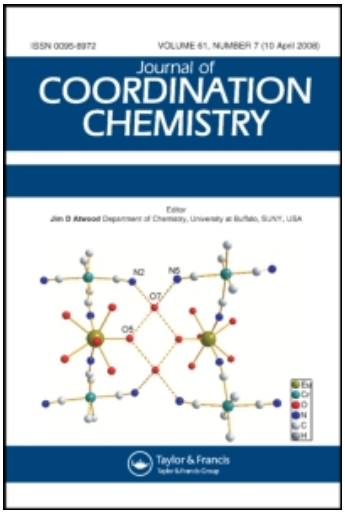

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

BONDING PROPERTIES OF CU(II)-N-CHROMOPHORES: SPECTROSCOPY AND ELECTRONIC STRUCTURES OF HISTAMINE COPPER(II) COMPLEXES. MOLECULAR STRUCTURES OF BIS (HISTAMINE) BIS (PERCHLORATO) COPPER (II) AND CHLOROETHYLENEDIAMINEHISTAMINE-COPPER(II) CHLORIDE

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To cite this Article Su, Chan-Cheng and Chang, Tsung-Yi(1994) 'BONDING PROPERTIES OF CU(II)-N-CHROMOPHORES: SPECTROSCOPY AND ELECTRONIC STRUCTURES OF HISTAMINE COPPER(II) COMPLEXES. MOLECULAR STRUCTURES OF BIS (HISTAMINE) BIS (PERCHLORATO) COPPER (II) AND CHLOROETHYLENEDIAMINEHISTAMINE-COPPER(II) CHLORIDE', Journal of Coordination Chemistry, 31: 1, 79 — 92
To link to this Article: DOI: 10.1080/00958979408022547
URL: http://dx.doi.org/10.1080/00958979408022547

J. Coord. Chem., 1994, Vol 31, pp. 79–92
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BONDING PROPERTIES OF CU(II)-N-CHROMOPHORES: SPECTROSCOPY AND ELECTRONIC STRUCTURES OF HISTAMINE COPPER(II) COMPLEXES. MOLECULAR STRUCTURES OF BIS (HISTAMINE) BIS (PERCHLORATO) COPPER (II) AND CHLOROETHYLENEDIAMINEHISTAMINE-COPPER(II) CHLORIDE

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(Received May 18, 1993; in final form August 2, 1993)

The crystal and molecular structures of $[Cu(hmH)_2(ClO_4)_2]$ (**1**) and [Cu(hmH)(en)Cl]Cl (**2**) (hmH = histamine; en = ethylenediamine) have been determined by three-dimensional X-ray diffraction data. Complex **1** crystallizes in monoclinic, $P2_1/c$, with a = 8.271(3), b = 13.659(4), c = 8.080(2) Å, β = 99.83(2)°, Z = 2, R = 0.039 and R_w = 0.048; complex **2** is orthorhombic, *Pbca*, with a = 10.093(3), b = 15.063(4), c = 16.819(5) Å, Z = 8, R = 0.035, and R_w = 0.038. The Cu(II) ion in **1** is coordinated centrosymmetrically by two histamine ligands forming an equatorial plane, Cu-N(ImH) 2.005(4) Å and Cu-N(NH_2) 2.035(4) Å, and by two perchlorate anions on the elongated z axis, Cu-O 2.608(4) Å. The Cu(II) ion in **2** is square pyramidal with one ethylenediamine, mean Cu-N 2.030 Å, and one histamine, Cu-N(ImH) 1.993(4) Å and Cu-N(NH_2) 2.041(4) Å, forming the basal plane and a chloride ion at the apex, Cu-Cl 2.609(2) Å. The puckered histamine chelate rings of both complexes are bound strongly by the imidazole moieties, but less by the amine sites. The imidazole rings are tilted from the CuN_4 coordination plane by 21.5° and 21.6° in **1** and **2**, respectively. Electronic and epr spectra of the histamine complexes have been examined. Bonding properties of histamine ligands are elucidated according to spectroscopic behaviour and electronic structures are deduced from a Gaussian analysis.

KEYWORDS: Copper(II), histamine, X-ray structure, electronic spectra, Gaussian analysis

INTRODUCTION

Imidazole groups have well been characterized in many copper proteins as the binding sites for metal ions.[1-4] The coordination properties of imidazole ligands, which play important roles in determining the stereochemistries and the functions of the complexes, have been the subject of considerable research.[4-5] Studies of the

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electronic spectra of imidazole copper(II) complexes can provide useful information on copper-imidazole interactions.[6,10] Schugar *et al.*[6] have demonstrated that there are two sets of imidazole π_1 and $\pi_2 \rightarrow d_{x^2-y^2}$ LMCT bands for the differently oriented imidazole ligands in $[Cu(ImH)_4(SO_4)]$.[11] We have shown that the degenerate d_{xz} and d_{yz} orbitals in $[Cu(ImH)_4(NO_3)_2]$[12] and $[Cu(ImH)_4(BF_4)_2]$.2hmpa,[9] both having equivalent imidazole ligands, are distinguished when the imidazole ligands become non-equivalent as in $[Cu(ImH)_4(ClO_4)_2]$,[13] which contains two sets of *trans* imidazole ligands (one with the imidazole ring approximately parallel to the CuN_4 coordination plane and the other nearly perpendicular). These spectroscopic features are not discernible for these imidazole complexes in solution, presumbaly due to reorientation of the imidazoles and/or dissociation of the ligands. Because of the chelate effect, studies of histamine complexes may overcome such difficulties and render investigation of solution species possible.

Herein, we report the molecular structures of the title complexes together with their spectroscopic and epr spectra and thus deduce bonding properties for histamine ligands.

EXPERIMENTAL

Materials and preparations

Histamine dihydrochloride (Aldrich), ethylenediamine (Fluka), $Cu(ClO_4)_2.6H_2O$ (Aldrich), and organic solvents were used as received. $Cu(OH)_2$[14] $Cu(en)_2(ClO_4)_2$,[15] and $[Cu(en)_2Cl(H_2O)]Cl$[16] were prepared according to the cited literature.

$[Cu(hmH)_2(ClO_4)_2]$[17] (1)

To a stirred methanol solution (10 cm^3) of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.741 g, 2 mmol), a 10 cm^3 methanolic solution of histamine dihydrochloride (0.736 g, 4 mmol) and $N(C_2H_5)_3$ (0.808 g, 8 mmol) was added, dropwise. After stirring at room temperature for 2 h, the blue reaction mixture was concentrated on a rotary evaporator. The violet blue precipitate obtained was recrystallized from methanol and then dried *in vacuo* over P_4O_{10}. Yield, 55%, m.p., 185°C (dec.). *Anal.*: Calcd. for $C_{10}H_{18}N_6O_8Cl_2Cu$: C, 24.78; H, 3.74; N, 17.33%. Found: C, 25.0; H, 3.40; N, 17.0%. IR: ν(N-H) 3318vs,br 3277vs, ν(C1-0) 1111vs 1057vs, ν(Cu-N, NH_2)337mw, ν(Cu-N, ImH) 249w. Molar conductivity: 163 ohm^{-1} cm^2 mol^{-1} (in CH_3OH). Columnar violet crystals suitable for X-ray structure determination were obtained by slow evaporation of a methanolic solution of the complex.

