X-Ray Evidence of Intermolecular Stacking Interactions in a Ternary Complex. Crystal and Molecular Structure † of the Complex Bis(*N*-benzyloxycarbonylglycinato)(2,2′-bipyridine)(propan-2-ol)-copper(II)

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The title compound, [Cu(bglyO)$_2$(bipy)(Pr^{i}OH)], crystallizes in the triclinic space group $P\bar{1}$ with four formula units in a cell of dimensions a = 22.199(11), b = 15.357(6), c = 10.223(4) Å, α = 103.78(3), β = 83.06(4), and γ = 88.89(4)°. The structure was solved by the heavy-atom method and refined by least-squares calculations to R = 0.095 for 3 437 counter data. It consists of two crystallographically independent, but chemically equivalent, Cu(bglyO)$_2$(bipy)(Pr^{i}OH) molecules, which are linked in dimeric units by hydrogen-bonding interactions. Each Cu atom shows a slightly distorted square-pyramidal five-co-ordination by the bidentate 2,2′-bipyridine (bipy) ligand and two *N*-benzyloxycarbonylglycinate (bglyO) ions in the equatorial plane, and by the propan-2-ol molecule in an apical position. The crystal packing is mainly determined by intermolecular stacking and hydrophobic interactions between 2,2′-bipyridine molecules and between phenyl groups, respectively. Its physical properties are also discussed in the light of its known crystal structure.

Being particularly interested in the donor properties of N-protected amino acids, where the protecting group is an acetyl, benzoyl, or tosyl group,[1] we have recently extended our previous investigations by studying the co-ordination ability of *N*-benzyloxycarbonyl-protected amino acids towards the copper(II) ion.[2] The complexes separated have dimeric structures with strong antiferromagnetic interactions between the copper(II) ions.[2]

In this paper we report a study on a mixed-ligand complex containing two different ligands with aromatic moieties, namely 2,2′-bipyridine and *N*-benzyloxycarbonylglycinate (bglyO) in order to provide evidence of intra- or intermolecular hydrophobic and stacking interactions. Such interactions, observed in solution [3] and in the solid state,[4–6] are considered very important; they enhance the stability of the ternary complexes and are responsible for the creation of distinct structural features.[3]

Experimental

Preparation of Bis(N-*benzyloxycarbonylglycinato*)(2,2′-*bipyridine*)(*propan*-2-*ol*)*copper*(II), [Cu(bglyO)$_2$(bipy)(Pr^{i}OH)].—A slight excess of 2,2′-bipyridine (bipy) was added to an aqueous methanolic (1 : 2) solution of [{Cu(bglyO)$_2$(H$_2$O)}$_2$],[2] the blue solution was concentrated at 70 °C, and then an equal amount of propan-2-ol was added. Blue crystals separated after 12 h (Found: C, 56.3; H, 5.2; N, 8.1; Pr^{i}OH, 8.5. Calc for $C_{33}H_{36}CuN_4O_9$: C, 56.9; H, 5.2; N, 8.1; Pr^{i}OH, 8.6%). Physical measurements were made as reported in ref. 1.

Carbon, hydrogen, and nitrogen were analysed with a C.Erba Elemental Analyser model 1106 by Mr. G. Pistoni. The propan-2-ol content was determined gravimetrically by thermogravimetric analysis with a Mettler TA 3000 instrument.

Table 1. Crystal data collection

(*a*) Crystal parameters [a] at 18 °C

Crystal system: triclinic	Space group: $P\bar{1}$ (C_i^1, no. 2)
a = 22.199(11) Å	α = 103.78(3)°
b = 15.357(6) Å	β = 83.06(4)°
c = 10.223(4) Å	γ = 88.89(4)°
U = 3 355.8 Å^3	Z = 4
Formula: $C_{33}H_{36}CuN_4O_9$	M = 696.22
D_m = 1.36 g cm^{-3} (flotation)	F(000) = 1 452
D_c = 1.38 g cm^{-3}	

(*b*) Data collection

Radiation: graphite-monochromated Mo-K_α (λ = 0.710 69 Å)
Reflections measured: $\pm h$, $\pm k$, $+l$
Scan type: ω—2θ
θ Range: 2—22°
Scan speed: 4.0° min^{-1}
Scan width: 1.5°
Background time: 10 s at beginning and end of the scan
Standards: 3 every 100 reflections (decrease in intensities of *ca.* 10%)
Collected reflections: 8 189
Observed reflections: 3 437 with $I > 2\sigma(I)$ [b]
Crystal size: ~0.20 × 0.15 × 0.04 mm
Absorption coefficient: 6.6 cm^{-1} (correction not applied)

[a] Unit-cell parameters and their e.s.d.s were derived from a least-squares fit to the setting angles of 24 automatically centred reflections (Mo-K_α radiation). [b] $\sigma(I)$ = (peak counts + total background counts)$^{\frac{1}{2}}$.

