

**BONDING PROPERTIES OF COPPER(II)-IMIDAZOLE
CHROMOPHORES: STRUCTURES AND ELECTRONIC
PROPERTIES OF TETRAKIS IMIDAZOLE COPPER(II)
COMPLEXES. MOLECULAR STRUCTURES OF
Cu(*N*-METHYLIMIDAZOLE)₄(ClO₄)₂ AND
[Cu(*N*-METHYLIMIDAZOLE)₄(H₂O)₂]Cl₂(H₂O)**

CHAN-CHENG SU,* KUO-YIH HWANG and JAN HUA CHEN

Department of Chemistry, National Taiwan Normal University, Taipei, Taiwan, R.O.C.

and

SUE-LEIN WANG, FEN-LING LIAO and JIA-CHERNG HORNG

Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan, R.O.C.

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Abstract—The crystal and molecular structures of [Cu(NMIm)₄(ClO₄)₂] (**1**) and [Cu(NMIm)₄(H₂O)₂]Cl₂·(H₂O) (**2**) (NMIm = *N*-methylimidazole) have been determined from three-dimensional X-ray diffraction data. The structure of **1** consists of discrete centrosymmetric [Cu(NMIm)₄(ClO₄)₂] units having a CuN₄ plane with a set of two *trans* *N*-methylimidazole ligands nearly perpendicular to the CuN₄ plane (dihedral angle 87.8°) and another set approximately parallel (dihedral angle 4.4°), and two perchlorates on the long *z*-axis with Cu—O length of 2.718(13) Å. The structure of **2** comprises two discrete structurally similar centrosymmetric [Cu(NMIm)₄(H₂O)₂] cations interconnected with Cl[−] ions and hydrate molecules by hydrogen bonds. The dihedral angles between the imidazole and the CuN₄ planes are 98.8° and 57.6° for one unit and 97.0° and 50.6° for another. Electronic and EPR spectra are reported for **1** and **2** and also for tetrakis complexes of imidazole, 4-methylimidazole, 4-phenylimidazole and benzimidazole. Analysis of the electronic spectra of **1** and **2** reveals that the former has *D*_{2h} symmetry with non-degenerate *d*_{xz} and *d*_{yz} orbitals, and the latter has *D*_{4h} symmetry with degenerate *d*_{xz} and *d*_{yz}. This is ascribed to the difference in donor abilities of the axial ClO₄[−] and H₂O ligands. In solution, all tetrakis species exhibit different structures depending on the donor abilities of the solvent molecules.

In our previous studies^{1,2} on the bonding properties of Cu^{II}-imidazole chromophores, we assigned the *d* orbitals of a number of tetrakis(imidazole)copper(II) and tetrakis(monosubstituted imidazole)copper(II) complexes by means of the Gaussian resolved solid-state *d*-*d* spectra. The layout

of the *d* orbitals exhibited noticeable differences depending on the orientations of the bonded imidazole ligands. The *d*_{xz} and *d*_{yz} orbitals are degenerate for complexes having *D*_{4h} local symmetry, namely, the four imidazole ligands are nearly perpendicular to or tilted ~45° towards the CuN₄ coordination plane, whilst the degeneracy of these two orbitals is lifted in complexes having *D*_{2h} local symmetry, namely, two *trans* imidazole ligands lie nearly parallel to the CuN₄ coordination plane and

* Author to whom correspondence should be addressed.

the other two remain approximately perpendicular. Based on the Gaussian resolved d - d spectrum, we have reported previously that the structure of $[\text{Cu}(\text{NMIm})_4(\text{ClO}_4)_2]$ (**1**) (NMIm = *N*-methylimidazole) belongs to the category of D_{2h} symmetry. Herein, we confirm the molecular structure of complex **1** by X-ray diffraction data. We also report the X-ray structure of a corresponding diaqua complex $[\text{Cu}(\text{NMIm})_4(\text{H}_2\text{O})_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (**2**) with two axial H_2O ligands, showing that the conformation of the complex is affected by the nature of the axial ligands. Studies are extended to elucidate the conformation and bonding of the tetrakis species in solutions.

EXPERIMENTAL

Materials and preparations

N-Methylimidazole (NMIm; Merck), benzimidazole (bzmH; Merck), imidazole (ImH; Merck), 4-phenylimidazole (4phImH; Aldrich), 4-methylimidazole (4MImH; Aldrich), $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Wako), NaClO_4 (Cica) and organic solvents were used as received. $[\text{Cu}(\text{NMIm})_4(\text{ClO}_4)_2]^2$ and $[\text{Cu}(\text{ImH})_4(\text{ClO}_4)_2]^3$ were prepared according to the cited literature. Anhydrous MeNO_2 for spectroscopic measurements was obtained by drying over MgSO_4 and then fractional distillation under reduced pressure ($55^\circ\text{C}/150$ Torr) and was stored over 4 \AA molecular sieves before use.

$[\text{Cu}(\text{NMIm})_4(\text{ClO}_4)_2]$ (**1**).² This complex was prepared according to the cited literature. Blue crystals suitable for X-ray structure determination were obtained by slow crystallization from an aqueous solution containing excess NaClO_4 .

$[\text{Cu}(\text{NMIm})_4(\text{H}_2\text{O})_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (**2**). This complex was prepared from an acetone solution containing stoichiometric amounts of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and *N*-methylimidazole. Yield 38%. M.p. 85°C . Found: C, 37.2; H, 5.7; N, 21.5. Calc. for $\text{C}_{16}\text{H}_{30}\text{N}_8\text{O}_3\text{Cl}_2\text{Cu}$: C, 37.1; H, 5.8; N, 21.7%. The violet crystals suitable for X-ray diffraction studies were obtained from a refrigerated MeCN and Me_2CO solution.

$\text{Cu}(4\text{phImH})_4(\text{ClO}_4)_2$. This violet complex was prepared from an MeOH solution containing stoichiometric amounts of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and 4-phenylimidazole. Yield, 81%. M.p. 208°C (dec). Found: C, 51.4; H, 3.6; N, 13.1. Calc. for $\text{C}_{36}\text{H}_{32}\text{N}_8\text{O}_8\text{Cl}_2\text{Cu}$: C, 51.5; H, 3.8; N, 13.3%.