$[Cu(hmH)_2(H_2O)Cl]Cl$

A methanolic solution (10 cm^3) of histamine dihydrochloride (1.0 g, 5.43 mmol) was added to a suspension of $Cu(OH)_2$ (0.530 g, 5.43 mmol) in 10 cm^3 of methanol. Bluish green solids appeared. After stirring for 1 h, 10 cm^3 of a methanolic solution of histamine dihydrochloride (1.0 g, 5.43 mmol) and $N(C_2H_5)_3$ (1.097 g, 10.83 mmol) was added dropwise. The reaction mixture finally became deep blue and clear. After reaction for 2 h at room temperature, the solution was filtered,

concentrated, and stored for two days to give a deep violet blue solid. The product was washed with H_2O and ether and then dried *in vacuo* over P_4O_{10}. Yield, 31%, m.p., 184°C (dec.). *Anal.*: Calcd. for $C_{10}H_{18}N_6Cl_2Cu.H_2O$: C, 32.05; H, 5.38; N, 22.42%. Found: C, 32.3; H, 5.15; N, 22.0%. IR: ν(O-H) 3468m, ν(N-H) 3337vs, br, 3306vs, 3233s, 3175s, δ(O-H) 1653m, ν(Cu-N, NH_2) 334w, ν(Cu-N, ImH) 245w, ν(Cu-Cl) 218m. Molar conductivity: 136 ohm^{-1} cm^2 mol^{-1} (in CH_3OH).

[Cu(hmH)(en)Cl]Cl (2)

A methanolic solution (10cm^3) of histamine dihydrochloride (1.0 g, 5.43 mmol) was added to a suspension of $Cu(OH)_2$ (0.530 g, 5.43 mmol) in 10 cm^3 of methanol. Bluish green solids appeared. After stirring for 1 h, a methanolic solution of ethylenediamine (0.326 g, 5.43 mmol) was added dropwise. The solution became deep blue and clear. After reaction at room temperature for 1 h, the reaction mixture was filtered. To the filtrate, ether was added to give violet-blue crystals. The product was filtered and washed with ether and then dried *in vacuo* over P_4O_{10}. Yield, 75%, m.p., 185°C (dec.). *Anal.*: Calcd. for $C_7H_{17}N_5Cl_2Cu$: C, 27.50; H, 5.60; N, 22.91%. Found: C, 28.05; H, 5.29; N, 22.7%. IR: ν(N-H) 3275m, 3221s, 3198s, ν(Cu-N, NH_2) 341w, ν(Cu-N, ImH) 235w, ν(Cu-N, en) 366m, 307w, ν(Cu-Cl) 218m. Molar conductivity: 136 ohm^{-1} cm^2 $mole^{-1}$ (in CH_3OH). Violet crystals suitable for X-ray structure determination were obtained by slow diffusion of either into a methanol solution of the complex.

Physical measurements

I.r. spectra were recorded in Nujol mulls or KBr pellets on a BIO-RAD FTS-40 FTIR. Jasco model 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 visible spectra into Gaussian components was performed on a VAX 6510 computer using the profile-fitting program *CUVFIT*.[18] E.p.r. spectra were obtained using a Bruker ER 200D spectrometer calibrated with DPPH (g = 2.0037). A MicroVax II computer-controlled Siemens R3m/V diffractometer was used for X-ray data collection. Elemental analyses were carried out by the microanalysis laboratories of Taiwan University, Taipei.

Structure determination and refinement

Details of crystal data and processing parameters are summarized in Table 1. Sixteen independent reflections with $11.94° \leq 2\theta \leq 27.09°$ for complex **1** and $12.44° \leq 2\theta \leq 24.15°$ for complex **2** were used for least-squares determinations of cell constants. Diffractometer examinations of the reciprocal lattice showed the space group to be $P2_1/c$ for complex **1** from the systematic absences, $0k0$, $k = 2n + 1$; $h0l$, $l = 2n + 1$ and $Pbca$ for **2** from $0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; $hk0$, $h = 2n + 1$. Intensity data ($\theta/2\theta$ scan, $2.5° \leq 2\theta \leq 50.0°$, $(\sin\theta/\lambda)_{max} \cong 0.6$) were corrected for Lorentz and polarization effects but not for absorption. Three standard reflections were monitored every 50 reflections and showed no signs of crystal deterioration. The structures were solved by direct methods using the *SHELXTL PLUS* program[19] and refined by full-matrix least-squares on F values.

Table 1 Summary of crystal data and processing parameters for $[Cu(hmH)_2(ClO_4)_2]$(**1**) and [Cu(hmH)(en)Cl]Cl (**2**).

formula	$C_{10}H_{18}N_6O_8Cl_2Cu$(**1**)	$C_7H_{17}N_5Cl_2Cu$(2)
M	484.7	305.7
crystal size (mm)	0.76 x 0.32 x 0.10	0.34 x 0.32 x 0.28
space group	$P2_1/c$, monoclinic	*Pbca*, orthorhombic
a(Å)	8.271(3)	10.093(3)
b(Å); β(°)	13.659(4); 99.83(2)	15.063(4); 90.0
c(Å)	8.080(2)	16.819(5)
V(Å^3)	899.4(5)	2557.1(13)
Z	2	8
ρ_{calcd}(g/cm^3)	1.790	1.588
μ (mm^{-1})	1.567	2.104
radiation (λ,Å)	MoKα(0.71073)	MoKα(0.71073)
independent refl.	1589 (1366 ≥ 3.0 $\sigma(I)$)	2254 (1373 ≥ 3.0 $\sigma(I)$)
extinction correction $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$		χ = 0.00005(6)
final R, R_w	0.039, 0.048	0.035, 0.038

Scattering factors and anomalous dispersion correction terms were taken from *International Tables for X-ray Crystallography.*[20] The quantity minimized was $\Sigma w(KF_o - F_c)^2$, with $w = [\sigma^2(F_o) + gF_o^2]^{-1}$, where g = 0.0021 for **1** and 0.0009 for *2*. All hydrogen atoms included in the refinement were placed in idealized positions (C-H = 0.96 Å, H-C-H = 109.4°) with a fixed U (0.08 Å^2) after the non-hydrogen atoms were refined anisotropically. All calculations were done on a MicroVax II-based Nicolet *SHELXTL PLUS* system.

