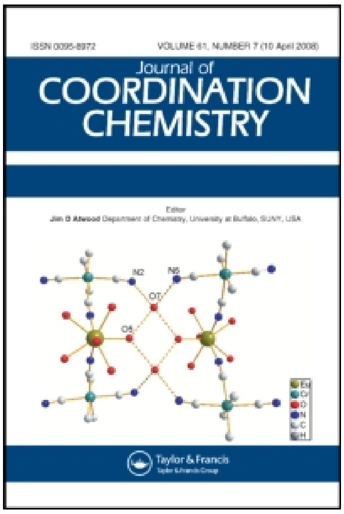

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BONDING PROPERTIES OF Cu(II)-IMIDAZOLE CHROMOPHORES: ELECTRONIC AND MOLECULAR STRUCTURE OF Cu(IMIDAZOLE)$_4$(CF$_3$SO$_3$)$_2$

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BONDING PROPERTIES OF Cu(II)-IMIDAZOLE CHROMOPHORES: ELECTRONIC AND MOLECULAR STRUCTURE OF $Cu(IMIDAZOLE)_4(CF_3SO_3)_2$

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The crystal and molecular structure of [Cu(imidazole)$_4$(CF$_3$SO$_3$)$_2$] has been determined using three-dimensional X-ray diffraction data. The complex crystallizes in the monoclinic space group $P2_1/n$ with $Z = 2$, $a = 9.116(4)$, $b = 9.560(1)$, $c = 14.664(5)$ Å, and $\beta = 106.19(3)°$. Least-squares refinement of the structure yields a final R value of 0.041 and R_w of 0.052 for 1607 independent reflections at 298 K. The copper(II) ion is coordinated centrosymmetrically by four imidazole ligands forming an equatorial plane, mean Cu-N 2.010 Å, and by two trifluoromethanesulfonate ions at the axial sites, Cu-O 2.593(5) Å. The dihedral angles between the imidazoles and the CuN$_4$ plane are 88.6° and 59.4°. Gaussian analyses of the electronic spectra of four *tetrakis*(imidazole)copper(II) complexes having O-donor counter ions yield the d orbital sequences as $d_{x^2-y^2} \gg d_{z^2} > d_{xy} > d_{xz} \geqq d_{yz}$, depending on the orientations of the imidazole nuclei. Energy differences between the antibonding d_{z^2} and non-bonding d_{xy} orbital correlate well with the Cu-O bond lengths and this supports the sequences of the d orbitals.

KEYWORDS: copper(II), imidazole, X-ray structure, electronic spectra, Gaussian analysis

INTRODUCTION

Interactions of histidyl residue with copper ions have been widely observed in many biological molecules and metalloproteins.[1–6] Considerable research effort has been focussed on low molecular weight copper-imidazole complexes in order to understand their stereochemistry and reactivity.[2–8] In our previous studies[9–11] of the bonding properties of copper-imidazole chromophores, we have shown that the conformations of the imidazole ligands in *tetrakis*-imidazole and *tetrakis*-monosubstituted imidazole copper(II) complexes are mainly affected by the donor abilities of both the imidazole ligands and the counter ions. Thus, imidazole and *N*-methylimidazole complexes with very weak σ donor anions, for example, [Cu(imidazole)$_4$(ClO$_4$)$_2$][12] and [Cu(*N*-methylimidazole)$_4$(ClO$_4$)$_2$],[11] comprise two sets of *trans* imidazole ligands, one parallel and another perpendicular to the CuN$_4$ coordination plane. Corresponding complexes with relatively stronger σ

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donor anions, such as [Cu(imidazole)$_4$(NO$_3$)$_2$][13] and [Cu(*N*-methylimidazole)$_4$(H$_2$O)$_2$]Cl$_2$(H$_2$O),[11] have all four imidazole ligands perpendicular or tilted ~45° with respect to the CuN$_4$ plane. Based on the energy levels of the d_π orbitals, only the parallel imidazole ligands have been found to be π-donors, and which participate in π interactions with the central copper ion and supply additional electron density to the central copper ion *via* the low lying d_π orbitals. Herein, we report the crystal and molecular structure of the title complex, and elucidate the electronic and bonding properties so as to substantiate our understanding of the roles of the axial anionic ligands on the orientations of the coordinated imidazole ligands.

