Bonding properties of Cu(II)–O chromophores: electronic and molecular structure of bis(imidazole)bis(*N*-methylacetamide)-bis(perchlorato)copper(II)

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Abstract

The crystal and molecular structure of bis(imidazole)bis(*N*-methylacetamide)bis(perchlorato)copper(II) has been determined using three-dimensional X-ray diffraction data. The complex crystallizes in monoclinic $P2_1/c$ with $Z=2$, $a=7.720(2)$, $b=16.169(3)$, $c=8.742(2)$ Å and $\beta=96.08(1)°$. Least-squares refinement of the structure yielded a final R value of 6.62% and a R_w of 7.55% for 1388 independent reflections at 294 K. The copper(II) ion is coordinated by six ligands to form a centrosymmetrically elongated octahedron with Cu–N(imidazole) 1.969(6), Cu–O(*N*-methylacetamide) 1.982(5) and Cu–O(ClO_4^-) 2.760(10) Å. The molecules are held together with hydrogen bonding between imidazole and perchlorate and between *N*-methylacetamide and perchlorate. The imidazole ligands, having donating nitrogens with mainly 'pyrrole' character as evident by the nearly equal bond lengths of the C–N(H) and C–N(Cu) bonds of the rings, form strong σ-bonds with the central copper ions. The *N*-methylacetamide ligand, having a very short C=O (1.159(12) Å) and a long N–C(=O) (1.330(13) Å) bond, suggests a canonical structure with restricted π-delocalization. The deconvoluted Gaussian component d–d bands of the title complex and the pyridine *N*-oxide analogues are analyzed and assigned with reference to their molecular structures. The bonding properties of Cu(II)–O are deduced: in elongated octahedral copper(II) complexes, pyridine *N*-oxide is a moderately strong σ-donor and a strong π-donor, whereas *N*-methylacetamide is merely a moderately strong σ-donor.

Introduction

The complexity of copper(II) stereochemistry has long been recognized [1]. It is understood that there are so many subtly balanced factors governing the formation of final structures of copper(II) complexes that deduction of prediction rules for the stereochemistry of copper(II) complexes seems exceedingly difficult. However, reviewing the most invoked factors, such as ligand field stabilization energy, the Pauling electroneutrality principle and the Jahn–Teller effect [2], we feel that the energies of the frontier orbitals should play a decisive role in determining the stereochemistry. In order to accomplish such a goal, analyses of bonding capabilities of individual ligands in copper(II) complexes of different stereochemistry are necessary. In reality, however, classification of ligands is needed. This will broaden the generality in practice for estimation of the energies of frontier orbitals. In this paper, we report our conclusion on the bonding properties of Cu(II)–pyridine *N*-oxide and Cu(II)–*N*-methylacetamide based on the energy levels of d orbitals in elongated octahedral complexes. Because the deconvolution processes cannot be reliable without knowing the structures of the complexes, we have undertaken the structure determination of the title complex by X-ray diffraction. The molecular structure of $[Cu(NMIm)_2(pyO)_2(ClO_4)_2]$ (1)** [3] has been reported previously. In order to ensure that the resulting Gaussian components are as reliable as possible, a curve fitting program was

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**Abbreviations used: HIm = imidazole; pyO = pyridine *N*-oxide; NMIm = *N*-methylimidazole; see also footnotes of Table 4.

employed and iteration was made until the reliability factor, *R*, was minimized.

Experimental

Materials

N-Methylacetamide (Aldrich), imidazole (Merck) and organic solvents of reagent grade were used as received. The preparation of compound **1** [3] and $[\mathrm{Cu(HIm)_2(pyO)_2(ClO_4)_2}]$ (**2**) [3] has been reported previously. $[\mathrm{Cu(HIm)_2(nma)_2(ClO_4)_2}]$ was prepared by the following procedure. Imidazole (4.00 mmol) in absolute EtOH was added slowly to an absolute EtOH solution of $[\mathrm{Cu(ClO_4)_2 \cdot 6H_2O}]$ (2.01 mmol) and *N*-methylacetamide (4.02 mmol). The solution was stirred at room temperature for 3 h. After addition of $\mathrm{CHCl_3}$, the solution was stored overnight in a refrigerator. The blue crystals obtained were dried *in vacuo* over $\mathrm{P_4O_{10}}$. Yield 51%. m.p. 174 °C. *Anal.* Found: C, 26.3; H, 3.84; N, 15.8. Calc. for $\mathrm{C_{12}H_{22}N_6O_{10}Cl_2Cu}$: C, 26.5; H, 4.07; N, 15.4%. The blue prisms suitable for X-ray structure determination were obtained by diffusion of $\mathrm{CH_2Cl_2}$ into an $\mathrm{CH_3CN}$ solution of the title compound. The density, determined by flotation in $\mathrm{CCl_4}$–$\mathrm{CHBr_3}$ mixture, was 1.64 g/cm^3 at room temperature.