RESULTS AND DISCUSSION

The bis(histamine)copper(II) complexes can readily be prepared by reactions of stoichiometric amounts of histamine with the appropriate copper salt. Attempts to prepare mixed ligand mono(histamine)copper(II) complexes with perchlorate anions were unsuccessful. The mixed ligand complex, [Cu(hmH)(en)Cl]Cl, was obtained by reaction of ethylenediamine with the blue-green species, $[Cu(hmH)Cl_2]$, in methanol solution. The chloride ions are important to stabilize the monohistamine species and render the formation of mixed ligand complexes possible. The final product is a five-coordinate square pyramidal complex with one chloride ion in the apical site (*vide infra*). In order to facilitate band assignments for electronic spectra, $[Cu(en)_2Cl(H_2O)]Cl$ and $[Cu(en)_2(ClO_4)_2]$ were also prepared. The molecular structures of these complexes are known from crystallographic studies.[15–16]

The molecular and crystal structures of $[Cu(hmH)_2(ClO_4)_2]$ (**1**) and [Cu(hmH)-(en)Cl)Cl (**2**) are shown in Figures 1–4. Selected bond lengths and angles are listed in Table 2. Atomic coordinates are given in Table 3. The copper ion of **1** is bound centrosymmetrically by two *trans* histamine chelates in the *xy* plane, Cu-N(imidazole) 2.005(4) Å and Cu-N(NH_2) 2.035(4) Å, and two perchlorate ions on the *z* axis, Cu-O 2.608(4)Å. The central copper ion lies on the inversion centre and the asymmetric unit consists of one half of the molecule. $[Cu(hmH)_2(ClO_4)_2]$ groups are connected by hydrogen bonds between imidazole N2 and perchlorate O2 atoms of a neighboring complex and between amine N3 and perchlorate O1 atoms of another neighboring complex (Fig. 2). The puckered six-membered histamine

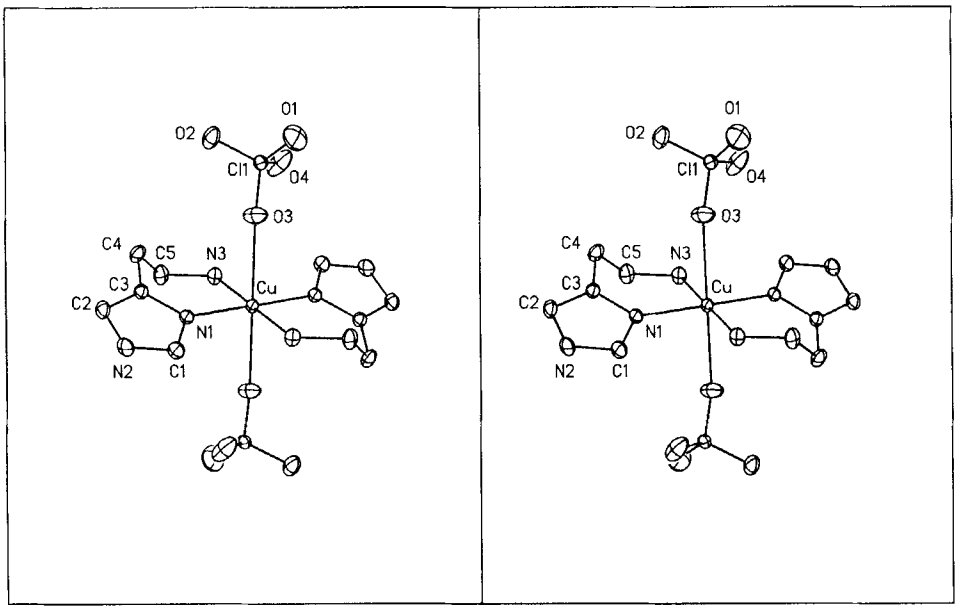

Figure 1 Stereoscopic drawing of $[Cu(hmH)_2(ClO_4)_2]$ with numbering scheme.

chelate ring is a little crowded so that the angle Cu-N3-C5 of 122.4(4)° is much larger than 109.5°, as expected for an sp^3 nitrogen atom; the Cu-N3 distance is slightly longer than the corresponding Cu-N of about 2.00 Å in bis(ethylenediamine)copper(II) complexes.[16,21] The binding of the imidazole moiety is comparable with that found for the tetrakis(4-methylimidazole)copper(II) complex.[10] It is

Table 2 Bond lengths (Å) and angles (°) for $[Cu(hmH)_2(ClO_4)_2]$ (**1**) and [Cu(hmH)(en)Cl]Cl (**2**)

	$[Cu(hmH)_2(ClO_4)_2]$		
Cu-N(1)	2.005(4)	Cu-N(3)	2.035(4)
Cu-O(3)	2.608(4)	N(1)-C(1)	1.335(7)
N(1)-C(3)	1.375(6)	N(2)-C(1)	1.323(7)
N(2)-C(2)	1.363(7)	N(3)-C(5)	1.470(7)
C(2)-C(3)	1.370(7)	C(3)-C(4)	1.491(7)
C(4)-C(5)	1.527(8)		
N(1)-Cu-N(3)	90.7(2)	N(1)-Cu-N(3A)	89.3(2)
N(1)-Cu-O(3)	85.8(1)	N(3)-Cu-O(3)	90.9(1)
	[Cu(hmH)(en)Cl]Cl		
Cu-N(1)	2.020(4)	Cu-N(2)	2.039(4)
Cu-N(3)	2.041(4)	Cu-N(4)	1.993(4)
Cu-Cl(1)	2.609(2)	N(3)-C(3)	1.493(8)
N(4)-C(5)	1.390(7)	C(3)-C(4)	1.462(9)
C(4)-C(5)	1.487(9)		
N(1)-Cu-N(2)	83.9(2)	N(1)-Cu-N(3)	86.4(2)
N(1)-Cu-N(4)	165.7(2)	N(2)-Cu-N(3)	169.7(2)
N(2)-Cu-N(4)	95.3(2)	N(3)-Cu-N(4)	93.3(2)
N(1)-Cu-Cl(1)	98.2(1)	N(2)-Cu-Cl(1)	91.3(1)
N(3)-Cu-Cl(1)	93.5(1)	N(4)-Cu-Cl(1)	96.1(1)

Table 3 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for $[Cu(hmH)_2(ClO_4)_2]$ and [Cu(hmH)(en)Cl]Cl