EXPERIMENTAL

Material and Methods

Imidazole (ImH) (Merck), 2,2-dimethoxypropane (Aldrich), and organic solvents of reagent grade were used as received. Cu(CF$_3$SO$_3$)$_2$·6H$_2$O was prepared from CuO and CF$_3$SO$_3$H. *Tetrakis*(imidazole)copper(II) complexes, [Cu(ImH)$_4$(NO$_3$)$_2$],[14] [Cu(ImH)$_4$(SO$_4$)],[15] and [Cu(ImH)$_4$(ClO$_4$)$_2$][16] were prepared according to the cited literature. The title complex, [Cu(ImH)$_4$(CF$_3$SO$_3$)$_2$], was prepared by the following procedure: [Cu(CF$_3$SO$_3$)$_2$·6H$_2$O] (1 mmol) and imidazole (4 mmol) were dissolved in acetonitrile containing 5% of 2,2-dimethoxypropane. After stirring the mixture at room temperature for 1 h, diethyl ether was added dropwise until precipitates began to appear. The solution was stored in a refrigerator for two days, yielding purple blue crystals. Yield, 83%. *Anal.*, calc. for C$_{14}$H$_{16}$N$_8$O$_6$F$_6$S$_2$Cu: C, 26.7; H, 1.92; N, 17.8%. Found: C, 26.9; H, 2.05; N, 17.6%.

Physical Measurements

IR spectra were recorded as Nujol mulls on a BIO-RAD FTS-40 FTIR spectrophotometer. A Shimadzu UV-3101PC double monochromator spectrophotometer was used for electronic spectra measurements. Spectra of solid samples were recorded as Nujol mulls on Whatman No. 1 filter paper. The deconvolution of visible spectra into Gaussian component bands was performed on a VAX 6510 computer using the profile-fitting program *CUVFIT*.[17,18] A VAX 3300 computer-controlled Enraf-Nonius CAD4 diffractometer was used for crystal data collection. 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 Twenty-five independent reflections with $24° < 2\theta < 28°$ were used for least-squares determination of the cell constants. The space group, $P2_1/n$, was unambiguously determined from systematic absences: $0k0$, $k = 2n + 1$; $h0l$, $h + l = 2n + 1$. The intensity data were corrected for Lorentz and polarization effects but not for absorption. Three standard reflections were monitored every 2 h and showed no

Table 1 Summary of crystal data and processing parameters for $[Cu(ImH)_4(CF_3SO_3)_2]$.

formula	$C_{14}H_{16}F_6N_8O_6S_2Cu$
M	634.0
crystal size (mm)	0.25 × 0.35 × 0.30
space group	$P2_1/n$, monoclinic
a(Å)	9.116(4)
b(Å); β (°)	9.560(1); 106.19(3)
c(Å)	14.664(5)
V(Å^3)	1227.2
Z	2
D_{calcd}(g/cm^3)	1.71
μ (mm^{-1})	1.14
radiation (λ, Å)	Mo Kα (0.71073)
maximum 2θ (°)	50.0
scan type	ω-θ
index range	$-10 \leq h \leq 10$, $0 \leq k \leq 11$, $0 \leq l \leq 17$
independent refl.	2305 (1607 with $I \geq 3.0\ \sigma(I)$)
final R, R_w	0.041, 0.052
largest shift Δ/σ	< 0.001

sign of crystal deterioration. The structure was solved by direct methods using Personal SDP software incorporating the SHELXS86 program[19,20] and refined by full-matrix least-squares on F values. Scattering factors and anomalous dispersion correction terms were taken from the *International Tables for X-ray Crystallography*.[21] The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$, with $w = 4F_o{}^2/\sigma^2(F_o^2)$. The hydrogen atoms included in the refinement were located in succeeding difference Fourier syntheses after the non-hydrogen atoms were refined anisotropically. All calculations were performed on a 80486/33 personal computer.