Physical measurements

IR spectra were recorded on Nujol mulls or KBr pellets on Perkin-Elmer models 983 and 567 spectrophotometers calibrated with polystyrene film. A Varian model 2300 Uv–Vis–NIR spectrophotometer was used for electronic spectra measurements. Solid samples were recorded on Nujol mulls on Whatman No. 1 filter paper. The deconvolution of solid visible spectra into Gaussian component bands was performed on a VAX 8530 computer using the profile-fitting program CUVFIT [4]. EPR spectra were obtained by using a Brucker ER 200D 10/12 model. Elemental analyses were carried out by the microanalysis laboratories of Taiwan University, Taipei.

Structure determination and refinement

A Micro.Vax II computer-controlled Nicolet R3m/V diffractometer was used for crystal and molecular structure determination. Details of crystal data and intensity collection are summarized in Table 1. Twenty independent reflections with $10 < 2\theta < 28°$ were used for least-squares determination of the cell constants. The space group, $P2_1/c$, was unambiguously determined from the systematic absences: $0k0$, $k = 2n + 1$; $h0l$, $l = 2n + 1$. $\theta/2\theta$ scan data were collected at room temperature (294 K) for two octants of the sphere ($-9 \leq h \leq 9$, $0 \leq k \leq 19$, $0 \leq l \leq 10$) out to the 2θ limit of 50.0° ($\sin\theta/\lambda \approx 0.6$). Three standard reflections were monitored every 50 reflections and showed no signs of crystal deterioration. No absorption corrections were made. The data were corrected for Lorentz and polarization effect. The structure was solved by direct methods using SHELXTL PLUS program [5] and refined by full-matrix least-squares on *F* values. Scattering form factors and anomalous-dispersion corrections terms were taken from the International Tables for X-ray Crystallography [6]. The quantity minimized was $\Sigma w(KF_o - F_c)^2$, with weights *w* equal to $[\sigma^2(F_o) + gF_o^2]^{-1}$, where $g = 0.0020$. 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. All calculations were done on a Micro Vax II-based Nicolet SHELXTL PLUS system.

