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ELECTRONIC AND BONDING PROPERTIES OF ACETYLACETONATO COPPER(II) COMPLEXES. MOLECULAR STRUCTURE OF [Cu(ACETYLACETONATO)(1,10-PHENANTHROLINE)(ClO_4)($0.5CH_3CN$)]

CHAN-CHENG SU,* SHU-PAO WU, CHIOU-YUH WU and TSUNG-YI CHANG

Department of Chemistry, National Taiwan Normal University, Taipei 11718, Taiwan

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Abstract—The preparation and characterization of mixed ligand complexes, [Cu(acac)(NN)(ClO_4)] (acac = acetylacetonate, NN = *N,N,N′,N′*-tetramethylethylenediamine, 2,2′-bipyridine, 1,10-phenanthroline (phen), and neocuproine), are reported. The structure of [Cu(acac)(phen)(ClO_4)($0.5CH_3CN$)] determined from three-dimensional X-ray diffraction data comprises discrete square pyramidal [Cu(acac)(phen)(ClO_4)] and [Cu(acac)(phen)(CH_3CN)](ClO_4) units, with the perchlorate or the CH_3CN on the apex. The CH_3CN is coordinated in an unusual bent mode with a Cu—N—C angle of 129.2(9)°. Analysis of the electronic spectra of the complexes suggests the sequence of *d* orbitals as $d_{xy} \gg d_{z^2} > d_{x^2-y^2} \sim d_{xz} > d_{yz}$. In these square pyramidal complexes, acetylacetonate ligands are π donors whilst heterocyclic diimines are not participated in π interactions.

The complexity of stereochemistry of copper(II) complexes has been well documented,[1] and many factors,[2–4] such as ligand field stabilization energies, the Pauling electroneutrality principle, the Jahn–Teller effect, semicoordination, counter ion effects, steric effects, *etc*., have been invoked to account for the complicated structures. Correlation of frontier orbitals with stereochemistry of transition metal complexes has been demonstrated in the literature.[5] Indeed, the *d* orbital energy levels reflect directly the geometries and the conformations of complexes. For instance, the different orientations of the imidazole ligands in [Cu(imidazole)$_4$(NO_3)$_2$][6] and [Cu(imidazole)$_4$(ClO_4)$_2$][7] have been ascribed to the imidazole π-donor ability,[8] and accordingly the layouts of the d_π orbitals are different for these two complexes. It is, therefore, valuable to study the bonding properties of ligands in order to correlate with the stereochemistry of complexes. To this end, investigation on the relative energies of d_π orbitals should be very useful in elucidation of the extent of π interactions between the central metal ion and the ligands.

Considerable research has taken place on acetylacetonate and related β-diketonate complexes.[9] For copper(II) acetylacetonate complexes, although there are controversies on the assignment of the electronic structures;[10–18] it seems that they generally agree with a sequence of *d* orbitals having the d_{xy} ground orbital and non-degenerate d_{yz} and d_{xz} orbitals. With a symmetry group of D_{2h} or C_{2v} for the square planar copper(II) β-diketonates, the d_{xz} and d_{yz} orbitals are expected to be non-degenerate. Accordingly, it is improper to infer that there are π interactions between the acetylacetonate ligand and the central copper ion simply based on the non-degeneracy of the d_{xz} and d_{yz} orbitals. In this paper, we report the bonding properties of acetylacetonate ligands in copper(II) complexes by referring to the energies of the d_π orbitals of mixed ligand acetylacetonatocopper(II) complexes. Since comparison of d_π orbitals would be meaningful only for complexes with similar structures, the structure of the

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*Author to whom correspondence should be addressed.

title complex has been determined by X-ray diffraction.

EXPERIMENTAL

Materials and preparations

Acetylacetone (Ferak), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (Merck), 2,2′-bipyridine (Merck), 1.10-phenanthroline (Merck), neocuproine (Merck), $Cu(ClO_4)_2 \cdot 6H_2O$ (Aldrich) and organic solvents are used as received. $[Cu(acac)_2]$[19] was prepared according to the cited literature.

$[Cu(acac)(tmen)(ClO_4)]$.[20] To 10 cm^3 MeOH solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (2.0 mmol), acetylacetone (2.0 mmol) and NH_3 (2.0 mmol) in 10 cm^3 MeOH were added, and after 30 min, tmen (2.0 mmol) in 10 cm^3 MeOH was added with stirring. After reaction at room temperature for 3 h, ether was added to the resulting solution to give purple precipitates. The product was recrystallized from dichloromethane and ether. Yield, 85%. M.p. 184°C (dec). Found: C, 35.0; H, 5.9; N, 7.2. Calc. for $C_{11}H_{23}N_2O_6ClCu$: C, 34.9; H, 6.1; N, 7.4%. Molar conductivity, 130 S cm^2 mol^{-1} in MeOH.

