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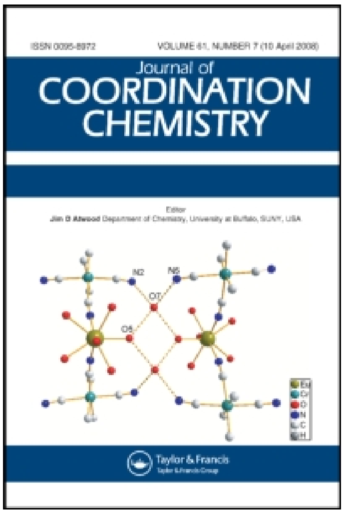

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BONDING PROPERTIES OF CU(II)-*N* CHROMOPHORES: PREPARATION, STRUCTURE, AND SPECTROSCOPIC PROPERTIES OF *N,N,N',N'*-TETRAMETHYLETHYLENEDIAMINE COPPER (II) COMPLEXES. MOLECULAR STRUCTURE OF BIS(4-METHYLPYRIDINE)PERCHLORATO-(*N,N,N',N'*-TETRAMETHYLETHYLENEDIAMINE) COPPER(II) PERCHLORATE

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BONDING PROPERTIES OF CU(II)-*N* CHROMOPHORES: PREPARATION, STRUCTURE, AND SPECTROSCOPIC PROPERTIES OF *N,N,N',N'*-TETRAMETHYLETHYLENEDIAMINE COPPER (II) COMPLEXES. MOLECULAR STRUCTURE OF BIS(4-METHYLPYRIDINE)PERCHLORATO-(*N,N,N',N'*-TETRAMETHYLETHYLENEDIAMINE) COPPER(II) PERCHLORATE

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N,N,N',N'-Tetramethylethylenediamine (tmen) copper(II) perchlorate and/or tetrafluoroborate complexes of the type Cu(tmen)L_2(anion)$_2$, where L represents imidazole, *N*-methylimidazole, 2-methylimidazole, 4-methylimidazole, 4-methylpyridine and NH_3, have been synthesized and characterized by analysis, and electronic, vibrational and epr spectroscopic measurements. The molecular structure of [Cu(tmen)(4Mpy)$_2$(ClO$_4$)](ClO$_4$) (4Mpy = 4-methylpyridine) has been determined using three-dimensional X-ray diffraction data. The complex salt is monoclinic, space group $P2_1/n$ with $Z = 4$, $a = 11.876(3)$, $b = 13.548(2)$, $c = 15.773(3)$Å and $\beta = 95.47(2)$°. Least-squares refinement of the structure yielded $R = 7.48\%$ and $R_w = 7.29\%$ for 1164 independent reflections at 297K. The Cu(II) ion is five coordinated (square pyramid) with the tmen and the 4-methylpyridine ligands on the basal plane, mean Cu-N(tmen) 2.074 Å and mean Cu-N(4Mpy) distances 2.008 Å, and one ClO_4^- at the apex, Cu-O 2.353(14) Å. Both 4-methylpyridine planes are nearly perpendicular to the CuN_4 coordination plane; dihedral angles are 92.5° and 98.0°. Based on spectroscopic data, similar structures are proposed for other tmen complexes. The bonding properties of the heterocyclic ligands to the tmen-Cu(II) core are elucidated and discussed by reference to the electronic structures of the complexes deduced from Gaussian analyses of their LF spectra.

KEYWORDS: Copper(II), *N,N,N',N'*-tetramethylethylenediamine, imidazole, 4-methylpyridine, X-ray structure, d-d spectra.

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INTRODUCTION

The bonding properties of copper(II)-imidazole are intriguing with respect to both structures and reactivities of copper ions in biological systems.[1-3] In previous studies,[4] we have found that in *tetrakis*(imidazole)copper(II) complexes, as the imidazole ring lies approximately parallel to the *xy* coordination plane, imidazole is a π-donor, but not when the ring is oriented nearly perpendicular to the *xy* plane. This is attributed to energetically favourable interactions of the copper d_{xz} and d_{yz} orbitals with the π_1 and π_2 orbitals rather than the π^* orbitals of the imidazole ligands.[5] The π-bonding capabilities of imidazole may be altered by changing the ligand environments and coordination numbers of the copper complexes. Herein, we report spectroscopic studies of *N,N,N',N'*-tetramethylethylenediamine copper(II) complexes and the molecular structure of the title complex, and elucidate the copper(II)-imidazole bonding properties based on electronic structures of the complexes.