		$[Cu(hmH)_2(ClO_4)_2]$		
	x/a	*y/b*	*z/c*	*U*(eq)
Cu	5000	5000	0	28(1)
N(1)	2937(4)	4522(3)	723(4)	33(1)
N(2)	988(5)	4248(3)	2200(5)	47(1)
N(3)	4855(5)	3917(3)	-1750(5)	41(1)
C(1)	2420(7)	4675(4)	2178(7)	45(2)
C(2)	526(6)	3780(4)	703(7)	44(2)
C(3)	1746(5)	3953(3)	-213(6)	36(1)
C(4)	1902(7)	3593(4)	-1921(7)	50(2)
C(5)	3597(7)	3147(4)	-1905(8)	51(2)
Cl(1)	2770(1)	6348(1)	-3843(1)	37(1)
O(1)	2569(8)	7357(4)	-3948(10)	116(3)
O(2)	1298(5)	5854(4)	-4627(5)	71(2)
O(3)	3087(6)	6118(4)	-2104(5)	72(2)
O(4)	4126(5)	6024(5)	-4560(6)	96(2)
		[Cu(hmH)(en)Cl]Cl		
	x/a	*y/b*	*z/c*	*U*(eq)
Cu	-46(1)	3576(1)	3202(1)	29(1)
Cl(1)	2386(1)	3556(1)	3729(1)	43(1)
Cl(2)	2126(1)	1286(1)	2417(1)	45(1)
N(1)	306(4)	3116(3)	2094(3)	36(1)
N(2)	236(4)	4789(3)	2691(3)	36(1)
N(3)	-387(4)	2285(3)	3510(3)	39(1)
N(4)	-858(4)	4047(3)	4197(2)	34(1)
N(5)	-1849(5)	4852(3)	5110(3)	49(2)
C(1)	1065(6)	3805(4)	1664(3)	46(2)
C(2)	408(5)	4684(3)	1813(3)	40(2)
C(3)	-871(8)	2048(4)	4321(4)	67(3)
C(4)	-410(7)	2638(4)	4953(4)	60(2)
C(5)	-970(6)	3548(4)	4889(3)	46(2)
C(6)	-1371(5)	4833(4)	4361(3)	39(2)
C(7)	-1595(7)	4038(4)	5445(3)	54(2)

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

noteworthy that the coordination of the NH_2 group is weakened, despite the fact that the pK_a value of the NH_2 (9.92[22]) is higher than that of the imidazole N1 site (6.14[22]). The imidazole nuclei tend to lie parallel to the CuN_4 coordination plane; the dihedral angle between the best planes is 21.5°. The dimensions of the histamine and perchlorate gorups are normal.

Complex **2** consists of a chloride ion and a five coordinated square pyramidal copper(II) cation interconnected by hydrogen bonds between the nitrogen and the chloride atoms as indicated in Figure 4. The ethylenediamine chelate ring in δ conformation is generally normal except that the Cu-N distances of 2.020(4) and 2.039(4)Å are slightly long.[16,21] The histamine chelate is quite similar to that in complex **1**; the bite angle of 93.3° is slightly larger, the angle Cu-N3-C3 of 121.0(3)° is again larger than 109.5°, and the Cu-N(NH_2) distance (2.041(4)Å) is longer than Cu-N(imidazole), (1.993(4)Å). Apparently, binding is stronger by the imidazole nucleus than by the amine group. The apical chloride completes the square pyramidal structure. The copper atom is 0.1332Å above the CuN_4 best plane, toward the chloride ion.

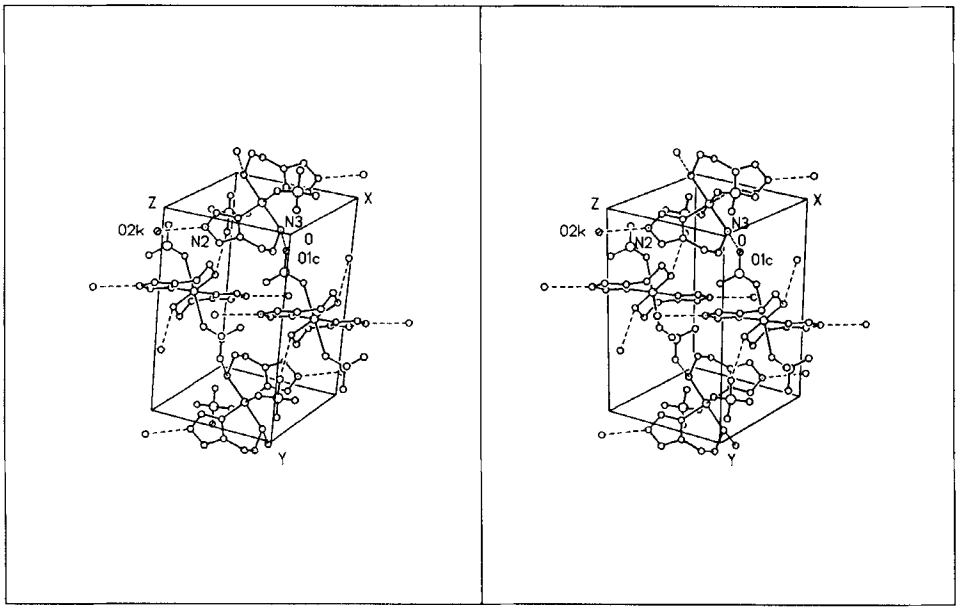

Figure 2 Stereoscopic drawing of the molecular packing of $[Cu(hmH)_2(ClO_4)_2]$ in the unit cell. Hydrogen bonds: N2....O2*k*, 2.951 Å and N3...O1*c*, 2.997 Å.

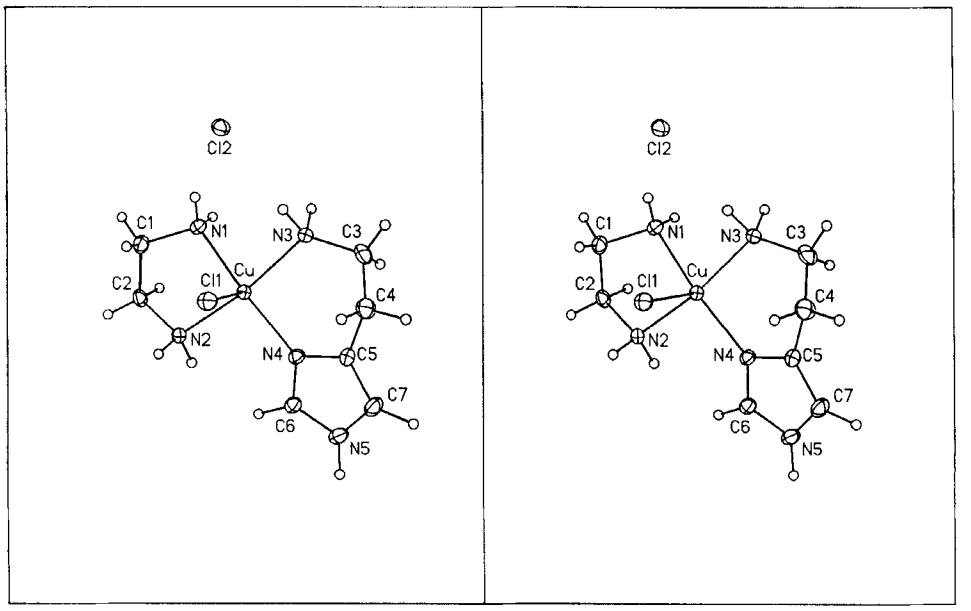

Figure 3 Stereoscopic drawing of [Cu(hmH)(en)Cl]Cl with numbering scheme.

