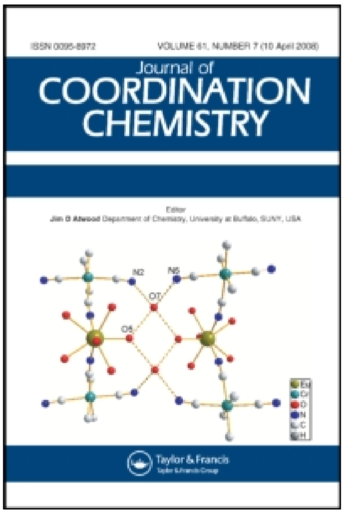

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ELECTRONIC STRUCTURES AND BONDING PROPERTIES OF MIXED LIGAND COPPER(II) COMPLEXES OF 2-(2-PYRIDYLETHYL)PICOLYLAMINE AND DIPICOLYLAMINE. MOLECULAR STRUCTURES OF (2,2'-BIPYRIDINE)[2-(2-PYRIDYLETHYL)PICOLYLAMINE]COPPER(II) PERCHLORATE AND (DIPICOLYLAMINE)(1,10-PHENANTHROLINE)COPPER(II) PERCHLORATE

Gin-Song Huang[a]; Chan-Cheng Su[a]; Sue-Lein Wang[b]; Fen-Lin Liao[b]; Kuan-Jiuh Lin[c]
[a] Department of Chemistry, National Taiwan Normal University, Taipei, Taiwan, ROC [b] Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan, ROC [c] Institute of Chemistry, Academia Sinica, Taipei, Taiwan, ROC

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ELECTRONIC STRUCTURES AND BONDING PROPERTIES OF MIXED LIGAND COPPER(II) COMPLEXES OF 2-(2-PYRIDYLETHYL)PICOLYLAMINE AND DIPICOLYLAMINE. MOLECULAR STRUCTURES OF (2,2′-BIPYRIDINE)[2-(2-PYRIDYLETHYL)PICOLYLAMINE]COPPER(II) PERCHLORATE AND (DIPICOLYLAMINE)(1,10-PHENANTHROLINE)COPPER(II) PERCHLORATE

GIN-SONG HUANG[a], CHAN-CHENG SU[a,*], SUE-LEIN WANG[b],
FEN-LIN LIAO[b] and KUAN-JIUH LIN[c]

[a]*Department of Chemistry, National Taiwan Normal University,
Taipei, Taiwan, ROC;* [b]*Department of Chemistry,
National Tsing Hua University, Hsinchu, Taiwan, ROC;*
[c]*Institute of Chemistry, Academia Sinica, Taipei, Taiwan, ROC*

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Mixed ligand copper(II) complexes of 2-(2-pyridylethyl)picolylamine (pepica) of [Cu(pepica)(picolinato)]$(ClO_4)(H_2O)$ and the [Cu(pepica)(L)]$(ClO_4)_2$ type, where L stands for 2,2′-bipyridine (bipy), 1,10-phenanthroline, neocuproine, and ethylenediamine, and dipicolylamine(dipica) of the [Cu(dipica)(L)]$(ClO_4)_2(H_2O)_n$ type, where L for 2,2′-bipyridine ($n = 0$), 1,10-phenanthroline (phen, $n = 0$), and neocuproine ($n = 1$), have been synthesized and characterized by elemental analyses, and IR, electronic and EPR spectroscopic measurements. The molecular structures of [Cu(pepica)(bipy)]$(ClO_4)_2$ (**1**) and [Cu(dipica)(phen)]$(ClO_4)_2$ (**2**) have been determined using three dimensional X-ray diffraction data. Complex **1** consists of discrete distorted square pyramidal [Cu(pepica)(bipy)] cations, with a *meridional* pepica ligand and one of the pyridine rings of the bipy ligand forming a basal plane. The other pyridine nucleus of the bipy is bound at the apex having an elongated bond distance of 2.255 Å and tilted off the normal z axis by ~ 15°. Complex **2** comprises discrete distorted trigonal bipyramidal [Cu(dipica)(phen)] cations, with

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[*] Corresponding author.

the two pyridine nuclei of the dipica ligand and one of the pyridine rings of the phen forming an equatorial trigonal plane and the remaining pyridine ring of the phen and the amine nitrogen of the dipica on the axial sites. The trigonal bipyramidal cation, distorted toward a square pyramidal structure, has an enlarged equatorial N(py)–Cu–N(py) angle of 132.4° and an elongated equatorial Cu–N(phen) bond of 2.156 Å. All of the complexes exhibit axial type EPR spectra. Gaussian resolved *d–d* spectra for these complexes, except the dipica–bipy and dipica–phen ones, yield an orbital sequence of $d_{x^2-y^2} \gg d_{z^2} > d_{xy} > d_{yz} \sim d_{xz}$. The bonding properties of the tridentate and the bidentate ligands are elucidated.

Keywords: 2-(2-pyridylethyl)picolylaminecopper(II); dipicolylaminecopper(II); X-ray structure; *d–d* spectra; EPR spectra; Gaussian analysis

INTRODUCTION

In the biomimetic studies of oxyhemocyanins, linear tridentate ligands with a central amine and two terminal heterocyclic nuclei, for example, derivatives of bis(2-pyridylethyl)amine,[1] have been reported as one class of chelates which successfully mimic peroxo-dicopper(II) complexes in biological systems.[2] The structures of these peroxo-dicopper(II) complexes have been suggested as possessing two square pyramidal copper(II) complexes bridged by the side-on $\eta^2 : \eta^2$ peroxo group with the tridentate ligand in a *facial* configuration with one of the pyridyl groups at the apex. Inspection of the structures of copper(II) complexes containing one linear 3 N tridentate ligand with a central amine reveals that these ligands tend to bind to copper(II) with a *meridional* configuration.[3] The *facial* binding mode is observed mainly in bis-copper(II) complexes.[4]

We have previously found that both the bis-copper(II) perchlorate complexes of dipicolylamine and 2-(2-pyridylethyl)picolylamine comprise mainly facially coordinated tridentate ligands.[4a] Their intraligand N(py)–Cu–N(py) angles are less than 90°. Consequently, there is no steric preference for these linear 3 N tridentate ligands to have a *meridional* or a *facial* coordination mode. The configurations of the tridentate ligands are therefore dependent on the coordination capabilities of other ligands present in the complexes. Herein, we report the molecular structures of the title mixed ligand copper(II) complexes and their electronic and bonding properties.