$\text{Cu}(\text{bzmH})_4(\text{ClO}_4)_2$.⁴ A MeOH solution (3 cm^3) of benzimidazole (3 mmol) was added to an aqueous solution (3 cm^3) of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.5 mmol) with stirring, and then heated in a water

bath to 60°C for 30 min. Perchloric acid (1 M) was added dropwise to the reaction mixture until the brown precipitate disappeared. The resulting blue solution was treated with NaClO_4 (4 g) and then refrigerated, giving blue crystals. Yield 72%. M.p. 270°C (dec). Found: C, 45.6; H, 3.3; N, 15.1. Calc. for $\text{C}_{28}\text{H}_{24}\text{N}_8\text{O}_8\text{Cl}_2\text{Cu}$: C, 45.8; H, 3.3; N, 15.3%.

Physical measurements

Electronic spectra were recorded with Jasco model 7850 and Perkin-Elmer lambda 9 spectrophotometers. Solid samples were measured as Nujol mulls on Whatman No. 1 filter paper. The deconvolution of the visible spectra into Gaussian component bands was performed on a VAX 6510 computer using the profile-fitting program CUVFIT.⁵ EPR spectra were measured using a Bruker ER 200D model spectrometer and calibrated with DPPH ($g = 2.0037$). Elemental analyses were carried out by the Microanalysis Laboratories of Taiwan University, Taipei.

X-ray structure determination and refinement

A Micro Vax II computer-controlled Siemens R3m/V diffractometer was used for crystal and molecular structure determination. Details of crystal data and intensity collection are summarized in Table 1. Diffractometer examination of the reciprocal lattice showed the space group to be $P2_1/n$ for **1** from the following systematic absences: $0k0$, $k = 2n + 1$; $h0l$, $h + l = 2n + 1$; and $P\bar{1}$ for **2** with no systematic absences. Intensity data [θ - 2θ , scan $2.5 \leq 2\theta \leq 50^\circ$, $(\sin \theta/\lambda)_{\text{max}} \approx 0.6$] were collected at 296 K for two octants of the sphere (**1**, $-9 \leq h \leq 9$, $0 \leq k \leq 12$, $0 \leq l \leq 17$; **2**, $-10 \leq h \leq 10$, $-11 \leq k \leq 10$, $0 \leq l \leq 16$) 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 structure was solved by direct methods using the SHELXTL PLUS program⁶ 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*.⁷ The extinction correction was $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$ with $\chi = 0.0014(7)$ for **1** and $\chi = 0.0021(4)$ for **2**. The quantity minimized was $\sum w(KF_0 - F_c)^2$, with weights w equal to $[\sigma^2 F_0 + gF_0^2]^{-1}$, where $g = 0.0003$ for **1** and $g = 0.0013$ for **2**. All hydrogen atoms included in the refinement were placed in idealized positions (C—H = 0.96 \AA H—C—H = 109.4°) with fixed $U(0.08 \text{ \AA}^2)$ after the non-hydrogen atoms were refined anisotropically. All calculations were done

Table 1. Summary of crystal data and processing parameters for [Cu(NMIm)₄(ClO₄)₂] (**1**) and [Cu(NMIm)₄(H₂O)₂]Cl₂·H₂O (**2**)

	[Cu(NMIm) ₄ (ClO ₄) ₂] (1)	[Cu(NMIm) ₄ (H ₂ O) ₂]Cl ₂ ·H ₂ O (2)
Formula	C ₁₆ H ₂₄ N ₈ O ₈ Cl ₂ Cu	C ₁₆ H ₃₀ N ₈ O ₃ Cl ₂ Cu
Formula weight	590.9	516.9
Crystal size (mm)	0.32 × 0.28 × 0.22	0.64 × 0.50 × 0.78
Space group	<i>P</i> 2 ₁ / <i>n</i> , monoclinic	<i>P</i> $\bar{1}$, triclinic
<i>a</i> (Å); α (°)	8.137(2); 90.00	9.224(3); 99.44(3)
<i>b</i> (Å); β (°)	10.541(3); 93.57(2)	9.365(3); 105.65(3)
<i>c</i> (Å); γ (°)	14.469(4); 90.00	15.564(5); 103.38(3)
<i>V</i> (Å ³)	1238.6(6)	1222.1(7)
<i>Z</i>	2	2
<i>D</i> _{calc} (g cm ⁻³)	1.584	1.405
μ (mm ⁻¹)	1.155	1.144
Radiation λ (Å)	Mo- <i>K</i> ₂ (0.71073)	Mo- <i>K</i> ₂ (0.71073)
Temperature (K)	296	296
Independent refl.	2199 (1487 \geq 3.0 σ (<i>I</i>))	4312 (3681 \geq 3.0 σ (<i>I</i>))
Final <i>R</i> , <i>R</i> _w	0.0583, 0.0595	0.0338, 0.0420
Largest and mean Δ/σ	0.001, 0.000	0.003, 0.001
Largest diff. peak (e Å ⁻³)	0.79	0.49
Largest diff. hole (e Å ⁻³)	-0.49	-0.36

on a Micro Vax II-based Nicolet SHELXTL PLUS system. Additional material deposited comprises atomic coordinates, structure factors, anisotropic thermal parameters and full lists of bond lengths and bond angles for complexes **1** and **2**.

RESULTS AND DISCUSSION

Description of structures

The crystal and molecular structures of [Cu(NMIm)₄(ClO₄)₂] (**1**) and [Cu(NMIm)₄(H₂O)₂]Cl₂(H₂O) (**2**) are shown in Figs 1 and 2. Important bond lengths and bond angles are listed in Table 2. The copper ion of **1** is bound centrosymmetrically by six ligands forming an elongated octahedron with four NMIm ligands in the *xy* plane, Cu—N(1) 1.990(5) and Cu—N(3) 2.031(5) Å, and the perchlorate ions on the long *z*-axis, Cu—O 2.718(13) Å. The central copper ion lies on the inversion centre and the asymmetric unit consists of only half of the molecules. The CuN₄ is co-planar, but the imidazole ligands are oriented in two sets, perpendicular and parallel; the dihedral angles between the best planes of the imidazole ring and CuN₄ are 87.8° for the N(1) set and 4.4° for the N(3) set. The bond distances and angles of the NMIm ligands and the loosely bound ClO₄⁻ are in the normal ranges.