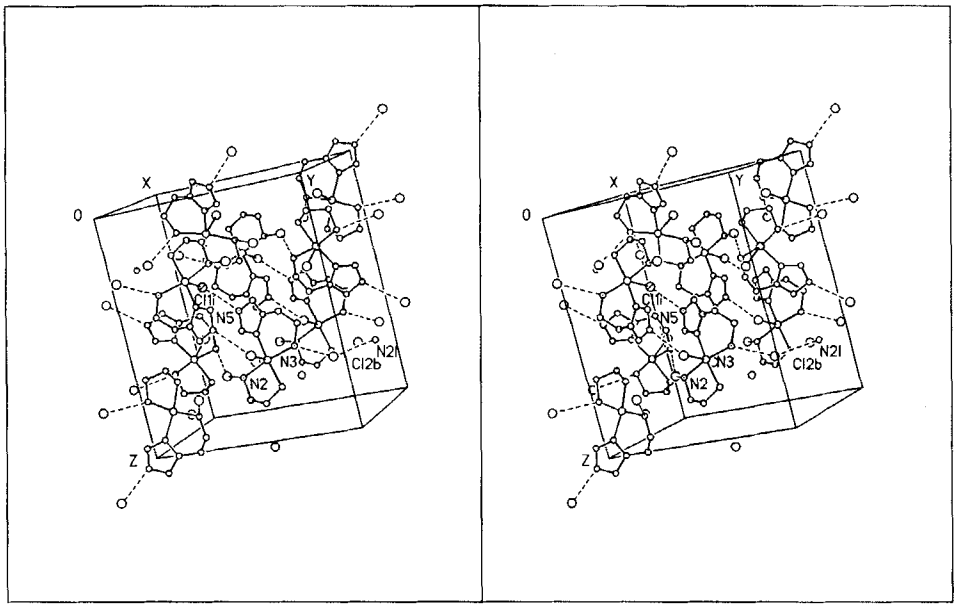

Figure 4 Stereoscopic drawing of the molecular packing of [Cu(hmH)(en)Cl]Cl in the unit cell. Hydrogen bonds: N2 ... Cl2, 3.286Å, N3 ... Cl2*b*, 3.317Å, N5 ... Cl1*i*, 3.141Å.

With the exception of $[Cu(hmH)_2Cl(H_2O)]Cl$, the structures of the complexes in Table 4 are confirmed by X-ray crystallography. The complexes, either five or six coordinate, contain a CuN_4 coordination plane with one or two ligands on the elongated z axis. LF band maxima in the region 529 to 588 nm are consistent with the structures. A similar coordination sphere is suggested for $[Cu(hmH)_2Cl(H_2O)]Cl$. The complex is a 1:1 electrolyte, as suggested from conductivity measurements. The H_2O ligand is likely coordinated to the central copper ion because one sharp O-H stretching can be observed. Another ν(O-H) mode is probably masked by the very strong N-H stretches. Two peaks are observed for ClO_4^- (ν_3) for complex **1** in agreement with the semi-coordinated perchlorates. In methanolic solution, the complexes retain their CuN_4 coordination plane, while the axial ligands may or may not be replaced by solvent molecules. This is supported by LF band maxima, ranging from 545 to 609 nm, and also by axial epr spectral data measured in an aqueous methanol matrix at 77K, as listed in Table 5. Values of g and A for the mixed ligand complexes are consistent with tetragonal structures. There are about nine lines for the nitrogen superhyperfine coupling. The value of g_{11} is increased and A_{11} is decreased as en is replaced by hmH.

Inspection of the electronic spectra results summarized in Table 4 reveals that three bands in the uv region appear only when histamine ligands are present and the intensities increase as the number of histamine ligands increases. The two very intense peaks at 203 and ~215 nm were assigned, respectively, as $\pi_2 \rightarrow \pi^*$ and $\pi_1 \rightarrow \pi^*$ transitions.[6-8]. The less intense peak at 305 nm was assigned $\pi \cdot \cdot \cdot d_x2_{-y}2$. The peaks at 245 nm, of which the intensities increased as the number of NH_2 groups increased, were assigned $\sigma(NH_2) \rightarrow d_x2_{-y}2$.[24-25] The assignments are in good

Table 4 Electronic spectral data for hmH-Cu(II) complexes.

Compound[a]	Mull	Methanol	Assignment
	λ_{max},nm	λ,nm(ε × 10^3)	
hmH		~210(5.40)	π_1(ImH) → π*(ImH)
		~203(5.40)	π_2(ImH) → π*(ImH)
$Cu(hmH)_2(ClO_4)_2$	551	598(0.09)	LF
	~320	305(0.47)	π(ImH) → $d_{x^2-y^2}$
	~250	245(3.80)	σ(NH_2) → $d_{x^2-y^2}$
		214(13.15)	π_1(ImH) → π*(ImH)
		203(11.8)	π_2(ImH) → π*(ImH)
$Cu(hmH)_2Cl(H_2O).Cl$	588	609(0.09)	LF
	~315	305(0.23)	π(ImH) → $d_{x^2-y^2}$
	~255	245(3.85)	σ(NH_2) → $d_{x^2-y^2}$
		214(13.1)	π_1(ImH) → π*(ImH)
		203(11.0)	π_2(ImH) → π*(ImH)
Cu(hmH)(en)Cl.Cl	573	577(0.08)	LF
	~325	305(0.24)	π(ImH) → $d_{x^2-y^2}$
	~270	245(5.95)	σ(NH_2) → $d_{x^2-y^2}$
		217(10.6)	π_1(ImH) → π*(ImH)
		203(7.73)	π_2(ImH) → π*(ImH)
$Cu(en)_2Cl(H_2O).Cl$	551	563(0.09)	LF
	(~235)[b]	234(5.83)	σ(NH_2) → $d_{x^2-y^2}$
$Cu(en)_2(ClO_4)_2$	529	546(0.07)	LF
	(~250)[b]	234(5.80)	σ(NH_2) → $d_{x^2-y^2}$

[a]hmH = histamine; en = ethylenediamine. [b]Ref. 23.

agreement with the report by Spiro *et al.*[26] Only one π → $d_{x^2-y^2}$ transition was identified. The second might be obscured by the intense σ(NH_2) → $d_{x^2-y^2}$ transition.

The LF spectra of the histamine complexes were deconvoluted into Gaussian components for detailed analysis of the energy levels of the *d* orbitals. Starting from a set of four trial peaks, computer-based curve fittings were carried out until a minimum value of the reliability factory, *R*,[27] was reached. Each of the histamine complexes had an excellent fit with $R < \sim 0.4\%$ and showed a resulting set comprising four Gaussian peaks as illustrated in Figure 5. The peak positions are presented in Table 6 along with their half-height widths and relative areas. Attempts to fit with three peaks were unsuccessful; *R* values could not be lowered while keeping reasonable half-height widths for component peaks.