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EXPERIMENTAL

Materials and Preparations

N-Methylimidazole (Aldrich), 2-methylimidazole (Merck), 4-methylimidazole (Aldrich), imidazole (Merck), 4-methylpyridine (Merck), 2,2-dimethoxypropane (Merck), *N,N,N',N'*-tetramethylethylenediamine (Aldrich), $Cu(ClO_4)_2.6H_2O$ (Aldrich), and organic solvents were used as received. $Cu(BF_4)_26H_2O$ was prepared from CuO and HBF_4. All complexes were prepared by the following general method. A 2,2-dimethoxypropane solution (12 cm^3) of $Cu(ClO_4)_2.6H_2O$ or $Cu(BF_4)_2.6H_2O$ (8.37 mmol) was stirred for ~40 min. When the solution turned pale green, methanol, containing 5% 2,2-dimethoxypropane, was added to make a total volume of 25 cm^3. Two cm^3 (0.67 mmol) of the anhydrous Cu(II) stock solution was added with stirring to a methanol solution of the *N*-donor unidentate ligand (1.34 mmol). After 20 min., *N,N,N',N'*-tetramethylethylenediamine (0.67 mmol) was added to the solution which was stirred for a further 20 min. Precipitates were formed by adding ether dropwise to the solutions. The bluish-purple products were filtered and dried *in vacuo* over P_4O_{10}. Yields were about 30–50%. Blue, columnar crystals of $[Cu(tmen)(4Mpy)_2(ClO_4)](ClO_4)$[6] suitable for X-ray structure determination were obtained from a refrigerated methanol solution containing 2 cm^3 of the anhydrous Cu(II) stock solution and 1 cm^3 of stoichiometric amounts of 4Mpy and tmen in methanol.

Physical Measurements

IR spectra were recorded as Nujol mulls or KBr pellets with a BIO-RAD FTS-40 FTIR. Jasco 7850 and Perkin-Elmer Lambda 9 spectrophotometers were used for electronic spectra measurements. Spectra of solid samples were recorded in Nujol mulls on Whatman No. 1 filter paper. Deconvolution of the visible spectra into Gaussian components was performed on a VAX 6510 computer using the profile-fitting program *CUVFIT*.[7] Epr spectra were obtained using a Bruker ER 200D 10/20 spectrometer and calibrated with DPPH (g = 2.0037). Elemental analyses were carried out by the microanalysis laboratories of Taiwan University, Taipei. A Micro Vax II computer-controlled Siemens R3m/V diffractometer was used for the crystal and molecular structure determination.

Structure Determination and Refinement

Details of crystal data and intensity collection are summarized in Table 1. Sixteen independent reflections with $8.35° \leq 2\theta \leq 26.43°$ were used for least-squares determination of the cell constants. Diffractometer examination of the reciprocal lattice showed the space group to be $P2_1/n$ from the systematic absences: $h0l$, $h+l \mp 2n+1$; $0k0$, $k \mp 2n+1$. Intensity data ($\theta/2\theta$ scan, $3.0° \leq 2\theta \leq 50.0°$, $(\sin\theta/\lambda)_{\max} \sim 0.6$) were collected at 297K for two octants of the sphere ($-14 \leq h \leq 0$, $0 \leq k \leq 16$, $-18 \leq l \leq 18$) and 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 structure was solved by direct methods using *SHELXTL PLUS* program[8] and refined by full-matrix least-squares on F values. Scattering form factors and anomalous dispersion correction terms were taken from the *International Tables for X-ray Crystallography.*[9] The quantity minimized was $\Sigma w(KF_o - F_c)^2$, with $w = [\sigma^2(F_o) + 0.0007F_o]^{-1}$. 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 the non-hydrogen atoms were refined anisotropically. A final difference map showed no unusual features (largest difference peak 0.86 e/Å^3 and largest difference hole −0.47 e/Å^3) All calculations were carried out on a Micro Vax II-based Nicolet *SHELXTL PLUS* system.

RESULTS AND DISCUSSION

Preparation of the *N,N,N',N'*-tetramethylethylenediaminecopper(II) complexes was carried out under anhydrous conditions to minimize the formation of the

Table 1 Summary of crystal data and intensity collection.

Empirical Formular	$CuC_{18}H_{30}Cl_2N_4O_8$
Crystal Size (mm)	0.36 x 0.20 x 0.18
Space Group	$P2_1/n$; Monoclinic
a (Å)	11.876(3)
b (Å); β (°)	13.548(2); 95.47(2)
c (Å)	15.773(3)
Volume (Å^3)	2526.2(9)
Z	4
D_{calcd} (g/cm^3)	1.485
μ (mm^{-1})	1.125
$F(000)$	1172
Radiation (λ, A)	MoK$_\alpha$(0.71073)
Reflection Collected	4987(1811 > 3.0$\sigma(I)$)
Independent Reflections	4485(1164 > 3.0$\sigma(I)$)
Min./Max. Transimission	0.8599/0.8811
Number of Parameters Refined	217
Final R, R_w	0.0748, 0.0729
Largest & Mean Δ/σ	0.021, 0.001

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Table 2 Analytical and physical data for *N,N,N',N'*-tetramethylethylenediamine copper(II) complexes.