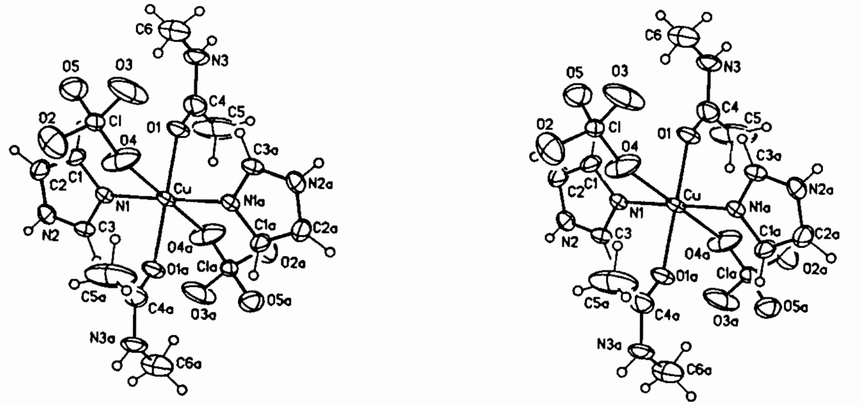
Results and discussion

The crystal and molecular structure of $[\mathrm{Cu(HIm)_2(nma)_2(ClO_4)_2}]$ is shown in Figs. 1 and 2. Bond lengths and bond angles are listed in Table 2. The atomic coordinates are given in Table 3. The copper ion is bound centrosymmetrically by six ligands forming an elongated octahedron with two perchlorates on the long *z* axis and two imidazoles and two *N*-methylacetamides on the *xy* plane. The central copper ion lies on the inversion center and the asymmetric unit consists of only half of the molecule. The discrete $[\mathrm{Cu(HIm)_2(nma)_2(ClO_4)_2}]$ molecules are interconnected by trifurcated hydrogen bonds [7] between imidazole, N(2), and perchlorates, O(5a), O(2a) and O(3b), of neighbouring complexes, and by bifurcated hydrogen bonds between perchlorates, O(2a) and O(3b), and the amide, N(3c), of the neighbouring complex in the next unit cell along the *a* axis. The bond distances and angles of the weakly bound perchlorates are in the normal range.

The short Cu–N(1) distance of 1.969(6) Å, suggesting strong interactions between the central copper ions and the coordinated imidazole ligands, lies at the lower end of the previously reported Cu–N(HIm) distances of imidazole–copper(II) compounds [8, 9] as shown in Table 4. By inspection of the bond lengths of the imidazole rings which bind to copper with a short Cu–N distance of less than *c.* 1.97 Å (Table 4), one sees that the C–N(Cu) bonds are longer than or nearly equal to the C–N(H) bonds. That means the donor nitrogen atoms of these imidazole ligands are mainly of 'pyrrole' character, $-\overset{|}{\mathrm{N}}-\mathrm{Cu}$, rather than the usually observed 'pyridine' one, $=\overset{|}{\mathrm{N}}\rightarrow\mathrm{Cu}$. This may be attributed to strong

TABLE 1. Summary of crystal data and intensity collection

Empirical formula	$C_{12}H_{22}N_6O_{10}Cl_2Cu$
Color, habit	blue transparent, prism
Crystal size (mm)	0.46×0.50×0.55
Space group	monoclinic, $P2_1/c$
Unit cell dimensions	
a (Å)	7.720(2)
b (Å)	16.169(3)
c (Å)	8.742(2)
β (°)	96.08(1)
Volume (Å^3)	1085.072(0)
Z	2
Formula weight	544.8
Density (calc.) (Mg/m^3)	1.667
Absorption coefficient (mm^{-1})	1.315
F(000)	558
Diffractometer used	Nicolet R3m/V
Radiation	Mo Kα (λ=0.71073 Å)
Temperature (K)	294
Monochromator	Highly oriented graphite crystal
2θ Range (°)	2.0–50.0
Scan type	$\theta/2\theta$
Scan speed (°/min in ω)	variable; 3.04–14.65
Scan range (ω)	1.20° plus Kα separation
Background measurement	stationary crystal and stationary counter at beginning and end of scan, each for 50.0% of total scan time
Standard reflections	3 measured every 50 reflections
Index ranges	$-9 \leqslant h \leqslant 9$, $0 \leqslant k \leqslant 19$, $0 \leqslant l \leqslant 10$
Reflections collected	2126 (1549 $I > 3.0\ \sigma(I)$)
Independent reflections	1911 (1388 $I > 3.0\ \sigma(I)$)
Solution	direct methods
Refinement method	full-matrix least-squares
Hydrogen atoms	riding model, fixed isotropic U
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0020F^2$
Final R indices (observed data)	R=6.62%, R_w=7.55%
Goodness-of-fit	1.83
Largest and mean Δ/σ	0.115, 0.028
Data-to-parameter ratio	9.8:1
Largest difference peak (e Å^{-3})	0.92
Largest difference hole (e Å^{-3})	−0.47



(a) (b)

Fig. 1. Stereoscopic diagram of the Cu coordination of $[Cu(HIm)_2(nma)_2(ClO_4)_2]$.

