitrogen donor ligands to form a CuN_4 coordination plane in mixed ligand diethylenetriamine copper(II) complexes. Since diethylenetriamine is merely a σ-donor ligand, designation of d orbitals is greatly simplified and any changes in the d_π levels should reflect directly the extent of π-interactions between the unidentate ligand and the central copper ion.

In this paper, we report mixed ligand diethylenetriamine copper(II) complexes with unidentate *N*-donor ligands including imidazoles, pyridines, and NH_3. The bonding properties of the unidentate ligands are elucidated by reference to electronic structures.

EXPERIMENTAL

Materials and Preparations

Diethylenetriamine (Aldrich), imidazole (Merck), *N*-methylimidazole (Aldrich), 2-methylimidazole (Merck), 4-methylimidazole (Merck), pyridine (Merck), 4-acetylpyridine (Merck), 3-methylpyridine (TCI), 4-methylpyridine (TCI), 2,2-dimethoxypropane (Merck), $Cu(ClO_4)_2.6H_2O$ (Aldrich), and organic solvents of reagent grade were used as received. $Cu(BF_4)_2.6H_2O$ was prepared from CuO and HBF_4. The CH_3OH used contains 5% 2,2-dimethoxypropane.

Cu(dien) (ImH) (BF$_4$)$_2$[13]

To 10 cm^3 of a CH_3OH solution of $Cu(BF_4)_2.6H_2O$ (1.90 g, 5.51 mmol), was added imidazole (1.12 g, 16.5 mmol). The solution was stirred at room temperature for 1 h and to this solution, a 10 cm^3 CH_3OH solution of diethylenetriamine (0.567 g, 5.50 mmol) was added. After reaction for 1 h, ether was added dropwise until the solution became cloudy. The solution was stored overnight to yield blue crystals. The product was recrystallized from CH_3OH and ether, and was dried *in vacuo* over P_4O_{10}. Yield, 40%, m.p., 262°C (dec). *Anal.*, calc. for $C_7H_{17}N_5F_8B_2Cu$: C, 20.6; H, 4.2; N, 17.1%. Found: C, 20.6; H, 4.1; N, 16.9%. Molar conductivity, 174 S cm^2 mol^{-1} in CH_3OH, 291 S cm^2 mol^{-1} in CH_3CN.

Cu(dien) (py) (BF$_4$)$_2$

This blue complex was prepared and recrystallized as described above, but by using pyridine. Yield, 67%, m.p., 220°C(dec.). *Anal.*, calc. for $C_9H_{18}N_4F_8B_2Cu$: C, 25.7; H, 4.3; N, 13.4%. Found: C, 25.6; H, 4.3; N, 13.3%. Molar conductivity, 147 S cm^2 mol^{-1} in CH_3OH, 325 S cm^2 mol^{-1} in CH_3CN.

Cu(dien) (3Mpy) (BF$_4$)$_2$

This blue complex was prepared and recrystallized as described above but by using 3-methylpyridine. Yield, 37%, m.p., 242°C(dec.). *Anal.*, calc. for $C_{10}H_{20}N_4F_8B_2Cu$: C, 27.7; H, 4.6; N, 12.9%. Found: C, 26.7; H, 4.4; N, 12.4%. Molar conductivity, 155 S cm^2 mol^{-1} in CH_3OH, 250 S cm^2 mol^{-1} in CH_3CN. Columnar crystals suitable for X-ray structure determination were hand-picked from solids before recrystallization.

Cu(dien) (4Mpy) $(BF_4)_2$

This blue complex was prepared and recrystallized as described above but by using 4-methylpyridine. Yield, 4%, m.p., 218°C(dec.). *Anal.*, calc. for $C_{10}H_{20}N_4F_8B_2Cu$: C, 27.7; H, 4.6; N, 12.9%. Found: C, 27.4; H, 4.1; N, 12.6%. Molar conductivity, 190 S cm^2 mol^{-1} in CH_3OH, 316 S cm^2 mol^{-1} in CH_3CN.

Cu(dien) (4acpy) $(BF_4)_2$

This blue complex was prepared and recrystallized as described above but by using 4-acetylpyridine. Yield, 21%, m.p., 185°C(dec.). *Anal.*, calc. for $C_{11}H_{20}N_4OF_8B_2Cu$: C, 28.6; H, 4.4; N, 12.1%. Found: C, 29.3; H, 4.0; N, 11.8%. Molar conductivity, 169 S cm^2 mol^{-1} in CH_3OH, 324 S cm^2 mol^{-1} in CH_3CN.

Cu(dien) $(NMIm)_2$ $(BF_4)_2$

This blue complex was prepared and recrystallized as described above but by using *N*-methylimidazole. Yield, 17%, m.p. 162°C(dec.). *Anal.*, calc. for $C_{12}H_{25}N_7F_8B_2Cu$: C, 28.6; H, 5.0; N, 19.4%. Found: C, 28.4; H, 4.7; N, 19.1%. Molar conductivity, 175 S cm^2 mol^{-1} in CH_3CN.

Cu(dien) (2MImH) $(ClO_4)_2$

This blue complex was prepared and recrystallized as described above but by using 2-methylimidazole and $Cu(ClO_4)_2.6H_2O$. Yield, 17%, m.p., 242°C(dec.). *Anal.*, calc. for $C_8H_{19}N_5O_8Cl_2Cu$: C, 21.5; H, 4.3; N, 15.6%. Found: C, 21.3; H, 4.1; N, 15.5%. Molar conductivity, 152 S cm^2 mol^{-1} in CH_3OH, 248 S cm^2 mol^{-1} in CH_3CN.

