

Copper(II) and Zinc(II) Co-ordination Compounds of Tridentate Bis(benzimidazole)pyridine ligands. Crystal and Molecular Structures of Bis[2,6-bis(1'-methylbenzimidazol-2'-yl)pyridine]copper(II) Diperchlorate Monohydrate and (Acetonitrile)[2,6-bis(benzimidazol-2'-yl)pyridine](perchlorato)copper(II) Perchlorate†

S. Bamidele Sanni, Helmut J. Behm, and Paul T. Beurskens

Crystallography Laboratory, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

Gerard A. van Albada and Jan Reedijk*

Department of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

Albert T. H. Lenstra

University of Antwerp (UIA), Department of Chemistry, Universiteitsplein 1, B2610, Wilrijk, Belgium

Anthony W. Addison and Mallayan Palaniandavar

Department of Chemistry, Drexel University, Philadelphia, Pa 19104, U.S.A.

Compounds are described of general formulae $\text{Cu}(\text{L}^1)\text{X}_2$, $\text{Cu}(\text{L}^1)_2\text{X}_2$, $\text{Cu}(\text{L}^2)\text{X}_2$, and $\text{Cu}(\text{L}^2)_2\text{X}_2$ with $\text{L}^1 = 2,6\text{-bis}(\text{benzimidazol-2'-yl})\text{pyridine}$, $\text{L}^2 = 2,6\text{-bis}(1'\text{-methylbenzimidazol-2'-yl})\text{pyridine}$, and $\text{X} = \text{Cl}$, Br , or ClO_4 . For comparison also a few zinc(II) halides were prepared and characterized. The compounds were structurally characterized by i.r., ligand-field, and e.s.r. spectra and for two representative cases $[\text{Cu}(\text{L}^1)(\text{CH}_3\text{CN})(\text{ClO}_4)](\text{ClO}_4)$ (1) and $[\text{Cu}(\text{L}^2)_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (2) also by X-ray diffraction techniques. Compound (1) crystallizes in space group $P2_1/c$ with $a = 14.061(1)$, $b = 20.638(1)$, $c = 8.273(1)$ Å, $\beta = 101.119(8)$, and $Z = 4$; $R = 0.0366$ for 4 265 observed reflections with $I > 2\sigma(I)$. Compound (2) crystallizes in space group $P2_1/c$ with $a = 8.4824(22)$, $b = 29.1965(29)$, $c = 16.7393(24)$ Å, $\beta = 95.836(17)^\circ$, and $Z = 4$; $R = 0.062$ for 3 165 observed reflections with $I > 3\sigma(I)$. The structure of (1) consists of one tridentate chelating L^1 ligand and CH_3CN , co-ordinated in a square-planar geometry ($\text{Cu-N } 1.96\text{--}2.03$ Å) with a perchlorato oxygen at 2.40 Å, thereby completing a five-co-ordinate geometry. A sixth ligand at 2.8 Å (from another perchlorate oxygen) is considered to be semico-ordinating. The structure of (2) consists of one tridentate and one bidentate L^2 , chelating in a five-co-ordinate geometry, again tetragonal pyramidal, with the apical ligand ($\text{Cu-N } 2.51$ Å) coming from the bidentate chelating L^2 . The sixth donor atom, again from a perchlorate oxygen, at 2.70 Å is considered to be semi-co-ordinating. Spectroscopic and magnetic data have been used to deduce structures for the other copper(II) compounds based on these two X-ray structures.

Co-ordination of copper(I) and copper(II) by benzimidazole-type ligands has been the subject of extensive investigation during the last decade.¹⁻⁴ General formulae of such chelating ligand types are $(\text{bzim-CH}_2)_n\text{X}(\text{CH}_2)_m\text{X}(\text{CH}_2\text{-bzim})_n$ where $\text{bzim} = \text{benzimidazolyl}$, $\text{X} = \text{N}$ ($n = 2$), S ($n = 1$), or O ($n = 1$), and $m = 2\text{--}5$. More advanced systems^{5,6} have the $(\text{CH}_2)_m$ part changed by co-ordinating units such as $\text{CH}_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_2$ or $(\text{CH}_2\text{CH}_2\text{OCH}_2)_2$. In all cases the donor atoms between the benzimidazole groups are forced to chelate to the metal, even in the cases⁴ of weakly binding ether and thioether groups. The benzimidazole groups are always co-ordinated to the metal ions.

In biological systems, co-ordinate bonds between copper and histidine imidazole ligands may be broken under certain conditions. Fairly good evidence for this is present for copper(I) plastocyanin,⁷ where at low pH one of the imidazoles is well separated from copper (and probably hydronated). A further example is the copper(I) state of the copper-zinc bovine superoxide dismutase.⁸

To create systems that contain a non-co-ordinating (benz)imidazole group in a synthetic analogue, we felt that another ligand group should be present, co-ordinating more

strongly than the thioether, ether, or tertiary amine groups. Therefore, we have developed a ligand system consisting of the general structure bzim-L-bzim , with L as a 2,6-disubstituted pyridine group.⁹ The two most simple ligands in this system have been synthesized, i.e. 2,6-bis(benzimidazol-2'-yl)pyridine and its *N*-methylated analogue. The present paper describes the co-ordination chemistry of these ligands with respect to Cu^{II} and, for comparison, Zn^{II} . Crystal structures for each ligand and for the ratio $\text{Cu:L} = 1:1$ and $1:2$ are reported. For the $1:2$ ratio, non-co-ordinated benzimidazole indeed occurs.

Experimental

Starting Materials.—Metal(II) salts were used as commercially available, without further purification. The ligand 2,6-bis(benzimidazol-2'-yl)pyridine (L^1) was synthesized according to the literature.⁹ The ligand 2,6-bis(1'-methylbenzimidazol-2'-yl)pyridine (L^2) was synthesized by methylation of the former compound by means of iodomethane and potassium hydroxide in acetone.¹⁰

Synthesis of the Co-ordination Compounds.—The ligand which was almost insoluble in ethanol or methanol was slurried in a ethanol-methanol mixture. To this mixture was added the metal salt dissolved in ethanol-methanol, in a $1:1$ and in a $1:2$ ratio. Upon adding the metal salt, the ligand dissolved in the

† Supplementary data available: see Instructions for Authors. *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii-xx.

mixture and deep green or blue colours developed, depending upon the counter ion used. Upon standing at room temperature a powder or crystals were formed, usual yields 60–75%. No precautions to prevent hydrolysis were taken. Preparations were carried out on a 0.01 molar scale. All compounds are listed in Table 1, together with their analytical data.

