Unusual Changes in Hyperfine Coupling Constants observed for Copper(II) Complexes with N,N-Bis(benzimidazol-2-ylmethyl)amine and its Homologues; X-Ray Crystal Structure Determinations of $[CuL^{Pr^i}(NO_3)(MeOH)]NO_3$, $[CuL^{Bu^i}(NO_3)(MeOH)]NO_3$, $[CuL^{Bu^n}(NO_3)]NO_3$, and $[CuL^{Bu^i}(NO_3)]NO_3$†

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Crystal structures of four copper(II) complexes, $[CuL^{Pr^i}(NO_3)(MeOH)]NO_3$ (5), $[CuL^{Bu^n}(NO_3)]NO_3$ (6), $[CuL^{Bu^i}(NO_3)]NO_3$ (7), and $[CuL^{Bu^t}(NO_3)(MeOH)]NO_3$ (9) were determined by X-ray diffraction methods, where L^{Bu^n}, L^{Bu^t}, L^{Bu^i}, and L^{Pr^i} represent the n-butyl, t-butyl, isobutyl, and isopropyl derivative, on the amine nitrogen atom, of L^H, N,N-bis(benzimidazol-2-ylmethyl)amine. These complexes consist of a mononuclear compound with a tridentate ligand (L^H or its derivative) and a bidentate nitrate ion. These show quite similar absorption spectra in methanol solution. However, remarkable differences were observed for $|A_{||}|$ values in e.s.r. spectra (frozen methanol solution) irrespective of the small change in the $g_{||}$ value. Bulky substituents, such as t-butyl, on the amine nitrogen atom decrease the $|A_{||}|$ value considerably $\{|A_{||}| = 160 \times 10^{-4}$ cm^{-1} for $[CuL^H(NO_3)]^+$ and $|A_{||}| = 110 \times 10^{-4}$ cm^{-1} for $[CuL^{Bu^t}(NO_3)(MeOH)]^+\}$, suggesting that the change of orientation of the lone pair orbital of the amine nitrogen atom produces a sizeable effect on $|A_{||}|$ values in these complexes.

The 'Type I' or 'blue copper proteins' have an extremely intense ($\varepsilon = 3\,000$—$5\,000$ dm^3 mol^{-1} cm^{-1}) absorption band near 600 nm, a very small hyperfine coupling constant in the $g_{||}$ region of the e.s.r. spectrum, and an unusually high reduction potential.[1-3] The molecular structures of two copper proteins, plastocyanin from poplar leaves[4] and azurin from *Pseudomonas aeruginosa*,[5] are known from X-ray crystallographic studies. The unique features of blue copper proteins have been substantially rationalized in terms of the structural studies; the intense absorption near 600 nm has been attributed to charge transfer from the cysteine sulphur to copper,[6-11] and the high reduction potentials to both the distorted tetrahedral structure and the co-ordination of sulphur atoms.[11-18]

Some e.s.r. parameters for blue copper proteins are listed in Table 1, together with those of several copper(II) complexes of low molecular weight. One of the most puzzling problems at present is the elucidation of the very low $|A_{||}|$ values for blue copper proteins. These copper proteins can be classified into two groups: (i) those showing an axial e.s.r. pattern, to which plastocyanin[19] and azurin[20] belong, and (ii) proteins showing a rhombic e.s.r. pattern, observed for stellacyanin[21] and mavicyanin.[22] It is known that $g_{||}$ values increase and $|A_{||}|$ values decrease when the geometry around the copper(II) ion changes from square planar to a distorted tetrahedral structure,[16,23-28] and that the change in $A_{||}$ is always associated with a sizeable change in $g_{||}$ (see Table 1). Thus, low $|A_{||}|$ values for the blue copper protein have been attributed to its unique structure. However these values are small compared with those of model compounds of low molecular weight, irrespective of their similar $g_{||}$ values.
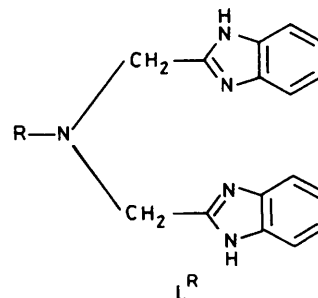
R = H, Me, Et, Pr^n, Pr^i, Bu^n, Bu^i, Bu^s, Bu^t, or CH$_2$Ph

Recently Nishida *et al.*[29] have prepared several copper(II) complexes with L^H [$= N,N$-bis(benzimidazol-2-ylmethyl)-amine][29] and its homologues, L^R, with substituents, R, on the amine nitrogen atom (R $=$ Me, Et, Pr^n, Pr^i, Bu^n, Bu^s, Bu^i, or Bu^t), and found that $|A_{||}|$ values in these complexes vary in the range $(110$—$160) \times 10^{-4}$ cm^{-1}, irrespective of the small change in $g_{||}$ values and the absorption spectroscopic properties. This suggests the presence of another important factor causing the drastic change in $|A_{||}|$ values of copper(II) complexes.

We have determined the crystal structures of four complexes, $[CuL^{Pr^i}(NO_3)(MeOH)]NO_3$ (5), $[CuL^{Bu^n}(NO_3)]NO_3$ (6), $[CuL^{Bu^i}(NO_3)]NO_3$ (7), and $[CuL^{Bu^t}(NO_3)(MeOH)]NO_3$ (9), and attempted to elucidate the origin for the unusual change in $|A_{||}|$ observed, and also that of the low $|A_{||}|$ values of blue copper proteins.

Experimental

Separation of Ligands.—An alkyliminodiacetic acid (0.02 mol) and 1,2-diaminobenzene (0.04 mol) were ground together, and the mixture heated at 160—170 °C for 3 h. The melt obtained was cooled to room temperature, and the wine-red glass dissolved in methanol (120 cm^3) by reflux, and further

Table 1. E.s.r. parameters

Copper enzyme	Source	$g_{\parallel}$	$g_{\perp}$	$10^4\lvert A_{\parallel}\rvert$ cm^{-1}	$10^4\lvert A_{\perp}\rvert$ cm^{-1}	Ref.
Plastocyanin	Spinach	2.226	2.053	63	17	19
Azurin	*Pseudomonas aeruginosa*	2.260	2.052	60	0	20
Stellacyanin	Lacquer	2.287	2.077, 2.025	35	29, 57	1, 2
Plantacyanin	Cucumber	2.232	2.114	50		22
Copper(II) complexes*						
$[Cu(H_2O)_6]^{2+}$		2.422	2.087	134	11	3
$[Cu(ox)_2]^{2-}$		2.318	2.071	164	8	3
$[Cu(Him)_4]^{2+}$		2.267	2.063	179		3
$[Cu(L^1)_2]^{2-}$		2.17		219		3
$[Cu(L^2)_2]$		2.182	2.049	192	11	16
$[Cu(L^3)_2]$		2.205	2.060	171	5	16
$[Cu(L^4)_2]$		2.267	2.068	108	33	16

* ox = Oxalate(2−), Him = imidazole, H_2L^1 = biuret, and HL^{2-4} = 2-(iminomethyl)-, 2-(isopropyliminomethyl)-, or 2(t-butyliminomethyl)-pyrrole respectively.

refluxed with charcoal (1 g) for 5 min. The mixture was filtered, and the filtrate evaporated to *ca.* 30 cm^3. A light brownish yellow solid was separated from the syrup by the addition of water (200—300 cm^3), and it crystallized on standing for 1 d. The crystals were collected by filtration, and washed with water. The ligands L^{Me}, L^{Bu^s}, and L^{CH_2Ph} were fine needles, the others yellow powders. They were dried under reduced pressure (2 mmHg, *ca.* 266 Pa) over P_2O_5 at 60 °C for 8 h.