Complex[a]	C(calcd.),%	H(calcd.),%	N(calcd.),%	mp, °C	cond.[b]
$[Cu(tmen)(NMIm)_2(ClO_4)](ClO_4)$	30.6(31.0)	4.84(5.16)	15.3(15.5)	128	194
$[Cu(tmen)(NMIm)_2(BF_4)](BF_4)$	31.8(32.5)	5.17(5.40)	16.4(16.2)	143	
$[Cu(tmen)(4MImH)_2(H_2O)](ClO_4)_2$	29.9(29.2)	5.17(5.35)	14.5(14.0)	125	169
$[Cu(tmen)(4MImH)_2(BF_4)](BF_4)$	31.9(32.5)	5.31(5.40)	15.8(16.2)	142	
$[Cu(tmen)(2MImH)_2(ClO_4)](ClO_4)$	31.4(31.0)	5.82(5.19)	15.2(15.5)	146	143
$[Cu(tmen)(ImH)_2(BF_4)](BF_4)(H_2O)$	27.9(28.4)	4.57(5.12)	16.3(16.5)	152	
$[Cu(tmen)(4Mpy)_2(ClO_4)](ClO_4)$	37.6(38.3)	5.39(5.35)	9.88(9.91)	193	176
$[Cu(tmen)(NH_3)_2(ClO_4)](ClO_4)$	17.4(17.4)	5.31(5.33)	14.4(13.6)	165	180

[a] Tmen = *N,N,N',N'*-tetramethylethylenediamine; NMIm = *N*-methylimidazole; 4MImH = 4-methylimidazole; 2MImH = 2-methylimidazole; ImH = imidazole; 4Mpy = 4-methylpyridine. [b] $Cm^2ohm^{-1}mol^{-1}$ in MeOH.

dihydroxo-bridged $[Cu_2(tmen)_2(\mu\text{-}OH)_2]^{2+}$ complex.[10] Since prolonged reaction of the 2,2-dimethoxypropane dehydrant with the starting hydrated copper(II) perchlorate or tetrafluoroborate resulted in severe side reactions, the unidentate ligands were added to the dehydrated Cu(II) solution when it just turned pale green. Although for steric reason the central copper(II) ions cannot accommodate two tmen ligands, addition of excess tmen to the reaction mixture should be avoided to minimize complications due to, presumably, reduction of the copper(II) complex or oxidation of the tmen ligand. The solid products contained only two *N*-donor unidentate ligands, even if excess amounts of the ligands were used. Analytical data and some physical properties are given in Table 2. The presence of H_2O molecules in the imidazole and the 4-methylimidazole complexes was verified by infrared spectra. The complexes are stable in a dry atmosphere.

The crystal and molecular structure of $[Cu(tmen)(4Mpy)_2(ClO_4)](ClO_4)$ is shown in Figures 1 and 2. Selected bond lengths and angles are listed in Table 3, and

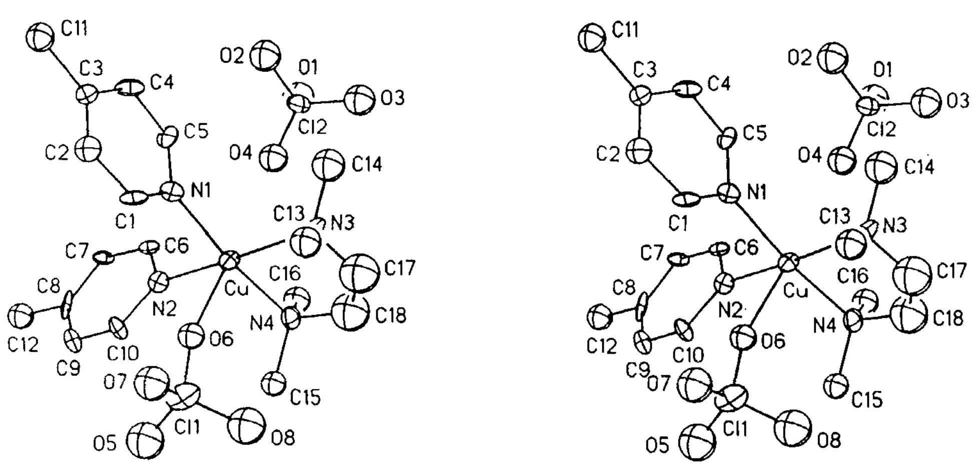

Figure 1 Stereoscopic diagram of $[Cu(tmen)(4Mpy)_2(ClO_4)_2]$.