LF spectra of the bis(ethylenediamine)copper(II) complexes were deconvoluted into three Gaussian component bands as shown in Figure 6. The results are presented in Table 6. Because the molecules possess D_{2h} symmetry, there must be

Table 5 Epr spectral data for hmH-Cu(II) complexes[a].

Compound	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$(Cu)[b]	$A_{\perp}$(N)[b]
$Cu(hmH)_2(ClO_4)_2$	2.234	2.053	198	14
$Cu(hmH)_2ClH_2O.Cl$	2.233	2.052	194	14
Cu(hmH)(en)Cl.Cl	2.218	2.057	197	12
$Cu(en)_2Cl(H_2O).Cl$	2.202	2.068	206	10
$Cu(en)_2(ClO_4)_2$	2.203	2.050	201	11

[a]X-band epr spectra measured at 77K in aqueous methanol. [b]10^{-4} cm^{-1}.

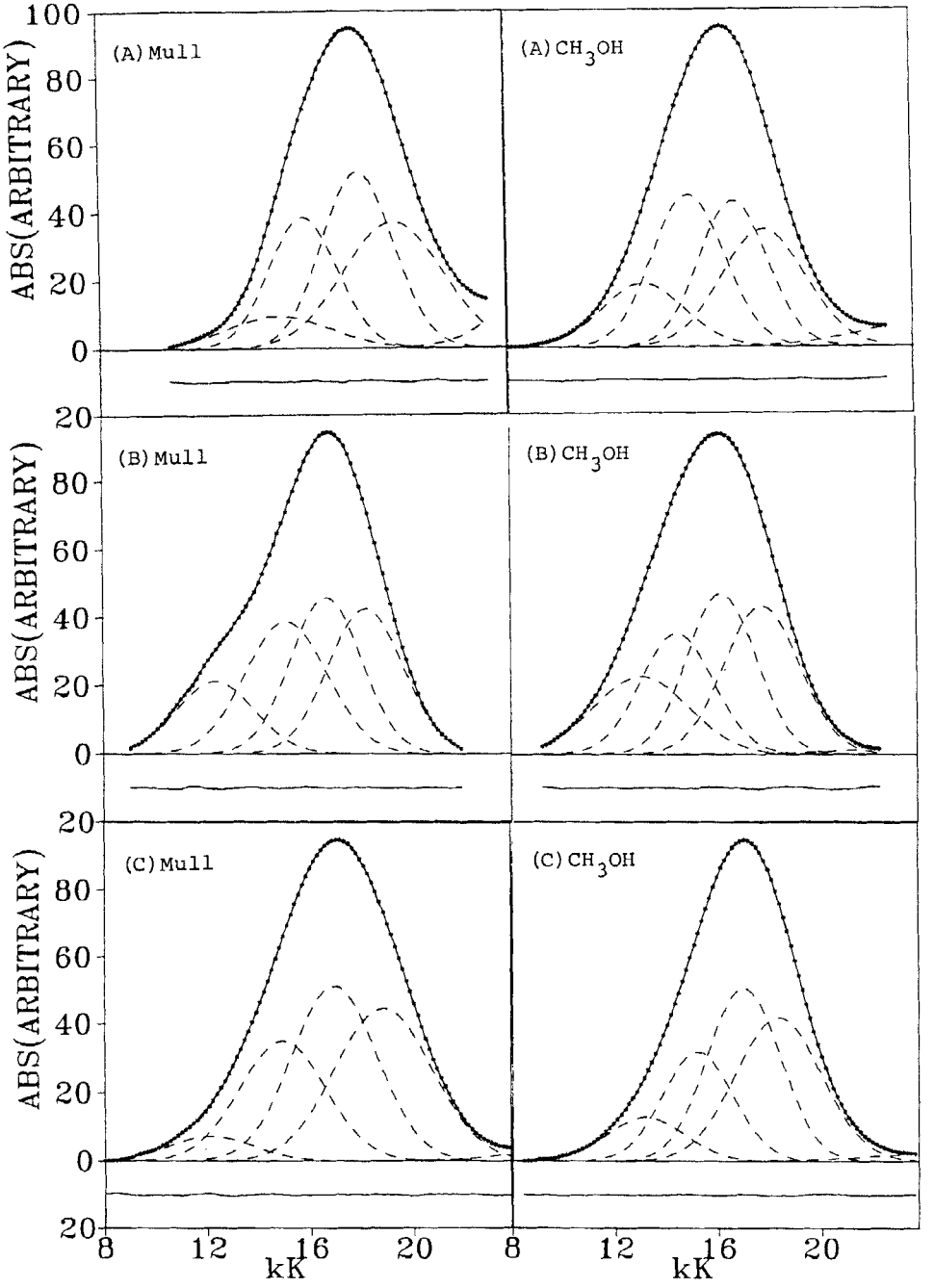

Figure 5 Visible spectra and Gaussian line-shape analysis with difference plots of (A) $[Cu(hmH)_2(ClO_4)_2]$; (B) $[Cu(hmH)_2Cl(H_2O)]Cl$; (C) [Cu(hmH)(en)Cl]Cl; (*) profile-fitting points; (---) Gaussian components; (——) observed spectrum.

Table 6 Gaussian band components for the visible spectra of the hmH-Cu(II) complexes.

band	ν/kK	area[a]	$\delta_{1/2}$[b]	ν/kK	area[a]	$\delta_{1/2}$[b]	assignment
$Cu(hmH)_2(ClO_4)_2$							
/mull (R = 0.33%)[c]				/CH_3OH(R = 0.34%)[c]			
I	15.2	0.89	4.69	13.6	1.46	3.81	d_{z^2}
II	16.2	2.41	3.13	15.4	3.06	3.33	d_{xy}
III	18.3	3.35	3.24	17.1	2.75	3.14	d_{xz}
IV	19.7	3.35	4.53	18.3	2.73	3.86	d_{yz}
$Cu(hmH)_2Cl_2(H_2O)$							
/mull (R = 0.35%)[c]				/CH_3OH(R = 0.42%)[c]			
I	12.6	1.47	3.53	13.4	1.92	4.34	d_{z^2}
II	15.4	2.83	3.72	14.8	2.30	3.34	d_{xy}
III	16.9	2.89	3.21	16.5	2.88	3.14	d_{xz}
IV	18.4	2.82	3.39	18.05	2.90	3.44	d_{yz}
$Cu(hmH)(en)Cl_2$							
/mull (R = 0.35%)[c]				/CH_3OH(R = 0.31%)[c]			
I	12.4	0.50	3.84	13.5	0.95	3.68	d_{z^2}
II	15.2	2.46	3.96	15.5	2.14	3.22	d_{xy}
III	17.2	3.54	3.88	17.3	4.49	3.31	d_{xz}
IV	19.1	3.50	4.42	18.6	3.42	3.92	d_{yz}
$Cu(en)_2(ClO_4)_2$							
/mull (R = 0.70%)[c]				/CH_3OH (R = 0.49%)[c]			
I	16.6	0.31	1.98	14.7	0.10	2.44	d_{z^2}
II	15.0	0.31	2.40	15.0	0.09	2.87	d_{xy}
III	19.0	9.38	5.01	18.3	9.81	4.66	d_{xz}; d_{yz}
$Cu(en)_2Cl(H_2O)\cdot Cl$							
/mull (R = 0.74%)[c]				/CH_3OH (R = 0.46%)[c]			
I	12.8	0.23	2.41	13.0	0.40	2.62	d_{z^2}
II	14.0	0.22	2.41	14.7	0.36	2.43	d_{xy}
III	18.1	9.55	5.44	17.75	9.24	4.77	d_{xz}; d_{yz}