Preparation of Copper(II) *Complexes.*—A methanol solution (10 cm^3) of the ligand (0.002 mol) was mixed with an equimolar amount of copper(II) nitrate (0.002 mol) in methanol (10 cm^3), and the mixture allowed to stand for several days at room temperature. The crystals precipitated were collected by filtration, and recrystallized from a hot methanol solution. The ten compounds thus obtained [$CuL^H(NO_3)_2(MeOH)$ (**1**); $CuL^{Me}(NO_3)_2(MeOH)$ (**2**); $CuL^{Et}(NO_3)_2(MeOH)$ (**3**); $CuL^{Pr^n}(NO_3)_2$ (**4**); $CuL^{Pr^i}(NO_3)_2(MeOH)$ (**5**); CuL^{Bu^n}-$(NO_3)_2$ (**6**); $CuL^{Bu^i}(NO_3)_2$ (**7**); $CuL^{Bu^s}(NO_3)_2$ (**8**); CuL^{Bu^t}-$(NO_3)_2(MeOH)$ (**9**); and $CuL^{CH_2Ph}(NO_3)_2(MeOH)$ (**10**)] were collected by filtration, and dried *in vacuo.* Analytical data for the new compounds are summarized in Table 2.

X-Ray Diffraction.—*Data collection.* The *X*-ray diffraction data were measured on a Rigaku AFC-5 automatic four-circle diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å) at 294 K and are collected in Table 3. Unit-cell parameters were determined from the least-squares fit of high angle reflections (2θ = 20—30°) (*cf.* Table 3). Intensity data were collected by the ω–2θ scan technique. For weak reflections, the intensity measurement was repeated up to three times depending on their intensities. Three standard reflections were monitored every 100 reflections, and showed good stability. The intensity data were corrected for Lorentz and polarization effects, but not for absorption. Independent reflections with [$\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)$] were considered as 'observed,' and used for the structure determination.

Structure solution and refinement. The structures of the present compounds were solved by the combined use of heavy-atom and direct methods,[30] and successive Fourier synthesis. The structures were refined by block-diagonal least-squares procedures. The reliability indices were $R = \Sigma\lVert F_o\rvert - \lvert F_c\rVert/\Sigma\lvert F_o\rvert$ and $R' = [\Sigma(w\lVert F_o\rvert - \lvert F_c\rVert)^2/\Sigma w\lvert F_o\rvert^2]^{\frac{1}{2}}$, where $w = 1$. Refinements were carried out by using isotropic thermal parameters initially, and then anisotropic ones for non-hydrogen atoms. Final difference Fourier maps of each complex showed no significant electron density (< 0.5 e Å^{-3}). All calculations were

Table 2. Elemental analyses of the copper(II) complexes

Complex	Analysis*/% H	C	N
(**1**) $CuL^H(NO_3)_2(MeOH)$	3.95 (3.85)	41.20 (41.10)	19.50 (19.75)
(**2**) $CuL^{Me}(NO_3)_2(MeOH)$	4.25 (4.15)	42.20 (42.30)	19.20 (19.20)
(**3**) $CuL^{Et}(NO_3)_2(MeOH)$	4.45 (4.40)	43.35 (43.45)	18.45 (18.70)
(**4**) $CuL^{Pr^n}(NO_3)_2$	4.25 (4.20)	45.25 (45.00)	19.30 (19.35)
(**5**) $CuL^{Pr^i}(NO_3)_2(MeOH)$	4.75 (4.70)	44.50 (44.55)	18.15 (18.20)
(**6**) $CuL^{Bu^n}(NO_3)_2$	4.55 (4.45)	46.10 (46.10)	18.65 (18.80)
(**7**) $CuL^{Bu^i}(NO_3)_2$	4.40 (4.45)	46.25 (46.10)	18.65 (18.80)
(**8**) $CuL^{Bu^s}(NO_3)_2$	4.55 (4.45)	46.05 (46.10)	18.85 (18.80)
(**9**) $CuL^{Bu^t}(NO_3)_2(MeOH)$	5.00 (4.90)	45.65 (45.60)	17.70 (17.75)
(**10**) $CuL^{CH_2Ph}(NO_3)_2(MeOH)$	4.40 (4.30)	49.10 (49.10)	16.65 (16.70)

* Calculated values in parentheses.

carried out on a Facom M-200 computer by the use of the local versions[31] of UNICS[32] and the ORTEP program;[33] the thermal ellipsoids of the ORTEP views in this paper were drawn at the 50% probability level. Atomic scattering factors were taken from ref. 34.
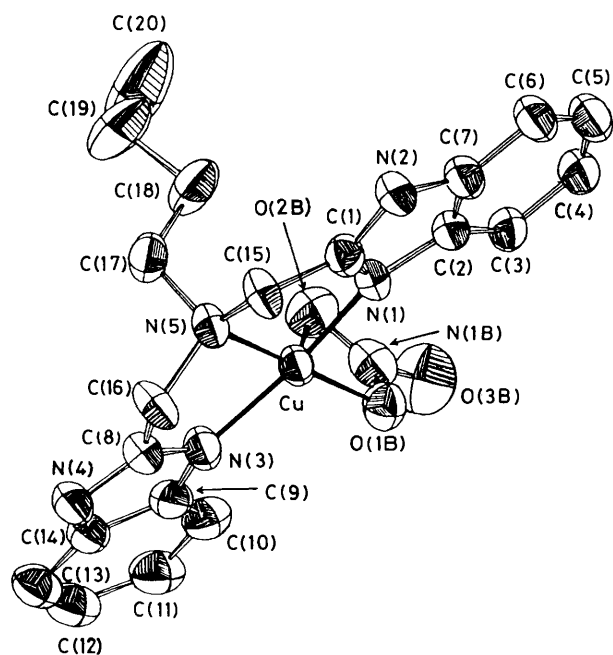
Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond parameters.

Results and Discussion

Molecular and Crystal Structures.—The ORTEP views of $[CuL^{Bu^n}(NO_3)]NO_3$ (**6**), $[CuL^{Bu^i}(NO_3)]NO_3$ (**7**), $[CuL^{Bu^t}(NO_3)(MeOH)]NO_3$ (**9**), and $[CuL^{Pr^i}(NO_3)(MeOH)]NO_3$ (**5**) are shown in Figures 1—4, respectively. The structure of (**10**), $[CuL^{CH_2Ph}(NO_3)(MeOH)]NO_3$, has already been reported.[29] The atomic co-ordinates, and selected bond distances and angles, are listed in Tables 4—7 and 8, respectively. The co-ordination spheres of the copper(II) ions are briefly illustrated in Figure 5.

Table 3. Crystal data for the complexes

Complex	(5)	(6)	(7)	(9)
Formula	$C_{20}H_{25}CuN_7O_7$	$C_{20}H_{23}CuN_7O_6$	$C_{20}H_{23}CuN_7O_6$	$C_{21}H_{27}CuN_7O_7$
M	539.0	521.0	521.0	553.0
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic
Space group	Pbca	$P2_1/c$	Pbca	Pbca
a/Å	16.136(5)	14.497(3)	29.55(1)	16.635(3)
b/Å	15.316(5)	14.401(3)	16.366(3)	18.768(4)
c/Å	18.901(3)	15.613(4)	9.380(2)	15.548(5)
β/°		137.51(1)		
U/Å³	4 671	2 202	4 536	4 855
D_m/g cm⁻³	1.53	1.53	1.49	1.53
D_c/g cm⁻³	1.53	1.57	1.53	1.51
Z	8	4	8	8
μ(Mo-K_α)/cm⁻¹	10.3	10.9	10.9	9.9
F(000)	2 232	1 076	2 152	2 296
Crystal dimensions/mm	0.3 × 0.3 × 0.5	0.2 × 0.3 × 0.4	0.3 × 0.4 × 0.5	0.4 × 0.4 × 0.4
Scan rate/° min⁻¹	8	8	8	8
Scan range (2θ)/°	2.5—55	2.5—50	2.5—50	2.5—50
Reflections collected	5 465	3 957	4 356	4 212
Independent reflections ($F_o > 3\sigma|F_o|$)	3 726	3 151	2 954	3 082
$R(=\Sigma||F_o| - |F_c||/\Sigma|F_o|)$	0.072	0.064	0.066	0.071
$R'[(=\Sigma||F_o| - |F_c||^2/\Sigma|F_o|^2)^{\frac{1}{2}}]$	0.070	0.067	0.073	0.075