Preparation of Single Crystals.—The powdered compound $\text{Cu}(\text{L}^1)(\text{ClO}_4)_2$ was redissolved in an ethanol-acetonitrile mixture. Upon standing at room temperature for some weeks single crystals of (1) formed as long green prisms. A piece cut from such a bar was used for diffraction measurements. For $\text{Cu}(\text{L}^2)_2(\text{ClO}_4)_2(\text{H}_2\text{O})$ the same procedure was followed using only ethanol, yielding (2).

Physical and Analytical Measurements.—Metal analyses were carried out by standard complexometric titrations and atomic absorption spectroscopy. The C, H, and N analyses were carried out by the Microanalytical Laboratory of University College, Dublin. Infrared spectra were obtained as Nujol mulls and as KBr pellets ($4000\text{--}200\text{ cm}^{-1}$) on a Perkin-Elmer 580B spectrophotometer. From the spectra information was obtained about the ligands, the anions, and possible solvent molecules. Ligand-field spectra were obtained by the diffuse-reflectance method on solid powders on a Perkin-Elmer 330 spectrophotometer. E.s.r. spectra of the powdered compounds were recorded

at room- and liquid-nitrogen temperatures with Varian E-3 and E-12 spectrometers operating at X -band frequencies (9 GHz). From these spectra useful information about the co-ordination geometry of the copper ions could be obtained.

Crystallography.—The single-crystal X -ray diffraction measurements were performed on Enraf-Nonius CAD-4 diffractometers using Mo-K_α radiation ($\lambda = 0.71069\text{ \AA}$) monochromated by graphite. The experimental densities were determined in a mixture of 1,1-dibromoethane and chloroform. Calculations were carried out on the Leiden University Amdahl V7B computer, and on the Nijmegen University computer using local sets of programs.

Crystal data. *Structure (1)*, $\text{C}_{21}\text{H}_{16}\text{Cl}_2\text{CuN}_6\text{O}_8$, $M = 614.8$, monoclinic, $a = 14.061(1)$, $b = 20.638(1)$, $c = 8.273(1)\text{ \AA}$, $\beta = 101.119(8)^\circ$, $U = 2355.72\text{ \AA}^3$ (determined by least-squares refinement from θ values of 25 accurately measured reflections), space group $P2_1/c$, $D_m = 1.72(1)\text{ Mg m}^{-3}$, $Z = 4$, $D_c = 1.73\text{ Mg m}^{-3}$, light green crystal, dimensions $0.40 \times 0.30 \times 0.30\text{ mm}$, $F(000) = 1246.3$, $\mu(\text{Mo-K}_\alpha) = 12.15\text{ cm}^{-1}$.

Structure (2), $\text{C}_{42}\text{H}_{36}\text{Cl}_2\text{CuN}_{10}\text{O}_9$, $M = 958.5$, monoclinic, $a = 8.4824(22)$, $b = 29.1965(29)$, $c = 16.7393(24)\text{ \AA}$, $\beta = 95.836(17)^\circ$, $U = 4123.6\text{ \AA}^3$ (determined by least-squares refinement from θ values of 25 accurately measured reflections), $\lambda(\text{Cu-K}_\alpha) = 1.54184\text{ \AA}$, space group $P2_1/c$, $D_m = 1.52(8)\text{ Mg m}^{-3}$, $Z = 4$, $D_c = 1.540\text{ Mg m}^{-3}$, light green crystal, dimensions $0.27 \times 0.24 \times 0.19\text{ mm}$, $F(000) = 1971.6$, $\mu(\text{Cu-K}_\alpha) = 24.1\text{ cm}^{-1}$.

Data collection and refinement. For crystal (1), 7670 reflections were measured with $2 < 2\theta < 31^\circ$, yielding 4265 significant independent reflections [$I > 2\sigma(I)$]. The data were corrected for Lorentz and polarization effects. No absorption correction was performed. Scattering factors, including anomalous dispersion, were taken from ref. 11. The copper position, located in a three-dimensional Patterson synthesis, was used as input in AUTOFOR, from which all the positions of the non-hydrogen atoms could be found. Refinements were carried out by common least-squares full-matrix methods. The positions of the hydrogen atoms, two of which had to be placed in fixed positions, were refined with fixed distances from the parent carbon or nitrogen atoms. The B_{iso} of the hydrogen atoms was refined as a group for the aromatic hydrogen atoms and the methyl hydrogen atoms, respectively. The function minimized during the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$ with

Table 1. Analytical data (%) with calculated values in parentheses

Compound	M	C	H	N
$\text{Cu}(\text{L}^1)(\text{CH}_3\text{CN})(\text{ClO}_4)_2$	10.1 (10.3)	40.3 (41.0)	2.5 (2.6)	13.5 (13.7)
$\text{Cu}(\text{L}^1)(\text{ClO}_4)_2(\text{H}_2\text{O})_2$		37.5 (37.4)	2.7 (2.8)	11.6 (11.5)
$\text{Cu}(\text{L}^1)_2(\text{ClO}_4)_2$	7.4 (7.2)	50.3 (51.6)	2.9 (3.0)	15.5 (15.8)
$\text{Cu}(\text{L}^1)(\text{NO}_3)_2(\text{H}_2\text{O})_2$	11.9 (11.9)	45.3 (42.7)	3.3 (3.2)	18.9 (18.3)
$\text{Cu}(\text{L}^1)\text{Cl}_2(\text{H}_2\text{O})_2$	13.1 (13.2)	49.6 (47.4)	3.4 (3.6)	13.8 (14.5)
$\text{Cu}(\text{L}^1)\text{Br}_2(\text{H}_2\text{O})_{0.5}$	12.1 (11.7)	42.2 (42.0)	2.7 (2.6)	13.0 (12.9)
$\text{Zn}(\text{L}^1)\text{Cl}_2(\text{H}_2\text{O})_2$	13.6 (13.5)			
$\text{Zn}(\text{L}^1)\text{Br}_2(\text{H}_2\text{O})$	10.5 (11.2)	41.6 (41.2)	2.6 (2.7)	12.6 (12.6)
$\text{Cu}(\text{L}^2)(\text{ClO}_4)_2(\text{H}_2\text{O})_2$	9.4 (9.9)	38.2 (39.5)	3.2 (3.3)	10.6 (10.9)
$\text{Cu}(\text{L}^2)_2(\text{ClO}_4)_2(\text{H}_2\text{O})$	6.9 (6.6)	53.0 (52.6)	3.6 (3.8)	14.7 (14.6)
$\text{Cu}(\text{L}^2)(\text{NO}_3)_2(\text{H}_2\text{O})_{0.5}$	11.6 (11.9)	45.4 (47.0)	3.3 (3.4)	17.6 (18.2)
$\text{Cu}(\text{L}^2)\text{Cl}_2(\text{H}_2\text{O})_4$	11.4 (11.6)			
$\text{Cu}(\text{L}^2)\text{Br}_2$	10.6 (11.3)	44.2 (44.8)	3.0 (3.0)	12.1 (12.4)
$\text{Zn}(\text{L}^2)\text{Cl}_2$	13.3 (13.7)			