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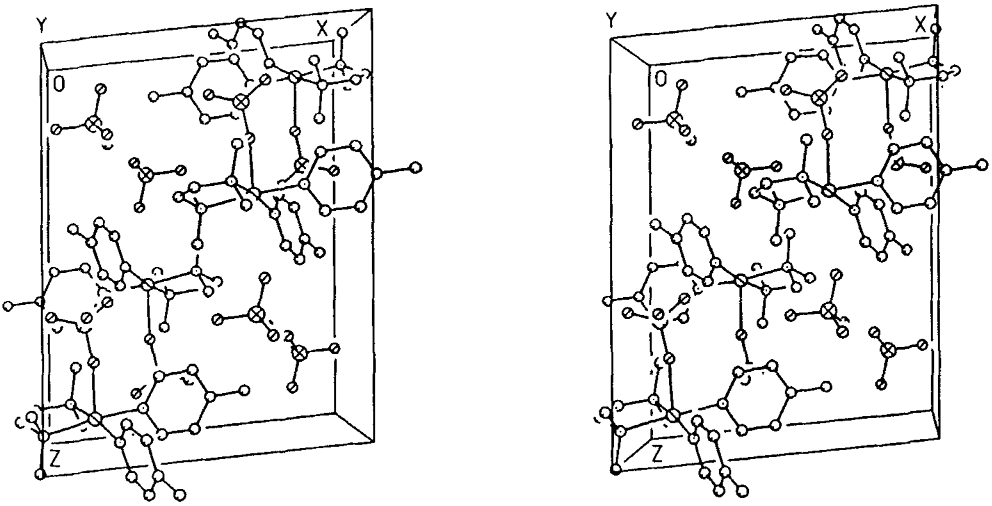

Figure 2 Stereoscopic drawing of the molecular packing in the unit cell.

Table 3 Selected bond lengths (Å) and angles (°).

Cu-N(1)	2.013(16)	Cu-N(2)	2.002(16)
Cu-N(3)	2.099(17)	Cu-N(4)	2.048(16)
Cu-O(6)	2.353(14)		
N(1)-Cu-N(2)	88.4(7)	N(1)-Cu-N(3)	92.6(7)
N(1)-Cu-N(4)	171.5(7)	N(2)-Cu-N(3)	173.8(7)
N(2)-Cu-N(4)	91.6(6)	N(3)-Cu-N(4)	86.4(7)
O(6)-Cu-N(1)	92.2(6)	O(6)-Cu-N(2)	91.2(6)
O(6)-Cu-N(3)	94.9(6)	O(6)-Cu-N(4)	92.2(6)
Cu-N(3)-C(17)	105.6(12)	Cu-N(4)-C(18)	107.6(14)
N(3)-(17)-C(18)	118.7(16)	N(4)-C(18)-C(17)	118.8(18)

atomic coordinates are given in Table 4. The crystals are built up of perchlorate anions and pentacoordinate copper cations with one tmen and two 4-methylpyridine ligands forming the basal plane and a perchlorate ion at the apex (2.353(14) Å) of a square pyramid. The second perchlorate ion is located on the other side of the plane is ~3.4 Å away from the copper atom. The four equatorial atoms, N(1), N(2), N(3) and N(4), are nearly coplanar; N(1), N(2), N(3) and N(4) lie 0.0474, 0.0048, 0.0041 and 0.0465Å, respectively, below the best least-squares plane through these four atoms and the central copper atom, whereas the copper atom is 0.1028 Å above it. The mean Cu-N(4Mpy) of 2.008 ± 0.006 Å is close to usual Cu-pyridine bond lengths.[11-17] The mean Cu-N(tmen) distance of 2.074 ± 0.025 Å is similar to that of 2.068 ± 0.014 Å reported for $[Cu(tmen)Cl_2]_2$,[18] and slightly longer than in $[Cu(tmen)(N\text{-methylformamide})_3](ClO_4)_2$[19] (2.031 ± 0.02 Å) and $[Cu(tmen)(SO_4)(H_2O)_2](H_2O)$[20](2.025 ± 0.01 Å), indicating that bonding in the title complex is affected by steric congestion due to the terminal methyl groups of tmen and the 4-methypyridine ligands. Although the ethylene C(17) and C(18)

Table 4 Atomic coordinates (x10^4) and equivalent isotropic displacement coefficients (Å^{2}x10^3).