[a] Relative peak area in arbitrary scale based on a sum of 10. [b] Half-width at $\varepsilon_{max}/2$. [c] Reliability factor defined as $R = \Sigma|y_{obs,i} - y_{calc,i}|/\Sigma y_{obs,i}$.

three components (the d_{xz} and d_{yz} orbitals are very close in energy). However, we were able to reach at least two resulting sets with low R values (less than 1%) and reasonable half-height widths for both complexes. The choice here is based on the single crystal polarized spectra,[28] and on data[29] estimated from circular dichroism measurements for $[Cu(\text{-pn})_2]^{2+}$, where -pn represents (-)$_D$-1, 2-diaminopropane.[30] It is noteworthy that the intensity for the high energy peak is much greater than the other two peaks, consistent with D_{2h} symmetry. Consequently, the sequence of the d orbitals can generally be assigned as $d_{x^2-y^2} >> d_{z^2} > d_{xy} > d_{xz} \sim d_{yz}$, where the x and y axes nearly coincide with the Cu-N bonds. The d_{xy} and d_{z^2} orbitals were assigned in the opposite sense for the mull spectrum of $[Cu(en)_2(ClO_4)_2]$ so as to agree with the value of 15.2 kK for the d_{xy} orbital based on CD measurements.[29-30] It is likely that the axial perchlorate anions bind so loosely that the d_{z^2} orbital is greatly stabilized.

The symmetry is much lower for the histamine complexes; C_2 for bis(histamine) copper(II) complexes and C_1 for [Cu(hmH)(en)Cl]Cl. Selection rules suggest that the peak intensities for the component bands should not vary much. Indeed, with the exception of the lowest energy peak, which is about half the size as the others, the areas of the other three peaks are nearly equal. As for the bis(ethylenediamine)copper(II) complexes, it is appropriate to set the x and y axes to be approximately coincident with the Cu-N bonds. Therefore, a $d_{x^2-y^2}$ ground state is

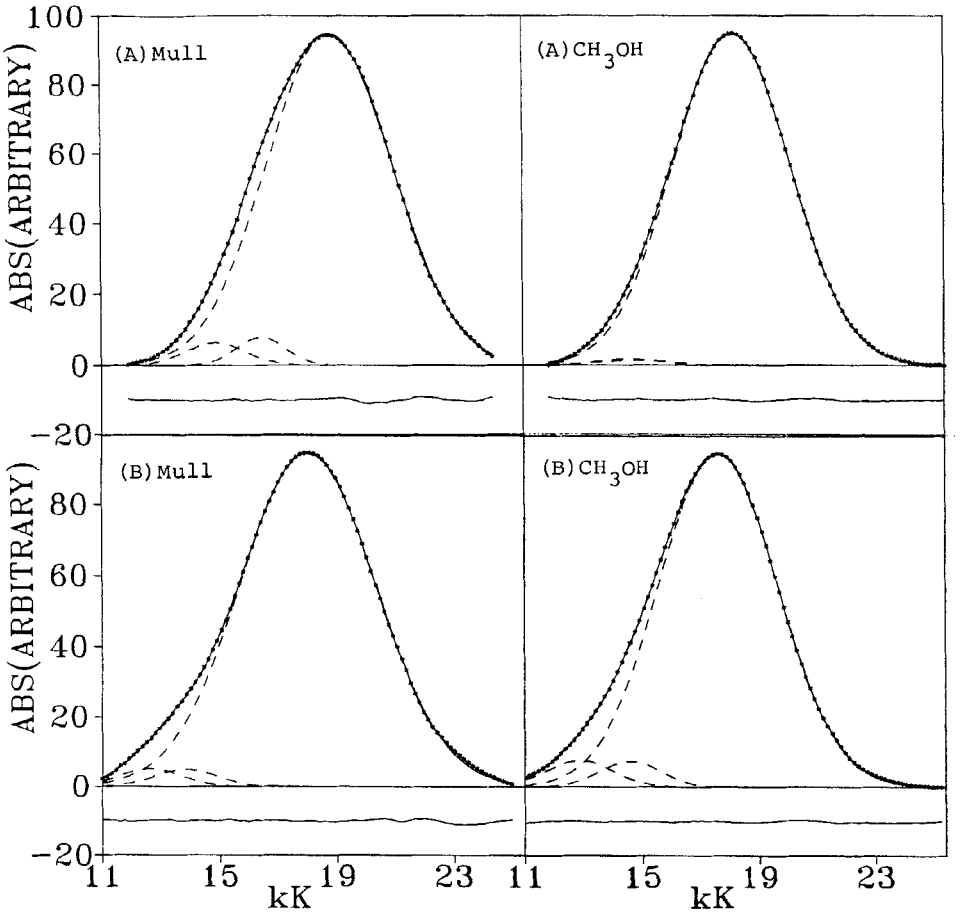

Figure 6 Visible spectra and Gaussian line-shape analysis with difference plots of (A) $[Cu(en)_2(ClO_4)_2]$; (B) $[Cu(en)_2Cl(H_2O)]Cl$; (*) profile-fitting points; (---) Gaussian components; (——) observed spectrum.

assumed. The lowest intensity peak can be assigned to a $d_{z^2} \rightarrow d_{x^2-y^2}$ transition as usually observed for elongated tetragonal copper(II) complexes. The sequence of the d orbitals is $d_{x^2-y^2} >> d_{z^2} > d_{xy} > d_{xz} > d_{yz}$, where the Cu-N(ImH) bond is defined as the x axis. This assignment is similar to that of the bis(ethylenediamine)copper(II) complexes, except that the d_{xz} and d_{yz} orbitals are well separated. This is attributable to π interactions in the copper-imidazole bonds, and is supported by the short Cu-N(ImH) distances.