EXPERIMENTAL

Materials and Preparations

2,2′-Bipyridine (Sigma), 1,10-phenanthroline (Merck), neocuproine (Sigma), ethylenediamine (Merck), picolinic acid (Sigma), $Cu(ClO_4)_2 \cdot 6H_2O$ (Merck), and organic solvents were used as received. 2-(2-Pyridylethyl)picolylamine and dipicolylamine[4a] were prepared according to the cited literature.

The mixed ligand dipica complexes were prepared by the following general procedure. To a stirred CH_3CN solution (5 cm^3) of $Cu(ClO_4)_2 \cdot 6H_2O$ (1.0 mmol), a solution of dipica (1.0 mmol) in CH_3CN (5 cm^3) was added dropwise, and then, a 5 cm^3 CH_3CN solution of the appropriate bidentate ligand (1.0 mmol) was added. After reaction at room temperature for 1 h, diethyl ether was allowed to diffuse very slowly into the reaction mixture. Blue crystalline products obtained after a few days were filtered and dried over P_4O_{10}.

For the pepica complexes, a similar preparation procedure was employed except for using CH_3OH instead of CH_3CN as the solvent. The blue precipitates obtained from the reaction mixture were filtered and dried over P_4O_{10}.

[Cu(dipica)(phen)](ClO$_4$)$_2$[†] Blue. Yield 63%. M.p. 248°C(dec.). IR (cm^{-1}): ν(N–H) 3242m; ν(C=N, C=C) 1612m 1586w 1574w; $\nu(ClO_4)$ 1090vs 930w 623s; δ[C–H(py)] 847s 774s 763s. *Anal.* Calcd. for $C_{24}H_{21}Cl_2N_5O_8Cu$(%): C, 44.9; H, 3.30; N, 10.9. Found: C, 44.9; H, 3.27; N, 10.8. The crystalline products were suitable for X-ray structure determination.

[Cu(dipica)(bipy)](ClO$_4$)$_2$[4b] Blue. Yield 65%. M.p. 252°C(dec.). IR (cm^{-1}): ν(N–H) 3237m; ν(C=N, C=C) 1611s 1601ms 1575m 1570m; $\nu(ClO_4)$ 1092vs 930mw 623s; δ[C–H(py)] 775ms 766s. *Anal.* Calcd. for $C_{22}H_{21}Cl_2N_5O_8Cu$(%): C, 42.8; H, 3.43; N, 11.3. Found: C, 42.7; H, 3.32; N, 11.3.

[Cu(dipica)(neoc)](H$_2$O)(ClO$_4$)$_2$ Blue. Yield 67%. M.p. 264°C(dec.). IR (cm^{-1}): ν(N–H) 3219mw; ν(C=N, C=C) 1609m 1589mw 1570mw; $\nu(ClO_4)$ 1094vs 932w 623s; δ[C–H(py)] 864s 777s 766s. *Anal.* Calcd. for $C_{26}H_{27}Cl_2N_5O_9Cu$(%): C, 45.4; H, 3.95; N, 10.2. Found: C, 45.3; H, 3.73; N, 10.5.

[Cu(pepica)(phen)](ClO$_4$)$_2$ Blue. Yield 67%. M.p. 213°C(dec.). IR (cm^{-1}): ν(N–H) 3215w; ν(C=N, C=C) 1614mw 1609m 1580w; $\nu(ClO_4)$ 1096vs 934w 625s; δ[C–H(py)] 847s 773s. *Anal.* Calcd. for $C_{25}H_{23}Cl_2N_5O_8Cu$(%): C, 45.8; H, 3.53; N, 10.7. Found: C, 45.7; H, 3.46; N, 10.8.

[Cu(pepica)(bipy)](ClO$_4$)$_2$ Blue. Yield 62%. M.p. 221°C(dec.). IR (cm^{-1}): ν(N–H) 3225mw; ν(C=N, C=C) 1614m 1605s 1597m; $\nu(ClO_4)$ 1095vs 932w 623s; δ[C–H(py)] 789ms 774ms 762s. *Anal.* Calcd. for $C_{23}H_{23}Cl_2N_5O_8Cu$(%): C, 43.7; H, 3.67; N, 11.1. Found: C, 43.6; H, 3.59; N, 11.1. Single crystals suitable for X-ray structure determination were obtained from slow diffusion of diethyl ether into a methanol solution of the complex.

[†] For abbreviations, see footnote a, Table IV.

[Cu(pepica)(neoc)](ClO$_4$)$_2$ Blue. Yield 63%. M.p. 232°C(dec.). IR (cm^{-1}): ν(N–H) 3219m; ν(C=N, C=C) 1609m 1595mw 1568mw; ν(ClO$_4$) 1092vs 932w 623s; δ[C–H(py)] 858s 768s. *Anal.* Calcd. for $C_{27}H_{27}Cl_2N_5O_8$-Cu(%): C, 47.4; H, 3.98; N, 10.2. Found: C, 47.4; H, 3.93; N, 10.4.

[Cu(pepica)(en)](ClO$_4$)$_2$ Blue. Yield 37%. M.p. 219°C(dec.). IR (cm^{-1}): ν(N–H) 3343m 3310m 3273m 3171w; ν(C=N, C=C) 1614m 1607ms 1576m; ν(ClO$_4$) 1088vs 932w 625s; δ[C–H(py)] 785m 772s. *Anal.* Calcd. for $C_{15}H_{23}$-$Cl_2N_5O_8Cu$(%): C, 33.6; H, 4.33; N, 13.1. Found: C, 33.8; H, 4.16; N, 12.6.