Figure 1. ORTEP view of $[CuL^{Bu^n}(NO_3)]^+$ (6)

Table 4. Atomic co-ordinates ($\times 10^4$) for (6)

Atom	x	y	z
Cu	4 982(1)	−48(1)	1 131(1)
N(1B)	6 116(6)	1 612(4)	1 546(6)
O(1B)	5 625(4)	933(3)	773(4)
O(2B)	6 065(5)	1 560(4)	2 297(5)
O(3B)	6 603(7)	2 276(4)	1 489(6)
N(1)	6 640(5)	−785(4)	2 218(5)
N(2)	7 615(5)	−2 154(4)	3 153(5)
C(1)	6 467(6)	−1 639(4)	2 376(6)
C(2)	8 029(6)	−708(4)	2 956(5)
C(3)	8 779(6)	43(5)	3 154(6)
C(4)	10 171(6)	−118(6)	3 969(6)
C(5)	10 765(7)	−989(6)	4 556(7)
C(6)	10 028(7)	−1 737(5)	4 365(7)
C(7)	8 629(6)	−1 567(5)	3 537(6)
N(3)	3 119(5)	392(4)	14(5)
N(4)	1 053(5)	60(4)	−889(5)
C(8)	2 313(6)	−260(4)	−215(6)
C(9)	2 354(6)	1 205(5)	−542(6)
C(10)	2 673(7)	2 094(5)	−608(6)
C(11)	1 657(7)	2 764(5)	−1 243(7)
C(12)	359(7)	2 551(5)	−1 773(7)
C(13)	32(7)	1 671(5)	−1 716(6)
C(14)	1 046(6)	996(5)	−1 104(6)
N(5)	4 320(5)	−1 132(3)	1 442(5)
C(15)	5 097(6)	−1 987(4)	1 725(6)
C(16)	2 811(6)	−1 238(5)	248(7)
C(17)	4 513(7)	−895(5)	2 509(7)
C(18)	5 884(9)	−475(6)	3 653(8)
C(19)	5 855(11)	−184(7)	4 593(9)
C(20)	6 638(16)	577(10)	5 334(14)
N(1C)	1 682(5)	578(4)	1 564(5)
O(1C)	2 562(5)	973(4)	1 716(5)
O(2C)	902(5)	1 064(4)	1 472(5)
O(3C)	1 555(6)	−274(4)	1 466(6)

As shown in Figures 1 and 5, the copper(II) co-ordination sphere of (6) consists of three nitrogen atoms of L^{Bu^n} [N(1), N(3), and N(5)] and two oxygen atoms of the bidentate nitrate ion [O(1B) and O(2B)]. The co-ordination geometry of (6) can be regarded as a highly distorted square pyramid whose basal plane is formed by N(1), N(3), N(5), and O(1B). The bidentate nitrate ion forms a weak co-ordination bond [Cu–O(2B), 2.631(5) Å] and an acute O(1B)–Cu–O(2B) angle [53.5(3)°]. A similar bidentate co-ordination of a nitrate ion was reported for $[Cu(bipy)_2(NO_3)]NO_3$ (bipy = 2,2'-bipyridine).[35]

As seen in Figures 3—5, the co-ordination structures of (9) and (5) are similar to each other. Their co-ordination geometries can be described as a highly distorted octahedron

with two axial co-ordination bonds [Cu–O(2B) and Cu–O(1A)]. In particular, (5) and (9) have the same space group (Pbca), similar unit-cell dimensions (see Table 3), and similar bond distances and angles (Table 8).

As illustrated in Figure 5, O(2B) and the substituent alkyl group in complexes (6), (9), (5), and (10) are located on the same

side of the basal, or equatorial, plane of the co-ordination sphere. In the case of (7), however, O(2B) is located on the opposite site to the Bu^i group. The methyl carbon atom of the

Bu^i group [C(19)] is in a proximal position to the copper(II) ion [Cu–C(19), 3.31 Å].

The co-ordination bond lengths of copper–benzimidazole

Table 5. Atomic co-ordinates ($\times 10^4$) for (7)

Atom	x	y	z
Cu	1 152.2(3)	495(1)	2 856(1)
N(1B)	681(2)	65(3)	668(7)
O(1B)	635(2)	−108(3)	1 876(6)
O(2B)	960(2)	547(4)	282(8)
O(3B)	456(2)	−319(4)	−282(7)
N(1)	847(2)	1 504(3)	3 311(6)
N(2)	936(3)	2 773(4)	4 119(7)
C(1)	1 112(3)	2 001(4)	4 046(7)
C(2)	477(3)	1 950(4)	2 858(8)
C(3)	106(3)	1 723(5)	2 047(9)
C(4)	−208(3)	2 324(6)	1 764(11)
C(5)	−154(3)	3 133(6)	2 255(11)
C(6)	213(3)	3 364(5)	3 074(10)
C(7)	527(3)	2 757(5)	3 358(8)
N(3)	1 595(2)	−362(3)	2 612(5)
N(4)	2 293(2)	−788(3)	3 092(6)
C(8)	1 971(2)	−224(4)	3 305(7)
C(9)	1 671(2)	−1 090(4)	1 839(6)
C(10)	1 380(3)	−1 537(4)	948(8)
C(11)	1 562(3)	−2 243(5)	371(9)
C(12)	2 010(3)	−2 501(6)	671(9)
C(13)	2 292(3)	−2 067(5)	1 580(8)
C(14)	2 102(2)	−1 358(4)	2 148(7)
N(5)	1 568(2)	834(3)	4 554(6)
C(15)	1 561(3)	1 757(4)	4 597(9)
C(16)	2 036(3)	520(4)	4 229(8)
C(17)	1 401(4)	537(5)	5 993(8)
C(18)	1 317(4)	−397(6)	6 056(9)
C(19)	832(5)	−583(8)	5 668(14)
C(20)	1 440(5)	−685(7)	7 566(11)
N(1C)	1 943(2)	1 234(4)	486(7)
O(1C)	1 887(2)	1 398(4)	−794(6)
O(2C)	1 693(2)	1 557(3)	1 384(6)
O(3C)	2 249(2)	775(4)	850(7)

Table 6. Atomic co-ordinates ($\times 10^4$) for (9)

Atom	x	y	z
Cu	3 602(1)	2 660.4(4)	317(1)
O(1A)	2 333(4)	2 709(3)	1 129(4)
C(1A)	1 734(7)	2 189(6)	1 276(7)
N(1B)	3 542(5)	3 210(3)	−1 158(4)
O(1B)	2 997(4)	3 166(3)	−581(3)
O(2B)	4 262(4)	2 953(3)	−1 078(3)
O(3B)	3 300(6)	3 518(3)	−1 774(3)
N(1)	3 351(4)	1 696(3)	−25(3)
N(2)	3 408(4)	540(3)	298(4)
C(1)	3 541(5)	1 217(4)	535(4)
C(2)	3 088(5)	1 300(4)	−688(4)
C(3)	2 813(5)	1 535(4)	−1 450(5)
C(4)	2 591(6)	998(5)	−2 003(5)
C(5)	2 640(6)	269(5)	−1 791(5)
C(6)	2 913(6)	36(4)	−1 038(4)
C(7)	3 124(5)	579(4)	−498(4)
N(3)	3 926(4)	3 508(3)	909(3)
N(4)	4 537(5)	3 931(3)	2 020(4)
C(8)	4 245(5)	3 352(4)	1 620(4)
C(9)	4 017(5)	4 245(4)	808(5)
C(10)	3 791(5)	4 686(4)	162(5)
C(11)	3 983(6)	5 407(4)	247(6)
C(12)	4 394(6)	5 666(5)	953(7)
C(13)	4 611(6)	5 228(5)	1 596(6)
C(14)	4 404(5)	4 512(4)	1 514(5)
N(5)	4 361(4)	2 127(3)	1 220(3)
C(15)	3 879(6)	1 445(4)	1 354(4)
C(16)	4 253(6)	2 611(4)	1 938(4)
C(17)	5 304(5)	2 006(4)	1 013(5)
C(18)	5 369(6)	1 544(5)	250(5)
C(19)	5 757(6)	2 716(5)	837(6)
C(20)	5 772(7)	1 615(6)	1 706(6)
N(1C)	969(5)	4 156(4)	1 484(4)
O(1C)	1 659(4)	4 184(3)	1 102(3)
O(2C)	742(5)	3 578(3)	1 780(4)
O(3C)	522(5)	4 681(4)	1 562(4)