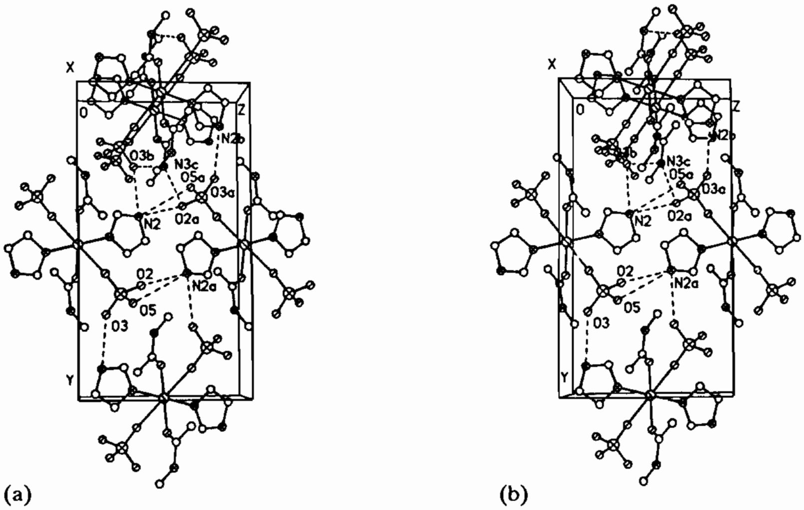


Fig. 2. Stereoscopic drawing of the molecular packing in the unit cell. One extra molecule located in the next unit cell along *a* axis is shown to illustrate the bifurcated H bonds, N3c...O2a, 3.194, and N3c...O3b, 3.344 Å, and the trifurcated H bonds, N2...O2a, 3.220, N2...O5a, 3.145 and N2...O3b, 3.014 Å.

Table 2. Bond lengths (Å) and angles (°) of $Cu(HIm)_2(nma)_2(ClO_4)_2$

Cu–N(1)	1.969(6)	Cu–O(1)	1.982(5)
Cu–N(1A)	1.970(6)	Cu–O(1A)	1.982(5)
Cu–O(4)	2.760(10)	Cu–O(4A)	2.760(10)
N(1)–C(1)	1.339(11)	N(1)–C(3)	1.307(9)
N(2)–C(2)	1.329(11)	N(2)–C(3)	1.306(10)
N(3)–C(4)	1.330(13)	N(3)–C(6)	1.378(13)
C(1)–C(2)	1.325(14)	C(4)–C(5)	1.382(19)
C(4)–O(1)	1.159(12)	Cl–O(2)	1.400(8)
Cl–O(3)	1.362(10)	Cl–O(4)	1.351(9)
Cl–O(5)	1.450(7)		
N(1)–Cu–O(1)	90.1(2)	N(1)–Cu–N(1A)	180.0(1)
O(1)–Cu–N(1A)	89.9(2)	N(1)–Cu–O(1A)	89.9(2)
O(1)–Cu–O(1A)	180.0(1)	N(1A)–Cu–O(1A)	90.1(2)
O(4)–Cu–N(1)	93.4(4)	O(4)–Cu–O(1)	81.0(4)
O(4)–Cu–N(1A)	86.6(4)	O(4)–Cu–O(1A)	99.0(4)
Cu–N(1)–C(1)	127.7(5)	Cu–N(1)–C(3)	126.7(5)
C(1)–N(1)–C(3)	105.6(6)	C(2)–N(2)–C(3)	106.9(7)
C(4)–N(3)–C(6)	122.3(9)	N(1)–C(1)–C(2)	108.8(8)
N(2)–C(2)–C(1)	107.5(9)	N(1)–C(3)–N(2)	111.2(6)
N(3)–C(4)–C(5)	119.5(10)	N(3)–C(4)–O(1)	121.4(9)
C(5)–C(4)–O(1)	118.9(10)	Cu–O(1)–C(4)	138.9(6)
O(2)–Cl–O(3)	113.0(6)	O(2)–Cl–O(4)	109.3(5)
O(3)–Cl–O(4)	112.9(6)	O(2)–Cl–O(5)	107.8(4)
O(3)–Cl–O(5)	106.2(6)	O(4)–Cl–O(5)	107.5(5)