[Cu(pepica)(pico)](H$_2$O)(ClO$_4$) Blue. Yield 33%. M.p. 193°C(dec.). IR (cm^{-1}): ν(N–H) 3154m; ν(C=N, C=C) 1632s 1604s 1570ms; ν(ClO$_4$) 1098vs 623s; δ[C–H(py)] 779m 768s. *Anal.* Calcd. for $C_{19}H_{12}ClN_4O_7Cu$(%): C, 44.2; H, 4.1; N, 10.9. Found: C, 44.8; H, 3.92; N, 11.2.

Physical Measurements

IR spectra were recorded as Nujol mulls or KBr pellets on a BIO-RAD FTS-40 FTIR. A Hitachi model U-3501 spectrophotometer was used for electronic spectra measurements. Reflectance spectra of solid samples were recorded with an integrating sphere attachment. Deconvolution of visible spectra into Gaussian component bands was performed on a VAX 6510 computer using the profile-fitting program CUVFIT.[5] EPR spectra were obtained using Bruker EMX 10 and ER200D spectrometers. 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 I. A crystal of [Cu(pepica)(bipy)](ClO$_4$)$_2$ (**1**) was selected for indexing and intensity data collection on a Siemens Smart-CCD diffractometer equipped with a normal focus, 3 kW sealed tube X-ray source, whereas data for [Cu(dipica)(phen)](ClO$_4$)$_2$ (**2**) were measured on an Enraf-Nonius CAD4 diffractometer. For **1**, intensity data were collected at 296 K in 1271 frames with increasing ω (width of 0.3° per frame). Unit cell dimensions were determined by a least-squares fit of 5142 reflections with $5° < 2\theta < 50°$. Absorption correction was based on 3385 symmetry-equivalent reflections ($-13 \le h \le 15$, $-10 \le k \le 9$, $-26 \le l \le 26$) using the SHELXTL PLUS (VMS) program package ($T_{\min,\max} = 0.746, 0.933$). On the basis of systematic absences, statistics of intensity distribution, and successful solution and refinement of the structure, the space group was determined to be $P2_1/c$.

TABLE I Summary of crystal data and processing parameters for **1** and **2**

$[Cu(C_{13}H_{15}N_3)(C_{10}H_8N_2)](ClO_4)_2$ (**1**)	$[Cu(C_{12}H_{13}N_3)(C_{12}H_8N_2)](ClO_4)_2$ (**2**)
Colour; habit: blue; columnar	Colour; habit: blue; columnar
Crystal size: 0.62 × 0.22 × 0.09 mm	Crystal size: 0.32 × 0.14 × 0.14 mm
Space group: monoclinic $P2_1/c$	Space group: monoclinic $P2_1/n$
$a = 12.98(2)$ Å	$a = 13.627(4)$ Å
$b = 8.89(1)$ Å; $\beta = 96.18(1)°$	$b = 9.259(3)$ Å; $\beta = 106.73(2)°$
$c = 22.61(3)$ Å	$c = 21.926(4)$ Å
$V = 2595(6)$ Å^3	$V = 2649(1)$ Å^3
$Z = 4$	$Z = 4$
$\rho_{calc} = 1.618\ g\,cm^{-3}$	$\rho_{calc} = 1.609\ g\,cm^{-3}$
$\mu = 1.106\ mm^{-1}$	$\mu = 1.085\ mm^{-1}$
$\lambda = 0.71073$ Å	$\lambda = 0.71069$ Å
Diffractometer: Siemens Smart-CCD	Diffractometer: Enraf-Nonius CAD4
Total refl. (unique): 11 288 (4537)	Total refl. (unique): 3533 (3429)
$R_{int} = 5.00\%$	
2θ range: 3.0–51.7°	2θ range: 3.16–44.84°
$R = 0.078$	$R = 0.053$
$R_w = 0.221$	$R_w = 0.153$
Hydrogen atoms: idealized positions	Hydrogen atoms: idealized positions
Number of parameters: 352	Number of parameters: 365
Solution: direct methods	Solution: direct methods
Refinement: full-matrix least-squares	Refinement: full-matrix least-squares

For **2**, intensity data ($\theta/2\theta$ scan, $3° \leq 2\theta \leq 45°$) were collected at 293 K for two octants of the sphere ($-14 \leq h \leq 14$, $0 \leq k \leq 9$, $0 \leq l \leq 22$) and corrected for Lorentz and polarization effects and for absorption ($T_{min,max} = 0.593, 0.787$). Twenty-five independent reflections with $13° < 2\theta < 25°$ 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 systematic absences.

Scattering factors and anomalous dispersion correction terms were taken from *International Tables for X-ray Crystallography* (1974).[6] The atom coordinates are shown in Table II.

RESULTS AND DISCUSSION

The mixed ligand dipica complexes were prepared from acetonitrile solution and analytically pure crystalline products were obtained directly from the reaction mixture by slow diffusion of ether. For pepica complexes, preparations were carried out in methanol solution. The precipitates from the reaction mixtures were filtered to yield the products. Attempts to prepare complexes by using other bidentate ligands such as picolylamine and *N,N'*-dimethylethylenediamine were unsuccessful. Although the pepica complexes

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$). $U(eq)$ is defined as one third of the trace of orthogonalized U_{ij} tensor