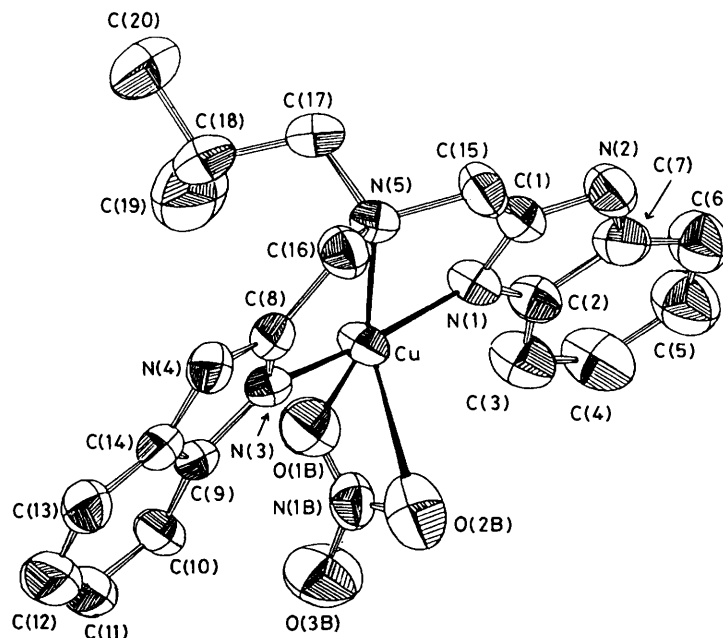**Figure 2.** ORTEP view of [CuL$^{Bu^i}$(NO$_3$)]$^+$ (7)

nitrogen atoms [N(1) and N(3)] (1.90—1.96 Å) fall in the range of those already reported for copper(II) complexes with benzimidazole-containing ligands.[29,36] The Cu–O(1B) and Cu–O(2B) bond lengths fall in the range 1.96—2.04 Å and 2.48—2.64 Å, respectively. The Cu–O(1A) distances decrease in the order (9) > (5) > (10) with consequent increase of the *trans*

Cu–O(2B) bond length. The bond distances and angles around N(5) seem to be affected by the alkyl group. The Cu–N(5) and N(5)–C(17) distances, except for those of (10), increase in the order (6) < (5) < (9). In the case of (9), the angles of Cu–N(5)–C(15), Cu–N(5)–C(16), and Cu–N(5)–C(17) differ remarkably from those of the other complexes.

The intermolecular contacts and the stacking modes of benzimidazole rings for (6) and (9) are shown in Figures 6—8. As seen in Figure 6, the two complex cations of (6) form a loosely bound dimeric unit, having an inversion centre. This situation is very similar to that in [Cu(bbt)X]ClO₄ observed by Nishida *et al.*[29] {bbt = 2-[bis(benzimidazol-2-ylmethyl)amino]ethanol, X = Cl or Br}. In the dimeric unit, there are contacts between copper(II) ions and nitrate oxygen atoms [Cu–O(1B′) and O(1B)–Cu′], which might be regarded as very weak co-ordination bonds since the distance (2.717 Å) is

Table 7. Atomic co-ordinates ($\times 10^4$) for (5)

| Atom	x	y	z
Cu	285.3(4)	1 466.9(4)	2 350.2(3)
O(1A)	1 074(3)	2 787(3)	2 308(3)
C(1A)	1 445(6)	3 315(5)	2 821(5)
N(1B)	−1 204(3)	1 497(4)	1 726(2)
O(1B)	−597(3)	2 045(3)	1 791(2)
O(2B)	−1 132(3)	777(3)	2 006(2)
O(3B)	−1 825(3)	1 736(4)	1 404(3)
N(1)	−141(3)	1 724(3)	3 294(2)
N(2)	72(3)	1 631(3)	4 457(3)
C(1)	370(3)	1 500(4)	3 799(3)
C(2)	−860(3)	2 021(4)	3 640(3)
C(3)	−1 593(4)	2 349(4)	3 367(3)
C(4)	−2 190(4)	2 608(5)	3 865(4)
C(5)	−2 044(4)	2 544(5)	4 597(4)
C(6)	−1 314(4)	2 228(5)	4 869(3)
C(7)	−724(4)	1 967(4)	4 369(3)
N(3)	958(3)	1 086(3)	1 554(2)
N(4)	2 096(3)	403(4)	1 202(3)
C(8)	1 664(4)	736(4)	1 750(3)
C(9)	912(4)	991(4)	816(3)
C(10)	293(4)	1 233(4)	335(3)
C(11)	422(5)	1 016(5)	−365(4)
C(12)	1 148(5)	557(5)	−578(4)
C(13)	1 762(5)	319(4)	−106(4)
C(14)	1 626(4)	557(4)	596(3)
N(5)	1 132(3)	706(3)	2 928(2)
C(15)	1 229(4)	1 169(4)	3 620(3)
C(16)	1 915(4)	708(4)	2 505(3)
C(17)	773(5)	−214(4)	3 055(4)
C(18)	581(3)	−678(4)	2 368(4)
C(19)	1 363(6)	−774(5)	3 515(5)
N(1C)	1 147(3)	4 190(4)	881(3)
O(1C)	1 424(3)	4 479(4)	1 438(3)
O(2C)	683(4)	3 537(4)	899(3)
O(3C)	1 313(4)	4 526(5)	313(3)
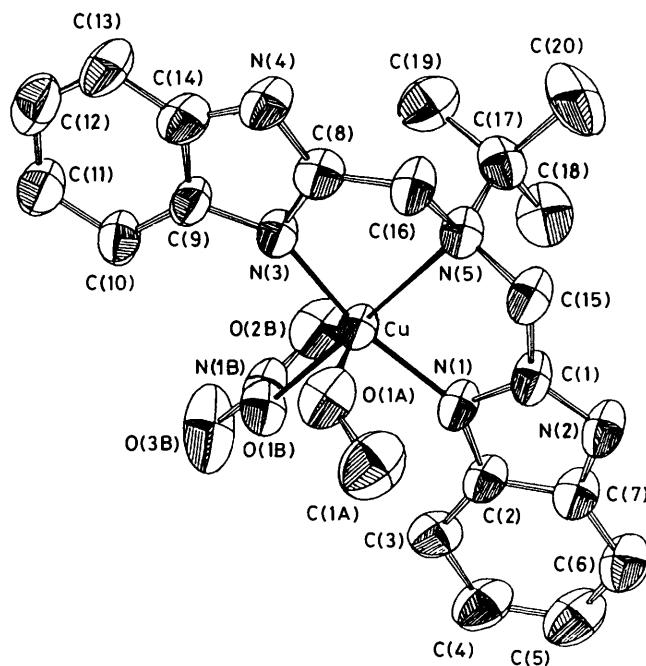
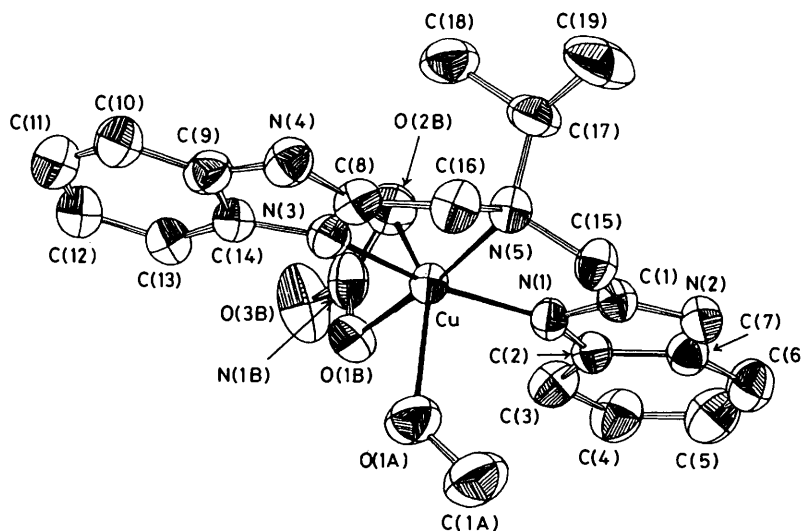**Figure 3.** ORTEP view of [CuL$^{Bu^i}$(NO₃)(MeOH)]⁺ (9)