TABLE 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$)

	x	*y*	*z*	U_{eq}[a]
Cu	5000	5000	0	51(1)
N(1)	3945(7)	4729(3)	1893(6)	53(2)
N(2)	2897(8)	4028(4)	3679(7)	71(2)
N(3)	1993(10)	7124(4)	−4469(9)	91(3)
C(1)	3418(15)	5255(5)	2933(10	90(4)
C(2)	2819(20)	4822(6)	4052(11)	111(5)
C(3)	3624(9)	3990(4)	2399(8)	62(2)
C(4)	2387(15)	6330(6)	−598(11)	94(4)
C(5)	1208(19)	5811(8)	−1420(25)	240(12)
C(6)	3104(17)	7670(7)	375(14)	131(6)
O(1)	3743(7)	6071(3)	−135(6)	75(2)
Cl	8076(2)	6644(1)	2404(2)	57(1)
O(2)	9384(10)	6395(5)	3542(9)	135(4)
O(3)	8557(16)	7297(5)	1561(14)	189(6)
O(4)	7543(11)	5985(5)	1526(12)	160(4)
O(5)	6602(9)	6923(4)	3165(8)	106(3)

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

hydrogen bonds between the imidazole and other atoms causing the imidazole ligand to become partially ionized. Here, the imidazole ligands of the title compound are subject to trifurcated hydrogen bonds. Since the dihedral angle between the imidazole rings and the equatorial coordination plane is 28.3°, π-interaction between the copper(II) and the imidazole is limited. Therefore, the short Cu–N bonds are mainly due to σ-donation by imidazole ligands.

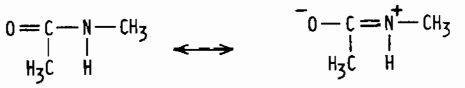
The bond lengths of the nma ligands are somewhat peculiar. First, the C=O of 1.159(12) Å is significantly shorter than that of the free nma (1.23(6) Å) [19] and the average peptide C=O (1.24(1) Å) [9]. Secondly, the N–C(=O) of 1.330(13) Å is significantly longer than that of the free nma (1.29(0) Å) [19] and slightly longer than the average peptide N–C(=O) of 1.31(0.009) Å [9]. Finally, the N–CH_3 of 1.378(12) Å is shorter than the normal N–C single bond, and the C–C(=O) of 1.382(19) Å is shorter than the normal C–C single bond.

TABLE 4. Selected bond lengths of Cu(II)–imidazole complexes

Complex[a]	Cu–N3	(H)N1–C2[b]	(Cu)N3–C2[b]	Remarks
$[Cu(HIm)_4(MeOAcO)_2]$[c]	1.913(7)	1.30(1)	1.39(1)	2-fold H-bond
$[Cu(HIm)(gly\text{-}gly\text{-}glyH)(H_2O)](H_2O)$[d]	1.95(1)			
$[Cu(HIm)(gly\text{-}gly)(H_2O)](3/2)(H_2O)$[d]	1.95(1)			
$[Cu(HIm)_2(gly\text{-}glyH)](ClO_4)$[d]	1.95(1); 1.96(1)			
$[Cu(HIm)_2(nma)_2(ClO_4)_2]$[e]	1.969(6)	1.306(10)	1.307(9)	3-fold H-bond
$[Cu(HIm)_2Cl_2]$[f]	1.973(12)	1.361(20)	1.391(20)	H-bond
$[Cu_3(HIm)_8(Im)_2(ClO_4)_4]$[g]	1.986(7)	1.403(17)	1.349(14)	H-bond
	1.987(7)	1.339(12)	1.334(11)	H-bond
	1.991(6)	1.347(12)	1.301(11)	H-bond
	2.009(6)	1.362(11)	1.356(11)	2-fold H-bond
$[Cu(HIm)_2Cl_2]$[f]	1.992(12)	1.357(27)	1.340(31)	
$[Cu(HIm)_4(ClO_4)_2]$[h]	1.998(4)	1.325(8)	1.311(9)	H-bond
	2.010(4)	1.331(9)	1.319(8)	2-fold H-bond
$[Cu(HIm)_4(NO_3)_2]$[i]	2.011(6)	1.337(11)	1.315(9)	H-bond
$[Cu(HIm)_4(SO_4)]$[j]	2.000(5)	1.337(6)	1.326(6)	H-bond
	2.021(5)	1.340(8)	1.305(7)	H-bond
$[Cu(HIm)_6(NO_3)_2]$[k]	2.012(2)	1.337(4)	1.321(4)	H-bond
	2.049(2)	1.333(4)	1.322(4)	H-bond
	2.593(3)	1.333(5)	1.319(5)	2-fold H-bond
$[Cu(HIm)_4(MeOAcO)_2]$[c]	2.045(7)	1.38(1)	1.30(1)	H-bond
$[Cu(HIm)_2(Im)Cl]$[l]	2.058(4)	1.375(9)	1.325(8)	H-bond