Atom	*x*/*a*	y/*b*	z/*c*	*U*(eq)*
Cu	1587(2)	7498(2)	8991(2)	42(1)
Cl(1)	1282(6)	8311(5)	6702(4)	76(3)
Cl(2)	8406(5)	3396(5)	8129(4)	59(2)
O(1)	7962(16)	4192(15)	7629(12)	125(7)
O(2)	7982(13)	2472(16)	7800(10)	107(5)
O(3)	9595(16)	3377(13)	8102(11)	112(6)
O(4)	8165(13)	3499(12)	8972(11)	93(5)
O(5)	2007(17)	7794(17)	6243(13)	137(8)
O(6)	1532(11)	8157(10)	7608(9)	67(4)
O(7)	1355(15)	9292(14)	6523(11)	110(6)
O(8)	236(18)	7921(15)	6459(13)	134(8)
N(1)	2357(14)	8708(12)	9510(11)	43(7)
N(2)	3117(14)	6916(11)	8889(12)	42(7)
N(3)	-24(14)	8015(12)	9216(13)	71(8)
N(4)	808(14)	6191(12)	8644(11)	54(7)
C(1)	2548(18)	9495(17)	9063(12)	47(9)
C(2)	3131(19)	10352(16)	9398(15)	61(10)
C(3)	3483(17)	10359(16)	10230(15)	51(9)
C(4)	3232(18)	9559(17)	10717(12)	52(9)
C(5)	2713(18)	8755(15)	10329(15)	54(9)
C(6)	3711(17)	6568(13)	9580(12)	38(8)
C(7)	4778(18)	6196(14)	9562(12)	37(8)
C(8)	5275(16)	6124(14)	8820(18)	52(10)
C(9)	4681(18)	6538(15)	8102(14)	51(9)
C(10)	3623(17)	6929(14)	8161(13)	44(9)
C(11)	4078(19)	11278(16)	10625(14)	75(8)
C(12)	6404(18)	5746(17)	8777(14)	83(8)
C(13)	-375(20)	8854(18)	8693(14)	90(9)
C(14)	-128(22)	8279(19)	10077(16)	109(10)
C(15)	965(18)	5835(16)	7785(13)	67(7)
C(16)	1186(15)	5349(12)	9255(11)	80(8)
C(17)	-766	7316	8882	163(14)
C(18)	-327(20)	6308(17)	8707(22)	160(15)

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

atoms are subject to significant thermal vibrations and the C(17)-N(3) and C(18)-N(4) distances are therefore shorter than the normal C-N bond length, the tmen chelate rings exhibit mainly the λ conformation with a torsion angle of 9.1°, revealing again the steric congestion of the ligands in the copper complex. Both 4-methylpyridine units are oriented approximately perpendicular to the CuN_4 coordination plane; the dihedral angles between the best planes are 92.5° and 98.0°. The bond distances and angles of the 4-methylpyridine ligands are in the normal ranges. The perchlorate anions show significant thermal vibrations but their dimensions are normal.

Infrared, visible and epr spectroscopic data for the tmen complexes are listed in Table 5. Two Cu-N stretches at ~300 cm^{-1} are assignable to the copper-pyridine and the copper-imidazole bonds.[21-22] The corresponding Cu-N(NH_3) stretches for the NH_3 complex are found at ~440 cm^{-1}.[23] The Cu-N modes tentatively assigned here are in agreement with the structure comprising a CuN_4 coordination plane. Two sharp OH stretches observed for the 4-methylimidazole perchlorate complex indicate that the H_2O is coordinated to the central copper ion. On the other hand,

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Table 5 Infrared, visible and epr spectroscopic data for *N*,*N*,*N'*,*N'*-tetramethylethylenediamine copper(II) complexes.

Complex[a]	Vibrational bands, cm^{-1} [b]		LF bands[c]	epr[d]
	υN-H(L)	υCu-N(L)	λ_{max},nm	$g_{\perp}$;$g_{\parallel}$
$[Cu(tmen)(NMIm)_2(ClO_4)](ClO_4)$		297m 282m	533 630sh	2.07;2.19
$[Cu(tmen)(NMIm)_2(BF_4)](BF_4)$		293sh 282s	532 630sh	2.07;2.18
$[Cu(tmen)(4MImH)_2(H_2O)](ClO_4)_2$[e]	3260s	284sh 274m	521 630sh	2.07; f
$[Cu(tmen)(4MImH)_2(BF_4)](BF_4)$	3330vs, br	288sh 278ms	521 630sh	2.07; f
$[Cu(tmen)(2MImH)_2(ClO_4)](ClO_4)$	3350s, br	313s 301s	510 630sh	g
$[Cu(tmen)(ImH)_2(BF_4)](BF_4)(H_2O)$[h]	3385s,br	293s 287s	529 630sh	2.07; f
$[Cu(tmen)(4Mpy)_2(ClO_4)](ClO_4)$		297mw 278m	538 630sh	2.06; f
$[Ci(tmen)(NH_3)_2(ClO_4)](ClO_4)$	3348s 3283s 3225ms 3194ms	463m 456sh	561br	2.07;2.19

[a]For abbreviations, see footnote of Table 2. [b]Measured in Nujol mulls. [c]Measured in Nujol mulls on Whatman No. 1 filter paper. [d]Powder spectrum at room temperature. [e]Water υO-H 3603s, 3495s cm^{-1}. [f]Tailing. [g] Here, g_{iso} = 2.085. [h] Water υO-H 3600m, br cm^{-1}.