Figure 4. ORTEP view of [CuL$^{Pr^i}$(NO₃)(MeOH)]⁺ (5)

Table 8. Selected bond distances (Å) and angles (°) in the co-ordination sphere of compounds (6), (7), (9), (5), and (10) with estimated standard deviations in parentheses

Complex	(6)	(7)	(9)	(5)	(10)
Cu–N(1)	1.942(5)	1.928(6)	1.932(6)	1 953(4)	1.943(5)
Cu–N(3)	1.946(5)	1.932(5)	1.916(6)	1.945(5)	1.940(6)
Cu–N(5)	2.068(7)	2.087(6)	2.138(6)	2.102(5)	2.109(6)
Cu–O(1A)			2.461(6)	2.390(5)	2.266(6)
Cu–O(1B)	1.987(7)	2.038(6)	1.965(5)	1.982(4)	1.998(4)
Cu–O(2B)	2.631(5)	2.482(7)	2.493(6)	2.602(5)	2.637(5)
N(1)–Cu–N(3)	165.1(3)	164.6(2)	166.2(2)	164.6(2)	163.4(2)
N(1)–Cu–N(5)	82.6(3)	83.0(2)	82.5(2)	82.3(2)	82.7(2)
N(1)–Cu–O(1A)			89.5(2)	92.8(2)	84.8(2)
N(1)–Cu–O(1B)	95.7(3)	99.5(2)	98.4(2)	98.3(2)	97.4(2)
N(1)–Cu–O(2B)	98.9(2)	94.5(2)	93.5(2)	90.0(2)	85.8(2)
N(3)–Cu–N(5)	83.0(3)	83.4(2)	84.7(2)	82.7(2)	82.0(2)
N(3)–Cu–O(1A)			88.0(2)	86.0(2)	93.2(2)
N(3)–Cu–O(1B)	98.4(3)	95.9(2)	94.9(2)	97.0(2)	99.2(2)
N(3)–Cu–O(2B)	93.4(2)	93.7(2)	96.4(2)	100.1(2)	104.1(2)
N(5)–Cu–O(1A)			100.8(2)	98.0(2)	105.4(2)
N(5)–Cu–O(1B)	176.1(3)	156.1(2)	174.5(2)	172.7(2)	157.2(2)
N(5)–Cu–O(2B)	130.2(3)	150.3(2)	114.5(2)	118.4(2)	104.2(2)
O(1A)–Cu–O(1B)			84.7(2)	89.3(2)	97.2(2)
O(1A)–Cu–O(2B)			144.7(2)	143.4(2)	147.5(2)
O(1B)–Cu–O(2B)	53.5(3)	53.6(2)	60.0(2)	54.3(2)	53.3(2)
Cu–O(1A)–C(1A)			131.5(6)	134.0(5)	131.0(7)
Cu–O(1B)–N(1B)	109.0(6)	103.4(5)	99.7(4)	107.7(3)	108.4(4)
Cu–O(2B)–N(1B)	79.6(4)	80.8(5)	76.0(4)	80.0(3)	79.1(3)
O(1B)–N(1B)–O(2B)	117.8(7)	122.0(7)	124.2(6)	117.9(5)	118.8(5)
Distances and angles around N(5)					
N(5)–C(15)	1.498(9)	1.512(9)	1.52(1)	1.495(8)	1.497(9)
N(5)–C(16)	1.507(6)	1.51(1)	1.451(9)	1.496(8)	1.494(8)
N(5)–C(17)	1.51(1)	1.52(1)	1.62(1)	1.542(8)	1.513(9)
C(15)–N(5)–C(16)	111.8(5)	111.0(6)	110.9(6)	112.3(4)	111.1(5)
C(15)–N(5)–C(17)	111.8(5)	106.9(6)	114.8(6)	109.6(5)	112.7(6)
C(16)–N(5)–C(17)	107.8(8)	111.7(6)	111.1(6)	113.7(5)	112.8(5)
Cu–N(5)–C(15)	108.2(6)	106.1(4)	99.9(5)	105.0(3)	107.1(4)
Cu–N(5)–C(16)	106.7(5)	107.2(4)	98.0(4)	105.7(3)	106.3(4)
Cu–N(5)–C(17)	110.3(4)	113.7(5)	120.5(4)	110.0(4)	106.4(4)
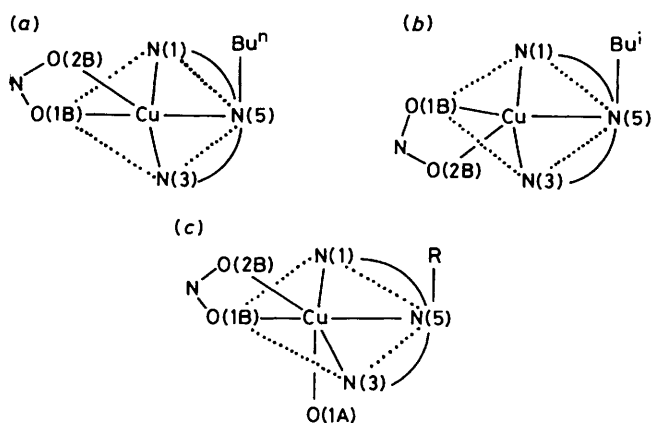
Figure 5. Illustration of the copper(ii) co-ordination spheres of (*a*) compound (6), (*b*) compound (7), and (*c*) compounds (9), (5), and (10)

close to that of the Cu–O(2B) co-ordination bond (2.631 Å). The benzimidazole rings, A and B′ (and B and A′) are stacked, with average interplane distance of 3.53 Å. From the above results, the dimerization is attributed to the intermolecular co-ordination bonds [Cu–O(1B′) and O(1B)–Cu′]. Furthermore, an attractive force operating between the stacked benzimidazole

rings cannot be disregarded, since the average interplane distance is nearly equal to those of [Cu(bbt)X]ClO₄,[29] which do not possess an interplane co-ordination bond in the bimolecular unit. The overlapping mode of the stacked benzimidazole rings is illustrated in Figure 7. This differs slightly from the mode in [Cu(bbt)X]ClO₄. Another stacking of benzimidazole rings is found between the rings A and A″ in Figure 7, and its overlapping mode is of a 'slipped' type.[37] The average interplane distance between A and A″ is 3.38 Å, being shorter than that between rings A and B′.