Cu(dien) (4MImH) $(ClO_4)_2$

This blue complex was prepared and recrystallized as described above but by using 4-methylimidazole and $Cu(ClO_4)_2.6H_2O$. Yield, 41%, m.p., 262°C(dec.). *Anal.*, calc. for $C_8H_{19}N_5O_8Cl_2Cu$: C, 21.5; H, 4.3; N, 15.6%. Found: C, 21.6; H, 4.2; N, 15.5%. Molar conductivity, 157 S cm^2 mol^{-1} in CH_3OH, 222 S cm^2 mol^{-1} in CH_3CN. Columnar crystals suitable for X-ray structure determination were hand-picked from solids before recrystallization.

Cu(dien) (NH_3) $(ClO_4)_2$

To 5 cm^3 of a CH_3OH solution of $Cu(ClO_4)_2.6H_2O$ (1.54 g, 4.17 mmol), 10 cm^3 CH_3OH solution of diethylenetriamine (0.478 g, 4.63 mmol) was added. After reaction for 1 h, a blue precipitate appeared. The solution became clear again by passing ammonia gas through it. Ether was added dropwise until the solution became cloudy. The solution was stored overnight to yield blue crystals. The product was dried *in vacuo* over P_4O_{10}. Yield, 32%, m.p., 190°C (dec.). *Anal.*, calc. for $C_4H_{16}N_4O_8Cl_2Cu$: C, 12.6; H, 4.2; N, 14.6%. Found: C, 12.9; H, 3.8; N, 14.4%. Molar conductivity, 149 S cm^2 mol^{-1} in CH_3OH, 296 S cm^2 mol^{-1} in CH_3CN.

Physical Measurements

I.r. spectra were recorded in Nujol mulls or KBr pellets on a BIO-RAD FTS-40 FTIR spectrometer. Jasco model 7850 and Perkin-Elmer lambda 9 spectrophotometers were used for electronic spectra measurements. Spectra of solid samples were recorded as Nujol mulls on Whatman No. 1 filter paper. Deconvolution of visible spectra into Gaussian component bands was performed on a VAX 6510 computer using the profile-fitting program *CUVFIT*.[14] E.p.r. spectra were obtained by using a Bruker ER 200D spectrometer and calibrated with DPPH (g = 2.0037). A Micro Vax II computer-controlled Siemens R3m/V diffractometer was used for crystal and molecular structure determination. Elemental analyses were carried out by the microanalysis laboratories of Taiwan University, Taipei.

Structure Determination and Refinement

Details of crystal data and intensity collection are summarized in Table 1. Seventeen independent reflections with $12.34° \leq 2\theta \leq 25.59°$ for **1** and fourteen with $11.18° \leq 2\theta \leq 23.27°$ for **2** were used for least-squares determination of the cell constants. The space groups of $P2_1/n$ for **1** and $P2_1/c$ for **2** were determined from systematic absences. Intensity data ($\theta/2\theta$ scan, $2.5° \leq 2\theta \leq 50.0°$, $(\sin \theta / \lambda)_{\max} \simeq 0.6$) were corrected for Lorentz and polarization effects but not for absorption. Three standard reflections were monitored every 50 reflections and showed no signs of crystal deterioration. The structures were solved by direct methods using *SHELXTL PLUS* program[15] and refined by full-matrix least-squares methods on F values. Scattering factors and anomalous dispersion correction terms were taken from the *International Tables for X-ray Crystallography*.[16] The quantity minimized was $\Sigma w(KF_o - F_c)^2$, with $w = [\sigma^2 F_o + gF_o^2]^{-1}$, where g = 0.0007 for **1** and 0.0056 for **2**. All hydrogen atoms included in the refinement were placed in idealized positions (C–H = 0.96 Å, H–C–H = 109.4°) with a fixed U (0.08 Å^2) after

Table 1 Summary of Crystal Data and Processing Parameters for [Cu(dien) (4MImH) $(ClO_4)_2$] (**1**) and [Cu(dien) (3Mpy) $(BF_4)_2$] (**2**)

formula	$C_8H_{19}N_5O_8Cl_2Cu$(**1**)	$C_{10}H_{20}N_4B_2F_8Cu$(**2**)
fw	447.7	433.5
crystal size (mm)	0.68 × 0.34 × 0.12	0.61 × 0.41 × 0.34
space group	$P2_1/n$, monoclinic	$P2_1/c$, monoclinic
a (Å)	8.496(2)	8.127(3)
b (Å); β(°)	17.290(4); 95.31(2)	14.204(5); 92.75(3)
c (Å)	11.655(2)	15.317(6)
V (Å^3)	1704.7(6)	1766.1(11)
Z	4	4
D_{calcd}(g/cm^3)	1.744	1.630
μ (mm^{-1})	1.645	1.316
radiation (λ, Å)	Mo K_α (0.71073)	Mo Kα (0.71073)
temperature (K)	296	296
independent refl.	3026 (2076 $\geq 3.0\sigma(I)$)	3130 (2070$\geq 3.0\sigma(I)$)
final R, R_w	0.0522, 0.0773	0.0662, 0.0773
largest & mean Δ/σ	0.005, 0.001	0.001, <0.001
largest diff. peak (eA^{-3})	0.79	0.95
largest diff. hole (eA^{-3})	− 0.46	− 0.74

the non-hydrogen atoms were refined anisotropically. All calculations were carried out on a Micro Vax II-based Nicolet *SHELXTL PLUS* system.