RESULTS AND DISCUSSION

The molecular and crystal structures of the title complex are shown in Figures 1 and 2. Selected bond lengths and bond angles are listed in Table 2. Atomic coordinates are given in Table 3. The copper ion is bound centrosymmetrically by six ligands to form an elongated octahedron with four imidazole ligands on the equatorial plane, Cu-N 2.021(3) and 1.998(5) Å, and two trifluoromethanesulfonate ions at the axial sites, Cu-O 2.593(5) Å. The central copper ion lies on the inversion centre and the asymmetric unit consists of only half of the molecule. The discrete $[Cu(ImH)_4(CF_3SO_3)_2]$ units are interconnected by hydrogen bonds between imidazole N2 and triflate O3 atoms of a neighbouring complex and between imidazole N4 and triflate O2 atoms of another neighboring complex. The N1 imidazole rings are oriented approximately perpendicular to the CuN_4 coordination plane; the dihedral angle is 88.6°. The N3 imidazoles are titled from the CuN_4 plane by 59.4°. The dimensions of the imidazoles and the trifluoromethanesulfonate ions are normal.

Table 4 lists visible and the infrared spectroscopic data of four *tetrakis*-imidazole copper(II) complexes, containing *O*-donor anionic ligands. Their structures[12,13,15] have been characterized by X-ray determinations to be elongated octahedra. Vibrational spectra exhibit one Cu-N stretch in the 300 cm^{-1} region[22,23] for the nitrato and the triflato complexes, and two for the sulfato and the

Table 2 Selected bond lengths (Å) and angles (°) for $[Cu(ImH)_4(CF_3SO_3)_2]$.

Cu-O(1)	2.593(5)
Cu-N(1)	2.021(3)
Cu-N(3)	1.998(5)
O(1)-Cu-N(1)	88.3(2)
O(1)-Cu-N(3)	92.0(2)
N(1)-Cu-N(3)	89.5(2)

Table 3 Atomic coordinates and thermal parameters (Å^2) for $[Cu(ImH)_4(CF_3SO_3)_2]$.

	x/a	*y/b*	*z/c*	*B**
Cu	0.000	0.500	0.500	2.38(2)
S1	0.2364(2)	0.2913(2)	0.35898(9)	2.65(3)
F1	0.5101(5)	0.3502(6)	0.4615(4)	7.6(1)
F2	0.4361(5)	0.1471(6)	0.4831(4)	8.9(1)
F3	0.5006(5)	0.1944(7)	0.3568(4)	9.4(1)
01	0.1803(4)	0.3452(6)	0.4338(3)	4.5(1)
02	0.2508(5)	0.3950(5)	0.2912(3)	5.0(1)
03	0.1688(5)	0.1617(5)	0.3195(4)	5.6(1)
N1	0.1635(5)	0.5047(5)	0.6256(3)	2.91(9)
N2	0.3854(6)	0.4718(6)	0.7292(4)	4.3(1)
N3	0.0858(5)	0.6755(5)	0.4615(3)	2.62(9)
N4	0.1854(5)	0.8264(5)	0.3852(3)	3.5(1)
C1	0.2961(7)	0.4457(7)	0.6405(4)	4.0(1)
C2	0.3044(8)	0.551(1)	0.7726(4)	5.7(2)
C3	0.1655(8)	0.572(1)	0.7085(5)	6.0(2)
C4	0.1394(7)	0.6947(6)	0.3879(4)	3.4(1)
C5	0.1627(7)	0.8950(7)	0.4607(4)	3.7(1)
C6	0.1006(7)	0.8005(6)	0.5074(4)	3.5(1)
C7	0.4305(7)	0.2426(7)	0.4178(5)	4.4(2)
H1	0.327	0.392	0.593	4.00
H2	0.488	0.439	0.757	4.00
H3	0.340	0.585	0.837	4.00
H4	0.081	0.626	0.721	4.00
H5	0.147	0.623	0.343	4.00
H6	0.225	0.867	0.336	4.00
H7	0.189	0.993	0.477	4.00
H8	0.068	0.820	0.563	4.00

* *B* is defined as: $(4/3)\cdot[a^2\cdot\beta(1,1) + b^2\cdot\beta(2,2) + c^2\cdot\beta(3,3) + ab(\cos\gamma)\cdot\beta(1,2) + ac\ (\cos\beta)\cdot\beta(1,3) + bc(\cos\alpha)\cdot\beta(2,3)]$.