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a broad featureless ν (O-H) band observed for the imidazole complex suggests the presence of water of crystallization. The N-H stretches of the imidazole complexes show various red shifts, indicating hydrogen bonds in the crystal.

The solid-state visible spectra of the 4-methylpyridine and the imidazole complexes are very similar with peak maxima in the region 510 to 538 nm and a pronounced flanking shoulder at 630 nm, the intensity ratio being 3:2, thus suggesting that the structures are virtually the same. This is also suggested by their axial epr spectra. Note particularly the nearly identical LF and epr data for the two *N*-methylimidazole complexes and for the two 4-methylimidazole complexes. Replacement of ClO_4^- anions by BF_4^- in these complexes does not change the structures of the copper cations. Although some of the spectra show tailing in the $g_{\parallel}$ region and the spectrum of the 2-methylimidazole complex appears to be nearly isotropic, it is apparent that these spectra have axial characteristics with $g_{\parallel} > g_{\perp} > 2$, indicating tetragonal symmetry with the unpaired $3d^9$ electron of Cu(II) in the $d_{x^2-y^2}$ orbital.[24] For the 2-methylimidazole complex, the nearly isotropic epr spectrum and the LF absorption maximum appearing at the highest frequency among this series of complexes (510 nm) suggest a structure with the axial ligands quite extensively, but not completely blocked by each of the 2-methyl groups of the 2-methylimidazole ligands. Since the LF envelope is similar to that of the other complexes, this complex is most likely square-pyramidal with the apical ClO_4^- loosely bound.

The solid state LF spectra of the tmen complexes were deconvoluted into Gaussian component peaks for a detailed analysis of the energy levels of the *d* orbitals. Starting from a set of three trial peaks, computer iterative processes for curve fitting were carried out until a minimum value of the reliability factor, R,[25] was reached. With the exception of the 2-methylimidazole complex where interference by CT bands was serious, each of the complexes had an excellent fit with $R < \sim 0.4\%$, and showed a resulting set comprising three Gaussian peaks; the peak positions are presented in Table 6 together with their half-height widths and relative maximum absorptions. Representative examples are shown in Figure 3. Attempts to fit with two peaks were unsuccessful; the R values were never lower than a few percent. Results with four component peaks were ruled out for the

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Table 6 Gaussian component bands for the visible spectra of *N,N,N',N'*-tetramethylethylenediamine copper(II) complexes.

band	υ, kK	ε_{max}[a]	$\delta_{1/2}$[b]	assignment
[Cu(tmen)(NH$_3$)$_2$(ClO$_4$)](ClO$_4$), ($R = 0.293\%$)[c]				
I	12.4	0.5	2.02	d_z2
II	16.0	19.9	2.89	d_{xy}
III	18.4	79.6	4.48	$d_{xz};d_{yz}$
[Cu(tmen)(4Mpy)$_2$(ClO$_4$)](ClO$_4$), (R = 0.244%)[c]				
I	14.6	4.6	2.00	d_z2
II	15.7	14.1	2.24	d_{xy}
III	18.5	81.2	4.57	$d_{xz};d_{yz}$
[Cu(tmen)(ImH)$_2$(BF$_4$)](BF$_4$)(H$_2$O), (R = 0.203%)[c]				
I	14.7	4.0	1.77	d_z2
II	15.7	23.4	2.38	d_{xy}
III	18.8	72.6	4.68	$d_{xz};d_{yz}$
[Cu(tmen)(NMIm)$_2$(ClO$_4$)](ClO$_4$), (R = 0.381%)[c]				
I	13.6	6.0	3.80	d_z2
II	15.5	18.9	2.36	d_{xy}
III	18.6	75.1	4.90	$d_{xz};d_{yz}$
[Cu(tmen)(NMIm)$_2$(BF$_4$)](BF$_4$), (R = 0.221%)[c]				
I	14.75	2.3	1.75	d_z2
II	15.5	25.1	2.62	d_{xy}
III	18.7	72.6	4.55	$d_{xz};d_{yz}$
[Cu(tmen)(4MImH)$_2$(H$_2$O)](ClO$_4$)$_2$, (R = 0.271%)[c]				
I	14.8	4.7	1.62	d_z2
II	15.8	17.5	2.18	d_{xy}
III	19.1	77.8	4.78	$d_{xz};d_{yz}$
[Cu(tmen)(4MImH)$_2$(BF$_4$), (R = 0.41%)[c]				
I	13.2	6.2	4.06	d_z2
II	15.8	23.2	2.47	d_{xy}
III	19.2	70.7	4.58	$d_{xz};d_{yz}$
[Cu(tmen)(2MImH)$_2$(ClO$_4$)](ClO$_4$), ($R = 0.95\%$)[c]				
I	14.7	3.4	2.13	d_z2
II	15.9	6.6	2.825	d_{xy}
III	19.6	90.0	5.67	$d_{xz};d_{yz}$