RESULTS AND DISCUSSION

The diethylenetriamine copper(II) complexes were prepared from methanol solution containing 5% 2,2-dimethoxypropane dehydrant by using a stoichiometric amount of dien and excess *N*-donor unidentate ligands. The presence of dehydrant facilitates the formation of crystalline products. Addition of excess unidentate ligands prior to dien may suppress the formation of the bis(diethylenetriamine)copper(II) complex. With the exception of the *N*-methylimidazole complex, which contains two unidentate ligands, the mixed ligand complexes isolated consist of only one unidentate *N*-donor. Attempts to prepare 2-methylimidazole and 4-methylimidazole complexes with BF_4^- counter ions were unsuccessful, the corresponding perchlorate complexes were obtained. The complexes are quite stable in a dry atmosphere. In methanol or acetonitrile solution, they are 2:1 electrolytes.

The crystal and molecular structures of complexes **1** and **2** are shown in Figures 1–4. Selected bond lengths and angles are listed in Table 2. The atomic coordinates are given in Table 3. The copper(II) ions of both complexes are bound by a tridentate dien and a unidentate *N*-donor ligand forming a CuN_4 square plane. Both complexes are of [4 + 1 + 1] elongated octahedral structure with the anions bound loosely on the long axis. The planar CuN_4 units are slightly tetrahedrally distorted. The deviations from the best least-squares plane through the four N atoms and the central copper ion are greater for **1** than for **2**: N1, - 0.1737, N2, - 0.1754, N3, 0.1681, N4, 0.1291, and Cu, 0.0519Å for **1**, and N1, - 0.0236, N2, - 0.0236, N3, 0.0230, N4, 0.0182, and Cu, 0.0059Å for **2**. The anions and the amine groups of the copper units are interconnected by hydrogen bonds as illustrated in Figures 2 and 4.

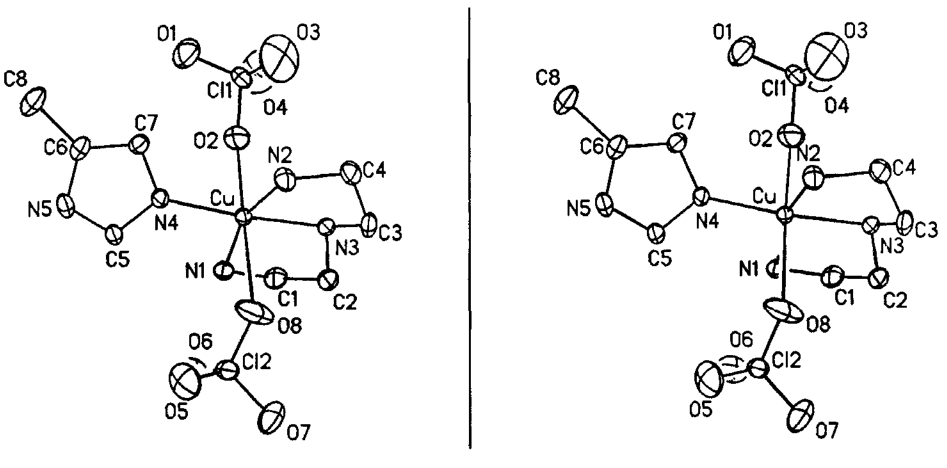

Figure 1 Stereoscopic drawing of [Cu(dien) (4MImH) $(ClO_4)_2$] with numbering scheme.

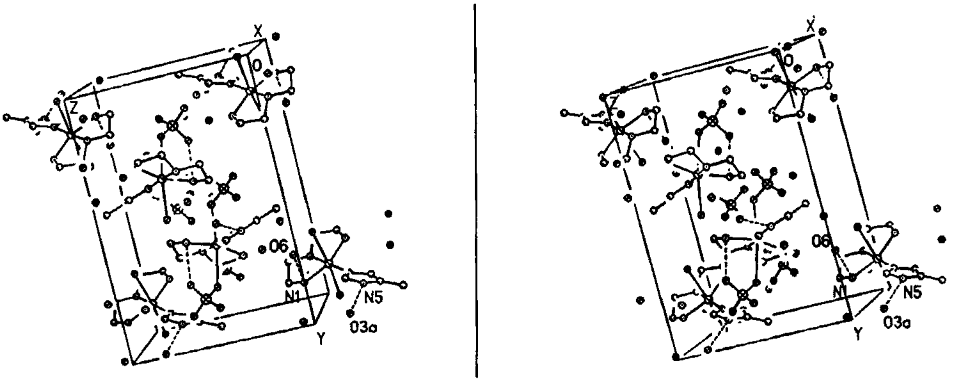

Figure 2 Stereoscopic drawing of the molecular packing of [Cu(dien) (4MImH) $(ClO_4)_2$] in the unit cell. Hydrogen bonds: N1. . . 06, 3.047Å and N5. . . 03a, 2.885Å.

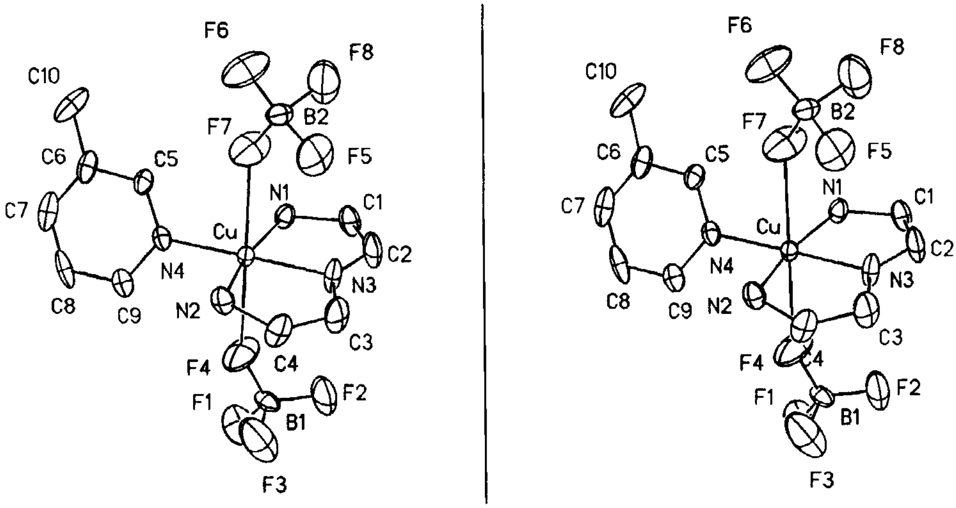

Figure 3 Stereoscopic drawing of [Cu(dien) (3Mpy) $(BF_4)_2$] with numbering scheme.