Table 4 Visible and IR spectroscopic data for *tetrakis*(imidazole)copper(II) complexes.

Compound	LF bands[a]	IR[b]		angle[c]/deg
	λ_{max},nm	ν Cu-N	ν N-H	
$[Cu(ImH)_4(NO_3)_2]$	528~650sh	291m[d]	3243vs,br[d]	98.6,94.6[e]
$[Cu(ImH)_4(CF_3SO_3)_2]$	543~650sh	280m	3422ms,br	88.2,59.4
$[Cu(ImH)_4(SO_4)]$	590	305m 272m	~3100vs,br	99.0,29.7[f]
$[Cu(ImH)_4(ClO_4)_2]$	550~650sh	310m 283m[d]	3356vs,br[d]	94.3,18.7[g]

[a] Measured in Nujol mulls on Whatman No.1 paper; sh = shoulder. [b] Measured in Nujol mulls; m = medium, ms = medium strong, vs = very strong, br = broad. [c] Dihedral angles between imidazole rings an CuN_4 plane. [d] Ref. 9. [e] Ref. 13. [f] Ref. 15. [g] Ref. 12.

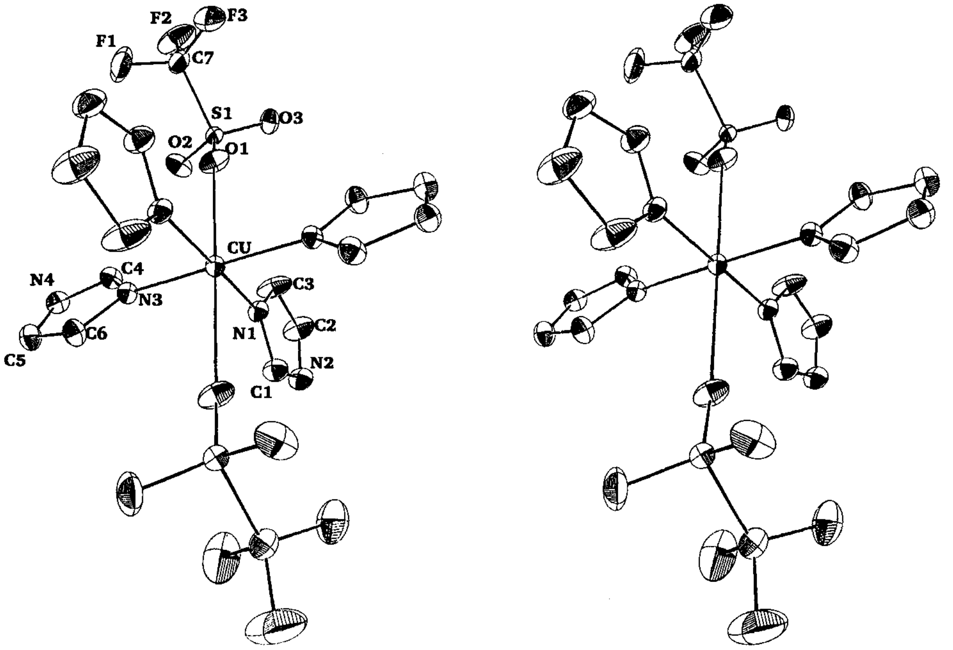

Figure 1 Stereoscopic drawing of $[Cu(ImH)_4(CF_3SO_3)_2]$ with atom numbering scheme.