Table 2. Fractional atomic co-ordinates ($\times 10^5$ for Cu and Cl, $\times 10^4$ for the other atoms) with estimated standard deviations (e.s.d.s) in the least significant digits in parentheses for structure (1)

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Cu	−23 141(2)	−1 365(1)	482(5)	C(27)	−3 016(3)	2 181(2)	2 272(5)
N(1)	−1 205(2)	190(1)	1 661(3)	C(28)	−2 718(2)	1 578(1)	1 911(4)
C(2)	−608(2)	426(1)	2 554(4)	C(29)	−3 342(2)	1 215(1)	775(3)
C(3)	182(2)	742(2)	3 691(4)	N(30)	−3 455(1)	−480(1)	−1 446(3)
N(11)	−1 783(1)	−995(1)	−553(3)	C(31)	−3 402(2)	−1 056(1)	−2 141(3)
C(12)	−2 438(2)	−1 328(1)	−1 604(3)	C(32)	−4 194(2)	−1 307(1)	−3 214(4)
N(13)	−2 082(2)	−1 890(1)	−2 036(3)	C(33)	−5 027(2)	−938(2)	−3 569(4)
C(14)	−1 139(2)	−1 937(1)	−1 228(4)	C(34)	−5 067(2)	−341(1)	−2 870(4)
C(15)	−435(2)	−2 406(1)	−1 271(5)	C(35)	−4 266(2)	−116(1)	−1 791(3)
C(16)	473(2)	−2 286(2)	−359(5)	Cl(1)	−22 398(5)	6 210(4)	−37 602(10)
C(17)	662(2)	−1 728(1)	598(4)	O(1)	−1 737(1)	321(1)	−2 245(3)
C(18)	−36(2)	−1 265(1)	649(4)	O(2)	−2 925(2)	1 068(1)	−3 383(4)
C(19)	−947(2)	−1 371(1)	−280(3)	O(3)	−2 737(3)	151(2)	−4 797(5)
N(21)	−3 270(1)	591(1)	153(3)	O(4)	−1 542(2)	941(2)	−4 481(4)
C(22)	−4 108(2)	486(1)	−880(3)	Cl(2)	−28 820(6)	−14 934(4)	28 719(10)
N(23)	−4 712(2)	994(1)	−955(3)	O(5)	−3 205(2)	−871(1)	2 211(3)
C(24)	−4 264(2)	1 464(1)	74(4)	O(6)	−2 820(2)	−1 918(1)	1 534(3)
C(25)	−4 563(2)	2 076(1)	458(4)	O(7)	−3 604(4)	−1 758(2)	3 623(6)
C(26)	−3 905(3)	2 432(2)	1 559(5)	O(8)	−2 030(3)	−1 460(2)	3 954(6)

Table 3. Fractional positional parameters with e.s.d.s for $[\text{Cu}(\text{L}^2)_2][\text{ClO}_4]_2 \cdot \text{H}_2\text{O}$ (2)