$[Cu(acac)(bipy)(ClO_4)]$. This blue complex was prepared by the procedure as described above but using bipy. Yield, 75%. M.p. 222°C (dec). Found: C, 42.5; H, 3.6; N, 6.5. Calc. for $C_{15}H_{15}N_2O_6ClCu$: C, 43.0; H, 3.8; N, 6.1%. Molar conductivity, 128 S cm^2 mol^{-1} in MeOH.

$[Cu(acac)(phen)(ClO_4)]$. This blue complex was prepared by the procedure as described above but using phen. Yield, 82%. M.p. 237°C (dec). Found: C, 46.0; H, 3.4; N, 6.3. Calc. for $C_{17}H_{15}N_2O_6ClCu$: C, 46.1; H, 3.6; N, 6.3%. Molar conductivity, 123 S cm^2 mol^{-1} in MeOH. The crystals suitable for X-ray structure determination were obtained by slow diffusion of ether into MeCN solution. The complex contains 0.5 MeCN.

$[Cu(acac)(phen)(ClO_4)(0.5CH_3CN)]$. Found: C, 46.5; H, 3.5; N, 7.5. Calc. for $C_{18}H_{16.5}N_{2.5}O_6ClCu$: C, 46.7; H, 3.6; N, 7.6%.

$[Cu(acac)(neoc)(ClO_4)]$. This deep green complex was prepared by the procedure as described above but using neoc. Yield, 65%. M.p. 202°C (dec). Found: C, 49.3; H, 4.0; N, 6.1. Calc. for $C_{19}H_{19}N_2O_6ClCu$: C, 48.4; H, 4.3; N, 5.9%. Molar conductivity, 135 S cm^2 mol^{-1} in MeOH.

Physical measurements

Electronic spectra were recorded on Perkin–Elmer Lambda 9 and Jasco model 7850 spectrophotometers. Solid samples were measured as Nujol mulls on Whatman No. 1 filter paper. Deconvolution of the visible spectra into Gaussian component bands was performed on a VAX 6510 computer using the profile-fitting program CUVFIT.[21] EPR spectra were obtained using a Bruker ER 200D spectrometer and calibrated with DPPH ($g = 2.0037$). IR spectra were recorded as Nujol mulls or KBr pellets on a BIO-RAD FTS-40 FTIR spectrometer. 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. Sixteen independent reflections with $10.64 \leqslant 2\theta \leqslant 23.90°$ were used for least-squares determination of the cell constants. Diffractometer examination of the reciprocal lattice showed the space group to be $P2_1/c$ from the systematic absences, $0k0$, $k = 2n+1$; $h0l$, $l = 2n+1$. Intensity data ($\theta/2\theta$ scan, $2.5 \leqslant 2\theta \leqslant 50.0°$, $(\sin\theta/\lambda)_{max} \simeq 0.6$) were collected at 296 K for two octants of the sphere ($-17 \leqslant h \leqslant 17$, $0 \leqslant k \leqslant 15$, $0 \leqslant l \leqslant 25$) 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 structures were solved by direct methods using the SHELXTL PLUS program[22] 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*.[23] All hydrogen atoms included in

Table 1. Crystal data and processing parameters for $Cu(acac)(phen)(ClO_4)(0.5CH_3CN)$

Formula	$C_{36}H_{33}Cl_2N_5O_{12}Cu_2$
fw	922.6
Crystal size (mm)	0.46 × 0.30 × 0.20
Space group	$P2_1/c$, monoclinic
a (Å)	14.997(4)
b (Å); β(°)	12.774(4); 106.93(2)
c (Å)	21.067(6)
V ($Å^3$)	3861(2)
Z	4
$D_{calc.}$ ($g\ cm^{-3}$)	1.587
μ (mm^{-1})	1.309
Radiation, λ (Å)	Mo-K_α (0.71073)
Independent refl.	6840 ($2693 \geqslant 3.0\sigma(I)$)
Final R, Rw	0.0556, 0.0594
Largest & mean Δ/σ	0.001, <0.001
Largest diff. peak/hole ($e\ A^{-3}$)	0.47/−0.35

the refinement were placed in idealized positions (C—H = 0.96 Å, H—C—H = 109.4°) with a fixed U (0.08 A^2) after non-hydrogen atoms were refined anisotropically. All calculations were done on a Micro Vax II-based Nicolet SHELXTL PLUS system. Selected bond lengths and angles are given in Table 2. Additional material deposited at the Cambridge Crystallographic Data Centre comprises atomic coordinates, structure factors, anisotropic thermal parameters, H atom coordinates, and a full list of bond lengths and angles.