Atom	*x/a*	*y/b*	*z/c*	*U(eq)*
1				
Cu(1)	7564(1)	7248(1)	1194(1)	55(1)
Cl(1)	6712(2)	−247(3)	−330(1)	73(1)
Cl(2)	1140(2)	4884(3)	1423(1)	76(1)
O(1)	7304(7)	−1263(11)	−628(4)	142(4)
O(2)	5818(6)	−182(13)	−735(5)	158(5)
O(3)	7337(13)	963(17)	−345(9)	281(11)
O(4)	6549(8)	−1020(17)	193(4)	197(7)
O(5)	408(6)	4315(8)	972(3)	119(3)
O(6)	1356(8)	3921(14)	1905(4)	178(5)
O(7)	482(8)	5995(12)	1700(5)	171(6)
O(8)	1895(9)	5605(22)	1249(5)	254(10)
N(1)	6774(4)	8478(7)	1737(3)	54(2)
N(2)	7794(5)	5939(7)	2054(3)	59(2)
N(3)	6279(5)	5995(8)	887(3)	60(2)
N(4)	8483(5)	6155(8)	695(3)	67(2)
N(5)	8752(5)	8750(7)	1233(3)	59(2)
C(1)	6388(7)	9836(10)	1588(4)	73(3)
C(2)	5933(7)	10 734(10)	1965(4)	79(3)
C(3)	5835(8)	10 196(13)	2531(5)	95(4)
C(4)	6194(6)	8837(12)	2684(3)	79(3)
C(5)	6675(5)	7954(10)	2287(3)	60(3)
C(6)	7129(5)	6477(10)	2437(3)	60(3)
C(7)	6949(7)	5712(12)	2927(4)	78(3)
C(8)	7413(9)	4282(14)	3024(4)	100(5)
C(9)	8074(8)	3730(12)	2635(4)	86(4)
C(10)	8244(8)	4626(10)	2173(4)	77(3)
C(11)	5323(6)	6613(11)	930(3)	68(3)
C(12)	4436(6)	5741(11)	857(3)	73(3)
C(13)	4508(8)	4213(12)	740(4)	81(4)
C(14)	5473(7)	3652(10)	653(4)	74(3)
C(15)	6345(6)	4530(9)	738(3)	63(3)
C(16)	7378(8)	3930(10)	623(4)	81(3)
C(17)	8035(7)	4942(12)	289(4)	83(4)
C(18)	9088(7)	7279(11)	388(4)	74(3)
C(19)	9366(6)	8545(10)	809(3)	65(3)
C(20)	10 223(6)	9474(12)	763(5)	83(4)
C(21)	10 406(7)	10 651(11)	1165(5)	85(4)
C(22)	9804(7)	10 832(11)	1610(5)	86(4)
C(23)	8966(6)	9843(10)	1628(4)	74(3)
2				
Cu	8189(1)	6927(1)	938(1)	44(1)
N(5)	9492(4)	7901(6)	1425(3)	45(1)
N(1)	7213(4)	8397(6)	1116(2)	45(1)
N(2)	6878(4)	5966(7)	463(3)	50(2)
N(4)	8835(4)	5243(6)	1614(2)	47(1)
N(3)	8580(4)	6405(6)	126(3)	48(1)
C(23)	10 086(4)	7119(7)	1919(3)	41(2)
C(7)	7037(6)	4982(8)	−41(3)	61(2)
C(1)	7384(5)	9416(8)	1569(3)	55(2)
C(11)	9531(7)	6560(10)	−635(5)	73(2)
C(14)	9053(7)	3009(9)	2181(4)	72(2)

TABLE II (*Continued*)

Atom	*x/a*	*y/b*	*z/c*	*U(eq)*
C(15)	9962(7)	3463(9)	2590(4)	72(2)
C(2)	6647(7)	10 374(9)	1626(4)	66(2)
C(16)	10 323(5)	4855(8)	2520(3)	54(2)
C(12)	9389(5)	6889(8)	−59(4)	58(2)
C(6)	6140(5)	7151(9)	217(3)	59(2)
C(9)	7996(6)	5192(9)	−866(4)	68(2)
C(5)	6269(5)	8300(7)	711(3)	48(2)
C(4)	5473(5)	9220(9)	753(4)	60(2)
C(22)	9790(5)	9218(8)	1313(3)	58(2)
C(13)	8512(6)	3920(8)	1700(4)	58(2)
C(3)	5693(6)	10 270(9)	1206(4)	67(2)
C(17)	11 260(6)	5473(11)	2933(3)	66(2)
C(19)	10 993(5)	7660(9)	2318(3)	53(2)
C(24)	9729(5)	5709(7)	2019(3)	40(2)
C(18)	11 570(5)	6764(11)	2835(3)	66(2)
C(20)	11 286(5)	9032(10)	2197(4)	63(2)
C(8)	7902(5)	5555(7)	−273(3)	47(2)
C(21)	10 699(6)	9799(9)	1700(4)	73(2)
C(10)	1195(8)	4293(11)	1041(4)	80(3)
Cl(1)	2229(2)	9092(2)	289(1)	63(1)
Cl(2)	5570(1)	4545(2)	1624(1)	58(1)
O(1)	2703(12)	8220(9)	758(4)	227(7)
O(2)	2628(11)	415(11)	361(6)	219(6)
O(4)	1334(10)	9301(23)	344(9)	303(10)
O(3)	7960(13)	1512(11)	298(4)	228(7)
O(6)	6375(6)	5644(8)	1840(3)	114(2)
O(7)	4638(6)	5152(12)	1584(4)	155(4)
O(8)	5673(5)	3995(7)	1042(3)	93(2)
O(5)	5828(5)	3452(8)	2096(3)	98(2)

of ethylenediamine and picolinato were obtained, preparations of the corresponding dipica complexes failed.

IR data are given in the experimental section. All of the complexes exhibit a peak with weak to medium intensities in the region 3240–3150 cm^{-1}, corresponding to the amine N–H stretching. The C=C and C=N stretches in the 1600–1550 cm^{-1} region and the C–H bending peaks in the 850–740 cm^{-1} region indicate the presence of pyridyl groups in these complexes. No apparent splitting was observed for the perchlorate ions at $\sim$ 1100 cm^{-1} suggesting that the perchlorate ions are not coordinated to the copper(II) ions. Since the far IR spectra are very complex and the Cu–N(py) stretching peaks are usually of weak intensity, no attempts have been made to assign the bands in this region. The water molecules in the neoc and the pico complexes show no apparent peaks in the 3400 cm^{-1} region. These peaks may be red-shifted and masked, due to hydrogen bonding, or may be too broad to be detected.