Complex **2** consists of two distinct centrosymmetric [Cu(NMIm)₄(H₂O)₂] cations and discrete

chlorides and water molecules interconnected by hydrogen bonds [Cl(1)···O(1), 3.133; Cl(1)···O(3), 3.149; Cl(2)···O(2), 3.153; Cl(2)···O(2a), 3.175 Å]. The Cu(1) ion at [0, 1/2, 1/2] is bound by two sets of *trans* NMIm ligands forming the equatorial plane, Cu(1)—N(1) 2.014(2) and Cu(1)—N(3) 2.035(2) Å, and by two water molecules on the axial sites, Cu—O 2.536(2) Å. The dihedral angles between the imidazole rings and the CuN₄ plane are 57.6° for the N(1) set and 98.8° for the N(3) set. The Cu(2) ion at [0,0,0] is structurally similar to the Cu(1) complex, Cu(2)—N(5) 2.030(2), Cu(2)—N(7) 2.013(3) and Cu—O 2.517(2) Å. The dihedral angles are slightly different from those of the Cu(1) unit, 97.0° for the N(5) set and 50.6° for the N(7) set. The dimensions of the NMIm ligands are in the normal ranges.

Spectroscopic studies

The EPR and electronic spectral data of **1** and **2**, along with some tetrakis complexes, are listed in Table 3. The powder EPR spectra of these complexes exhibit typical axial features of $g_{\parallel} > g_{\perp} > 2$, consistent with elongated tetragonal or square planar structures and indicative of the $d_{x^2-y^2}$ ground state.¹⁰ The mull LF spectra in the range of 510–563 nm also agree with the structures.¹¹ However, the spectral contours are similar for NMIm and ImH complexes as one category, and the other complexes as a second category. The former is a broad

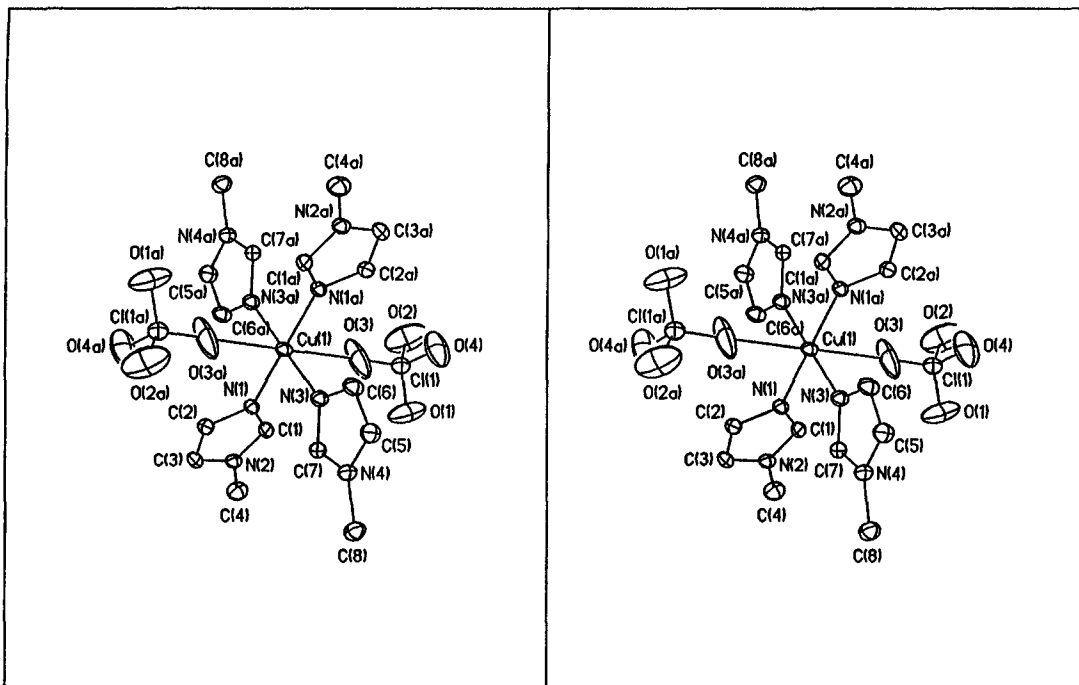


Fig. 1. Stereoscopic drawing of the molecular structure of $[\text{Cu}(\text{NMIm})_4(\text{ClO}_4)_2]$ with numbering scheme.

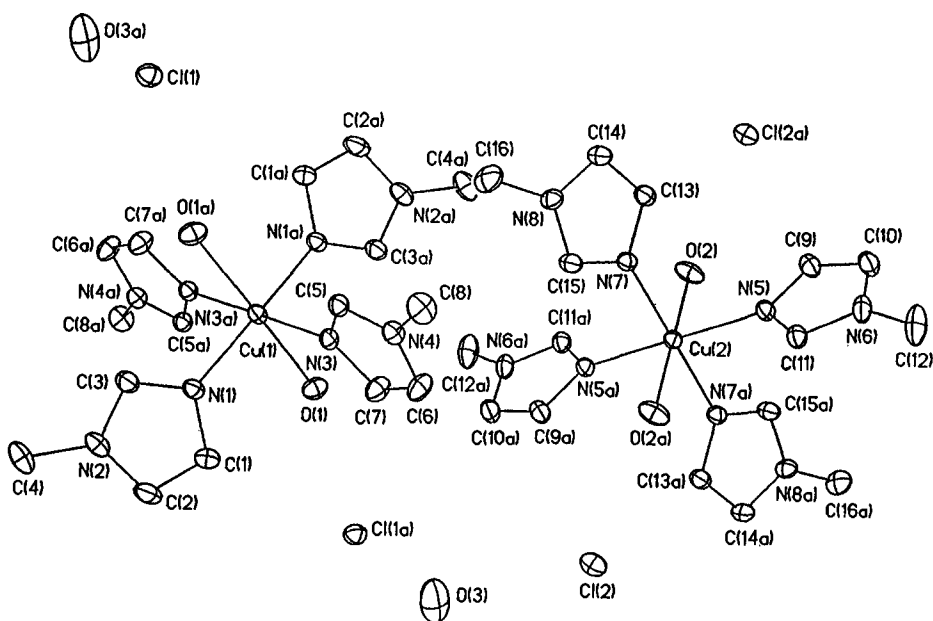


Fig. 2. The molecular structure of $[\text{Cu}(\text{NMIm})_4(\text{H}_2\text{O})_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$ with numbering scheme.