RESULTS AND DISCUSSION

Structure description

The title phen complex consists of two discrete five-coordinate square pyramidal copper(II) units, [Cu(acac)(phen)(ClO$_4$)] and [Cu(acac)(phen)(CH$_3$CN)](ClO$_4$), as shown in Fig. 1. Both units contain a [Cu(acac)(phen)] basal plane packed nearly parallel in the crystal with the apical ClO$_4^-$ and CH$_3$CN sitting in the opposite directions (Fig. 2). The basal atoms are nearly coplanar; the deviations from the least-squares plane through the CuN$_2$O$_2$ atoms are N(1) 0.0223, N(2) 0.0107, O(1) 0.0250, O(2) 0.0136 and Cu(1) −0.0716 Å for the Cu(1) unit, and N(3) −0.0787, N(4) 0.0377, O(3) 0.0317, O(4) −0.0778 and Cu(2) 0.0871 Å for the Cu(2) unit. The O(1) atom of the Cu(1) unit located on the z axis of the Cu(2) unit is ~3.3 Å away from the Cu(2) atom. The mean Cu—N(phen) distance of 2.00 Å and the bite angle of ~82° for the phen ligand are close to the corresponding average values for phen copper(II) complexes.[24–26] The dimensions of the phen ligands are normal. The mean Cu—O(acac) distance of 1.90 Å is similar to that of 1.92 Å for [Cu(acac)$_2$][27] and 1.91 Å for [Cu(acac)(phen)(hfac)] and [Cu(acac)(phen)(H$_2$O)](hfac)(H$_2$O)[28] (hfac = hexafluoroacetylacetonate), but is significantly shorter than that of 1.95 Å for [Cu(acac)$_2$(quinoline)].[29] The acac chelates in the title complex exhibit a mean C$\overset{\cdots}{—}$O distance of 1.29 Å slightly longer than 1.260 Å for the [Cu(acac)$_2$] complex, whereas a mean C$\overset{\cdots}{—}$C of 1.38 Å is slightly shorter than the corresponding 1.404 Å. The mean ∠O—Cu—O bite angle of ~95° is the largest among some known acac complexes[30] and the binding oxygen atoms, therefore, lie closer to the x axis than the y axis by ~0.13 Å, where the y axis is defined to be bisecting the chelate rings. The dihedral angles between the planes of OCuO and OCCCO are 14.8 and 5.3° for the Cu(1) and Cu(2) units, respectively. These evidences suggest that it is more likely for the acac π orbitals to overlap with the copper d_{xz} orbital than with the d_{yz} orbital. It is noteworthy that the axial CH$_3$CN ligand is bound in a bent fashion toward O(2) (∠Cu(1)—N(5)—C(18) 129.2°). The dimensions of the linear acetonitrile ligand with

Table 2. Bond lengths (Å) and angles (°) for Cu(acac)(phen)(ClO$_4$)(0.5CH$_3$CN)

Cu(1)—N(1)	1.994(8)	Cu(1)—N(2)	2.014(7)
Cu(1)—O(1)	1.900(7)	Cu(1)—O(2)	1.899(6)
Cu(1)—N(5)	2.484(11)	Cu(2)—N(3)	1.989(8)
Cu(2)—N(4)	1.998(9)	Cu(2)—O(3)	1.897(7)
Cu(2)—O(4)	1.899(7)	Cu(2)—O(9)	2.479(16)
C(2)—O(1)	1.276(14)	C(4)—O(2)	1.283(14)
C(22)—O(3)	1.290(14)	C(24)—O(4)	1.301(16)
C(2)—C(3)	1.399(19)	C(3)—C(4)	1.375(18)
C(22)—C(23)	1.341(16)	C(23)—C(24)	1.398(19)
N(5)—C(18)	1.115(17)		
O(1)—Cu(1)—O(2)	95.0(3)	O(1)—Cu(1)—N(1)	172.2(4)
O(2)—Cu(1)—N(1)	90.2(3)	O(1)—Cu(1)—N(2)	92.3(3)
O(2)—Cu(1)—N(2)	171.0(3)	N(1)—Cu(1)—N(2)	82.1(3)
O(1)—Cu(1)—N(5)	91.5(3)	O(2)—Cu(1)—N(5)	89.0(3)
N(2)—Cu(1)—N(5)	96.1(3)	N(1)—Cu(1)—N(5)	94.4(3)
Cu(1)—N(5)—C(18)	129.2(9)	O(3)—Cu(2)—O(4)	95.4(3)
O(3)—Cu(2)—N(3)	90.0(3)	O(4)—Cu(2)—N(3)	168.7(4)
O(3)—Cu(2)—N(4)	172.1(4)	O(4)—Cu(2)—N(4)	91.6(4)
N(3)—Cu(2)—N(4)	82.5(4)	O(3)—Cu(2)—O(9)	94.4(5)
O(4)—Cu(2)—O(9)	102.4(4)	N(3)—Cu(2)—O(9)	87.1(4)
N(4)—Cu(2)—O(9)	87.7(5)	Cu(2)—O(9)—Cl(2)	138.6(8)
N(5)—C(18)—C(19)	178.2(13)		