[a] HIm = imidazole; Im = imidazolate; MeOAcO = $CH_3OCH_2CO_2^-$; gly-glyH = $NH_2CH_2CONHCH_2CO_2^-$; gly-gly = $NH_2CH_2CON^-CH_2CO_2^-$; gly-gly-glyH = $NH_2CH_2CON^-CH_2CONHCH_2CO_2^-$; nma = *N*-methylacetamide. [b] Numbering of the imidazole ring as (H)N1–C2–N3(Cu)–C4–C5. [c] Ref. 10. [d] Ref. 11. [e] This work. [f] Ref. 12. [g] Ref. 13. [h] Ref. 14. [i] Ref. 15, average of the four imidazole ligands. [j] Ref. 16. [k] Ref. 17. [l] Ref. 18.

It is usually observed that the amide C=O distance lengthens and the N–C(=O) distance shortens as the amide oxygen binds to metal ions, attributable to the delocalization of π-bonds throughout the amide skeleton and the metal ion. Here, the short C=O and the long N–C(=O) distances are indications of restricted delocalization of π-electrons, that means, resonance structure **I** (Scheme 1) is preferred and π-interaction between the copper ion and the amide ligands must be very limited. In addition, the Cu–O(nma) of 1.982(5) Å, which is nearly the same as many known Cu–O(amide) bond distances [20–22], is longer than the Cu–O(pyO) (1.948(4) Å) of compound **1**, where π-interaction between copper and pyridine oxide has been suggested based on the short Cu–O bond distance and the coplanarity of the Cu–O–N(py) and the equatorial coordination planes [3]. Moreover, the shortening of C(5)–C(4) and N(3)–C(6) bond lengths due to disorder of the nma ligand suggests that the nma ligands are pivoting around the Cu–O axis by about 20° off the average nma plane. These facts indicate that the Cu–O(nma) bond of the title compound is mainly of σ-type and is very limited or no π-interaction at all, despite the observation that the molecular plane of the coordinated nma is nearly perpendicular to the equatorial coordination plane (86.2°).



$$O=\underset{H_3C}{C}-\underset{H}{N}-CH_3 \longleftrightarrow {}^{-}O-\underset{H_3C}{C}=\underset{H}{\overset{+}{N}}-CH_3$$

(I) (II)

Scheme. 1.

In order to elucidate the bonding properties of the copper–oxygen bonds, analysis of spectroscopic data of the complexes appears to be of particular value. The visible spectra of the title complex and the pyO compounds **1** and **2** were deconvoluted into Gaussian component bands. Starting from a set of three or four trial peaks, iteration process for curve fitting was carried out until a minimum value of the reliability factor was reached. Each of the complexes had an excellent fit (R = 0.2112, 0.2271, and 1.16%) and showed a resulting set consisting of three Gaussian peaks as shown in Fig. 3; the peak positions are presented in Table 5 together with their half-height width and relative max. absorptions. Note the differences of the Gaussian component bands; the most intense peak of the nma complex appears at the high energy end, while that of the pyO complexes appear at the center. The assignment of the component peaks was based on (i) the close resemblance of their structures, i.e. all have D_{2h} chromophore with two N-donors of imidazole, two O-donors of neutral ligands, and two O-donors of ClO_4^-; (ii) the π-interaction specific to the d_{xz} orbital for the pyO complexes, but not for the nma complex, as illustrated in Fig. 4. If there was no π-interaction involved in the coordination bonds, a plausible order of d orbitals for an elongated octahedral structure would be $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz} = d_{yz}$, and one would expect that the d_π orbitals of these complexes should hardly be affected by the coordinated ligands, that is, the energy levels of the d_{xy} orbitals of these complexes should be of nearly the same energy as is the case also for the d_{xz} and d_{yz} orbitals. On the other hand, the $d_{x^2-y^2}$ and d_{z^2} energy levels of d_σ character should show significant variation upon the coordination of different ligands. In the pyO complex, π-interaction has been suggested for the Cu–O(pyO) bonds and, therefore, the d_{xz} orbital, which interacts with the p_π of pyO oxygen, is raised in energy and is coincidentally degenerate with the d_{xy} orbital in the pyO complexes. In the nma complex, the d_π levels are not varied because there is essentially no π-interaction between the central copper and the coordinated ligands. Note, particularly, that the energy difference between d_{xy} an d_{yz} is 2.6 kK for both nma and pyO