Table 2. Important bond lengths (Å) and angles (°) for [Cu(NMIm)₄(ClO₄)₂] (1) and [Cu(NMIm)₄(H₂O)₂]Cl₂·H₂O (2)

[Cu(NMIm) ₄ (ClO ₄) ₂] (1)			
Cu—N(1)	1.990(5)	Cu—N(3)	2.031(5)
Cu—O(3)	2.718(13)		
N(1)—Cu(1)—N(3)	89.9(2)	N(1)—Cu(1)—N(3a)	90.1(2)
N(1)—Cu(1)—O(3)	92.4(4)	N(3)—Cu(1)—O(3)	88.9(4)
[Cu(NMIm) ₄](H ₂ O) ₂]Cl ₂ ·H ₂ O (2)			
Cu(1)—N(1)	2.014(2)	Cu(1)—N(3)	2.035(2)
Cu(2)—N(5)	2.030(2)	Cu(2)—N(7)	2.013(3)
Cu(1)—O(1a)	2.536(2)	Cu(2)—O(2a)	2.517(2)
N(1)—Cu(1)—N(3)	90.4(1)	N(1)—Cu(1)—N(3a)	89.6(1)
N(1)—Cu(1)—O(1a)	92.9(1)	N(3)—Cu(1)—O(1a)	88.5(1)
N(5)—Cu(2)—N(7)	90.9(1)	N(5)—Cu(2)—N(7a)	89.1(1)
N(5)—Cu(2)—O(2a)	90.4(1)	N(7)—Cu(2)—O(2a)	89.2(1)

asymmetric peak, whereas the latter has an apparent flanking shoulder at the lower energy side of the main peak.

The complexes show different LF spectral behaviour in solution, as illustrated in Fig. 3. In nitromethane, red shifts of the LF bands were observed when excess free imidazole ligands were added to the solution, suggesting no dissociation of the tetrakis complexes in nitromethane. In acetonitrile and in methanol or aqueous methanol, however, addition of excess ligand causes the LF peaks to be blue-shifted to the highest frequency limit as indicated in Table 3, along with the ligand to Cu²⁺ ratio, and then red-shifted if ligands are further added. Apparently, the complexes dissociate in these solutions. Addition of proper amounts of free ligands is necessary to ensure the existence of tetrakis species in these solutions. It is remarkable that the LF spectra of the tetrakis species in nitromethane are somewhat broader than those of the corresponding tetrakis species in acetonitrile and in methanol or aqueous methanol.

The presence of tetrakis species in solution is further supported by their axial glass EPR spectra. No superhyperfine coupling was observed for the species in acetonitrile. In some cases, as illustrated in Fig. 4, there are nine weak lines for the species in frozen aqueous methanol and methanol, and five particularly intense lines together with some weak

lines for the species in frozen nitromethane. This fact may suggest that the species in methanol contain four electronically equivalent imidazoles, but the species in nitromethane consist of two sets of electronically non-equivalent imidazole ligands.

The solid state electronic spectra for [Cu(NMIm)₄(ClO₄)₂] (1) and [Cu(NMIm)₄(H₂O)₂]Cl₂·H₂O (2) are very similar to those for [Cu(ImH)₄(ClO₄)₂]^{1,12} and [Cu(ImH)₄(NO₃)₂]^{1,13} respectively. First, the energy separation of the two LMCT bands, assigned as $\pi_2 \rightarrow \text{Cu}^{\text{II}}$ and $\pi_1 \rightarrow \text{Cu}^{\text{II}}$,¹⁴⁻¹⁶ is larger for complex 1 than for complex 2. This is attributable to the π -donation of the π_1 orbitals¹⁷ of the parallel imidazole ligands of complex 1 to the copper d_{xz} orbital.^{1,2} Secondly, complex 1 exhibits a broad LF band with λ_{max} at 563 nm, whereas complex 2 has an LF band with λ_{max} at 585 nm and a low energy shoulder at ~ 700 nm. The 563 nm band was resolved previously² into four Gaussian component bands, suggesting the sequence of the d orbitals as $d_{x^2-y^2} \gg d_{z^2} > d_{xy} > d_{xz} > d_{yz}$, where Cu—N(3) was defined as the x -axis. The non-degeneracy of d_{xz} and d_{yz} orbitals is consistent with the molecular structure of 1 having D_{2h} local symmetry. Deconvolution of the LF bands of complex 2 is less satisfactory, because the complex comprises two distinct molecular structures in crystals. Since the LF band envelope of complex 2 is similar to that of [Cu(ImH)₄(NO₃)₂],¹ an analogous d orbital sequence with degenerate d_{xz} and d_{yz} is expected.

The solid state LF spectra of Cu(4phImH)₄

* See footnote *c* of Table 4.

Table 3. EPR and visible spectral data for tetrakis(imidazole)copper(II) complexes