Atom	x	y	z	S.o.f.*	Atom	x	y	z
Cu	0.075 42(12)	0.132 54(3)	0.219 86(6)	1.0	C(29)	0.403 8(10)	0.142 8(3)	0.400 5(5)
Cl(1)	0.285 8(3)	0.098 86(8)	0.028 83(15)	1.0	N(31)	0.011 2(7)	0.069 2(2)	0.191 1(3)
O(11)	0.281 1(8)	0.113 36(24)	0.111 7(4)	1.0	C(32)	−0.084 9(9)	0.062 3(2)	0.123 1(4)
O(12)	0.134 3(10)	0.105 8(3)	−0.012 5(5)	1.0	C(33)	−0.126 6(10)	0.017 6(3)	0.100 1(5)
O(13)	0.388 9(11)	0.127 1(4)	−0.006 5(7)	1.0	C(34)	−0.069 2(12)	−0.018 2(3)	0.147 6(5)
O(14)	0.365 1(36)	0.057 3(10)	0.022 9(19)	0.5	C(35)	0.034 9(10)	−0.010 4(2)	0.215 5(5)
O(15)	0.272 9(40)	0.051 7(8)	0.035 7(16)	0.5	C(36)	0.069 7(9)	0.035 0(2)	0.237 0(4)
Cl(2)	−0.156 8(4)	0.358 0(1)	0.222 3(2)	0.5	C(30)	0.204 4(12)	−0.014 9(3)	0.397 7(5)
O(21)	−0.010 9(4)	0.380 2(1)	0.220 3(2)	0.5	Ligand B			
O(22)	−0.131 6(4)	0.313 0(1)	0.248 9(2)	0.5	N(11)	0.161 5(7)	0.256 6(2)	0.328 6(4)
O(23)	−0.237 5(4)	0.357 7(1)	0.144 8(2)	0.5	C(12)	0.106 6(8)	0.213 2(2)	0.319 6(4)
O(24)	−0.247 8(4)	0.381 4(1)	0.274 3(2)	0.5	N(13)	0.142 6(7)	0.194 8(2)	0.250 9(3)
O(25)	−0.065 7(7)	0.378 7(1)	0.295 9(3)	0.5	C(14)	0.226 0(9)	0.228 4(2)	0.214 3(4)
O(26)	−0.138 4(7)	0.387 8(1)	0.161 5(3)	0.5	C(15)	0.235 0(9)	0.266 8(2)	0.262 5(5)
O(27)	−0.320 6(7)	0.363 9(1)	0.244 3(3)	0.5	C(16)	0.312 5(12)	0.306 7(3)	0.242 1(6)
O(28)	−0.120 5(7)	0.316 0(1)	0.216 1(3)	0.5	C(17)	0.380 7(14)	0.305 3(3)	0.171 1(7)
O(w)	0.664 3(21)	0.239 3(5)	0.274 2(9)	1.0	C(18)	0.375 3(12)	0.266 1(4)	0.122 5(6)
Ligand A					C(19)	0.293 6(11)	0.227 0(3)	0.142 7(5)
N(11)	−0.216 9(7)	0.115 1(2)	0.015 7(3)		C(20)	0.129 7(10)	0.289 2(2)	0.392 1(5)
C(12)	−0.129 3(8)	0.106 6(2)	0.086 1(4)		N(21)	−0.312 9(7)	0.084 8(2)	0.290 0(4)
N(13)	−0.085 3(7)	0.144 5(2)	0.126 0(3)		C(22)	−0.202 8(9)	0.081 0(2)	0.355 1(4)
C(14)	−0.149 6(9)	0.180 1(2)	0.079 1(4)		N(23)	−0.180 5(8)	0.038 3(2)	0.380 4(4)
C(15)	−0.231 2(8)	0.162 4(2)	0.009 4(4)		C(24)	−0.281 4(11)	0.012 4(3)	0.327 1(5)
C(16)	−0.307 6(11)	0.189 9(3)	−0.048 1(5)		C(25)	−0.367 0(10)	0.041 5(3)	0.272 1(5)
C(17)	−0.303 6(11)	0.236 3(3)	−0.033 1(6)		C(26)	−0.478 5(11)	0.025 3(4)	0.212 5(6)
C(18)	−0.228 9(11)	0.254 1(3)	0.037 5(6)		C(27)	−0.500 6(14)	−0.021 1(4)	0.211 0(7)
C(19)	−0.147 5(9)	0.226 9(2)	0.094 1(5)		C(28)	−0.416 0(17)	−0.049 8(4)	0.262 9(9)
C(20)	−0.275 5(10)	0.082 8(3)	−0.045 9(5)		C(29)	−0.306 2(14)	−0.035 0(3)	0.323 2(7)
N(21)	0.236 2(7)	0.031 5(2)	0.371 9(4)		N(31)	−0.054 9(7)	0.150 1(2)	0.344 4(3)
C(22)	0.177 4(9)	0.053 1(2)	0.304 0(4)		C(32)	0.033 5(8)	0.185 1(2)	0.378 1(4)
N(23)	0.222 1(7)	0.096 6(2)	0.301 5(3)		C(33)	0.069 9(10)	0.188 3(2)	0.459 7(5)
C(24)	0.320 7(8)	0.104 0(2)	0.371 6(4)		C(34)	0.016 3(10)	0.155 5(3)	0.510 7(5)
C(25)	0.327 3(9)	0.063 4(2)	0.416 1(4)		C(35)	−0.075 2(10)	0.120 2(3)	0.476 8(4)
C(26)	0.414 0(11)	0.060 9(3)	0.491 3(5)		C(36)	−0.109 7(8)	0.118 8(2)	0.394 6(4)
C(27)	0.492 0(11)	0.099 4(3)	0.517 4(5)		C(30)	−0.375 7(10)	0.126 3(3)	0.248 6(5)
C(28)	0.488 8(10)	0.139 4(3)	0.474 4(5)					

* Disordered oxygen pairs: O(14), O(15); O(21), O(25); O(22), O(26); O(23), O(27); O(24), O(28). S.o.f. = Site occupation factor.

Table 4. Relevant bond distances (Å) and angles (°) in $[\text{Cu}(\text{L}^1)(\text{CH}_3\text{CN})(\text{ClO}_4)][\text{ClO}_4]$ with e.s.d.s in parentheses

Cu–N(1)	1.966(2)	N(11)–C(19)	1.390(3)	C(18)–C(19)	1.378(4)	C(26)–C(27)	1.377(5)
Cu–N(11)	2.023(2)	C(12)–N(13)	1.338(3)	N(21)–C(22)	1.333(3)	C(27)–C(28)	1.365(4)
Cu–N(21)	2.028(2)	C(12)–C(31)	1.454(4)	N(21)–C(29)	1.397(3)	C(28)–C(29)	1.378(4)
Cu–N(30)	1.959(2)	N(13)–C(14)	1.369(3)	C(22)–N(23)	1.342(3)	N(30)–C(31)	1.330(3)
Cu–O(1)	2.396(2)	C(14)–C(15)	1.389(6)	C(22)–C(35)	1.449(4)	N(30)–C(35)	1.349(3)
Cu–O(5)	2.817(3)	C(14)–C(19)	1.403(4)	N(23)–C(24)	1.362(4)	C(31)–C(32)	1.384(4)
N(1)–C(2)	1.117(3)	C(15)–C(16)	1.375(5)	C(24)–C(25)	1.387(4)	C(32)–C(33)	1.381(4)
C(2)–C(3)	1.463(4)	C(16)–C(17)	1.395(4)	C(24)–C(29)	1.411(4)	C(33)–C(34)	1.366(4)
N(11)–C(12)	1.330(3)	C(17)–C(18)	1.376(4)	C(25)–C(26)	1.379(5)	C(34)–C(35)	1.376(4)
N(1)–Cu–N(11)	100.65(9)	O(1)–Cu–O(5)	167.14(7)	N(13)–C(14)–C(19)	106.1(2)	C(25)–C(24)–C(29)	122.1(3)
N(1)–Cu–N(2)	99.39(9)	Cu–N(11)–C(12)	111.8(2)	C(15)–C(14)–C(19)	122.2(3)	C(24)–C(25)–C(26)	116.3(3)
N(1)–Cu–O(1)	93.25(9)	Cu–N(11)–C(19)	142.2(2)	C(14)–C(15)–C(16)	116.9(5)	C(25)–C(26)–C(27)	121.3(3)
N(1)–Cu–O(5)	98.35(9)	Cu–N(21)–C(22)	111.3(2)	C(15)–C(16)–C(17)	120.9(4)	C(26)–C(27)–C(28)	122.8(3)
N(1)–Cu–N(30)	176.5(1)	Cu–N(21)–C(29)	142.5(2)	C(16)–C(17)–C(18)	122.2(3)	C(27)–C(28)–C(29)	117.6(3)
N(11)–Cu–N(21)	159.80(9)	Cu–N(30)–C(31)	119.3(2)	C(17)–C(18)–C(19)	117.6(3)	N(21)–C(29)–C(24)	108.1(2)
N(11)–Cu–N(30)	79.85(9)	Cu–N(30)–C(35)	119.2(2)	N(11)–C(19)–C(14)	107.9(2)	C(24)–C(29)–C(28)	119.8(3)
N(11)–Cu–O(1)	87.34(8)	Cu–N(1)–C(2)	174.1(2)	C(14)–C(19)–C(18)	120.1(3)	C(31)–N(30)–C(35)	121.5(2)
N(11)–Cu–O(5)	85.10(8)	Cu–O(1)–Cl(1)	131.9(1)	C(22)–N(21)–C(29)	105.5(2)	N(30)–C(31)–C(32)	120.4(3)
N(21)–Cu–N(30)	79.99(9)	Cu–O(5)–Cl(2)	125.3(1)	N(21)–C(22)–N(23)	112.1(3)	C(31)–C(32)–C(33)	118.4(3)
N(21)–Cu–O(1)	94.02(8)	N(1)–C(2)–C(3)	178.7(3)	N(21)–C(22)–C(35)	120.0(2)	C(32)–C(33)–C(34)	120.6(3)
N(21)–Cu–O(5)	89.55(8)	C(12)–N(11)–C(19)	106.0(2)	C(22)–H(23)–C(24)	108.3(2)	C(33)–C(34)–C(35)	118.9(3)
N(30)–Cu–O(1)	90.22(8)	N(11)–C(12)–N(13)	112.0(2)	N(23)–C(24)–C(29)	106.0(2)	N(30)–C(35)–C(34)	120.2(3)
N(30)–Cu–O(5)	78.22(8)	C(12)–N(13)–C(14)	107.9(2)				