As shown in Figure 8, only the 'slipped' type of stacking between the rings B and B′ is observed in the crystal of (9). This may be due to steric hindrance of the methanol molecule. The stacking is also found in the crystal of (5), and the overlapping mode and average interplane distances between the stacked benzimidazole rings (3.55 Å) are almost the same as those of (9). No intermolecular contact between benzimidazole rings is observed for (7). This seems to be attributed to the very large dihedral angle between the two benzimidazole rings of L^{Bu^i} (18.8°), since the dihedral angles of the other complexes are less than 10° [8.2, 9.4, 9.8, and 6.9° for (6), (9), (5), and (10), respectively]. Thus, the unique molecular structure of this complex may contribute to the absence of the stacking of benzimidazole rings.

Magnetic and Spectroscopic Properties.—The copper(ii) complexes studied here show ordinary magnetic moments at
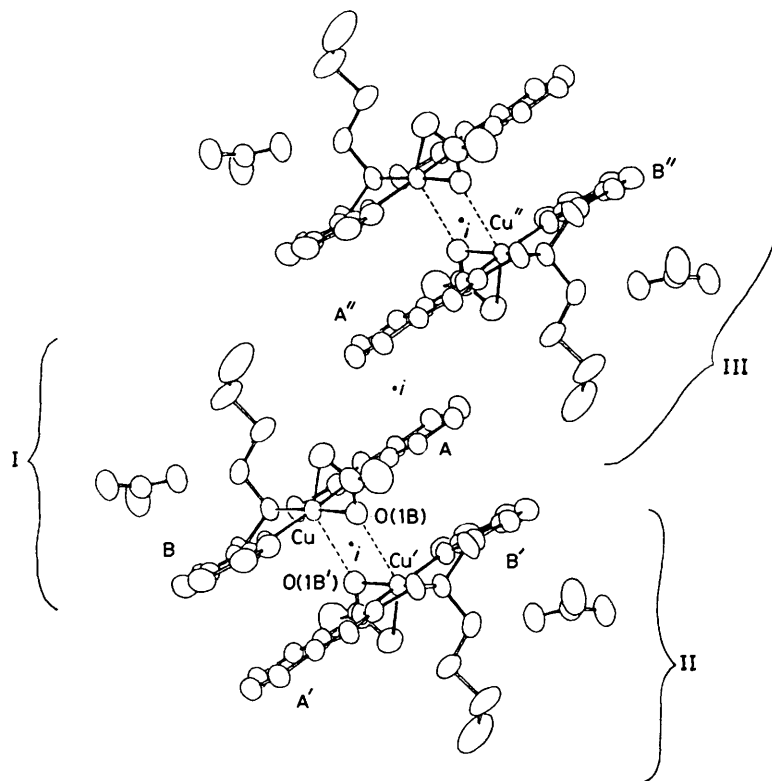
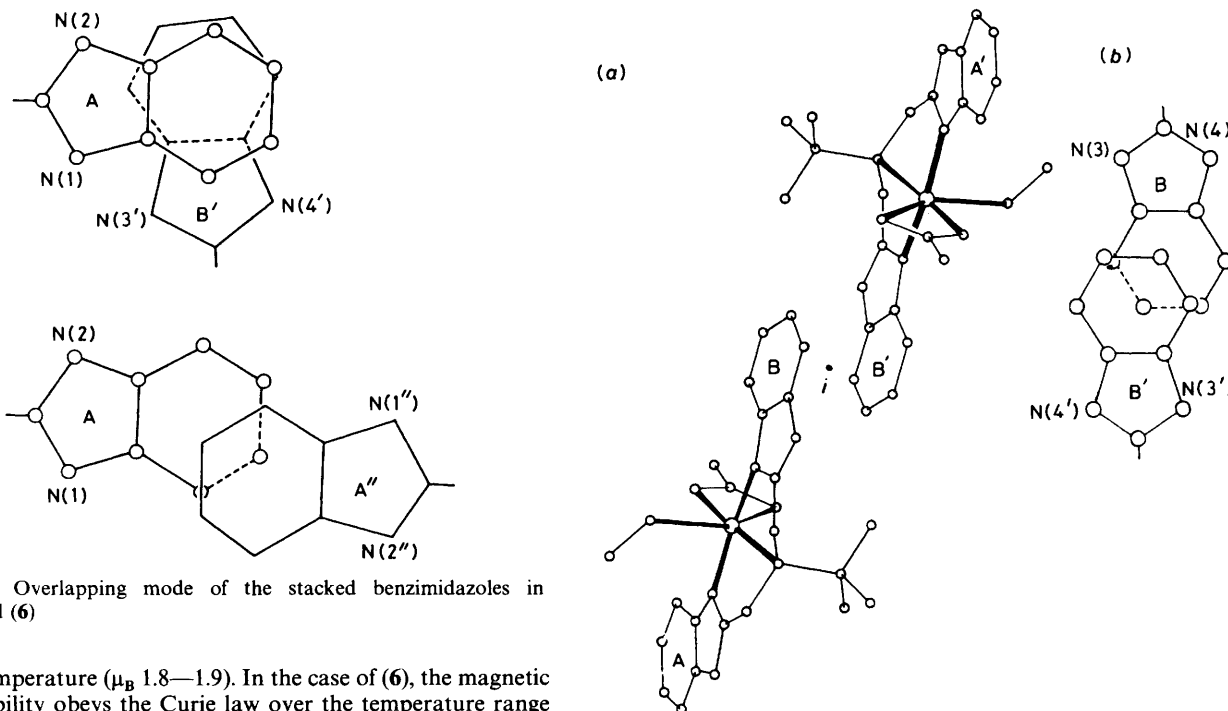**Figure 6.** ORTEP view of intermolecular contacts in the crystal of (6)

Figure 7. Overlapping mode of the stacked benzimidazoles in compound (6)

Figure 8. (a) Perspective view of intermolecular contacts in compound (9), and (b) overlapping mode of the stacked benzimidazole rings

room temperature (μ_B 1.8—1.9). In the case of (6), the magnetic susceptibility obeys the Curie law over the temperature range 90—295 K, giving $\theta = 0$, where θ denotes the Weiss constant.

The d–d bands of Nujol mull transmittance spectra of (1), (2), and (3) are similar to those of the six-co-ordinate complexes verified by X-ray analysis [(5), (9), and (10), see Table 9], and their band maxima are in the range (14.5—14.9) $\times$ 10^3 cm^{-1} (see Table 9). This suggests that the methanol molecule in each complex co-ordinates to the copper(II) ion, forming a six-co-ordinate complex. In the solid state, (4) and (8) are likely to be
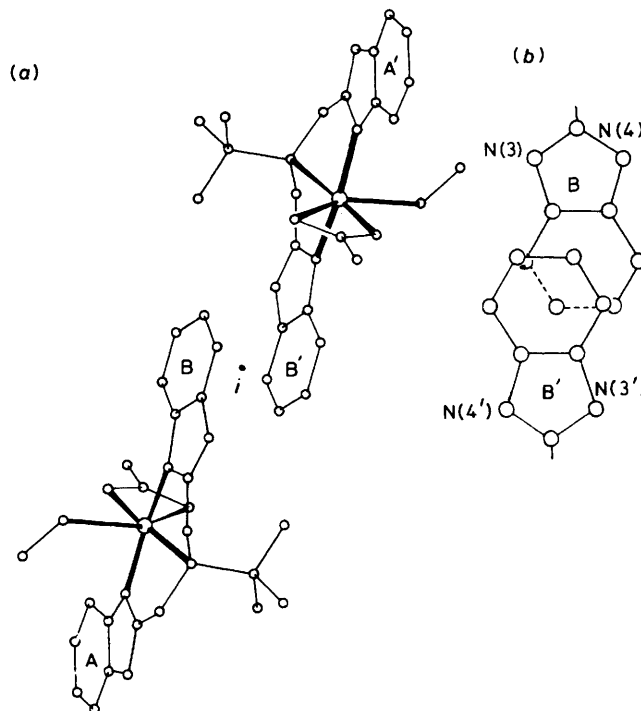
five-co-ordinate complexes, because their d–d bands are similar to those of (6) and (7) [band maxima (15.5—15.6) $\times$ 10^3 cm^{-1}]. The band maxima in the methanol solution are all observed in