Compound ^a /state (ligand :Cu ²⁺)	EPR ^b				LF band ^c λ_{\max} (ϵ), nm
	g	g_{\perp}	A_{\parallel}	A_{\perp}^N	
[Cu(NMIm) ₄ (ClO ₄) ₂] /powder ^d	2.244	2.053	189		563 ^e
/MeNO ₂ (4:1)	2.251	2.047	189		576(70)
	(2.256	2.055	192) ^f		
/MeCN ^g (5:1)	2.260	2.057	185		578(52)
/aq. MeOH (30:1)	2.256	2.056	187	14	604(60)
[Cu(ImH) ₄ (ClO ₄) ₂] /powder ^d					560
/MeNO ₂ (4:1)	2.252	2.065	191		564(67)
/MeCN ^g (5:1)	2.250	2.058	189		576(50)
/aq. MeOH (17:1)	2.256	2.053	190	14	599(59)
	(2.255	~ 2	206	14) ^h	
[Cu(NMIm) ₄ (H ₂ O) ₂]Cl ₂ · H ₂ O /powder	2.262	2.065	188		585 700sh ⁱ
[Cu(4phImH) ₄ (ClO ₄) ₂] /powder	2.242	2.043	195		529 640sh
/MeNO ₂ (4:1)	2.254	2.047	189		564(128)
/MeCN (5:1)	2.255	2.051	185		578(92)
/MeOH (60:1)	2.256	2.049	183		593(69)
[Cu(bzmH) ₄](ClO ₄) ₂ /powder	2.235	2.041	198		516 640sh (526 641sh) ^j
MeNO ₂ (4:1)	2.253	2.049	189	14	564(71)
/MeCN (5:1)	2.247	2.067	188		584(82)
/MeOH (60:1)	2.250	2.054	183	15	604(85)
[Cu(4MImH) ₄ (ClO ₄) ₂] /powder ^a	2.233	2.053	203		510 637sh
/MeNO ₂ (4:1)	2.251	2.047	191		575(82)
/MeCN ^g (5:1)	2.248	2.049	194		573(65)
/aq. MeOH (15:1)	2.258	2.052	183	14	598(80)

^a For abbreviations, see Experimental section.

^b X-band EPR spectra measured at 77 K with hyperfine coupling constants in 10⁻⁴ cm⁻¹.

^c Solid state visible spectra were recorded as Nujol mulls on Whatman No. 1 filter paper. Both solid and solution spectra were taken at room temperature.

^d Ref. 1.

^e LMCT ~ 250–~ 310 nm.

^f Ref. 8.

^g Ref. 2.

^h Ref. 9.

ⁱ LMCT ~ 250–~ 290 nm.

^j Ref. 4.

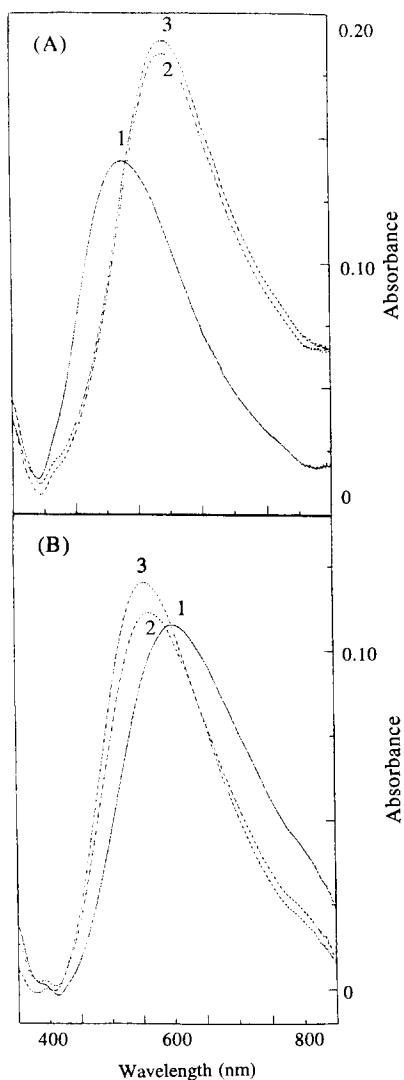


Fig. 3. The LF spectra of *N*-methylimidazole-Cu^{II} complex in: (A) MeNO₂ with [Cu²⁺] = 2.00 mM and [NMIm]/[Cu²⁺] at 4 (1), 6 (2) and 8 (3); (B) aq MeOH with [Cu²⁺] = 2.00 mM and [NMIm]/[Cu²⁺] at 4 (1), 15 (2) and 30 (3).

(ClO)₂ and Cu(bzmH)₄(ClO₄)₂ complexes were deconvoluted into Gaussian component bands. Starting from a set of two trial peaks, computer iteration processes for curve fitting were carried out until a minimum value of the reliability factor, *R*,* was reached. Each of the complexes had an excellent fit, with *R* ~ 0.7%, and exhibited a resulting set comprising two Gaussian peaks, as shown in Fig. 5. The peak positions are presented in Table 4, along with their half-height widths and relative peak areas. The very intense high energy component peak can be assigned as a

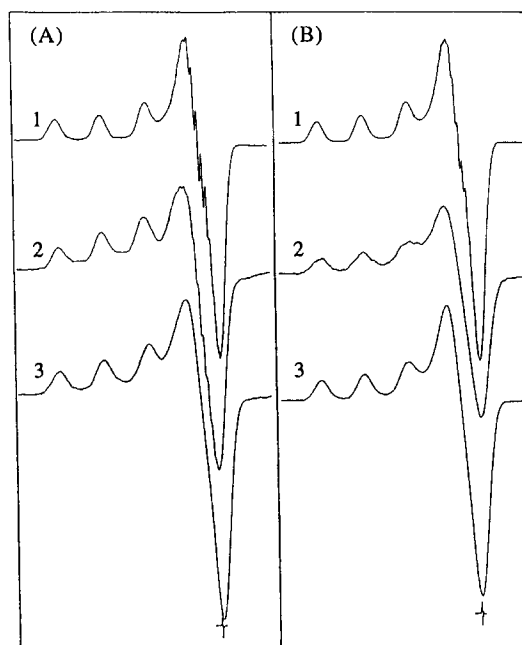


Fig. 4. The X-band EPR spectra measured at 77 K for: (A) [Cu(bzmH)₄(ClO₄)₂] and (B) [Cu(4phImH)₄(ClO₄)₂] in MeNO₂ (1), MeOH (2) and MeCN (3).

$d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ transition and the weak low energy peak as a $d_{xy} \rightarrow d_{x^2-y^2}$ transition. Here, the weak $d_{z^2} \rightarrow d_{x^2-y^2}$ transition peak could not be resolved. Attempts to resolve into three or four peaks resulted in larger *R* values. Since these two complexes exhibit the λ_{\max} at higher energy regions (bzmH, 516 nm; 4phImH, 529 nm) than expected from their *pK_a* values (bzmH, 5.53; 4phImH, 5.70),^{18, 20} it is likely that the perchlorate ions may bind loosely or not bind to the axial positions. Presumably the small $d_{z^2} \rightarrow d_{x^2-y^2}$ transition peak is buried in the large $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ transition band. The sequence of *d* orbitals is assigned as $d_{x^2-y^2} \gg d_{xy} > d_{xz} \sim d_{yz}$ for these complexes, consistent with the structure having effective *D*_{4h} symmetry.