Table 5. Bond lengths (Å) and angles (°) with e.s.d.s for $[\text{Cu}(\text{L}^2)_2][\text{ClO}_4]_2 \cdot \text{H}_2\text{O}$ (**2**)

	Ligand A	Ligand B			
Cu–N(13)	2.004(5)	1.958(5)			
Cu–N(23)	2.042(5)		Cu–O(11)	2.698(7)	
Cu–N(31)	1.973(5)	2.510(5)			
				Ligand A	Ligand B
N(11)–C(12)	1.351(8)	1.354(8)	N(11)–C(15)	1.391(9)	1.359(10)
N(11)–C(20)	1.446(9)	1.472(10)	C(12)–N(13)	1.325(8)	1.333(9)
C(12)–C(32)	1.466(9)	1.461(10)	N(13)–C(14)	1.382(8)	1.389(9)
C(14)–C(15)	1.394(10)	1.377(10)	C(14)–C(19)	1.389(10)	1.381(12)
C(15)–C(16)	1.367(11)	1.398(12)	C(16)–C(17)	1.376(13)	1.375(16)
C(17)–C(18)	1.385(13)	1.403(15)	C(18)–C(19)	1.368(12)	1.395(14)
N(21)–C(22)	1.350(9)	1.365(9)	N(21)–C(25)	1.377(9)	1.368(10)
N(21)–C(30)	1.456(10)	1.468(10)	C(22)–N(23)	1.328(9)	1.326(9)
C(22)–C(36)	1.471(10)	1.475(10)	N(23)–C(24)	1.386(8)	1.394(10)
C(24)–C(25)	1.399(10)	1.400(11)	C(24)–C(29)	1.394(11)	1.401(12)
C(25)–C(26)	1.393(11)	1.387(12)	C(26)–C(27)	1.354(13)	1.367(16)
C(27)–C(28)	1.370(13)	1.359(18)	C(28)–C(29)	1.371(12)	1.371(18)
N(31)–C(32)	1.346(9)	1.357(8)	N(31)–C(36)	1.326(8)	1.354(9)
C(32)–C(33)	1.398(10)	1.372(10)	C(33)–C(34)	1.372(11)	1.390(12)
C(34)–C(35)	1.386(12)	1.379(12)	C(35)–C(36)	1.396(10)	1.377(10)
N(13A)–Cu–N(13B)	101.7(7)		N(31A)–Cu–N(13B)	178.5(6)	
N(23A)–Cu–N(13B)	99.1(9)		N(13A)–Cu–N(31B)	107.7(8)	
N(31A)–Cu–N(31B)	105.1(6)		N(23A)–Cu–N(31B)	80.7(7)	
	Ligand A	Ligand B		Ligand A	Ligand B
N(13)–Cu–N(23)	159.1(2)	—	N(13)–Cu–N(31)	79.8(2)	—
N(23)–Cu–N(31)	79.4(2)	—	O(11)–Cu–N(23)	87.2(2)	—
O(11)–Cu–N(31)	79.8(2)	165.8(2)	O(11)–Cu–N(13)	86.8(1)	100.4(2)
Cu–N(13)–C(12)	112.6(4)	121.1(4)	Cu–N(13)–C(14)	140.7(4)	133.4(5)
Cu–N(23)–C(22)	110.9(4)	—	Cu–N(23)–C(24)	139.6(4)	—
Cu–N(31)–C(36)	119.2(4)	—	Cu–N(31)–C(32)	118.3(4)	—
C(12)–N(11)–C(15)	106.4(5)	107.2(6)	C(12)–N(11)–C(20)	128.5(6)	126.9(6)
C(15)–N(11)–C(20)	124.9(6)	125.4(6)	N(11)–C(12)–N(13)	112.9(6)	111.5(6)
N(11)–C(12)–C(32)	128.6(6)	127.9(6)	N(13)–C(12)–C(32)	118.4(6)	120.2(6)
C(12)–N(13)–C(14)	105.5(5)	105.5(5)	N(13)–C(14)–C(15)	109.2(6)	108.5(6)
N(13)–C(14)–C(19)	129.9(6)	129.5(6)	C(15)–C(14)–C(19)	120.9(6)	122.0(7)
N(11)–C(15)–C(16)	106.0(6)	107.3(6)	N(11)–C(15)–C(16)	132.0(7)	130.4(7)
C(14)–C(15)–C(16)	122.0(7)	122.4(8)	C(15)–C(16)–C(17)	116.7(8)	115.8(8)
C(16)–C(17)–C(18)	121.8(9)	122.3(10)	C(17)–C(18)–C(19)	121.8(8)	121.0(10)
C(14)–C(19)–C(18)	116.7(7)	116.5(8)	C(22)–N(21)–C(25)	106.0(6)	106.6(6)
C(22)–N(21)–C(30)	128.4(6)	129.0(6)	C(25)–N(21)–C(30)	125.5(6)	124.2(6)
N(21)–C(22)–N(23)	113.1(6)	113.3(6)	N(21)–C(22)–C(36)	128.4(6)	126.0(6)
N(23)–C(22)–C(36)	118.5(6)	120.6(6)	C(22)–C(23)–C(24)	105.7(5)	104.2(6)
N(23)–C(24)–C(25)	107.9(6)	109.7(7)	N(23)–C(24)–C(29)	131.3(7)	130.1(8)
C(25)–C(24)–C(29)	120.8(6)	120.2(8)	N(21)–C(25)–C(24)	107.2(6)	106.1(7)
N(21)–C(25)–C(26)	131.9(7)	131.5(8)	C(24)–C(25)–C(26)	120.9(7)	122.4(8)
C(25)–C(26)–C(27)	116.4(8)	115.7(9)	C(26)–C(27)–C(28)	123.7(8)	122.5(11)
C(27)–C(28)–C(29)	121.1(8)	123.4(11)	C(24)–C(29)–C(28)	117.1(8)	115.7(9)
C(32)–N(31)–C(36)	122.5(5)	117.4(6)	C(12)–C(32)–N(31)	109.5(5)	113.4(6)
C(12)–C(32)–C(33)	131.4(6)	124.1(6)	N(31)–C(32)–C(33)	119.1(6)	121.6(6)
C(32)–C(33)–C(34)	119.1(7)	120.7(7)	C(33)–C(34)–C(35)	120.6(7)	117.9(7)
C(34)–C(35)–C(36)	117.9(7)	119.1(7)	C(22)–C(36)–N(31)	109.7(6)	115.4(6)
C(22)–C(36)–C(35)	129.5(6)	121.2(7)	N(31)–C(36)–C(35)	120.6(6)	123.3(7)