Table 9. Effective magnetic moments, electronic spectra, electric conductance, and e.s.r. parameters of compounds

| Complex | $\mu_{eff}{}^{a}$ | d–d Peak/cm^{-1} ^{b,c} | | $\Lambda_{M}{}^{c,d}$ | E.s.r. parameters ^{c,e} | | |
		Nujol	MeOH solution		$g_{\parallel}$	$g_{\perp}$	$10^{-4}\lvert A_{\parallel}\rvert/cm^{-1}$
(1)	1.89	14.7	14.7(99)	127	2.272		160
(2)	1.85	14.9	14.6(107)	126	2.278	2.058	147
(3)	1.85	14.5	14.7(108)	118	2.281	2.058	142
(4)	1.82	15.6	14.7(111)	111	2.277	2.058	140
(5)	1.84	14.9	14.7(112)	102	2.279	2.057	129
(6)	1.83	15.5	14.7(107)	111	2.277	2.056	142
(7)	1.83	15.6	14.6(106)	117	2.281	2.058	141
(8)	1.84	15.4	14.6(113)	101	2.281	2.058	129
(9)	1.84	14.6	14.6(105)	97	2.286	2.059	110
(10)	1.85	14.5	14.6(105)	114	2.285	2.057	140

^{a} μ_{eff} at 295 K. ^{b} Molar absorption coefficient (ϵ/mol^{-1} cm^{2}) in parentheses. ^{c} Methanol solution at 1×10^{-3} mol dm^{-3}. ^{d} Λ_{M} (at 25 ± 1 °C) in Ω^{-1} cm^{2} mol^{-1}. ^{e} Frozen methanol solution at liquid nitrogen temperature.
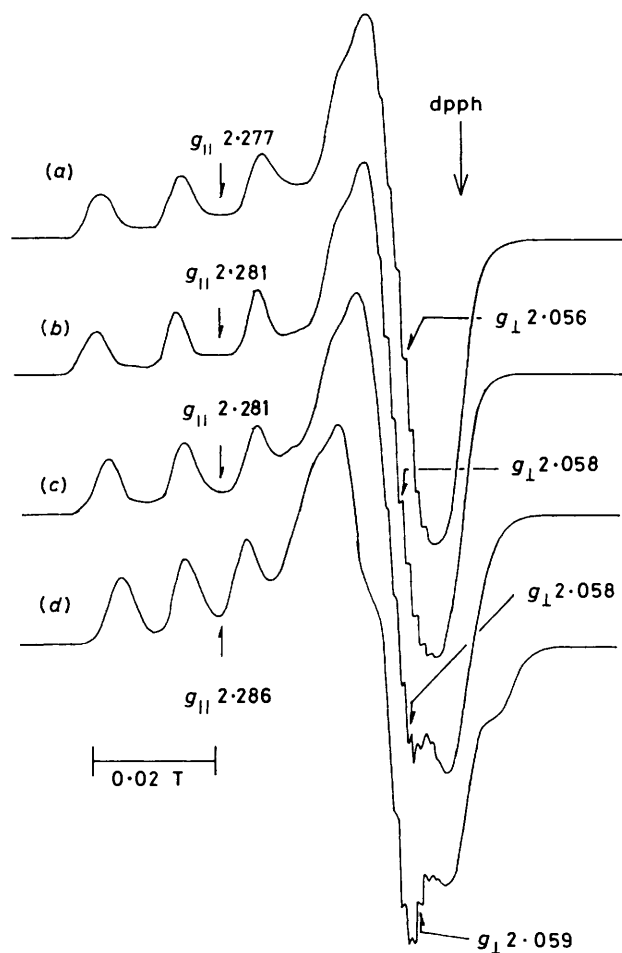

Figure 9. E.s.r. spectra (methanol solution, 77 K): (a) compound (6), (b) compound (7), (c) compound (8), and (d) compound (9) (dpph = diphenylpicrylhydrazyl)

Figure 10. Trend observed between $\lvert A_{\parallel}\rvert$ value and Cu–N(5) bond distance

the range (14.6—14.7) $\times$ 10^{3} cm^{-1}, similar to those of the solid-state spectra of the six-co-ordinate complexes.

The molar conductivities (Λ_{M} 97—127 Ω^{-1} cm^{2} mol^{-1}) indicate that the complexes are 1:1 electrolytes in methanol,[38] suggesting that one of the two nitrate ions in each complex co-ordinates to the copper(II) ion. The absorption spectral and electrical conductance data at the same concentration (1×10^{-3}
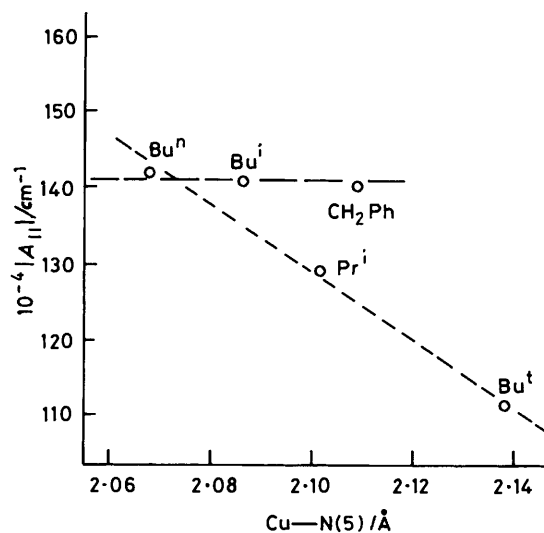
mol dm^{-3}) suggest that the co-ordination number of all the complexes is six with a composition of $[CuL^{R}(NO_{3})(MeOH)]^{+}$.

E.S.R. Spectra.—E.s.r. spectra in frozen methanol solutions of complexes (6), (7), (8), and (9) are shown in Figure 9, and the parameters are summarized in Table 9. The spectral patterns of all the complexes ($g_{\parallel} > 2.1 > g_{\perp} > 2.0$) indicate that copper(II) ions are in the $(3d_{x^{2}-y^{2}})^{1}$ ground state due to tetragonal symmetry.[39] Seven hyperfine lines ($\lvert A_{N}\rvert = 1.2$ mT) due to the nuclear spin of three nitrogen atoms ($I = 1$) of the ligand are observed in the $g_{\parallel}$ region, except for complex (1). The spectral shapes of (2), (3), and (10) are similar to that of (6). The spectra of (4) and (5) resemble those of (7) and (8), respectively. The $g_{\parallel}$ values are in the range 2.272—2.286, not varying throughout the series. In contrast, $\lvert A_{\parallel}\rvert$ values decrease markedly in the order, (1) > (2) > (3), (4), (6), (7) and (10) > (5), (8) > (9), with increase of the bulkiness of the substituent groups on the aliphatic amine nitrogen atom; *i.e.*, H < Me < non-α-branched group (Et, Pr^{n}, Bu^{n}, Bu^{i}) < α-branched group (Pr^{i}, Bu^{s}) < three-α-branched (Bu^{t}). In the case of (6), (7), (9), (5), and (10), a trend is observed between $\lvert A_{\parallel}\rvert$ values and Cu–N(5) distance, as shown in Figure 10. There is also trend between the $\lvert A_{\parallel}\rvert$ value and the average angles of Cu–N(5)–C(15) and Cu–N(5)–C(16), as illustrated in Figure 11. The largest
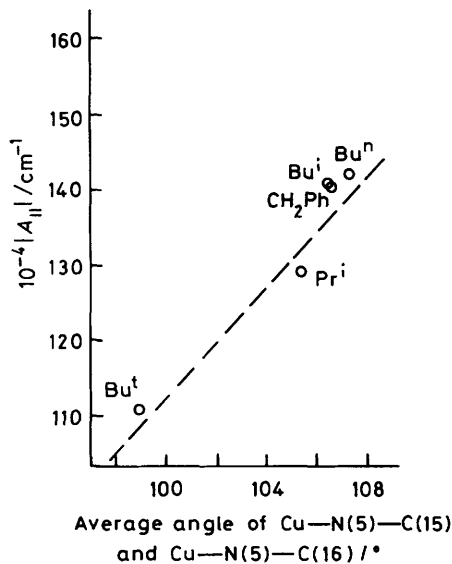
Figure 11. Trend observed between $|A_{\parallel}|$ value and the average angle of Cu–N(5)–C(15) and Cu–N(5)–C(16)