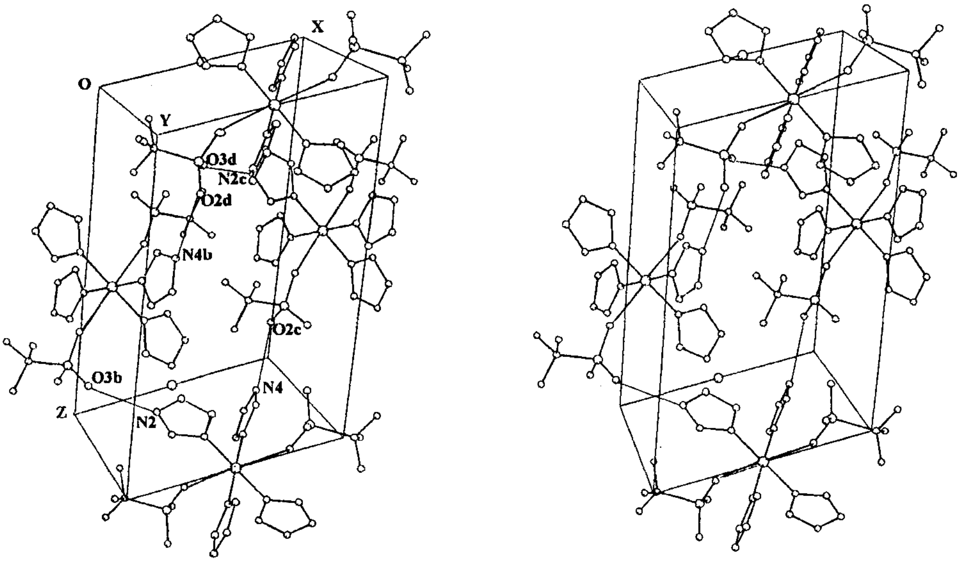

Figure 2 Stereoscopic drawing of the molecular packing of $[Cu(ImH)_4(CF_3SO_3)_2]$ in the unit cell; hydrogen bonds: N2... O3b, 2.855 Å and N4 ... O2c, 2.881 Å.

perchlorato complexes. This suggests that the four perpendicular imidazole ligands in the nitrato complex are equivalent, and the four imidazole ligands, two perpendicular and two canted by ~30°, in the triflato complex are also equivalent. In the latter two complexes, the two sets of imidazole ligands, perpendicular and nearly parallel, are non-equivalent. In other words, the former two complexes consist of a C_4 symmetry axis, but the latter complexes comprise a C_2 axis. The imidazole N-H stretches appear as broad bands in a wide range from ~3400 to ~3100 cm^{-1} indicating various degrees of hydrogen bonding in these complexes.

Visible spectra of these complexes show λ_{max} values in the region 528 to 590 nm. Absorption peak positions and the spectroscopic contours are very similar for the nitrato and the title complexes as one category (Fig. 3), strongly suggesting that both complexes are virtually equivalent in coordination bonding and in local symmetry as well. The spectra for the perchlorato and the sulfato complexes as another category are different from the previous two spectra. The sulfato complex exhibits a broad asymmetric absorption with tailing on the low energy side. The perchlorato complex also show a broad asymmetric peak with a barely discernible low energy shoulder. Apparently, bonding in the complexes of these two categories must be different. It is worth mentioning that the quality of the mull spectra in this study is greatly improved by using a double monochromator spectrophotometer. Particularly, the low absorptivity regions are well defined, thus affording more reliable Gaussian analysis (*vide infra*).

The visible spectra were deconvoluted into Gaussian component bands for detailed analysis of bonding. Computer iteration processes for curve-fitting resulted in three component peaks for the nitrato and the triflato complexes and four peaks for the sulfato and the perchlorato ones in agreement with their structures, namely, the former complexes possess a C_4 axis and the latter a C_2 axis. The results of curve fitting are improved with the reliability factor, R,[24] being less than 0.5% for each complex as shown in Figure 3. Peak positions are listed in Table 5 together with

Table 5 Gaussian component bands for the visible septra of *tetrakis*(imidazole)copper (II) complexes.

band	$\nu/10^3$ cm^{-1}	area[a]	$\delta_{1/2}$[b]	assignment
[Cu(ImH)$_4$(NO$_3$)$_2$] (R = 0.43%)[c]				
I	14.7	19.5	2.92	d_{z^2}
II	16.85	18.6	3.27	d_{xy}
III	19.4	61.9	4.41	d_{xz},d_{yz}
Cu(ImH)$_4$(CF$_3$SO$_3$)$_2$] (R = 0.38%)				
I	14.9	18.2	2.86	d_{z^2}
II	16.7	9.6	3.17	d_{xy}
III	18.7	72.2	4.16	d_{xz},d_{yz}
[Cu(ImH)$_4$(SO)$_4$)] (R = 0.41%)				
I	13.55	14.3	2.79	d_{z^2}
II	15.55	32.5	3.13	d_{xy}
III	17.4	26.9	3.07	d_{xz}
IV	19.0	26.3	3.47	d_{yz}
[Cu(ImH)$_4$(ClO$_4$)$_2$] (R = 0.47%)				
I	15.0	18.3	3.03	d_{z^2}
II	16.3	23.4	3.22	d_{xy}
III	18.2	32.9	3.17	d_{xz}
IV	20.1	25.4	3.32	d_{yz}