the weighting scheme $w = \sigma_f^{-2}$. The final residual indices are $R = 0.0366$ ($\Sigma|\Delta F|/|F_o|$) and $R' = 0.0460$ ($\{[\Sigma w(\Delta F^2)/\Sigma w|F_o|^2]^{1/2}\}$). The positional parameters are listed in Table 2.

For compound (**2**) 11 676 reflections were measured up to $\theta = 70^\circ$ in the range $-10 \leq h \leq 10$, $-30 \leq k \leq 0$, $-20 \leq l \leq 0$. Of these 8 493 were unique reflections of which 3 165 had $I > 3\sigma(I)$; empirical absorption corrections were made following the method described by North *et al.*¹³ The position of the copper atom was located from the Patterson map using PATSYS¹⁴ and automatically input to DIRDIF.¹⁵ The positions of all non-hydrogen atoms were obtained in two DIRDIF runs. The high isotropic thermal parameters of the oxygen atoms indicated that the two independent perchlorate ions and the water molecule were disordered. A Fourier map

calculated without the oxygen atoms revealed a significant extended region of electron density for one of the oxygen atoms, O(14), of the first perchlorate ion and all the disordered oxygen atoms of the second perchlorate ion. Consequently, two oxygen peaks [O(14) and O(15) each with occupancy of 0.5] were input [instead of O(14)], while the second perchlorate ion was distributed in two orientations with an occupancy of 0.5 for each atom. An additional empirical absorption correction was applied using DIFABS.¹⁶ All hydrogen atoms except those of the methyl groups and the water molecule were located from the Fourier difference map. The methyl-hydrogen atoms were fixed at expected positions. The hydrogen of the water molecule could not be located. Block refinements were made using SHELX.¹⁷ The hydrogen atoms had fixed isotropic thermal parameters of

0.06 Å². The function minimized was $\Sigma w(F_o - F_c)^2$ with $w = 1/[\sigma^2(F_o) + 0.0025F_o^2]$ and $\sigma(F_o)$ from counting statistics. The final conventional agreement factors were $R = 0.062$ and $R' = 0.065$ for the 3 165 'observed' reflections. The maximum shift to error ratio in the last full-matrix least-squares cycle was less than 0.06 for all atoms except those of the disordered perchlorate ion. The final Fourier difference map showed no peaks higher than 0.5 e Å⁻³. Plots were made with PLUTO.¹⁸ Final atomic co-ordinates of the non-hydrogen atoms are given in Table 3. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

Molecular Structure of Compound (1).—The geometry of compound (1) is depicted in Figure 1. Relevant bond lengths and distances are given in Table 4. The copper(II) is tetragonally co-ordinated by three nitrogens from the ligand and one nitrogen from an acetonitrile molecule. The axial ligands are the two oxygen atoms of the perchlorate anions; one of these oxygens [O(1)] is rather close to the Cu ion [2.396(2) Å], whereas the other is at a much longer, but still semico-ordinating, distance [Cu—O 2.817(3) Å]. For this discussion we consider Cu...L contacts between 2.5 and 2.9 Å as semico-ordinating. Most literature values^{19–24} for asymmetric bis-(oxygen) co-ordination are usually closer together, *i.e.* the short bond often lies between 2.45 and 2.60 Å, whereas the long bond

usually varies from 2.60 to 2.80 Å. The plane of the four nitrogen atoms is almost a square, as seen from the bonding angles in Table 4. The atoms do not significantly deviate from the plane. The nearest Cu atom in the lattice lies at 6.55 Å. The cell has four molecules, two of which are opposite to each other with a distance between the planes of about 5.0 Å. The packing is mainly determined by van der Waals forces, although two relatively strong hydrogen bonds are also present, between the N—H groups of the benzimidazoles and the O atoms of the perchlorate anions. The respective distances are N(23)...O(5') 2.924(3) Å with an N—H...O angle of 153.7°, and N(13)...O(6'') 2.839(3) Å with an N—H...O angle of 135.9°.