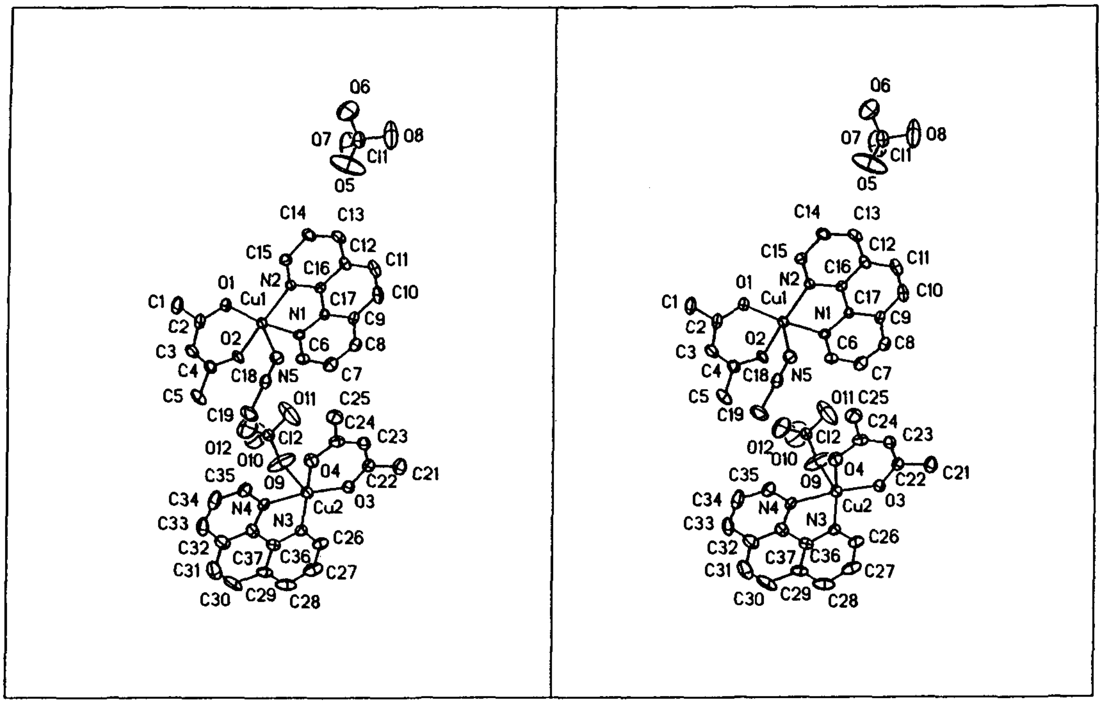

Fig. 1. Stereoscopic drawing of the molecular structure of [Cu(acac)(phen)(ClO_4)($0.5CH_3CN$)] with numbering scheme.