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

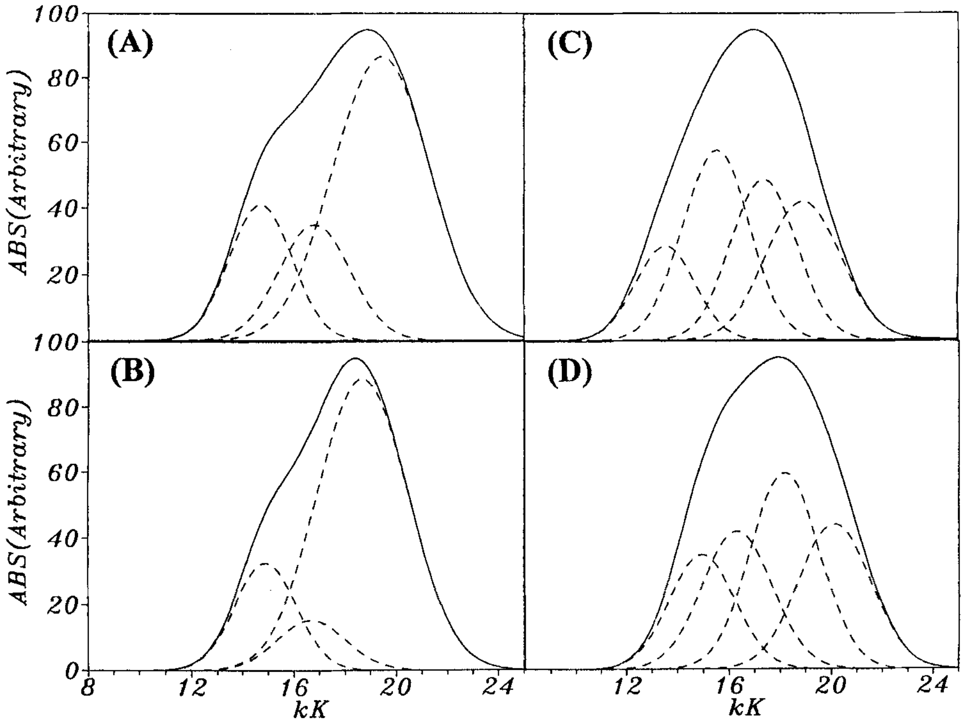

Figure 3 Visible spectra and Gaussian line-shape analysis of (A) [Cu(ImH)$_4$(NO$_3$)$_2$]; (B) [Cu(ImH)$_4$(CF$_3$SO$_3$)$_2$]; (C) [Cu(ImH)$_4$(SO$_4$)]; (D) [Cu(ImH)$_4$(ClO$_4$)$_2$]; (----) Gaussian components; (—) observed spectrum.

half-height widths and relative peak areas. The sequence of the d orbitals can be assigned as $d_{x^2-y^2} \gg d_{z^2} > d_{xy} > d_{xz} \geqq d_{yz}$, as in many tetragonal CuN$_4$X$_2$ complexes.[25] The puzzling small $d_{z^2} \rightarrow d_{x^2-y^2}$ transition peaks previously resolved for the nitrato and the perchlorato complexes[9] are artifacts due to poor data. Here, the improved resolution gave the d_{z^2} and d_{xy} Gaussian component bands of nearly equal intensities. This can be ascribed to low local symmetries for these complexes.