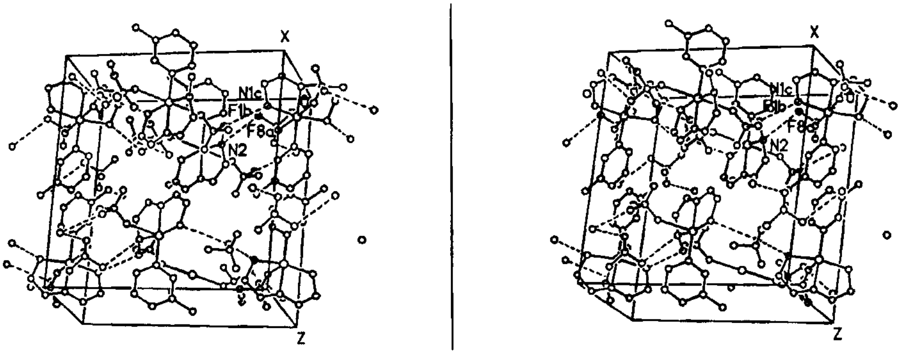

Figure 4 Stereoscopic drawing of the molecular packing of [Cu(dien) (3Mpy) $(BF_4)_2$] in the unit cell. Hydrogen bonds: N2. . . F8a, 2.956Å, N2. . . F1b, 3.092Å, N1c. . . F1b, 3.217Å.

Table 2 Bond lengths (Å) and Angles (°) for [Cu(dien) (4MImH) $(ClO_4)_2$] (**1**) and [Cu(dien) (3Mpy) $(BF_4)_2$] (**2**).

	[Cu(dien) (4MImH) $(ClO_4)_2$]		
Cu-N(1)	2.022(6)	Cu-N(2)	2.024(7)
Cu-N(3)	1.995(5)	Cu-N(4)	1.967(5)
Cu-O(2)	2.617(8)	Cu-O(8)	2.701(8)
N(1)-Cu-N(2)	161.5(3)	N(1)-Cu-N(3)	83.9(2)
N(2)-Cu-N(3)	83.9(2)	N(1)-Cu-N(4)	97.6(2)
N(2)-Cu-N(4)	96.1(2)	N(3)-Cu-N(4)	174.4(2)
N(1)-Cu-O(2)	84.2(3)	N(2)-Cu-O(2)	108.2(3)
N(3)-Cu-O(2)	85.1(2)	N(4)-Cu-O(2)	89.6(2)
N(1)-Cu-O(8)	89.9(3)	N(2)-Cu-O(8)	76.8(3)
N(3)-Cu-O(8)	91.3(2)	N(4)-Cu-O(8)	94.1(2)
O(2)-Cu-O(8)	173.4(3)		
	[Cu(dien) (3Mpy) $(BF_4)_2$]		
Cu-N(1)	2.006(7)	Cu-N(2)	2.016(7)
Cu-N(3)	2.011(7)	Cu-N(4)	1.996(7)
Cu-F(4)	2.556(10)	Cu-F(7)	2.579(9)
N(1)-Cu-N(2)	167.5(3)	N(1)-Cu-N(3)	84.1(3)
N(1)-Cu-N(4)	96.5(3)	N(2)-Cu-N(3)	83.7(3)
N(2)-Cu-N(4)	95.8(3)	N(3)-Cu-N(4)	177.5(3)
N(1)-Cu-F(4)	91.8(3)	N(2)-Cu-F(4)	90.1(3)
N(3)-Cu-F(4)	88.0(3)	N(4)-Cu-F(4)	89.6(3)
N(1)-Cu-F(7)	85.4(3)	N(2)-Cu-F(7)	93.0(3)
N(3)-Cu-F(7)	93.5(3)	N(4)-Cu-F(7)	88.9(3)
F(4)-Cu-F(7)	176.6(3)		

The constraints of the tridentate dien ligand force the coordination of the two terminal nitrogen atoms to bend towards the central nitrogen atom. The bite angles are close to 84°. The planar tridentate dien requires the two ethylenediamine chelate rings in a δ and a λ conformation, with torsion angles of ~27° for **1** and ~5° for **2**. The small torsion angles in **2** are due to large thermal vibrations for the ethylene C2 and C3 atoms. The dimensions of the dien ligands are otherwise normal. Large thermal vibrations are also observed for the 3Mpy C7, C8 and C10 atoms. The lengths of the Cu–N coordination bonds of the dien, mean 2.012Å, are in agreement with those reported for other dien[4–12] and ethylenediamine[2,17] complexes. The Cu–N(3Mpy) distance of 1.996(7)Å is close to the typical Cu–N(pyridine) interaction of ~2.0 Å,[18–22] with a dihedral angle of 57.7° between the pyridine ring and the CuN_4 plane. A corresponding dihedral angle of 66.2° for [Cu(terpyridine) (3Mpy) $(BF_4)_2$] has been reported.[23] The Cu–N(4MImH) distance of 1.967(5)Å is significantly shorter than usual Cu–N(imidazole) bonds in tetragonal complexes.[24–28] The dihedral angle between the imidazole ring and the CuN_4 coordination plane is 41.2°, which is much smaller than the angle of 85.3° observed for [Cu(terpyridine) (4MImH) (H_2O) (BF_4)] (BF_4).[23] Large thermal vibrations are observed for the anions, but bond lengths and angles are in normal ranges.