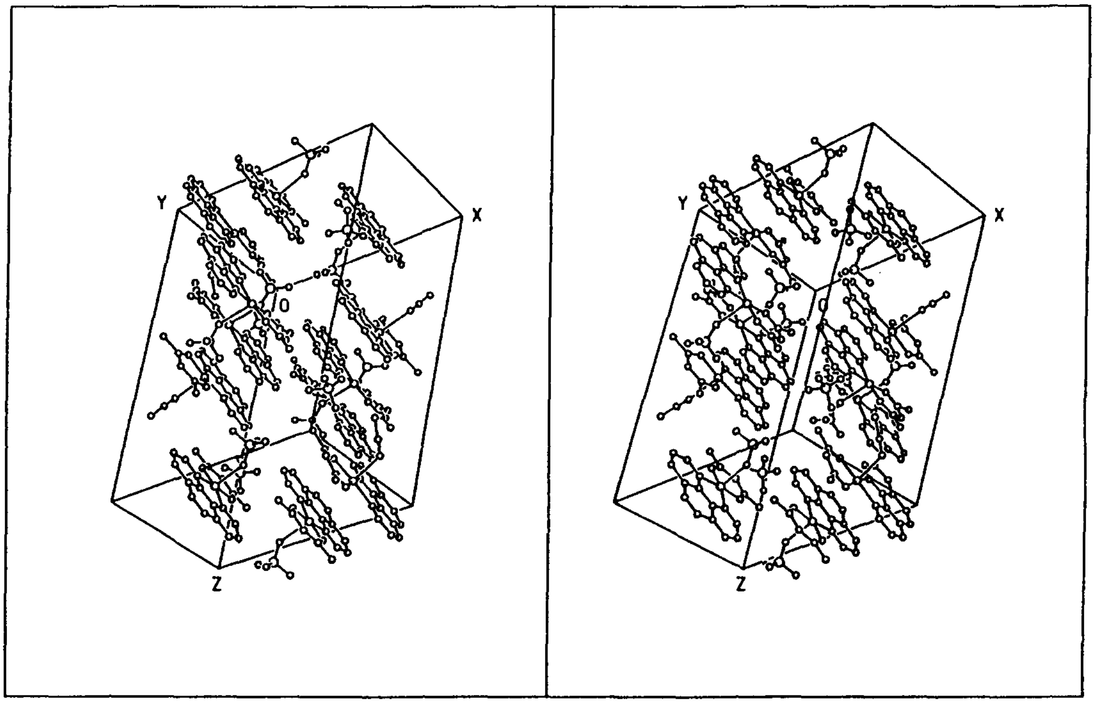

Fig. 2. Stereoscopic drawing of the molecular packing of [Cu(acac)(phen)(ClO_4)($0.5CH_3CN$)] in the unit cell.

Table 3. Infrared spectral data for acetylacetonato copper(II) complexes[a]

Compound[b]	ν(C=O)	ν(C=C)	ν(Cu—O)	ν(Cu—N)	ν(Cl—O)
Cu(acac)(tmen)(ClO_4)	1587s	1522s	454m 293w	424m	1098vs 1080vs
Cu(acac)(phen)(ClO_4)	1586s	1520s	448m 309m	268m	1113vs 1084vs
Cu(acac)(bipy)(ClO_4)	1578s	1522s	448m 301m		1113vs 1086vs
Cu(acac)(neoc)(ClO_4)	1580s	1519s	453m 291w	305w 284m	1107vs 1069vs
Cu$(acac)_2$	1578s (1578)[c]	1528s (1527)[c]	453s 298s (455 290.5)[d]		

[a] Measured as Nujol mulls or KBr pellets.

[b] acac = acetylacetonate, tmen = *N,N,N′,N′*-tetramethylethylenediamine, phen = 1,10-phenanthroline, bipy = 2,2′-bipyridine, neoc = neocuproine.

[c] Ref. 31.

[d] Ref. 35.

C≡N bond length of 1.115 Å and ∠N(5)—C(18)—C(19) of 178.2° are normal. The dimensions of the perchlorate anions are also in the normal ranges.

Infrared, EPR and electronic spectroscopy

The infrared spectral data for the acac complexes are listed in Table 3. Two strong peaks appearing in the ~1590 and ~1520 cm^{-1} regions are assignable to the ν(C=O) and ν(C=C), respectively.[31] The corresponding peaks for [Cu$(acac)_2$] were observed at ~1578 and ~1528 cm^{-1},[31-34] indicating that the π-systems of the acac ligands are somewhat disturbed in the mixed ligand complexes as compared with those in [Cu$(acac)_2$]. Two very strong peaks in the 1100 and 1080 cm^{-1} regions suggest semicoordination of the perchlorate anions for the mixed ligand complexes in agreement with the X-ray structure for the phen complex. The ν(Cu—O) are tentatively assigned at ~450 and ~290 cm^{-1} as those for [Cu$(acac)_2$].[35] The Cu—N stretches are assigned in the 300 cm^{-1} region for the diimines,[36-38] and somewhat higher frequency for the tmen.

The EPR spectral data are given in Table 4. Although the powder spectra are of axial type,[39] $g_\parallel > g_\perp > 2$, the glass spectra of the mixed ligand complexes, except the neoc one, exhibit the fine structures of rhombic spectral features, indicating that the complexes are essentially square pyramidal as the phen complex. The g_z value is much higher for the neoc complex, whereas the hyperfine coupling constant, A_z(Cu), is much lower, suggesting tetrahedral distortion[40,41] of the basal plane for the neoc complex, where steric congestion must be serious.

Table 4. EPR spectral data for acetylacetonato copper(II) complexes[a]

Compound[b]	g_z	g_y	g_x	A_z(Cu)[c]	A_y(Cu)[c]	A_y(N)[c]	A_x(N)[c]
Cu(acac)(tmen)(ClO_4)	2.240 (2.189)	2.059 (2.103)	~2.00	190	~12	~12	
Cu(acac)(phen)(ClO_4)	2.249 (2.182)	2.059 (2.066)	2.020	189	~12	~12	~11
Cu(acac)(bipy)(ClO_4)	2.249 (2.183)	2.058 (2.073)	2.017	190	~12.5	~12.5	~11
Cu(acac)(neoc)(ClO_4)	2.299 (2.218)	[d] (2.083)		161	[d]		

[a] X-band EPR spectra measured at 77 K in aqueous CH_3OH (1 : 1). Powder data in parentheses.

[b] For abbreviations, vide footnote *b* of Table 3.

[c] 10^{-4} cm^{-1}.