The orientations of the imidazole ligands in tetrakis complexes can be ascribed to two major governing factors: (1) the donor ability of the equatorial imidazole ligands; and (2) the donor ability of the axial ligands. Since the σ -donor abilities of NMIm and ImH are similar, justified from their *pK_a* values (NMIm, 6.98; ImH, 6.90),²¹ it is expected that the bondings in the structurally similar [Cu(NMIm)₄(ClO₄)₂] and [Cu(ImH)₄(ClO₄)₂] are alike. Indeed, these two complexes have a set of

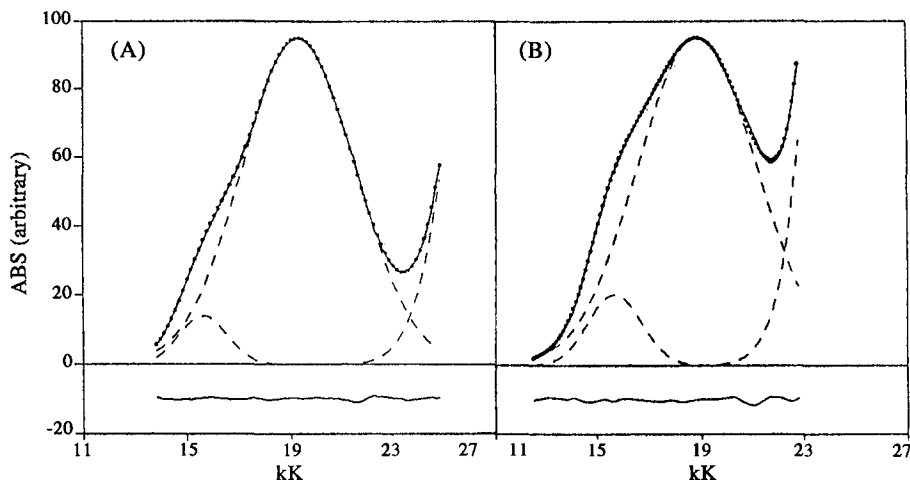


Fig. 5. The solid state visible spectra and Gaussian line-shape analysis with difference plots of: (A) $[\text{Cu}(\text{bzmH})_4(\text{ClO}_4)_2]$, $R = 0.48\%$ and (B) $[\text{Cu}(4\text{phImH})_4(\text{ClO}_4)_2]$, $R = 0.70\%$. (—) Observed spectrum; (---) Gaussian components; (*) profile-fitting points.

two *trans* imidazole nuclei oriented nearly parallel to the CuN_4 coordination plane, facilitating π -donation from ligand π orbitals to the low lying copper d_{xz} orbital. When the extremely weak σ -donor, ClO_4^- , is replaced by H_2O , the π -donation from the equatorial NMIm is no longer demanded by the central copper ion, in accord with the electroneutrality principle. The complex then adopts a less crowded conformation, with the four NMIm ligands nearly perpendicular to the CuN_4 plane, and is electronically of D_{4h} symmetry.

In this context, one would expect that the perchlorate complexes of 4phImH and bzmH, which are weaker σ -donors than ImH and NMIm, would have structures with D_{2h} symmetry. However, these complexes are likely to have D_{4h} symmetry. Presumably, steric congestion is serious in crystals for these bulky ligands. It is therefore intriguing to investigate the tetrakis species in solutions. Again, the LF spectra were deconvoluted into Gaussian component peaks for detailed analysis. The results are presented in Table 4. Each spectrum of the tetrakis species had an excellent fit, as shown in Fig. 6. The resulting sets for the species of all of the imidazole complexes in CH_3CN and CH_3OH or aqueous CH_3OH consist of three Gaussian peaks, suggesting that the sequence of the d orbitals is $d_{x^2-y^2} \gg d_{z^2} > d_{xy} > d_{xz} \sim d_{yz}$ and the species have D_{4h} symmetry. On the other hand, there are four

peaks for the species in CH_3NO_2 , indicating that the d -orbital sequence is $d_{x^2-y^2} \gg d_{z^2} > d_{xy} > d_{xz} > d_{yz}$ and the species have D_{2h} symmetry. This is in agreement with the results of EPR spectral data. Obviously, the orientations of the imidazole ligands in tetrakis complexes depend on the donor abilities of the solvents. The donor number²² of nitromethane is much lower than those of acetonitrile, methanol and water.

CONCLUSIONS

We have demonstrated that the orientations of the *N*-methylimidazole ligands in tetrakis copper(II) complexes are controlled by the axial ligands. This stems mainly from the σ -donor capabilities of the axial ligands, and therefore the bonding abilities of the equatorial *N*-methylimidazole ligands are affected. Accordingly, the Cu^{II} -imidazole bonding properties are greatly dependent on the solvent molecules. The imidazole ligands are dissociated in donating solutions, such as acetonitrile, methanol and H_2O . However, in the very weak donating nitromethane solution, the four imidazole ligands, and other substituted imidazoles as well, do not dissociate, and coordinate firmly in a particular conformation. This may imply that the