Molecular Structure of Compound (2).—The geometry of compound (2) is depicted in Figures 2 (stereo drawing) and 3 (one unit split into two halves for clarity, with the applied numbering system). Table 5 lists the more relevant interatomic distances and bond angles. The copper(II) ion is square-

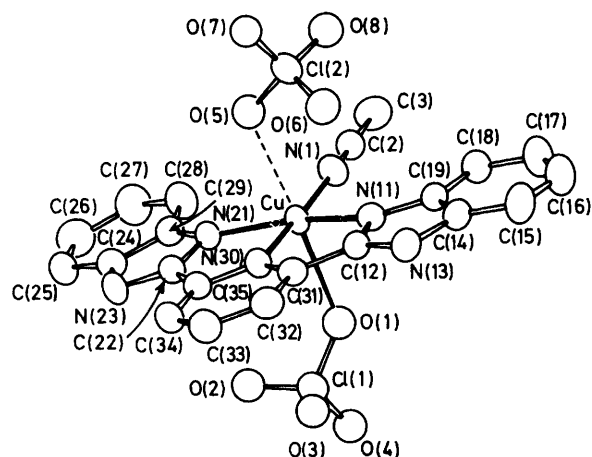


Figure 1. ORTEP representation of $[\text{Cu}(\text{L}^1)(\text{CH}_3\text{CN})(\text{ClO}_4)](\text{ClO}_4)$ with thermal ellipsoids of 50% probability, showing the numbering scheme. The oxygen atoms of the perchlorate molecules have an arbitrary isotropic B value (2.0 nm²) for clarity

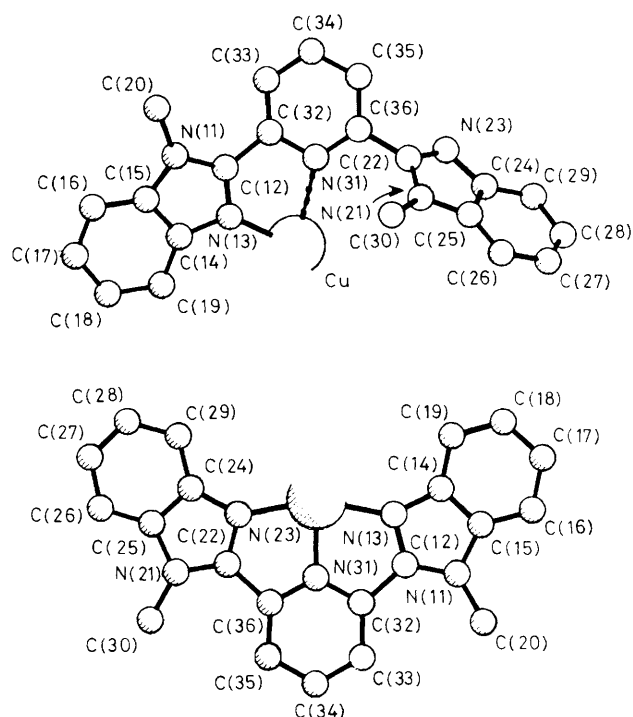


Figure 3. Crystallographic atomic numbering scheme for $[\text{Cu}(\text{L}^2)_2]^{2+}$. For clarity the ClO_4 has been omitted and the two parts of the molecule are plotted separately. Top: ligand B. Bottom: ligand A

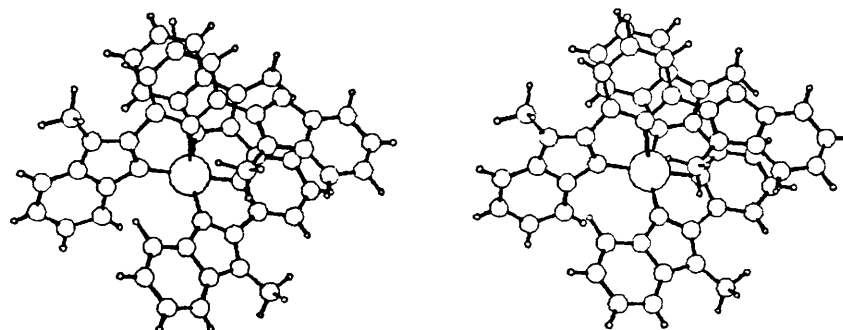


Figure 2. Stereoview of the cation $[\text{Cu}(\text{L}^2)_2]^{2+}$. The semico-ordinating perchlorate has been omitted for clarity

Table 6. Ligand-field data and e.s.r. parameters ($G = 10^{-4}$ T)

Compound	Colour	Ligand-field (reflectance)/ 10^3 cm^{-1}	E.s.r. (at 77 K)			
			g_{\perp}	g_{\parallel}	A_{\parallel}/G	g_{iso}
$\text{Cu}(\text{L}^1)(\text{CH}_3\text{CN})(\text{ClO}_4)_2$	Green	15.5				2.07^a
$\text{Cu}(\text{L}^1)(\text{ClO}_4)_2(\text{H}_2\text{O})_2$	Green	14.9	2.06	2.31^b	165^b	
$\text{Cu}(\text{L}^1)_2(\text{ClO}_4)_2$	Green	14.2, 7.25	2.07	2.25	155	
$\text{Cu}(\text{L}^1)(\text{NO}_3)_2(\text{H}_2\text{O})_2$	Dark green	13.9				2.07^a
$\text{Cu}(\text{L}^1)\text{Cl}_2(\text{H}_2\text{O})_2$	Light green	14.1	2.06	2.24		
$\text{Cu}(\text{L}^1)\text{Br}_2(\text{H}_2\text{O})_{0.5}$	Green	13.2	2.07	2.22		
$\text{Zn}(\text{L}^1)\text{Cl}_2(\text{H}_2\text{O})_2^c$	Green-yellow	d	2.07	2.26	130	
$\text{Zn}(\text{L}^1)\text{Br}_2(\text{H}_2\text{O})^c$	Green-yellow	12.1	2.06	2.24	160	
$\text{Cu}(\text{L}^2)(\text{ClO}_4)_2(\text{H}_2\text{O})$	Green	15.0	2.03	2.23	167	
$\text{Cu}(\text{L}^2)(\text{ClO}_4)_2(\text{H}_2\text{O})_2$	Green	15.3				2.07^a
$\text{Cu}(\text{L}^2)(\text{NO}_3)_2(\text{H}_2\text{O})_{0.5}$	Green	14.6				2.07^a
$\text{Cu}(\text{L}^2)\text{Cl}_2(\text{H}_2\text{O})_4$	Green	13.7	2.08	2.27		
$\text{Cu}(\text{L}^2)\text{Br}_2$	Green	12.6	2.07	2.22		