distortion around the N(5) atom was observed for complex (9) which has the smallest $|A_{\parallel}|$ value, *i.e.* angle C(15)–N(5)–C(17) is far from 109° and Cu–N(5)–C(17) is the largest among the complexes studied here. Based on the above discussion, we may assume that the orientation of the lone pair orbital of the N(5) atom is one of the most important factors in controlling the $A_{\parallel}$ value for the present complexes.

As shown in Table 1, the distorted tetrahedral copper(II) complexes show larger $g_{\parallel}$ values and smaller $|A_{\parallel}|$ values than those of the square-planar complexes. This has been attributed to a change in the Fermi contact constant due to the mixing of d_{z^2} and $4s$ orbitals in the tetrahedral symmetry, as pointed out by Yokoi and Addison.[16a] In this study, however, the remarkable change in $A_{\parallel}$ values was observed irrespective of the change in $g_{\parallel}$ value, the behaviour being greatly different from that discussed by Yokoi and Addison. Although the intrinsic origin for the present result is not known at present, our data provide an important key to the explanation of the very low $|A_{\parallel}|$ values for the blue copper proteins.

References

1 R. Malkin and B. G. Malmstrom, *Adv. Enzymol.*, 1970, 33, 177.
2 J. A. Fee, *Struct. Bonding (Berlin)*, 1975, 23, 1.
3 E. I. Solomon, K. W. Penfield, and D. E. Wilcox, *Struct. Bonding (Berlin)*, 1983, 53, 1.
4 J. M. Guss and H. C. Freeman, *J. Mol. Biol.*, 1983, 169, 521.
5 G. E. Norris, B. F. Anderson, and E. N. Baker, *J. Am. Chem. Soc.*, 1986, 108, 2784.
6 E. I. Solomon, J. W. Hare, and H. B. Gray, *Proc. Natl. Acad. Sci. USA*, 1976, 73, 1389.
7 D. R. McMillan, *Bioinorg. Chem.*, 1978, 8, 179.
8 E. I. Solomon, J. W. Hare, D. M. Dooley, J. H. Dawson, P. J. Stephens, and H. B. Gray, *J. Am. Chem. Soc.*, 1980, 102, 168.
9 K. W. Penfield, R. R. Gay, R. S. Himmelwright, N. C. Eickman, V. A. Norris, H. C. Freeman, and E. I. Solomon, *J. Am. Chem. Soc.*, 1981, 103, 4382.
10 D. L. Tennet and D. R. McMillan, *J. Am. Chem. Soc.*, 1979, 101, 2507; D. R. McMillan and M. C. Morris, *Proc. Natl. Acad. Sci. USA*, 1981, 78, 6567.
11 G. S. Patterson and R. H. Holm, *Bioinorg. Chem.*, 1975, 4, 257.
12 R. D. Bereman, J. R. Dorfman, J. Bordner, D. P. Rilleman, P. McCarthy, and G. D. Shields, *J. Inorg. Biochem.*, 1982, 16, 47.
13 R. D. Bereman, M. R. Churchill, and G. D. Shields, *Inorg. Chem.*, 1979, 18, 3117.
14 D. E. Nikles, M. J. Powers, and F. L. Urbach, *Inorg. Chim. Acta*, 1979, 37, L499.
15 J. S. Thompson, T. J. Marks, and J. A. Ibers, *Proc. Natl. Acad. Sci. USA*, 1977, 74, 3114; *J. Am. Chem. Soc.*, 1979, 101, 4180.
16 (a) H. Yokoi and A. W. Addison, *Inorg. Chem.*, 1977, 16, 1341; (b) A. W. Addison, T. N. Rao, and E. Sinn, *ibid.*, 1984, 23, 1957.
17 K. D. Karlin and J. Zubieta, *Inorg. Perspect. Biol. Med.*, 1979, 2, 127.
18 P. W. R. Corfiels, C. Ceccarelli, M. D. Glick, I. W. May, L. A. Ochrymowycz, and D. B. Rorabacher, *J. Am. Chem. Soc.*, 1985, 107, 2399.
19 W. E. Blumberg and J. Peisach, *Biochim. Biophys. Acta*, 1966, 126, 269.
20 A. S. Brill, G. Bryce, and H. J. Maria, *Biochim. Biophys. Acta*, 1969, 154, 342.
21 B. G. Malmostrom, B. Reinhammer, and T. Vanngard, *Biochim. Biophys. Acta*, 1970, 205, 48.
22 A. Marechesini, M. Minell, H. Merkle, and P. M. H. Kroneck, *Eur. J. Biochem.*, 1979, 101, 77.
23 U. Sakaguchi and A. W. Addison, *J. Chem. Soc., Dalton Trans.*, 1979, 600.
24 H. Yokoi, *Bull. Chem. Soc. Jpn.*, 1974, 47, 3037.
25 Y. Murakami, Y. Matsuda, and K. Sakata, *Inorg. Chem.*, 1971, 10, 1728.
26 R. C. Roseberg, C. A. Root, D. K. Bernstein, and H. B. Gray, *J. Am. Chem. Soc.*, 1975, 97, 2092.
27 F. G. Herring, D. J. Patmore, and A. Stone, *J. Chem. Soc., Dalton Trans.*, 1975, 711.
28 Y. Nishida, N. Oishi, and S. Kida, *Inorg. Chim. Acta*, 1979, 32, 7.
29 Y. Nishida, K. Takahashi, and S. Kida, *Mem. Fac. Sci. Kyushu Univ., Ser. C*, 1981, 13(1), 27; Y. Nishida, K. Takahashi, and S. Kida, *ibid.*, 1982, 13(2), 343; K. Takahashi, Y. Nishida, and S. Kida, *Polyhedron*, 1984, 3, 113.
30 P. Main, M. M. Woolfson, and G. Germain, 'Computer Program for the Automatic Solution of Crystal Structure,' Universities of York, England and Louvain, Belgium, 1971.
31 S. Kawano, *Rep. Comp. Cent. Kyushu Univ.*, 1980, 13, 39.
32 'Universal Crystallographic Computer Program System,' ed. T. Sakurai, The Crystallographic Society of Japan, Tokyo, 1967.
33 C. K. Johnson, Report No. 3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1965.
34 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
35 H. Nakai, *Bull. Chem. Soc. Jpn.*, 1980, 53, 1321.
36 A. W. Addison, P. J. Burke, K. Henrick, T. N. Rao, and E. Sinn, *Inorg. Chem.*, 1983, 22, 3645; J. V. Dagdigian, V. McKee, and C. A. Reed, *ibid.*, 1982, 21, 1332; V. McKee, M. Zvagulis, J. V. Dagdigian, M. G. Patch, and C. A. Reed, *J. Am. Chem. Soc.*, 1984, 106, 4765.
37 K. Aoki and H. Yamazaki, *J. Am. Chem. Soc.*, 1980, 102, 6878; B. E. Fischer and R. Bau, *Inorg. Chem.*, 1978, 17, 27.
38 W. J. Geary, *Coord. Chem. Rev.*, 1971, 7, 81.
39 B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, 1970, 5, 153.