[a] Relative band height in arbitary scale based on a sum of 100.
[b] Width at $\varepsilon_{max}/2$.
[c] Reliability factor defined as $R = \Sigma|y_{obs,i} - y_{calc,i}|\Sigma y_{obs,i}$.

following reasons: first, the fit could not be improved by assuming two peaks for the most intense highest energy one. In some cases, four peaks finally merged into three. Secondly, there should be only three component peaks for the NH$_3$, the 4Mpy, and the NMIm complexes, because copper d_{xz} and d_{yz} orbitals can not participate in π-interactions due to either no ligand π-orbitals for the NH$_3$ ligands or the nearly perpendicularly oriented heterocyclic ligand plane for the 4Mpy and the NMIm complexes.[26] For other imidazole complexes, the imidazole rings also must lie approximately perpendicular to the CuN$_4$ coordination plane to avoid steric hindrance imposed by the methyl groups of the tmen ligand.

Because the structures of the complexes consist of a CuN$_4$ square plane and the unsaturated heterocyclic rings of the unidentate ligands are approximately perpendicular to it, the highest energy peak with greatest intensity can be assigned to the $d_{xz},d_{yz} \rightarrow d_x2\text{-}_y2$ transition, and the lowest energy peak to the $d_z2 \rightarrow d_x2 - {}_y2$ transition. This results in the same energy level sequence, $d_x2 - {}_y2 > d_z2 > d_{xy} >$

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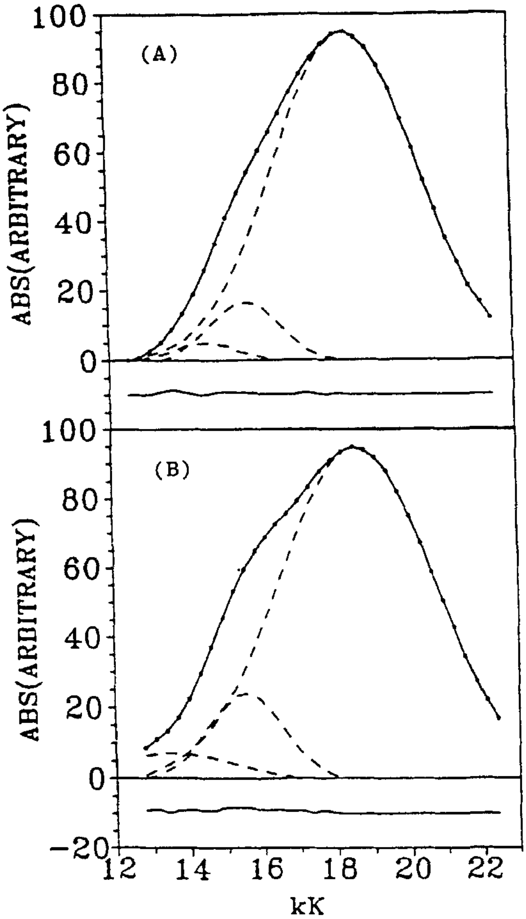

Figure 3 Solid state visible spectra and Gaussian line-shape analysis with difference plots of (A) [Cu(tmen)(4Mpy)$_2$(ClO$_4$)$_2$], R = 0.244%, and (B) [Cu(tmen)(NMIm)$_2$(ClO$_4$)$_2$], R = 0.381%; (*) profile-fitting points; (---) Gaussian components; (——) observed spectrum.

$d_{xz} = d_{yz}$, as reported in the literature for square-pyramidal or elongated octahedral copper(II) complexes.[27–28] Because both d_{xz} and d_{yz} orbitals do not participate in π-interactions and the $d_{x^2-y^2}$ orbital binds with four N-donor atoms, the transition energies for $d_{xz},d_{yz} \rightarrow d_{x^2-y^2}$ must reflect the σ-donor abilities of the unidentate ligands. Indeed, as shown in Figure 4, the transition energies appear at 18.5-19.6 kK for these complexes and parallel the pK_a values of the imidazole ligands and, in turn, the σ-bonding abilities of the unidentate ligands. The transition energies for $d_{z^2} \rightarrow d_{x^2-y^2}$ for these complexes show larger variations, ranging from 13.2 to 16.0 kK, because the energy level of d_{z^2} is sensitive to the axial bond lengths as well as the nature of the axial ligands.