Infrared data are listed in Table 4. There are multiple peaks with strong to medium intensities in the ~3150 to ~3350 cm^{-1} region assignable for N–H stretches for the dien ligand.[29] For the NH_3 and the imidazole complexes, the N–H stretches of the unidentate ligands are mixed in this region. Variation of the peak positions indicates (possibly) hydrogen bonds involved in the dien and the anions as observed in the 3Mpy and the 4MImH complexes. The Cu-N(dien) stretches were tentatively assigned (consistently) at ~390, ~350 and ~320 cm^{-1}. Cu–N

Table 3 Atomic Coordinates (× 10^4) and Equivalent Isotropic Displacement Coefficients* (Å^2 × 10^3) for [Cu(dien) (4MImH) $(ClO_4)_2$] (**1**) and [Cu(dien) (3Mpy) $(BF_4)_2$] (**2**).

		[Cu(dien) (4MImH) $(ClO_4)_2$]		
	x/a	*y/b*	*z/c*	*U(eq)*
Cu	1152(1)	6470(1)	4195(1)	39(1)
Cl(1)	3373(2)	4706(1)	3406(2)	55(1)
Cl(2)	3512(2)	6917(1)	57(2)	53(1)
N(1)	245(7)	6070(4)	5624(5)	48(2)
N(2)	2218(7)	7165(4)	3102(5)	60(2)
N(3)	3022(6)	6733(3)	5288(4)	42(2)
N(4)	- 568(6)	6126(4)	3065(5)	45(2)
N(5)	- 2895(7)	5860(4)	2205(6)	61(2)
C(1)	1492(10)	6067(5)	6608(6)	64(3)
C(2)	2533(9)	6751(5)	6490(6)	61(3)
C(3)	3743(9)	7448(5)	4894(7)	60(3)
C(4)	3797(10)	7383(5)	3608(8)	66(3)
C(5)	- 2110(8)	6119(5)	3176(6)	54(3)
C(6)	- 1850(9)	5711(4)	1432(6)	52(3)
C(7)	- 418(9)	5889(4)	1949(6)	48(2)
C(8)	- 2367(12)	5412(6)	232(8)	84(4)
O(1)	2396(10)	4265(6)	2622(7)	127(4)
O(2)	2433(9)	5096(5)	4141(8)	121(4)
O(3)	4284(19)	5187(11)	2983(12)	284(10)
O(4)	4196(15)	4215(7)	4108(12)	225(7)
O(5)	2319(9)	6625(5)	- 738(6)	117(4)
O(6)	2852(9)	7614(4)	560(7)	100(3)
O(7)	3856(9)	6382(4)	948(5)	103(3)
O(8)	4837(8)	7133(5)	- 486(8)	125(4)
		[Cu(dien) (3Mpy) $(BF_4)_2$]		
	x/a	*z/b*	*z/c*	*U(eq)*
Cu	2548(1)	423(1)	7682(1)	40(1)
F(1)	- 2338(7)	2205(7)	7713(6)	142(4)
F(2)	- 1080(14)	1589(7)	8954(6)	177(5)
F(3)	- 157(16)	2742(7)	8330(8)	213(7)
F(4)	16(12)	1488(8)	7719(6)	188(5)
N(4)	2322(8)	408(5)	6378(4)	55(2)
N(2)	4027(9)	1562(5)	7770(5)	64(3)
N(3)	2704(11)	483(6)	8995(4)	76(3)
N(1)	1190(9)	- 731(5)	7874(4)	63(2)
B(1)	- 1032(12)	1928(7)	8188(8)	68(4)
C(9)	1725(11)	1163(7)	5942(6)	70(3)
C(8)	1567(16)	1152(10)	5028(8)	104(5)
C(7)	2113(14)	388(10)	4585(7)	98(5)
C(6)	2704(12)	- 393(8)	5019(6)	81(4)
C(5)	2776(10)	- 347(6)	5911(5)	60(3)
C(4)	4235(13)	1856(7)	8674(6)	83(4)
C(3)	3579(17)	1217(8)	9287(6)	108(5)
C(2)	2070(18)	- 311(7)	9336(7)	103(5)
C(1)	1114(12)	- 934(7)	8803(6)	75(3)
C(10)	3244(13)	- 1261(10)	4562(8)	122(6)
F(5)	6591(13)	- 405(5)	8703(6)	148(4)
F(6)	7481(8)	- 1253(8)	7552(7)	165(5)
F(7)	4992(10)	- 727(7)	7605(6)	163(4)
F(8)	5888(21)	- 1809(6)	8428(7)	224(7)
B(2)	6278(13)	- 1004(7)	8022(7)	63(4)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4 IR Data for dien-Cu(II) Complexes[a].