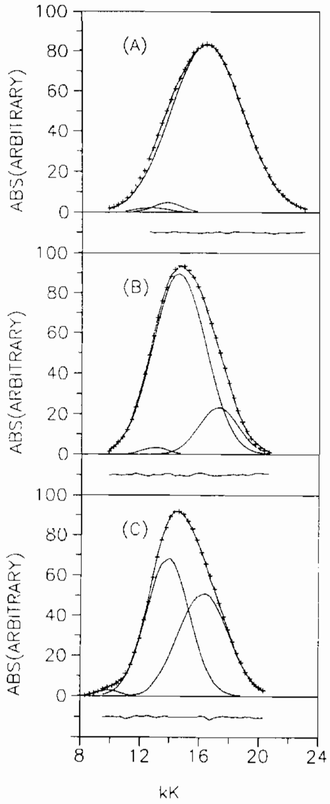


Fig. 3. Visible spectra and Gaussian line-shape analysis with difference plots of (A) $[Cu(HIm)_2(nma)_2(ClO_4)_2]$, $R = 0.2112\%$; (B) $[Cu(HIm)_2(pyO)_2(ClO_4)_2]$, $R = 0.2271\%$; (C) $[Cu(NMIm)_2(pyO)_2(ClO_4)_2]$, $R = 1.16\%$. +, curve-fitting point.

TABLE 5. Gaussian component bands for the visible spectra of Cu(II)–imidazole complexes

Band	ν (kK)	λ_{max}[a]	$\delta_{1/2}$[b]	Assignments
$[Cu(HIm)_2(nma)_2(ClO_4)_2]$ ($R = 0.2112\%$)[c]				
I	12.7	3	2.5	d_{z^2}
II	13.8	5	2.2	d_{xy}
III	16.4	92	5.6	d_{xz}; d_{yz}
$[Cu(HIm)_2(pyO)_2(ClO_4)_2]$ ($R = 0.2271\%$)[c]				
I	12.9	3	2.1	d_{z^2}
II	14.6	77	4.2	d_{xy}; d_{xz}
III	17.2	20	3.1	d_{yz}
$[Cu(NMIm)_2(pyO)_2(ClO_4)_2]$ ($R = 1.16\%$)[c]				
I	9.8	2	1.9	d_{z^2}
II	13.9	56	3.4	d_{xy}; d_{xz}
III	16.5	42	3.9	d_{yz}

[a] Relative band height in arbitrary scale based on a sum of 100. [b] Half-width at $\epsilon_{max}/2$. [c] R is the reliability factor defined as $R = \Sigma|y_{obs,\,i} - y_{calc,\,i}|/\Sigma y_{obs,\,i}$.