[d] Axial spectrum with $g_\perp$ 2.070 and $A_\perp$ (Cu) ~14 × 10^{-4} cm^{-1}.

Although no superhyperfine coupling was observed for the neoc complex, the superhyperfine splittings in the *xy* plane are clearly discerned in separate regions for the phen and bipy complexes. There are eight lines for the A_y(Cu) and A_y(N) with two humps and somewhat distorted trace in the low field region presumably interfered with $A_{\parallel}$(Cu) and essentially about five lines for the A_x(N) as illustrated in Fig. 3. For the tmen complex, the eight lines for the A_y(Cu) and A_y(N) superhyperfine were observed but not the A_x(N). Such apparent separation of the g_x and g_y values is not observed for the structurally similar square pyramidal [Cu(en)(phen)(H_2O)](ClO_4)$_2$ and [Cu(en)(bipy)(H_2O)](ClO_4)$_2$ complexes.[26] Obviously, the out-of-plane d_π orbitals must be interacting with the acac ligand and are non-degenerate.

The electronic spectral data for the acac complexes together with the relevant mixed ligand ethylenediamine complexes[26] are shown in Table 5. All of the complexes exhibit the LF band maximum in mulls in a narrow range 560–572 nm, except the neoc complex, which appears at ~100 nm longer wavelength. The LF band maxima suggest that the bonding strengths of the N-donor ligands are consistent with their σ-donating capabilities, namely, tmen is stronger than the diimines. The much lower λ_{max} for the neoc complex indicates that the basal plane must be greatly distorted due to steric congestion. In CH_3OH solution, the LF band maxima red-shifted by ~30 nm, which should be stemmed from replacement of the axial anions by solvent molecules, consistent with the conductivity measurements. The bidentate ligands are non-dissociative in CH_3OH solution, because the LF band maxima are virtually unaffected by addition of excess bidentate ligands.

The intraligand and the LMCT transitions for the acac ligand are assigned in the ~300 and ~250 nm regions, respectively.[42,43] The $\pi \rightarrow \pi^*$ intraligand transitions appearing in the ~270 and ~220 nm regions for phen and ~310 and ~240 nm for bipy are essentially not varied as compared with those of the corresponding ethylenediamine complexes. Since no π interactions have been suggested for the ethylenediamine complexes,[26] there must be virtually no π interactions participated in the diimine–copper bondings in the mixed ligand acac complexes. The intraligand and the LMCT transitions for the acac ligands, however, are varying for these complexes, indicating that there are π interactions involved in the acac–copper bondings.

Electronic structures and bonding properties

As evident from the visible, EPR and infrared spectral data, the complexes are of square pyramidal structure with a CuN_2O_2 basal plane and a loosely bound apical perchlorate. It is usually observed that the bonding abilities of O-donor ligands are weaker than N-donors for copper(II) complexes. The acetylacetonate ligands in this study, however, exert ligand field strengths as strong as ethylenediamine ligands. This is due to π