In view of the structural similarity of the four *tetrakis*-imidazole complexes listed in Table 6, the following effects on the energy levels are expected: (1) $d_{x^2-y^2}$ orbitals are sensitive to the Cu-N bond strengths, and all of the d-d transitions shift accordingly; (2) the non-bonding d_{xy} level is unchanged and the shift in the

Table 6 Bond distances and $\Delta(d_{xy}$-$d_{z^2})$ energy gap of *tetrakis*(imidazole)copper(II) complexes.

Compound	Cu-O, Å	Cu-N, [a]Å	$\Delta(d_{xy}$-$d_z{}^2)^b$
[Cu(ImH)$_4$(NO$_3$)$_2$]	2.566[a]	2.011[c]	2.15
[Cu(ImH)$_4$(CF$_3$SO$_3$)$_2$]	2.593	2.010	1.8
[Cu(ImH)$_4$(SO$_4$)]	2.574	2.011[d]	2.0
[Cu(ImH)$_4$(ClO$_4$)$_2$]	2.625	2.004[e]	1.3

[a] Mean bond distances. [b] In 10^3 cm^{-1}. [c] Ref. 13. [d] Ref. 15. [e] Ref. 12.

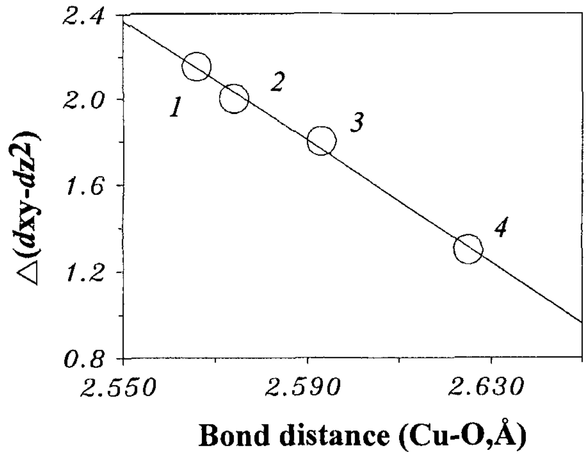

Figure 4 Plot of $\Delta(d_{xy}\text{-}d_{z^2})$ *vs.* Cu-O bond length of *tetrakis*(imidazole)copper(II) complexes: 1, $[Cu(ImH)_4(NO_3)_2]$; 2, $[Cu(ImH)_4(SO_4)]$;3, $[Cu(ImH)_4(CF_3SO_3)_2]$; 4, $[Cu(ImH)_4(ClO_4)_2]$.

$d_{xy} \rightarrow d_{x^2-y^2}$ transition reflects mainly the varying $d_{x^2-y^2}$ level; (*3*) the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition reflects both the Cu-O bond strengths and the $d_{x^2-y^2}$ levels. It is therefore anticipated that the energy difference between the d_{z^2} and d_{xy} levels should vary with the Cu-O bond strengths. This relationship is illustrated by the linear plot of the energy gaps, $\Delta(d_{xy} - d_{z^2})$, *versus* the Cu-O distances as shown in Figure 4. The linear plot indicates that the layouts of the *d* orbitals are mainly affected by the donor abilities of the anionic ligands, and may further imply that the assignment for the *d* orbitals is correct.

Since the Cu-O bond distance and the $\Delta(d_{xy} - d_{z^2})$ for the sulfato complex lie between those for the nitrato and the triflato complexes, bonding and therefore conformations of these three complexes are expected to be similar. The conformation of the sulfato complex, however, is different from that of the other two complexes. The inconsistency here seems to disagree with our previous conclusion[9-11] on the relationship between the orientations and the bondings of the imidazole ligands. Inspection of the low λ_{max} for the sulfato complex reveals that the imidazole ligands in this complex exert weak ligand field strength. Although the σ donor ability is somewhat stronger for the sulfates than for the triflate ligands, additional electron density is required by the central copper ion owing to the weakened σ donor ability of the imidazole ligands in the sulfato complex. The two approximately parallel imidazole ligands in the sulfato complex, bound as π donors with the d_{xz} orbital, can provide additional electron density to the copper ion. This is in agreement with the electroneutrality principle.

SUPPLEMENTARY MATERIAL

Additional material comprising structure factors, anisotropic thermal parameters, and full lists of bond lengths and angles are available from the authors on request.

Acknowledgements

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