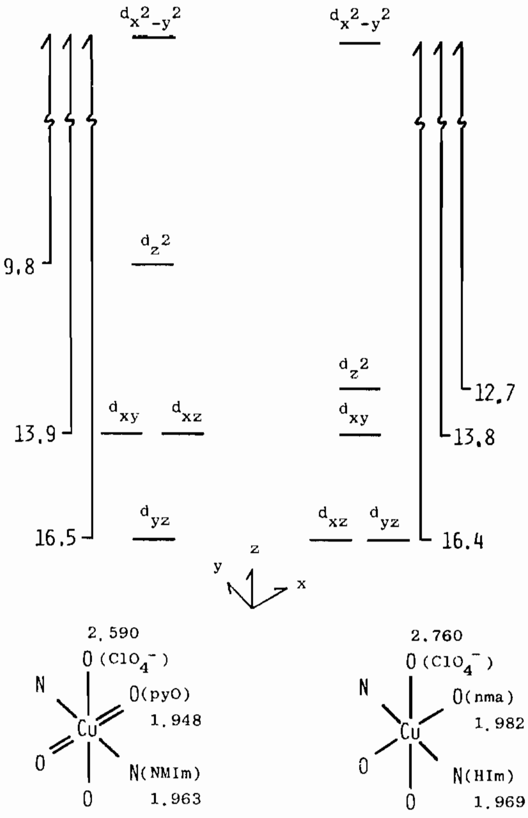


Fig. 4. Energy level diagrams for d orbitals of $[Cu(HIm)_2(nma)_2(ClO_4)_2]$, without π-interaction in the coordination sphere, and $[Cu(NMIm)_2(pyO)_2(ClO_4)_2]$, with Cu–O(pyO) π-bonds, in a field of D_{2h} symmetry.

complexes, strongly suggesting that the d_{xy} level of the nma complex is not varied, and accordingly, there is no π-interaction in the Cu–O(nma) bonds consistent with the previous conclusion. The results may be attributed to the far lying *N*-methylacetamide π and π^* orbitals from the d_{xy} orbital energetically.

Because the bond lengths of Cu–O(pyO) and Cu–O(ClO_4^-) of compound **1** are somewhat shorter than those of the corresponding Cu–O(nma) and Cu–O(ClO_4^-) of the nma complex, both $d_{x^2-y^2}$ and d_{z^2} of compound **1** should be somewhat higher in energy than those of the nma complex. Consequently, all of the d–d absorptions of compound **1** are higher in energy than the corresponding absorptions in the nma complex. In Fig. 4. as we set the d_π orbitals of these complexes at the same energy level, the $d_{x^2-y^2}$ and d_{z^2} orbitals of compound **1** do lie higher than those of the nma complex consistent with the fact that Cu–O(ClO_4^-) and Cu–O(pyO) are shorter in the pyO complex. Likewise, the high lying d_σ orbitals of compound **2** suggest the similarity in structure for both pyO complexes.

The low intensities of both $d_{z^2} \rightarrow d_{x^2-y^2}$ and $d_{xy} \rightarrow d_{x^2-y^2}$ transitions are puzzling because they are vibronically allowed. An analogous situation has been observed in the polarized crystal spectra of $Cu(HIm)_6(NO_3)_2$ [17] which also belongs to a D_{2h} symmetry.

The assignment of $d_{x^2-y^2}$ as the ground state for both complexes is in accordance with their powder EPR spectra, which are of axial type [2] with $g_\parallel > g_\perp > 2$ [23] ($g_\perp$ 2.060, $g_\parallel$ 2.272, $A_\parallel$ 157 G for the nma complex and $g_\perp$ 2.075, $g_\parallel$ 2.279, $A_\parallel$ 160 G for the pyO compound **1**). Because of the interference of the imidazole vibrational peaks, attempts to correlate the characteristic amide IR spectral data with the structure of the amide ligands were not very successful. Nevertheless, the amide I and II bands were tentatively assigned at 1607 and 1573 cm^{-1}, respectively, and the N–H stretching at 3362 cm^{-1}. The red shift of the ν(N–H), as compared with that of the free nma measured in non-polar solvent [24], is a reflection of hydrogen bonding in the nma ligand. The red shift of the amide I peak, however, must be attributed to the mass increment owing to the binding of amide oxygen to the central copper ion.

Our investigation has demonstrated that the bonding capability of pyridine *N*-oxide is greater than that of *N*-methylacetamide in accord with the results reported in the literature [25–27]. Direct comparison of the λ_{max} of d–d band envelopes (700 nm for the pyridine *N*-oxide complexes; 610 nm for the *N*-methylacetamide complex) cannot lead to the correct coordination strength of the ligands, particularly when π-interaction is involved in the bonding. In conclusion, pyridine *N*-oxide is a moderately strong σ-donor and is also a strong π-donor, whereas *N*-methylacetamide is merely a moderately strong σ-donor in elongated octahedral copper(II) complexes.

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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