Compound[b]	νN-H(dien)	νCu-N(dien)	νCu-N(L)
$[Cu(dien)(ImH)(BF_4)_2]$[c]	3348s 3298s 3155m	384mw 353mw 322mw	347mw
$[Cu(dien)(4MImH)(ClO_4)_2]$[d]	3341s 3291m 3246s 3140m	388mw 353m 320mw	344sh
$[Cu(dien)(2MImH)(ClO_4)_2]$[e]	3366s 3343s 3294ms 3281ms 3256ms 3144m	390m 326mw	336mw
$[Cu(dien)(NMIm)_2](BF_4)_2$[f]	3348s 3298s 3279s	378mw 353w 322mw	370w
$[Cu(dien)(3Mpy)(BF_4)_2]$[g]	3345s 3293s 3274m 3165m	390m 355m 324m	345m
$[Cu(dien)(4Mpy)(BF_4)_2]$[h]	3348s 3293s 3267s 3161m	390m 355m 322m	341mw
$[Cu(dien)(py)(BF_4)_2]$[i]	3343s 3289s 3173m	384mw 353m 322w	343mw
$[Cu(dien)(4acpy)(BF_4)_2]$[j]	3354s 3337s 3275s	395mw 357mw	334mw
$[Cu(dien)(NH_3)(ClO_4)_2]$[k]	3356s 3341s 3291s 3250s	380mw 320mw	446sh

[a] Measured in Nujol mulls or KBr pellets. [b]dien = diethylenetriamine; ImH = imidazole; 4MImH = 4-methylimidazole; 2MImH = 2-methylimidazole; NMIm = *N*-methylimidazole; 3Mpy = 3-methylpyridine; 4Mpy = 4-methylpyridine; py = pyridine; 4acpy = 4-acetylpyridine. [c]νN-H(ImH) masked; $\nu(BF_4)$ 1092vs, 521s. [d]νN-H(ImH) masked; $\nu(ClO_4)$ 1094vs, 621s. [e]νN-H(ImH), masked; $\nu(ClO_4)$ 1125vs, 1065vs, 621s. [f]$\nu(BF_4)$ 1076vs, 521s, [g]$\nu(BF_4)$ 1092vs, 523s; δ(py) 413m. [h]$\nu(BF_4)$, 1092vs, 521s; δ(py) 420vw. [i]$\nu(BF_4)$ 1092vs, 521s; δ(py) 430m. [j]ν(C=O) 1705s; $\nu(BF_4)$ 1092vs, 521s; δ(py) 430mw. [k]νN-H(NH_3) masked; $\nu(ClO_4)$, 1095vs, 625s.

stretches for the unidentate ligands are tentatively assigned at ~340 cm^{-1}. Cu-N(NH_3), however, appears at much higher frequency.[30]

Electronic spectral data for the mixed ligand dien-Cu(II) complexes are presented in Table 5. Band maxima of the LF spectra for the complexes with one unidentate ligand, both measured as mulls and in solution, appear in a range of 536 to 596 nm, suggesting that the structures are elongated octahedral with a square planar CuN_4 unit. The square pyramidal complex [Cu(dien) $(NMIm)_2)$] $(BF_4)_2$[31] exhibits a λ_{max} at a lower energy of 612 nm whilst the solution spectrum shows λ_{max} at 580 nm, indicating that the solution species contains only one NMIm ligand. The NH_3

Table 5 Visible and Epr Data for dien-Cu(II) Complexes.

Compound[a]	LF bands	E.p.r.[b]		
	λ_{max}(ε),nm	$g_\perp$	$g_\parallel$	$A_\parallel$(Cu)[c]
$[Cu(dien) (ImH) (BF_4)_2]$	575/mull 580(94)/MeOH	2.050	2.215	197
$[Cu(dien) (4MImH) (ClO_4)_2]$	572/mull 580(98)/MeOH	2.050	2.212	196
$[Cu(dien) (2MImH) (ClO_4)_2]$	596/mull 585(103)/MeOH	2.049	2.210	196
$[Cu(dien) (NMIm)_2] (BF_4)_2$	612/mull 580(100)/MeOH	2.049	2.213	194
$[Cu(dien) (3Mpy) (BF_4)_2]$	563/mull 570(113)/MeCN	2.051	2.205	200
$[Cu(dien) (4Mpy) (BF_4)_2]$	571/mull 572(104)/MeCN	2.051	2.209	197
$[Cu(dien) (py) (BF_4)_2]$	568/mull 570(97)/MeCN	2.050	2.207	198
$[Cu(dien) (4acpy) (BF_4)_2]$	536/mull 571(141)/MeCN	2.052	2.210	199
$[Cu(dien) (NH_3) (ClO_4)_2]$	553/mull 577(86)/MeOH	2.049	2.208	198

[a] For abbreviations, see Table 4. [b]X-band epr spectra measured at 77 K in aqueous methanol for NH_3 and imidazole complexes and in CH_3CN for pyridine complexes. [c]10^{-4}cm^{-1}.

complex with λ_{max} at 553 nm shows strong σ-donation by the NH_3 ligand (pK_a 9.26).[32]

For the species in CH_3OH or CH_3CN, the axial anions are completely replaced by the solvent molecules as indicated by the high conductivity in solution. The unidentate *N*-donor ligands are non-dissociative in CH_3CN solution, because addition of excess unidentate ligands results in a red shift of the d-d spectra. The NH_3 and the imidazole ligands are also non-dissociative in CH_3OH solution. The pyridine ligands, however, are dissociative in CH_3OH, because addition of the pyridine ligands causes a blue shift of the d-d bands. The identity of the solution species is also supported by the axial epr data measured in frozen matrix at 77 K as presented in Table 5. No superhyperfine coupling in the $g_\perp$ region was observed for these complexes. The $A_\parallel$ values are only marginally smaller for the imidazole complexes with respect to the pyridine species. This fact[22,23] is consistent with the slightly larger tetrahedral distortion for the 4MImH complex than for the 3Mpy case. Electronically, however, these complexes are essentially square planar. The $g_\parallel$ values are slightly but significantly smaller for the pyridine complexes than for the imidazole cases. Because $g_\parallel = 2-8r_\parallel\lambda/E(d_{xy}-d_{x^2-y^2})$,[30,34] the smaller $g_\parallel$ values for pyridine complexes may suggest the d_{xy} level be lowered, consistent with the results of the ligand field spectra (*vide infra*). Note that the epr parameters for the NMIm complex are comparable with other complexes, suggesting again the solution species comprising only one NMIm ligand.