The molecular structures of **1** and **2** are shown in Figures 1 and 2, respectively. Selected bond lengths and angles are given in Table III. For

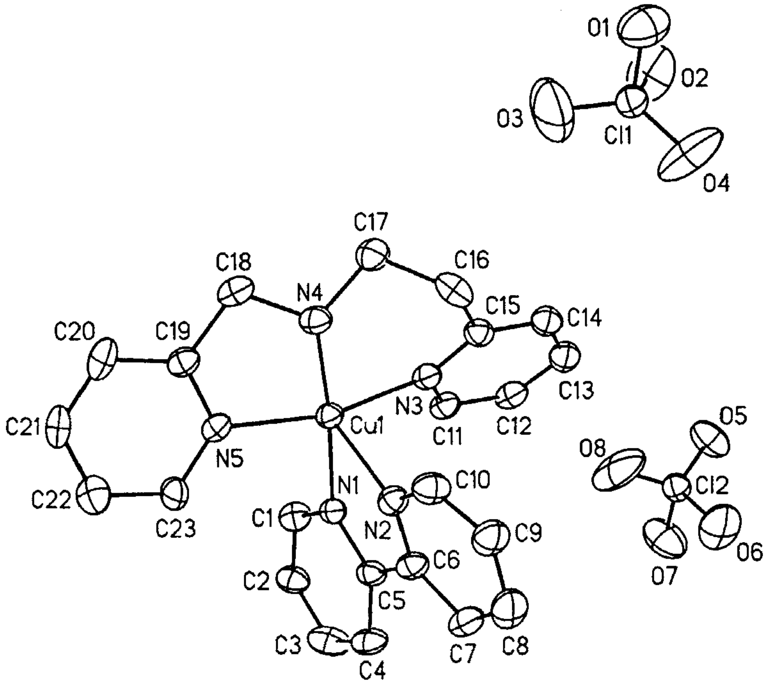

FIGURE 1 Molecular structure of **1** with numbering scheme.

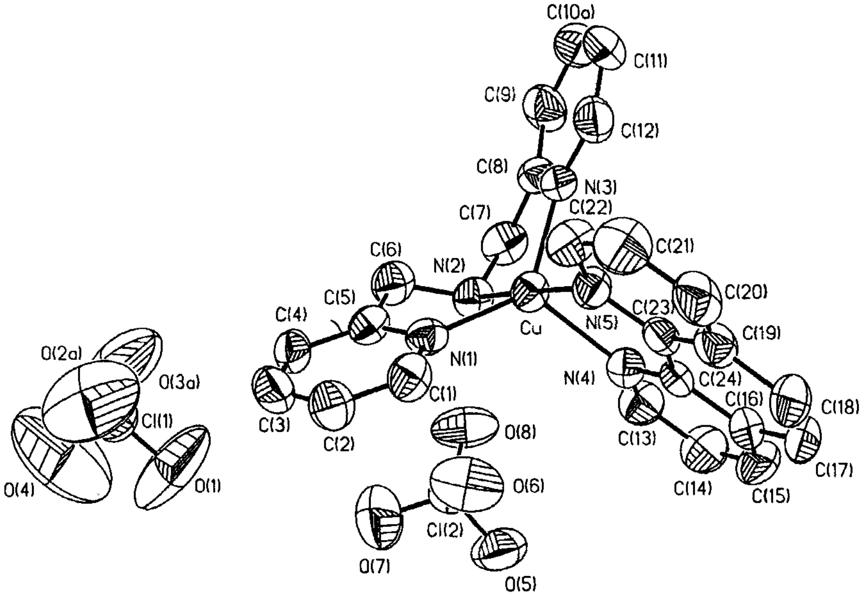

FIGURE 2 Molecular structure of **2** with numbering scheme.

TABLE III Selected bond lengths (Å) and angles (°) for **1** and **2**

1			
Cu(1)-N(1)	2.016(5)	Cu(1)-N(2)	2.255(6)
Cu(1)-N(3)	2.056(6)	Cu(1)-N(4)	1.993(6)
Cu(1)-N(5)	2.020(6)		
N(1)-Cu(1)-N(2)	77.5(2)	N(1)-Cu(1)-N(3)	92.8(2)
N(2)-Cu(1)-N(3)	92.3(2)	N(1)-Cu(1)-N(4)	173.5(2)
N(2)-Cu(1)-N(4)	102.1(2)	N(3)-Cu(1)-N(4)	93.6(3)
N(1)-Cu(1)-N(5)	92.8(2)	N(2)-Cu(1)-N(5)	105.6(2)
N(3)-Cu(1)-N(5)	162.0(2)	N(4)-Cu(1)-N(5)	81.1(3)
C(17)-N(4)-C(18)	113.2(6)		
2			
Cu-N(1)	2.018(5)	Cu-N(2)	1.999(5)
Cu-N(3)	2.058(5)	Cu-N(4)	2.157(5)
Cu-N(5)	2.004(5)		
N(1)-Cu-N(2)	82.0(2)	N(1)-Cu-N(3)	132.4(2)
N(2)-Cu-N(3)	81.9(2)	N(1)-Cu-N(4)	121.1(2)
N(2)-Cu-N(4)	99.4(2)	N(3)-Cu-N(4)	105.6(2)
N(1)-Cu-N(5)	97.2(2)	N(2)-Cu-N(5)	179.1(2)
N(3)-Cu-N(5)	99.0(2)	N(4)-Cu-N(S)	80.5(2)
C(6)-N(2)-C(7)	114.2(6)		

complex **1**, the copper ion is bound by the *meridional* tridentate pepica and the bipy to form a distorted square pyramidal structure, of which the Cu(1)-N(2) bond (2.255 Å) is elongated and inclined toward the Cu(1)-N(1) bond. The small N(1)-Cu(1)-N(2) bond angle of 77.5° results in a ~ 15° lean of the Cu(1)-N(2) bond from the normal to the basal plane. The deviations from the least-squares plane through the N(1)N(3)N(4)N(5) atoms are N(1) 0.1539, N(3) −0.1534, N(4) 0.1739, N(5) −0.1743, and Cu(1) 0.1411 Å, indicating that the structure is slightly distorted toward a trigonal bipyramid. The dihedral angles between the N(1)N(3)N(4)N(5) basal plane and the N(1), N(3) and N(5) pyridine nuclei are 76.3°, 27.5°, and 18.5°, respectively. There is a bifurcated hydrogen bond between the amine N(4) and the perchlorate O(5) and O(7) [N(4)-H····O(5), 2.110 Å, N(4)-H····O(7), 2.326 Å]. Although the isotropic coefficients are somewhat large, due to poor crystal quality, the dimensions of the structure are in the normal ranges. The largest difference peak of 1.82 eÅ^{-3} is located near the Cl(2) atom.