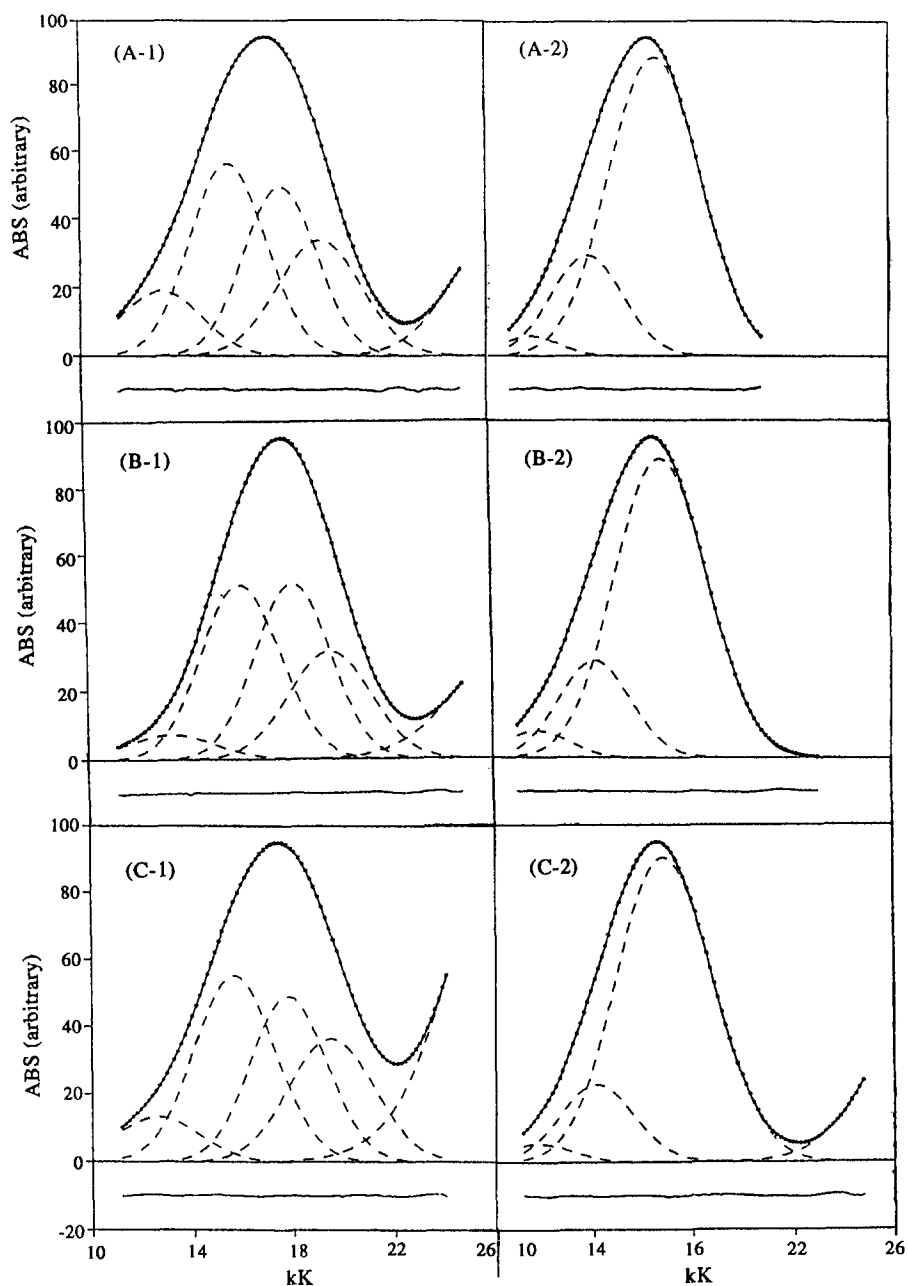


Fig. 6. The solution visible spectra and Gaussian line-shape analysis with difference plots of: (A-1) $[\text{Cu}(\text{NMIIm})_4(\text{ClO}_4)_2]$ in MeNO_2 , $R = 0.39\%$; (A-2) $[\text{Cu}(\text{NMIIm})_4(\text{ClO}_4)_2]$ in aq. MeOH , $R = 0.35\%$; (B-1) $[\text{Cu}(\text{ImH})_4(\text{ClO}_4)_2]$ in MeNO_2 , $R = 0.28\%$; (B-2) $[\text{Cu}(\text{ImH})_4(\text{ClO}_4)_2]$ in aq. MeOH , $R = 0.32\%$; (C-1) $[\text{Cu}(4\text{MIImH})_4(\text{ClO}_4)_2]$ in MeNO_2 , $R = 0.30\%$; (C-2) $[\text{Cu}(4\text{MIImH})_4(\text{ClO}_4)_2]$ in aq. MeOH , $R = 0.39\%$. (—) Observed spectrum; (---) Gaussian components; (*) profile-fitting points.

Table 4. Gaussian component bands for the visible spectra of tetrakis(imidazole)copper(II) complexes

Band	$\nu(10^3 \text{ cm}^{-1})$	Area ^a	$\delta_{1,2}$ ^b	Assignment
Cu(NMIm)₄(ClO₄)₂				
/MeNO ₂ (<i>R</i> = 0.39%) ^c				
I	13.1	12.8	3.80	<i>d</i> _{z²}
II	15.8	35.0	3.53	<i>d</i> _{xy}
III	17.9	29.2	3.37	<i>d</i> _{xz}
IV	19.4	23.0	3.89	<i>d</i> _{yz}
/aqueous MeOH (<i>R</i> = 0.35%) ^c				
I	11.8	3.2	2.66	<i>d</i> _{z²}
II	14.1	20.3	3.40	<i>d</i> _{xy}
III	16.8	76.5	4.25	<i>d</i> _{xz} ; <i>d</i> _{yz}
/MeCN (<i>R</i> = 0.44%) ^c				
I	14.6	9.3	4.0	<i>d</i> _{z²}
II	15.1	18.5	3.6	<i>d</i> _{xy}
III	17.7	72.2	3.9	<i>d</i> _{xz} ; <i>d</i> _{yz}
Cu(ImH)₄(ClO₄)₂				
/MeNO ₂ (<i>R</i> = 0.28%) ^c				
I	13.25	5.9	4.09	<i>d</i> _{z²}
II	16.1	36.1	3.64	<i>d</i> _{xy}
III	18.1	34.5	3.44	<i>d</i> _{xz}
IV	19.55	23.5	3.83	<i>d</i> _{yz}
/aqueous MeOH (<i>R</i> = 0.32%) ^c				
I	11.95	4.7	3.02	<i>d</i> _{z²}
II	14.3	19.6	3.41	<i>d</i> _{xy}
III	16.95	75.7	4.23	<i>d</i> _{xz} ; <i>d</i> _{yz}
/MeCN (<i>R</i> = 0.28%) ^c				
I	12.7	4.8	2.99	<i>d</i> _{z²}
II	14.7	10.4	2.64	<i>d</i> _{xy}
III	17.5	84.8	4.25	<i>d</i> _{xz} ; <i>d</i> _{yz}
Cu(4phImH)₄(ClO₄)₂				
/Mull (<i>R</i> = 0.70%) ^c				
I	15.7	8.7	2.41	<i>d</i> _{xy}
II	18.9	91.3	5.39	<i>d</i> _{xz} ; <i>d</i> _{yz}
/MeNO ₂ (<i>R</i> = 0.14%) ^c				
I	13.15	4.6	3.60	<i>d</i> _{z²}
II	16.0	39.1	3.70	<i>d</i> _{xy}
III	17.9	32.8	3.34	<i>d</i> _{xz}
IV	19.5	23.5	3.45	<i>d</i> _{yz}
/MeCN (<i>R</i> = 0.41%) ^c				
I	12.7	3.8	2.46	<i>d</i> _{z²}
II	14.6	11.1	2.62	<i>d</i> _{xy}
III	17.4	85.1	4.20	<i>d</i> _{xz} ; <i>d</i> _{yz}
Cu(bzmH)₄(ClO₄)₂				
/Mull (<i>R</i> = 0.48%) ^c				
I	15.65	5.8	2.14	<i>d</i> _{xy}
II	19.4	94.2	5.10	<i>d</i> _{xz} ; <i>d</i> _{yz}
/MeNO ₂ (<i>R</i> = 0.31%) ^c				
I	13.6	6.7	3.60	<i>d</i> _{z²}
II	16.1	38.0	3.65	<i>d</i> _{xy}
III	18.1	29.7	3.25	<i>d</i> _{xz}
IV	19.7	25.6	3.75	<i>d</i> _{yz}
/MeOH (<i>R</i> = 0.33%) ^c				
I	11.2	7.9	4.22	<i>d</i> _{z²}
II	14.1	14.3	3.70	<i>d</i> _{xy}
III	16.9	77.8	4.88	<i>d</i> _{xz} ; <i>d</i> _{yz}