It is noteworthy that the λ_{max} values for the 3-methylpyridine complex (563 nm/mull and 570 nm/CH_3CN) are at higher energy than those for the 4-methylimidazole complex (572 nm/mull and 580 nm/CH_3OH), despite the fact that the 3-methylpyridine ligand (pK_a 5.68[32]) is a weaker σ-donor than 4-methylimidazole (pK_a 7.35[35]). In fact, all of the pyridine complexes exhibit λ_{max} values at higher energy than those for the imidazole complexes by ~10 nm. This fact suggests that the d orbitals of these structurally similar tetragonal complexes are likely affected by the heterocyclic unidentate ligands. This could be either due to ascending d_{xz} orbital energy resulting from π-donation by imidazole ligands or descending d_{xy} orbital energy from π-accepting by pyridine ligands. The former may be ruled out because steric effects prevent the imidazole nucleus from lying parallel with the CuN_4 plane. The latter is supported by the visible spectrum of the 4-acetylpyridine complex. The λ_{max} of 536 nm most likely stems from the strong π-accepting pyridine ligand due to the presence of the 4-acetyl group.

In order to elucidate the π-interactions of the heterocyclic ligands, the visible spectra were deconvoluted into Gaussian components for detailed analysis of the d orbitals. Because of the tetragonal octahedral structure of the complexes where the heterocyclic unidentate ligands are not likely to lie parallel with the CuN_4 coordination plane, three peaks were assumed for the curve fitting processes. After computer iteration, each of the complexes had an excellent fit with the reliability factor, R,[36] less than ~0.7%, and showed a resulting set comprising three Gaussian component peaks. The results are illustrated in Figure 5. The peak positions are presented in Table 6 together with their half-height widths and relative peak areas. As reported in tetragonal CuN_4X_2 complexes,[17,25,28,37] the sequence of the d orbitals is designated as $d_{x^2-y^2} >> d_{z^2} > d_{xy} > d_{xz} \sim d_{yz}$. The intensities of the component peaks are very similar to those of tetragonal $[Cu(ImH)_4(NO_3)_2]$;[28] the highest energy peak has the greatest intensity and the lowest energy peak the smallest intensity. The intensity of the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition in some cases is very

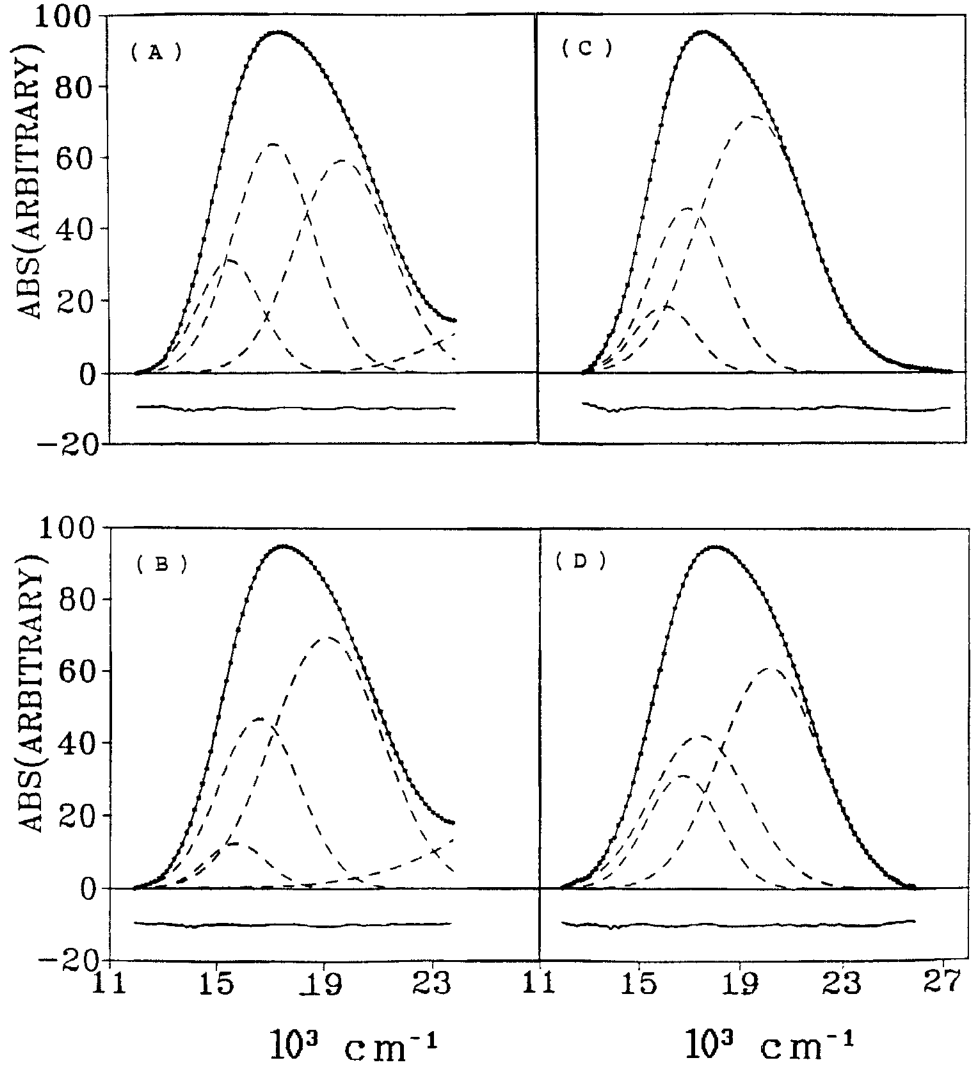

Figure 5 Visible spectra and Gaussian line-shape analysis with differences plots of (A) [Cu(dien)(NH_3)(ClO_4)$_2$]; (B) [Cu(dien)(4MImH)(ClO_4)$_2$]; (C) [Cu(dien)(ImH)(BF_4)$_2$]; (D) [Cu(dien)(3Mpy)(BF_4)$_2$]; (*) profile-fitting points; (---) Gaussian components; (—) observed spectrum.