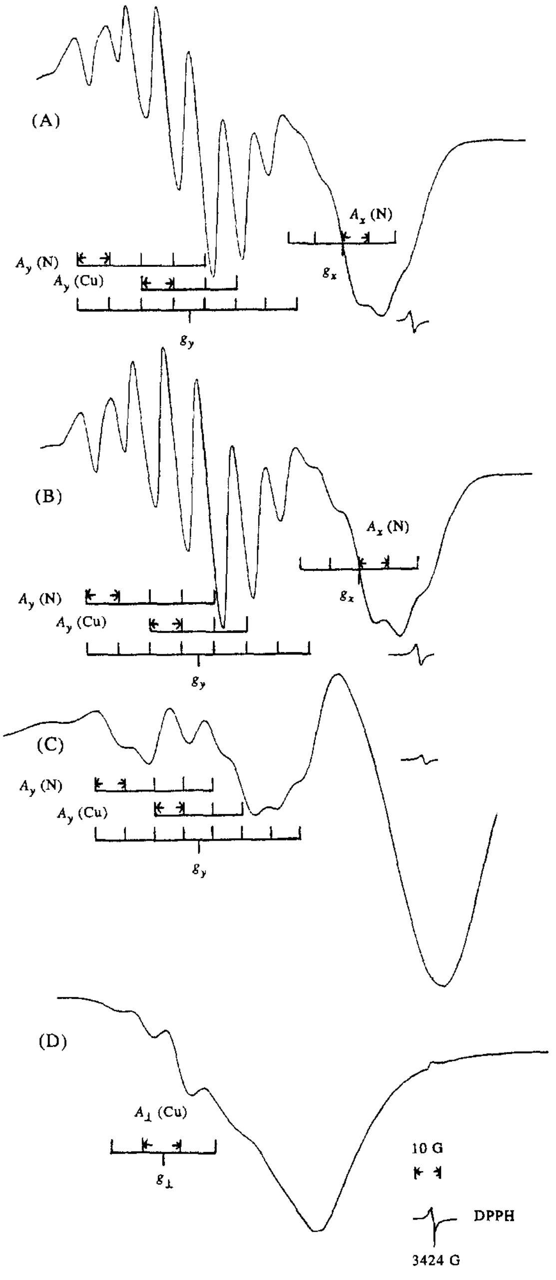

Fig. 3. The high field region of X-band EPR spectra measured at 77 K in aqueous MeOH (1 : 1) for (A) Cu(acac)(phen)(ClO_4); (B) Cu(acac)(bipy)(ClO_4); (C) Cu(acac)(tmen)(ClO_4); (D) Cu(acac)(neoc)(ClO_4). Slightly decomposition of the phen complex was observed, but exhibited no apparent interference in this region.

Table 5. Electronic spectral data for acetylacetonato copper(II) complexes

Compound[a]	Mull λ_{max}(nm)	Solution[b] λ (nm) ($\varepsilon \times 10^3$)	Assignment
Cu(acac)(tmen)(ClO_4)	561	595(0.13)	LF
	[553][c]	[586(0.12)][c]	LF
		302(15.1)	π(acac) → π^*(acac)
		255(13.8)	π(acac) → d_{xy}
Cu(acac)(phen)(ClO_4)	572	610(0.07)	LF
		293(20.8)	π(acac) → π^*(acac)
		272(35.1)	π(phen) → π^*(phen)
		250sh(18.5)	π(acac) → d_{xy}
		223(41.5)	π(phen) → π^*(phen)
Cu(en)(phen)(H_2O)(ClO_4)$_2$	568	588(0.08)	LF
		272(33.7)	π(phen) → π^*(phen)
		225(35.8)	π(phen) → π^*(phen)
Cu(acac)(bipy)(ClO_4)	570	603(0.07)	LF
		308sh(12.0)	π(bipy) → π^*(bipy) π(acac) → π^*(acac)
		297(15.5)	π(bipy) → π^*(bipy) π(acac) → π^*(acac)
		243(10.6)	π(acac) → d_{xy} π(bipy) → d_{xy}
Cu(en)(bipy)(H_2O)(ClO_4)$_2$	560	585(0.07)	LF
		311(14.0)	π(bipy) → π^*(bipy)
		302(14.3)	π(bipy) → π^*(bipy)
		242(16.8)	π(bipy) → π^*(bipy)
Cu(acac)(neoc)(ClO_4)	680	713(0.10)	LF
		294sh(20.7)	π(acac) → π^*(acac)
		271(40.7)	π(neoc) → π^*(neoc)
		~250sh	π(acac) → d_{xy}
		228(55.7)	π(neoc) → π^*(neoc)
Cu(acac)$_2$	555 675	636(0.05)	LF
		294(23.5)	π(acac) → π^*(acac)
		[297(23.5)][d]	π(acac) → π^*(acac)
		241(14.2)	π(acac) → d_{xy}
		[241.2(15.2)][d]	π(acac) → d_{xy}

[a] For abbreviations, see footnote *b* of Table 3.

[b] Measured in CH_3OH. Brackets indicate literature data.

[c] Ref. 44.

[d] Ref. 42.

interactions in the acac–copper bonds, as suggested from the acac $\pi \rightarrow \pi^*$ intraligand spectral data. In order to reveal the acac–copper bondings, the LF spectra were deconvoluted into their Gaussian component bands. Starting from a set of three trial peaks, computer iteration processes were performed until a minimum value of the reliability factor, R,[45] was reached. Each complex had an excellent fit, with the R factor within ~0.5%, and showed a resulting set of three Gaussian component peaks as shown in Fig. 4. The peak positions along with the half-height widths and the relative peak areas are listed in Table 6. Attempts to fit with two component bands were unsuccessful. Attempts to fit with four peaks resulted in merging of the components into three bands.

It is important to note the peak areas of the component bands. The highest and the lowest energy peaks have smaller peak areas, while the central peak is larger than the other two peaks. Since these mixed ligand complexes possess C_1 symmetry, it is anticipated that there will be four *d–d* transition bands with similar intensities. Consequently, the central large peak is owing to two accidentally degenerate transitions. For the square pyramidal mixed chelate copper(II) complexes, if there are no π interactions involved in the coordination bondings, such as [Cu(en)(phen)(H_2O)]