The structure of **2** comprises discrete trigonal bipyramidal copper cations and perchlorate anions. The copper atom is bound by the pyridyl groups of the dipica and one of the pyridine groups of the phen to form a trigonal plane, and the amine of the dipica and another pyridine of the phen on the axial sites. The complex ion is distorted toward a square pyramidal structure with an enlarged N(1)-Cu-N(3) angle of 132.4° and an elongated

Cu–N(4) bond of 2.157 Å. The two axial bonds are slightly shorter than the two equatorial pyridyl bonds. The Cu–N(4) bond tilts toward the Cu–N(5) bond by ~ 10°. There is a weak hydrogen bond between the amine and the perchlorate [N(2)···· O(8), 2.973 Å]. The thermal vibrations are large for the perchlorate oxygen atoms, but the dimensions of the complex are in the normal ranges.

The coordination bond distances and angles of $[Cu(dien)(bipy)](NO_3)_2$ and $[Cu(dien)(phen)](NO_3)_2$[3i] are closely related to those of **1** and **2**. The structures of the dien complexes can be viewed as intermediates between square pyramidal **1** and trigonal bipyramidal **2**. Two terminal nitrogen atoms of the tridentate ligand bind to the central copper ion with a N–Cu–N angle of 162° for **1**, 156° for the dien complexes, and 132° for **2**. The coordination bond opposite to this N–Cu–N angle varies as 2.255 Å for **1**, ~2.21 Å for the dien complexes, and 2.157 Å for **2**. For these four complexes, the mean bond distances of the Cu–N bonds excluding the elongated one are essentially equal.

Electronic and EPR spectroscopic data for the pepica and dipica complexes are listed in Table IV along with the electronic data for the dien complexes. The reflectance LF spectra of the pepica complexes and $[Cu(dipica)(neoc)](H_2O)(ClO_4)_2$ exhibit very similar envelopes with a main peak at 597–660 nm and a pronounced shoulder or a small peak on the low energy side of ~810 to ~900 nm, suggesting strongly that the structures of these complexes are square pyramidal. The solution LF spectra of these complexes have similar features in the same energy range, indicating that the solution species are also of square pyramidal structure. Reflectance spectra of $[Cu(dipica)(phen)](ClO_4)_2$ and $[Cu(dipica)(bipy)](ClO_4)_2$ appear as one broad peak at ~ 760 nm with shoulders on both sides at ~ 600 and ~ 900 nm, in agreement with the spectroscopic contours for trigonal bipyramidal complexes.[7] Their solution visible spectra are similar to the reflectance spectra except that for the phen complex the intensity on the high energy side increases.

The $\pi \rightarrow \pi^*$ transitions for the pepica and dipica ligands at ~255 nm observed for the complexes except the phen and neoc ones, for which the peaks are obscured, are blue-shifted as compared with those for free pepica and dipica at 261 nm. For the intraligand transitions of the bipy at 237 and 282 nm, the phen at 229 and 266 nm, and the neoc at 231 and 268 nm, considerable blue-shifts were observed as compared with the corresponding transitions of the dien complexes or other square pyramidal copper(II) complexes.[8] Apparently, the heterocyclic moieties of the pepica and dipica complexes participate in π-interactions with the copper d_π orbitals.

TABLE IV Electronic and EPR spectroscopic data for copper(II) complexes of pepica and dipica

Compound[a]	*UV–VIS*[b] $\lambda_{max}(\varepsilon \times 10^3)$, nm	*EPR*[c]	
		$g_{\parallel}$; $A_{\parallel}^{Cu}$	$g_{\perp}$; $A_{\perp}^{N}$
[Cu(pepica)(bipy)]$(ClO_4)_2$	616 810/refl. 237(16.8) 258(16.2) 281(13.6) 628(0.11) 850sh/soln.	(2.140;[d] 2.231; 177	2.062;[d]) 2.067;[e]
[Cu(pepica)(phen)]$(ClO_4)_2$	660 900sh/refl. 228(40.9) 265(35.5) 627(0.10) 850sh/soln.	(2.280;[d] 2.232; 175	2.076;[d]) 2.067;[e]
[Cu(pepica)(neoc)]$(ClO_4)_2$	627 820sh/refl. 204(32.3) 231(47.7) 268(33.4) 604(0.10) 850sh/soln.	(2.239;[d] 2.216; 188	2.100;[d]) 2.056; 14
[Cu(dipica)(neoc)]$(H_2O)(ClO_4)_2$	610 830sh/refl. 205(38.5) 231(42.8) 268(30.4) 613(0.19) 820sh/soln.	([d]; [d] 2.224; 186	2.081;[d]) 2.038;[e]
[Cu(pepica)(en)]$(ClO_4)_2$	597 840sh/refl. 255(14.6) 593(0.15)830sh/soln.	(2.199;[d] 2.211; 191	2.075;[d]) 2.065; 12
[Cu(pepica)(pico)]$(H_2O)(ClO_4)$	631 917/refl. 258(14.1) 653(0.10) 900sh/soln.	(2.237;[d] 2.246; 187	2.078;[d]) 2.056;[e]
[Cu(dipica)(bipy)]$(ClO_4)_2$	600sh 759 900sh/refl. [602 820/solid][f] 237(16.8) 254(14.3) 282(12.7) 630sh 719(0.12) 850sh/soln. [400 676 826/CH_3OH][f]	([d] ;[d] 2.232; 191	2.115;[d]) 2.059[g]; 12 2.007[h]
[Cu(dien)(bipy)]$(ClO_4)_2$	[245(16.9) 297(15.4) 312sh 637(0.09) 825sh/CH_3CN][i]		
[Cu(dipica)(phen)]$(ClO_4)_2$	600sh 756 900/refl. 229(41.2) 266(34.2) 643(0.10) 750sh 850sh/soln.	(2.293;[d] 2.232; 195	2.093;[d]) 2.059[g]; 12 2.006[h]
[Cu(dien)(phen)]$(ClO_4)_2$	[207(27.1) 228(36.9) 270(35.0) 613(0.11) 825sh/CH_3CN][i]		