small. The same situation was observed in the single crystal polarized spectrum of the tetragonal octahedral complex [Cu(ImH)$_6$ (NO_3)$_2$].[37]

The energy difference of the d_{xy} and the degenerate d_{xz} and d_{yz} orbitals can serve as an indication of π-interactions between the ligand π-orbitals and the copper d_π orbitals. Taking the energy difference of 2.6×10^3 cm^{-1} for the NH_3 complex as a reference, a difference of 2.6×10^3 cm^{-1} for the imidazole complexes suggests no π-interactions in these complexes. The differences of 2.2×10^3 cm^{-1} for the

Table 6 Gaussian Component Bands for the Visible Spectra of dien-Cu(II) Complexes.

band	$\nu/10^3$cm^{-1}	area[a]	$\delta_{1/2}$[b]	assignment
[Cu(dien) (NH$_3$) (ClO$_4$)$_2$] (R = 0.50%)[c]				
I	15.6	15.8	2.82	d_{z^2}
II	17.2	40.8	3.55	d_{xy}
III	19.8	43.4	4.09	$d_{xz};d_{yz}$
[Cu(dien) (ImH) (BF$_4$)$_2$] (R = 0.76%)[c]				
I	16.1	9.2	2.81	d_{z^2}
II	17.0	27.8	3.43	d_{xy}
III	19.6	62.9	4.91	$d_{xz};d_{yz}$
[Cu(dien) (4MImH) (ClO$_4$)$_2$] (R = 0.35%)[c]				
I	15.7	6.3	2.70	d_{z^2}
II	16.6	31.5	3.56	d_{xy}
III	19.1	62.2	4.75	$d_{xz};d_{yz}$
[Cu(dien) (2MImH) (ClO$_4$)$_2$] (R = 0.35%)[c]				
I	15.7	12.2	2.73	d_{z^2}
II	16.7	35.0	4.05	d_{xy}
III	19.3	52.8	5.00	$d_{xz};d_{yz}$
[Cu(dien) (3Mpy) (BF$_4$)$_2$] (R = 0.63%)[c]				
I	16.7	18.0	3.34	d_{z^2}
II	17.4	33.0	4.49	d_{xy}
III	20.1	49.0	4.62	$d_{xz};d_{yz}$
[Cu(dien) (4Mpy) (BF$_4$)$_2$] (R = 0.70%)[c]				
I	16.4	14.4	4.85	d_{z^2}
II	16.6	20.8	3.19	d_{xy}
III	19.3	64.8	5.13	$d_{xz};d_{yz}$
[Cu(dien) (py) (BF$_4$)$_2$] (R = 0.27%)[c]				
I	13.1	10.3	2.68	d_{z^2}
II	16.1	25.7	3.12	d_{xy}
III	18.3	64.0	5.73	$d_{xz};d_{yz}$
[Cu(dien) (4acpy) (BF$_4$)$_2$] (R = 0.292%)[c]				
I	17.0	15.8	2.94	d_{z^2}
II	17.8	31.6	4.77	d_{xy}
III	20.1	51.6	4.65	$d_{xz};d_{yz}$

[a] Relative peak area in arbitrary scale based on a sum of 100.
[b] Half-width at $\varepsilon_{max}/2$. [c] Reliability factor defined as $R = \Sigma|Y_{obs,i} - Y_{calc,i}|/\Sigma Y_{obs,i}$.

pyridine complex and 2.3 × 10^3 cm^{-1} for the 4-acetylpyridine complex are indications of π-accepting properties for these ligands. The 4-methylpyridine and the 3-methylpyridine ligands, however, do not participate in π-interaction.

In conclusion, we have demonstrated that the imidazole ligands are simply σ-donors in the tetragonal, mixed ligand dien-Cu(II) complexes. This may be ascribed to the strong σ-donating abilities of both dien and imidazole ligands so that no additional electron density is demanded by the central copper(II) ion. For the pyridine complexes, however, electron density may be released to the π-accepting ligands *via* π-interactions in accord with the electroneutrality principle. The results of this study further support a previous report[23] that terpyridine is a π-acceptor in mixed ligand, terpyridine copper(II) complexes. Such a π-accepting interaction is strong enough to affect the orientations of the *trans* ligand. The 4MImH ligand in [Cu(terpyridine) (4MImH) (H$_2$O) (BF$_4$)] (BF$_4$) lies nearly perpendicular to the CuN$_4$ coordination plane, and acts as a π-donor. 3Mpy is a potential π-acceptor and is tilted from the CuN$_4$ plane by 66.2° in [Cu(terpyridine) (3Mpy) (BF$_4$)$_2$] so as to avoid competing with terpyridine for withdrawing electron density from the central copper ion.

Supplementary Material

Additional material comprising structure factors, anisotropic thermal parameters, and H atom coordinates are available from the authors on request.

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