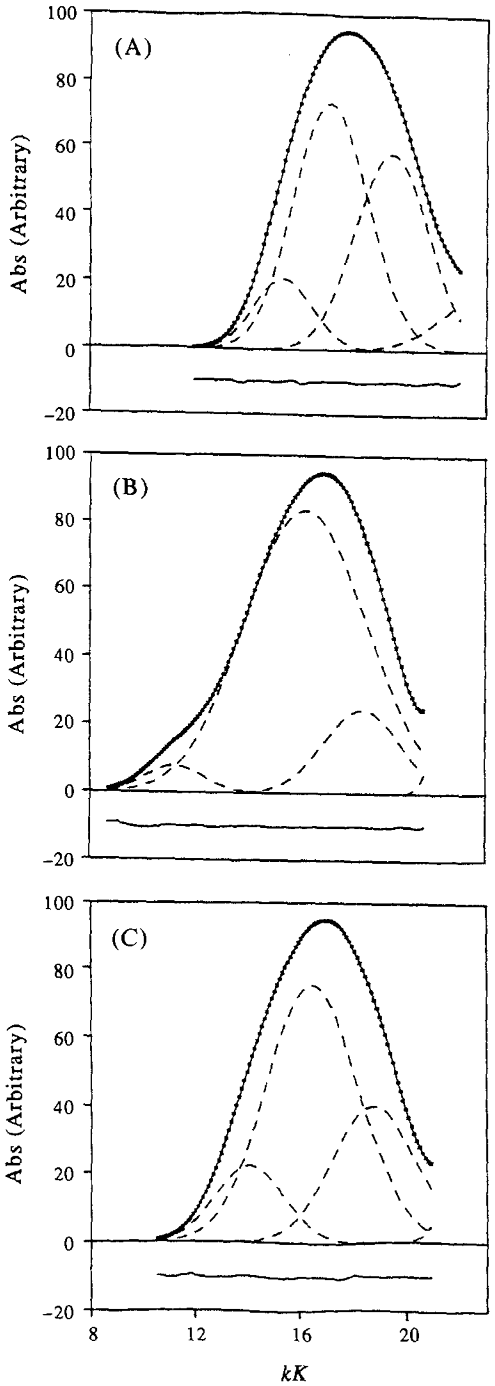

Fig. 4. The solid state visible spectra and Gaussian lineshape analysis with difference plots of (A) [Cu(acac)(tmen)(ClO_4)], $R = 0.35\%$; (B) [Cu(acac)(phen)(ClO_4)], $R = 0.47\%$; (C) [Cu(acac)(bipy)(ClO_4)], $R = 0.40\%$. (——) observed spectrum ; (– – –) Gaussian components ; (*) profile-fitting points.

Table 6. Gaussian component bands for the visible spectra of acetylacetonato copper(II) complexes

Band	ν (kK)	Area[a]	$\delta_{1/2}$[b]	Assignment
Cu(acac)(tmen)(ClO_4)($R = 0.35\%$)[c]				
I	15.4	11.3	2.58	d_{z^2}
II	17.2	49.9	3.23	$d_{x^2-y^2}$; d_{xz}
III	19.5	38.8	3.14	d_{yz}
Cu(acac)(phen)(ClO_4)($R = 0.47\%$)[c]				
I	11.3	3.9	2.68	d_{z^2}
II	16.3	81.1	5.35	$d_{x^2-y^2}$; d_{xz}
III	18.4	15.0	3.34	d_{yz}
Cu(acac)(bipy)(ClO_4)($R = 0.40\%$)[c]				
I	14.1	13.1	3.10	d_{z^2}
II	16.5	58.9	4.07	$d_{x^2-y^2}$; d_{xz}
III	18.8	28.0	3.64	d_{yz}

[a] Relative peak area in arbitrary scale based on a sum of 100.

[b] Half-height width.

[c] Reliability factor defined as $R = \Sigma|y_{\mathrm{obs},i} - y_{\mathrm{calc},i}|/\Sigma y_{\mathrm{obs},i}$.

(ClO_4)$_2$ and [Cu(en)(bipy)(H_2O)](ClO_4)$_2$ complexes,[26] the sequence of the d orbitals is expected to be $d_{xy} \gg d_{z^2} > d_{x^2-y^2} > d_{yz} > d_{xz}$, where the y axis is bisecting the chelate rings. Since both ultraviolet and EPR spectral data (*vide supra*) suggest π interactions between the acac ligand and the central copper ion, it is the d_{xz} orbital, which raises in energy due to interaction with the acac ligand and accidentally becomes degenerate with the $d_{x^2-y^2}$ orbital. Therefore, the sequence of the d orbitals can be assigned as $d_{xy} \gg d_{z^2} > d_{x^2-y^2} \sim d_{xz} > d_{yz}$.

In conclusion, we suggest that acac ligands interact with the copper ion in square pyramidal complexes as π donors, because the d_{xz} orbital is greatly raised in energy upon interacting with the acac ligand. This is consistent with the observed g_y values and the accompanying superhyperfine coupling with the acac ligand. In addition, the energy difference of ~2.3 kK between the $d_{x^2-y^2}$ and d_{yz} orbitals is in good agreement with those of the mixed ligand en-diimine copper(II) complexes.[26]

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