It is interesting to compare the $d_{xy} \rightarrow d_{x^2-y^2}$ transition for the tmen complexes, because the d_{xy} orbital, having d_π symmetry, may interact with the π orbitals of the

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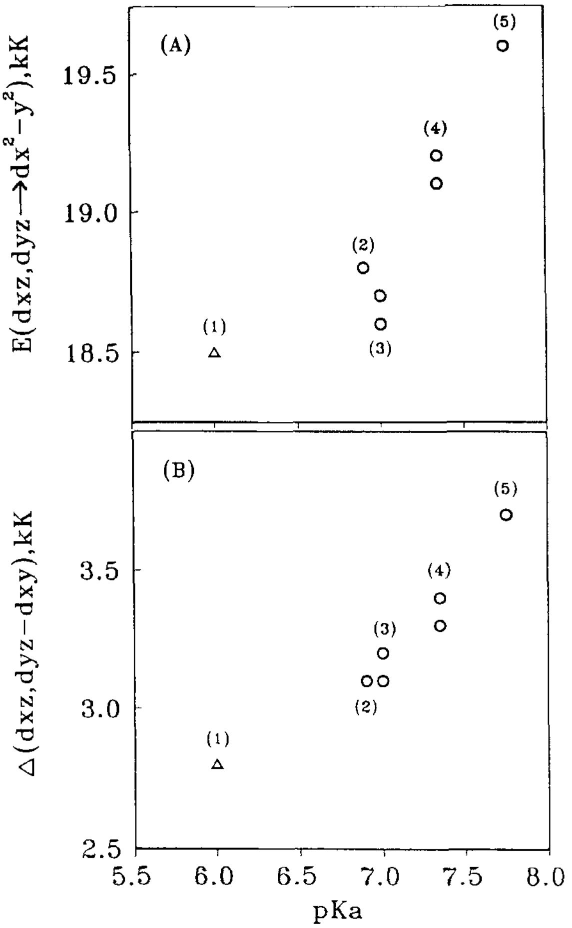

Figure 4 (A) $d_{xy}, d_{yz} \rightarrow d_{x^2-y^2}$ transition energy and (B) energy difference, $d_{xz}d_{yz} - d_{xy}$, *vs* pK$_a$ of the unidentate ligands, L, for [Cu(tmen)L$_2$(anion)]$^+$ complexes; (1) 4-methylpyridine, (2) imidazole, (3) *N*-methylimidazole, (4) 4-methylimidazole, (5) 2-methylimidazole.

approximately perpendicularly oriented 4-methylpyridine and imidazole ligands. If there were no π-interactions in these complexes, their transition energies, $d_{xy} \rightarrow d_{x^2-y^2}$, would hardly vary. One would expect the $d_{xy} \rightarrow d_{x^2-y^2}$ transition energies be nearly the same for these complexes. However, because the energy level of $d_{x^2-y^2}$ orbital rises as the pK$_a$ values of the unidentate ligands increase, the energy increment may be adjusted by comparison of the energy difference between the d_{xy} and the degenerate d_{xz} and d_{yz} orbitals. As shown in Figure 4, the difference for the 4-methylpyridine complex is 2.8 kK, which is very close to the corresponding energy difference of 2.9 kK for ethylenediaminecopper(II) complexes, [Cu(en)L$_2$(ClO$_4$)$_2$], where L stands for imidazoles and pyridines.[17] Therefore, there is essentially no π-interaction in the 4-methylpyridine complex, as with the ethylenediamine complexes. The corresponding energy differences for the imidazole complexes vary from 3.0 to 3.7 kK, suggesting that the bonding capabilities of the imidazole ligands range from merely σ-donors to those with various extent of π-donating ability depending on their pK_a values. This can be ascribed to π-interactions between the d_{xy} and the π_1 and π_2 orbitals of the imidazole ligands.[29] Because both d_{xy} and the π_1 and π_2 orbitals are filled, their reactions alone are not allowed. It is likely that the empty copper $4p_x$ and $4p_y$ orbitals are also involved in π-interactions with the ligand π_1 and π_2 orbitals. These interactions are symmetry allowed but energetically less favourable.

Attempts to employ the NH_3 complex as reference for comparison are not proper here. The σ-donation ability of the NH_3 ligand in the NH_3 complex is not as strong as anticipated from its pK_a value. We suspect that the bonding in the NH_3 complex is complicated, perhaps due to hydrogen bonds.

In conclusion, we have demonstrated that in tmen copper(II) complexes, imidazoles are weak π-donor ligands, but not 4-methylpyridine. The π-donating properties of imidazole ligands are consistent with previous results.[4] It is less favourable energetically for π-donor ligands to interact with the copper d_{xy} orbital. In these complexes, however, π-interactions seem to be demanded by the central copper ion, namely, the steric congestion imposed by the tmen ligand prevents the ligands from donating enough σ-electron density to the central copper ion. Accordingly, π-donation provides additional electron density in accord with the electroneutrality principle.

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Supplementary material

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

Acknowledgements

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