[a] Pepica = 2-(2-pyridylethyl)picolylamine; dipica = dipicolylamine; dien = diethylenetriamine; bipy = 2,2′-bipyridine; phen = 1,10-phenanthroline; en = ethylenediamine; pico = picolinate. [b] Solution spectra measured in $CH_3OH : H_2O = 2:1$; ε in M^{-1} cm^{-1}. [c] X-band glass EPR spectra measured at 77 K in $CH_3OH : H_2O$ (2 : 1) matrix; powder data in parentheses; hyperfine coupling constants in $10^{-4} cm^{-1}$. [d] Not observed. [e] Not well resolved. [f] Ref. 4c. [g] g_y. [h] g_x. [i] Ref. 3o.

In accord with the square pyramidal structures, the pepica complexes and the dipica–neoc complex exhibit typical axial powder and glass EPR spectra.[9] Surprisingly, the dipica–phen and dipica–bipy complexes show axial-rhombic glass EPR spectra, despite the fact that the structures of these two complexes are trigonal bipyramidal as in the X-ray structure of **2**. These two complexes may have axial structures in the CH_3OH–H_2O (2 : 1) matrix at 77 K. This suggests that all of the complexes, except the dipica–phen and dipica–bipy ones, are electronically square pyramidal with a $d_{x^2-y^2}$ (or d_{xy}) ground state and the ligand field strengths along the x and y axes are alike or nearly so. The high $g_{\|}$ and $g_{\perp}$ values for the phen and the bipy complexes are comparable with those of the corresponding dien complexes[10] and reflect the weak σ-donation capabilities in the basal plane for the pepica and dipica complexes. [Cu(pepica)(pico)](ClO_4)(H_2O) exhibits a high $g_{\|}$ value of 2.246 as a result of the low energy LF band at 653 nm, whereas the pepica–en complex shows a low $g_{\|}$ value of 2.211 as a consequence of high energy LF at 593 nm. The superhyperfine splittings in the $g_{\perp}$ region are well resolved for some complexes. The pepica–neoc complex having a pattern of 1 : 3 : 6 : 8 : 8 : 6 : 3 : 1 suggests coupling with the copper ion and two pyridyl nitrogen atoms; the pepica–en complex with 1 : 2 : 3 : 3 : 2 : 1 indicates coupling with the copper ion and one pyridyl nitrogen. A pattern of 1 : 3 : 6 : 7 : 6 : 3 : 1 in the g_y region for the dipica–phen and dipica–bipy complexes suggests coupling with three heterocyclic nitrogen atoms.

The solution LF spectra of the square pyramidal complexes were deconvoluted into Gaussian component peaks for detailed analysis of the energy levels of the d orbitals. Starting from a set of three trial peaks for these complexes, computer iteration processes for curve fitting were carried out until a minimum value of the reliability factor, R,[‡] was reached. Each of the solution spectra had an excellent fit with $R < 0.5\%$ and showed a resulting set comprising three Gaussian component peaks. Representative examples are shown in Figure 3. Peak positions are listed in Table V together with their half-height widths and relative areas.

All of the pepica complexes and the dipica–neoc complex show three component peaks of a similar intensity pattern, namely, the highest energy peak with a largest peak area and the lowest energy one with a smallest area. This agrees with the component peaks for square pyramidal copper(II) complexes,[3o,10,11] and the sequence of the d orbitals is assigned accordingly as $d_{x^2-y^2} \gg d_{z^2} > d_{xy} > d_{yz} \sim d_{xz}$. The coordinate system is defined with x and y axes lying parallel to the least-squares plane of the tridentate nitrogen atoms and the bidentate nitrogen *trans* to the tridentate amine, with y along the tridentate pyridyl bond direction and with z orthogonal to x and y. The degeneracy of the d_{yz} and d_{xz} orbitals may be lifted on account of the difference of the coordinated ligands along the x and y axes. Because of the axial type EPR spectra observed for these complexes, it is likely that the energy levels of the d_{yz} and d_{xz} orbitals are equally affected by the coordinated ligands.

[‡] See footnote c, Table V.

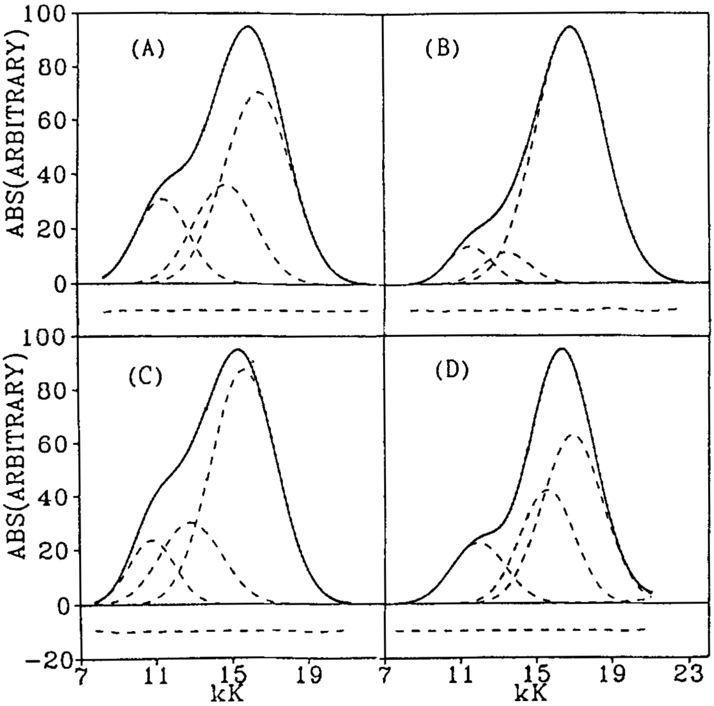

FIGURE 3 Solution visible spectra and Gaussian line-shape analysis with difference plots of: (A) $[Cu(pepica)(bipy)](ClO_4)_2$, $R = 0.26\%$; (B) $[Cu(pepica)(en)](ClO_4)_2$, $R = 0.51\%$; (C) $[Cu(pepica)(pico)](ClO_4)(H_2O)$, $R = 0.38\%$; (D) $[Cu(dipica)(neoc)](ClO_4)_2$, $R = 0.26\%$; (—), observed spectrum; (---), Gaussian components; (*) profile-fitting points.