Comparing the energy levels for the structurally similar bis(ethylenediamine)copper(II) and histaminecopper(II) complexes, one would expect that the energy levels for the non-bonding d_{xy} orbitals should be comparable for these complexes. While setting the d_{xy} orbitals at the same energy level, the d_{yz} orbitals for the histamine complexes are of 3.7 ± 0.2 kK less energy. This is close to the energy difference of

4.05 ± 0.05 kK for the d_{xy} and the degenerate d_{xz} and d_{yz} orbitals of the bis(ethylenediamine)copper(II) complexes. Note that the energy of the d_{xz} orbital is greater than the non-bonding d_{yz} orbital, indicating that the imidazole moieties in the histamine complexes are acting as π-donors.

The energies of the histamine $\pi_1 \rightarrow \pi^*$ and $\pi_2 \rightarrow \pi^*$ transitions also indicate π-donation behaviour of the imidazole moiety. Since the imidazole π_2 orbital is composed primarily of the 2p(π) orbitals of the nitrogen atoms whereas the π_1 orbital is mainly located on the carbon atoms,[6-8,31] π-interaction between π_2 and d_π should be more efficient than the corresponding π_1 and d_π interaction, and therefore perturb π_2 to a larger extent than π_1. The energy difference for these two $\pi \rightarrow \pi^*$ transitions is ~1.7 kK for free histamine. The difference of ~2.6 kK for the coordinated histamine ligands suggests that the imidazole π orbitals are involved in Cu-N bonds as π-donors.

In conclusion, we have demonstrated that the imidazole nucleus of histamine is a π-donor in copper(II) complexes in the solid state and in solution. The imidazole moiety is bound strongly but the amine end is weakened owing to the steric effect of the six-membered chelate ring. It is somewhat surprising that the amine site (of high pK_a), rather than the imidazole site, is weakened. We believe that the histamine chelate with a low pK_a imidazole binding site cannot provide enough σ electron density to the central copper ion, and therefore additional electron density may be supplied from the imidazole nucleus *via* π-bonds in accord with the electroneurality principle.

Supplementary material

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

Acknowledgements

We thank Prof. T.-Y. Dong for use of his Perkin-Elmer Lambda 9 spectrophotometer and Prof. S.-L. Wang for assistance with X-ray work. Financial support from the National Science Council of the Republic of China (NSC82-0208-M003-003) is gratefully acknowledged.

References

1. T.G. Spiro, ed., *Copper Proteins*, (John Wiley, New York, 1981).
2. K.D. Karlin and J. Zubieta, (eds.), *Copper Coordination Chemistry: Biochemical & Inorganic Perspectives*, (Adenine Press, Guilderland, NY, 1983).
3. K.D. Karlin and J. Zubieta, (eds.), *Biological and Inorganic Copper Chemistry*, Vol. I and II, (Adenine Press, Guilderland, NY, 1986).
4. B.J. Hathaway in *Comprehensive Coordination Chemistry*, G. Wilkinson, R.D. Gillard and J. A. McCleverty (eds.), (Pergamon Press, Oxford, 1987), Vol. 5, pp. 533–774.
5. R.J. Sundberg and R.B. Martin, *Chem. Rev.*, **74**, 471 (1974).
6. T.G. Fawcett, E.E. Bernarducci, K. Krogh-Jespersen and H.J. Schugar, *J. Amer. Chem. Soc.*, **102**, 2598 (1980).

7. E. Bernarducci, W.F. Schwindinger, J.L. Hughey, IV, K. Krogh-Jespersen and H.J. Schugar, *J. Amer. Chem. Soc.*, **103**, 1686 (1981).
8. E. Bernarducci, P.K. Bharadwaj, K. Krogh-Jespersen, J.A. Potenza and H.J. Schugar, *J. Amer. Chem. Soc.*, **105**, 3860 (1983).
9. C.-C. Su, T.-T. Hwang, O.Y.-P. Wang, S,-L. Wang and F.-L. Liao, *Transition Met. Chem.*, **17**, 91 (1992); hmpa = hexamethylphosphoramide.
10. C.-C. Su, J.H. Chen, K.-Y. Hwang, S.-J. Liu, S.-W. Wang, S.-L. Wang and S.-N. Liu, *Inorg. Chim. Acta*, **196**, 231 (1992).
11. G. Fransson and B.K.S. Lundberg, *Acta Chem Scand.*, **26**, 3969 (1972).
12. D.L. McFadden, A.T. McPhail, C.D. Garner and F.E. Mabbs *J. Chem. Soc., Dalton Trans.*, 47 (1976).
13. G. Ivarsson, *Acta Chem. Scand.*, **27**, 3523 (1973).
14. G. Braure, *Handbook of Preparative Inorganic Chemistry*, 2nd Ed., (Academic Press, New York, NY, 1965), Vol. 2, pp. 1013–4.
15. I.M. Proctor, B.J. Hathaway and P. Nicholls, *J. Chem. Soc. (A)*, 1678 (1968).
16. R.D. Ball, D. Hall, C.E.F. Richard and T.N. Waters, *J. Chem. Soc. (A)*, 1435 (1969).
17. U. Sakaguchi and A.W. Addison, *J. Chem. Soc., Dalton Trans.*, 600 (1979).
18. S.L. Wang, P.C. Wang and Y.P. Nieh, *J. Appl. Crystallogr.*, **23**, 520 (1990).
19. G.M. Sheldrick, *SHELXTL PLUS User Manual*, (Nicolet XRD Corporation, Madison, WI, 1986).
20. *International Tables for X-ray Crystallography*, Vol. 4, (Kynoch Press, Birmingham, UK, 1974).
21. B.W. Brown and E.C. Lingafelter, *Acta Cryst.*, **17**, 254 (1964).
22. P.R. Huber, R. Griesser, B. Prijs and H. Sigel, *European J. Biochem.*, **10**, 238 (1969).
23. V.M. Miskowski, J.A. Thick, R. Solomon, and H. J. Schugar, *J. Amer. Chem. Soc.*, **98**, 8344 (1976).
24. B.P. Kennedy and A.B.P. Lever, *J. Amer. Chem. Soc.*, **95**, 6907 (1973).
25. H. Yokoi and T. Isobe, *Bull. Chem. Soc. Japn.*, **42**, 2187 (1969).
26. D.S. Caswell and T.G. Spiro, *J. Amer. Chem. Soc.*, **108**, 6470 (1986).
27. See footnotes in Table 5.
28. B. J. Hathaway, D.E. Billing, P. Nicholls and I.M. Procter, *J. Chem. Soc. (A)*, 319 (1969).
29. H. Yokoi and T. Isobe, *Bull. Chem. Soc. Japn.* **41**, 2835 (1968).
30. R.D. Gillard, *J. Inorg. Nulc. Chem.*, **26**, 1455 (1964).
31. J. Del Bene and H.H. Jaffe, *J. Chem. Phys.*, **48**, 4050 (1968).