^a Asymmetric signal. ^b Only observed as frozen solution in MeOH. ^c Doped in copper compound. ^d Weak signal.

pyramidally co-ordinated by two different ligands. The first ligand binds in a tridentate manner, very similar to L^1 in compound (1). The Cu–N (benzimidazole) distances are similar to those in structure (1) and to literature values.^{1–4} The second ligand, on the other hand, has a very unusual co-ordination mode. One nitrogen, N(13B), binds strongly [like acetonitrile in compound (1)] and completes the square of four nitrogen atoms around Cu^{II} , whereas a second nitrogen, N(31B), binds at a semico-ordinating distance of 2.510(5) Å [like one of the perchlorates in compound (1)]. The third nitrogen, N(23B), does not bind to copper at all; this is very unusual for a strongly donating ligand group like benzimidazole. This non-co-ordinating behaviour of this benzimidazole nitrogen in a sense resembles the low-pH form of copper(II) plastocyanin. It would be interesting to study this behaviour also in solution; however, our compounds decomposed under such conditions.

In addition to the above described co-ordination by five nitrogen atoms and similarly to compound (1), there is a perchlorate oxygen at a rather long distance [*trans* to N(31B), *i.e.* Cu–O(11) 2.698(7) Å]. Another difference between the two compounds originates from the fact that ligand L^2 has no acidic hydrogens, and therefore no hydrogen bonds are observed. As a result the perchlorate counter anions have serious disorder. There exists one hydrogen bond between the lattice water molecule and one perchlorate oxygen: O(W)–O(22) 2.82(2) Å, or the disordered equivalent, O(W)–O(28) 3.10(2) Å. The other packing forces are of van der Waals nature. The three rings of each of the ligands are not coplanar and the relative orientations seem to be mainly determined by the co-ordination to the copper. Ligand A has benzimidazole planes with dihedral angles with the pyridine ring of 7.6(2) and 14.8(2)°. In ligand B the co-ordinating benzimidazole ring makes an angle of 33.6(2)° with the pyridine ring, and the non-co-ordinating benzimidazole makes an angle of 41.4(2)° with the pyridine ring.

General Discussion of the Structures and Spectroscopic Information.—The compounds obtained with both ligands all have the general formula $\text{Cu}(\text{ligand})(\text{anion})_2(\text{solvent})_n$ and $\text{Cu}(\text{ligand})_2(\text{anion})_2(\text{solvent})_n$. As is seen from the *X*-ray structure of compound (2), two tridentate ligands cannot bind to copper in an octahedral manner, since one of the ligands appears to be only bidentate. Synthesis of the 1:2 species appeared possible only in the case of the ClO_4^- counter ion and only using an excess of the ligands L^1 and L^2 . On the other hand, in a related study on the iron(II) compounds of L^1 , L^2 , and similar ligands, 1:2 products were more easily formed.²⁵ The larger ionic radius of iron(II) compared with copper(II) is likely

to be responsible for this observation. In addition, Jahn-Teller effects are probably involved.

In Table 6 the ligand-field and e.s.r. spectra of the compounds are listed, together with those for a few samples of zinc halides, doped with Cu^{II} . The pure zinc compounds without copper dopants have also been prepared and characterized as white products, for which n.m.r. spectra show the presence of all the ligand peaks, hardly shifted compared to the free ligand. This phenomenon has been observed before for related ligands.² The ligand-field spectra of all the compounds show maxima at rather low energy [*i.e.* the absorption at 15 500 cm^{-1} for compound (1) with a square-pyramidal geometry is the highest]. The two absorptions for $\text{Cu}(\text{L}^1)_2(\text{ClO}_4)_2$ at 14 200 and 7 250 cm^{-1} , in combination with the e.s.r. parameters (Table 6), suggest a geometry slightly different from that of compound (2) (Figures 2 and 3). Therefore, an octahedrally based six-co-ordinated geometry cannot be excluded for this compound. All other compounds in Table 6 have a 1:1 copper:ligand ratio, and a structure with a tridentate co-ordinating ligand, with two additional ligands from anion and/or water molecule, yielding a square-pyramidally based five-co-ordinate geometry, with a sixth ligand at best at a very large distance, similar to the *X*-ray structure depicted in Figure 1. The fact that several compounds do not show a resolved e.s.r. hyperfine structure is attributed to exchange-narrowing effects, resulting from the solid-state effect, where the copper ions are influencing each other.²⁶ Given the ligand structure and the *X*-ray structure of (1), it is most unlikely that the ligand has anything but a *mer* orientation in all 1:1 products.

Infrared spectra of the compounds show the presence of bands due to the ligand, the counter ions, and the solvent molecules (acetonitrile and water). The water peaks are usually broad and coincide with the N–H peaks of ligand L^1 . The C–N stretch for CH_3CN is observed as a weak band (doublet) at 2 260 and 2 300 cm^{-1} ; this is in accord with earlier work on co-ordinated acetonitrile.²⁷ The ClO_4 peaks are all rather broad and at best agree with semi-co-ordination to the metal or hydrogen-bond formation to a water molecule. The nitrate N–O stretching is observed as a triplet, in agreement with one monodentate co-ordinating NO_3^- and the other one, at best, semico-ordinating.²⁸

In the far-i.r. spectra several bands are observed below 350 cm^{-1} which are likely to originate from Cu–N and (for certain compounds) Cu–Cl vibrations. No attempts were undertaken to make detailed assignments.

In conclusion, our aim to create a system where a benzimidazole ligand group in a chelate does not bind to a

metal has been reached. Whether the ligand L^2 can change its geometry, *e.g.* by rotation about the C—C bond [C(36)—C(22) in Figure 3], is not yet clear. Such a rotation, however, has been proposed by Freeman and co-workers⁷ for the histidine ligand in copper(1) plastocyanin. Further studies are scheduled, *e.g.* of the compound in solution and of the related copper(1) complexes, which will hopefully lead to a more complete understanding of this problem.

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