Table 4. (Continued)

Band	$\nu(10^3 \text{ cm}^{-1})$	Area ^a	$\delta_{1,2}$ ^b	Assignment
/MeCN (<i>R</i> = 0.41%) ^c				
I	11.7	1.9	2.76	<i>d</i> _{z²}
II	14.05	10.4	2.84	<i>d</i> _{xy}
III	17.15	87.7	4.16	<i>d</i> _{xz} ; <i>d</i> _{yz}
Cu(4MImH)₄(ClO₄)₂				
/MeNO ₂ (<i>R</i> = 0.30%) ^c				
I	12.6	9.0	3.89	<i>d</i> _{z²}
II	15.7	36.2	3.76	<i>d</i> _{xy}
III	17.8	29.9	3.50	<i>d</i> _{xz}
IV	19.5	24.9	3.92	<i>d</i> _{yz}
/aq. MeOH (<i>R</i> = 0.39%) ^c				
I	11.75	3.5	3.26	<i>d</i> _{z²}
II	14.2	16.1	3.55	<i>d</i> _{xy}
III	17.0	80.4	4.46	<i>d</i> _{xz} ; <i>d</i> _{yz}

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

^b Half-width at $\epsilon_{\text{max}}/2$.

^c Reliability factor defined as $R = \sum |y_{\text{obs},i} - y_{\text{calc},i}| / \sum y_{\text{obs},i}$.

imidazole moiety of the histidyl residue in copper proteins may bind firmly to the copper(II) ions.

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REFERENCES

- C.-C. Su, T.-T. Hwang, O. Y.-P. Wang, S.-L. Wang and F.-L. Liao, *Transition Met. Chem.* 1992, **17**, 91.
- 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* 1992, **196**, 231.
- J. B. Hodgson, G. C. Percy and D. A. Thornton, *J. Molec. Struct.* 1980, **66**, 81.
- M. Goodgame and L. I. B. Haines, *J. Chem. Soc. (A)* 1966, 174.
- S.-L. Wang, P. C. Wang and Y. P. Nieh, *J. Appl. Cryst.* 1990, **23**, 520.
- G. M. Sheldrick, *SHELXTL PLUS User Manual*. Nicolet XRD Corporation, Madison, WI (1986).
- International Tables for X-ray Crystallography*, Vol. 4. Kynoch Press, Birmingham (1974).
- U. Sagaguchi and A. W. Addison, *J. Chem. Soc., Dalton Trans.* 1979, 600.
- H. L. Van Camp, R. H. Sands and J. A. Fee, *J. Chem. Phys.* 1981, **75**, 2098.
- B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.* 1970, **5**, 143.

11. B. J. Hathaway, *J. Chem. Soc., Dalton Trans.* 1972, 1196.
12. M. E. Bridson and W. R. Walker, *Aust. J. Chem.* 1970, **23**, 1973.
13. D. L. McFadden, A. T. McPhail, C. D. Garner and F. E. Mabbs, *J. Chem. Soc., Dalton Trans.* 1976, 47.
14. E. Bernarducci, P. K. Bharadwaj, K. Krogh-Jespersen, J. A. Potenza and H. J. Schugar, *J. Am. Chem. Soc.* 1983, **105**, 3860.
15. E. Bernarducci, W. F. Schwindinger, J. L. Hughey IV, K. Krogh-Jespersen and H. J. Schugar, *J. Am. Chem. Soc.* 1981, **103**, 1686.
16. T. G. Fawcett, E. E. Bernarducci, K. Krogh-Jespersen and H. J. Schugar, *J. Am. Chem. Soc.* 1980, **102**, 2598.
17. J. Del Bene and H. H. Jaffe, *J. Chem. Phys.* 1968, **48**, 4050.
18. G. Schwarzenbach and K. Lutz, *Helv. Chim. Acta* 1940, **23**, 1162.
19. F. A. Walker, M.-W. Lo and M. T. Ree, *J. Am. Chem. Soc.* 1976, **98**, 5552.
20. A. Albert, *Meth. Heterocycl. Chem.* 1963, **1**.
21. F. Jiang, F. McCracken and J. Peisach, *J. Am. Chem. Soc.* 1990, **112**, 9035.
22. V. Gutmann, *The Donor-Acceptor Approach to Molecular Interactions*. Plenum, New York (1978).