The energy differences between the $d_{x^2-y^2}$ and the degenerate d_{yz} and d_{xz} orbitals may serve to estimate the σ-donation abilities of the tridentate ligands. The $d_{yz}, d_{xz} \rightarrow d_{x^2-y^2}$ transitions of 16.9 kK for the dipica-neoc complex and $\sim$ 16.7 kK for pepica complexes, except the pico one, are smaller than those of $\sim$ 17.5 kK for dien complexes.[3o] Both dipica and pepica are weaker σ-donors than dien, in agreement with the smaller p*Ka* values for the pyridyl moieties than for the amines. Because the p*Ka* value of 5.4 for the pyridyl moiety of pico[12] is comparable with that of bipy, and thus their σ-donation abilities, the abnormally low $d_{yz}, d_{xz} \rightarrow d_{x^2-y^2}$ transition of 15.6 kK for the pico complex may be attributed to a drastic change of the coordinated atoms in the basal plane. It is probable that this complex is composed of a *facial* pepica ligand with the picolyl chelate and pico forming a basal plane with ethylpyridine moiety at the apex. A CuN_3O basal plane would explain the low $d_{yz}, d_{xz} \rightarrow d_{x^2-y^2}$ transition and, moreover, the

TABLE V Gaussian component bands for the visible spectra of mixed ligand pepica–copper(II) and dipica–copper(II) complexes[a]

Band	ν (kK)	*Area*[b]	$\delta_{1/2}$[c]	*Assignment*
[Cu(pepica)(bipy)](ClO$_4$)$_2$ ($R^d = 0.26\%$)				
I	11.5	19.1	3.28	d_{z^2}
II	14.8	26.1	3.80	d_{xy}
III	16.5	54.8	4.11	$d_{xz}\ d_{yz}$
[Cu(pepica)(phen)](ClO$_4$)$_2$ ($R = 0.43\%$)				
I	11.7	19.7	3.08	d_{z^2}
II	15.0	25.9	3.12	d_{xy}
III	16.6	54.4	3.81	$d_{xz}\ d_{yz}$
[Cu(pepica)(neoc)](ClO$_4$)$_2$ ($R = 0.37\%$)				
I	11.7	12.3	3.08	d_{z^2}
II	15.4	25.8	3.38	d_{xy}
III	17.0	61.9	3.58	$d_{xz}\ d_{yz}$
[Cu(dipica)(neoc)](H$_2$O)(ClO$_4$)$_2$ ($R = 0.26\%$)				
I	12.0	16.6	3.34	d_{z^2}
II	15.6	31.2	3.33	d_{xy}
III	16.9	52.2	3.74	$d_{xz}\ d_{yz}$
[Cu(pepica)(en)](ClO$_4$)$_2$ ($R = 0.51\%$)				
I	11.5	7.8	2.66	d_{z^2}
II	13.5	7.0	2.78	d_{xy}
III	16.8	85.2	4.20	$d_{xz}\ d_{yz}$
[Cu(pepica)(pico)](H$_2$O)(ClO$_4$) ($R = 0.38\%$)				
I	10.8	12.5	2.83	d_{z^2}
II	12.8	21.4	3.75	d_{xy}
III	15.6	66.1	4.00	$d_{xz}\ d_{yz}$

[a] For abbreviations, see Table IV. Spectra measured in CH$_3$OH : H$_2$O = 2 : 1. [b] Relative peak area in arbitrary scale based on a sum of 100. [c] Half-height width at $\varepsilon_{\max}/2$. [d] Reliability factor defined as $R = \sum|y_{\mathrm{obs},i} - y_{\mathrm{calc},i}|/\sum y_{\mathrm{obs},i}$.

failure to prepare the corresponding dipica–pico complex. By the same token, [Cu(pepica)(en)(ClO$_4$)$_2$], having an absorption at 593 nm and superhyperfine coupling with only one pyridyl atom, may possibly have a structure consisting of a *facial* pepica with the picolyl chelate and en in the basal plane. Again, this would account for the failure to prepare the dipica–en complex.

The π-interactions of the bidentate ligands may be elucidated from the energy difference between the potential d_π orbitals, namely, d_{xy} and degenerate d_{yz} and d_{xz} orbitals. The energy difference $\Delta(d_{yz}, d_{xz} - d_{xy})$ of 3.0 kK for [Cu(dien)(phen)](ClO$_4$)$_2$ and [Cu(dien)(bipy)](ClO$_4$)$_2$,[30] for which no π-interaction has been suggested, may serve as a reference. The phen, bipy, and neoc complexes of pepica and [Cu(dipica)(neoc)](ClO$_4$)$_2$ show energy differences of ~ 1.6 and 1.3 kK, respectively, strongly suggesting that the phen, bipy, and neoc ligands in these complexes are strong π-acceptors, in agreement with the observed blue-shifts of their intraligand $\pi \rightarrow \pi^*$ transitions.

The structures of the mono-dipica and mono-pepica copper(II) complexes depend mainly on the tridentate ligands, which tend to bind to the equatorial positions. The bidentate ligands, such as phen, bipy, and neoc, are unable to replace one of the terminal pyridyl groups of the tridentate ligands and therefore bind perpendicularly to give a square pyramidal structure. Such a coordination mode may stabilize the complex by decreasing the d_{xy} orbital *via* the π-accepting interaction of the bidentate pyridyl group. The strong en ligand can affect the binding mode of the pepica ligand by replacing ethylpyridine, and binds to equatorial sites. However, it is not clear why the pico ligand, which is not a strong σ-donor, also tends to bind in the basal plane.

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