X-*Ray Data Collection*.—Single crystals suitable for *X*-ray analysis proved very difficult to grow, mainly because of their small thickness. A fragment of a large, plate crystal, sealed in a glass fibre was directly transferred, in a random orientation, to a Philips PW 1100 automated four-circle diffractometer. Details specific to unit-cell determination and data collection, which were carried out at room temperature using Mo-K_α

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† *Supplementary data available* (No. SUP 56002, 28 pp.): intermolecular interactions, bond distances and angles within the ligands, thermal parameters, least-squares planes, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Non-S.I. unit employed: B.M. = 9.274 × 10^{-24} J T^{-1}.

Table 2. Final atomic co-ordinates with e.s.d.s in parentheses

Atom *	x	y	z	Atom	x	y	z
Cu(1)	0.397 0(1)	0.419 7(2)	0.266 3(3)	Cu(2)	0.114 5(1)	0.604 5(2)	0.220 1(3)
N(1)	0.418 0(6)	0.359 3(10)	0.406 9(16)	N(5)	0.027 9(6)	0.605 5(10)	0.308 0(15)
C(1)	0.382 8(9)	0.316 0(14)	0.479 2(21)	C(31)	0.011 4(9)	0.599 5(13)	0.426 3(22)
C(2)	0.400 1(10)	0.272 2(14)	0.574 7(23)	C(32)	−0.054 8(9)	0.595 1(13)	0.485 7(21)
C(3)	0.465 6(10)	0.272 6(15)	0.592 5(23)	C(33)	−0.092 6(9)	0.594 5(13)	0.384 3(21)
C(4)	0.501 8(8)	0.320 8(13)	0.518 4(20)	C(34)	−0.076 8(9)	0.598 6(12)	0.255 2(19)
C(5)	0.479 9(8)	0.363 1(13)	0.428 8(20)	C(35)	−0.011 3(7)	0.604 7(10)	0.213 2(17)
N(2)	0.484 9(5)	0.449 1(10)	0.258 7(16)	N(6)	0.074 4(5)	0.616 6(10)	0.059 8(16)
C(6)	0.512 2(9)	0.496 1(14)	0.177 5(22)	C(36)	0.099 2(8)	0.630 3(13)	−0.055 3(21)
C(7)	0.577 6(10)	0.512 2(14)	0.175 3(22)	C(37)	0.068 6(9)	0.641 2(13)	−0.165 5(21)
C(8)	0.605 6(9)	0.479 6(14)	0.269 7(22)	C(38)	0.003 9(9)	0.640 1(14)	−0.136 3(22)
C(9)	0.579 2(8)	0.428 4(13)	0.351 8(20)	C(39)	−0.023 8(8)	0.626 8(12)	−0.018 5(19)
C(10)	0.513 8(8)	0.413 9(11)	0.342 1(18)	C(40)	0.009 3(7)	0.615 8(11)	0.088 3(17)
O(1)	0.311 5(5)	0.392 5(9)	0.302 6(14)	O(9)	0.194 0(4)	0.575 0(8)	0.109 0(12)
O(2)	0.296 9(5)	0.305 0(9)	0.098 8(15)	O(10)	0.160 2(4)	0.440 2(8)	0.038 4(14)
C(11)	0.281 6(9)	0.347 6(13)	0.212 0(23)	C(41)	0.200 2(8)	0.496 3(13)	0.036 0(19)
C(12)	0.210 2(8)	0.359 9(12)	0.280 5(19)	C(42)	0.261 1(8)	0.476 2(13)	−0.055 5(19)
N(3)	0.172 2(5)	0.305 4(10)	0.185 1(17)	N(7)	0.269 5(5)	0.382 3(10)	−0.118 8(16)
C(13)	0.160 5(9)	0.222 1(14)	0.197 0(21)	C(43)	0.247 1(9)	0.353 0(16)	−0.237 2(24)
O(3)	0.177 5(6)	0.186 8(11)	0.280 0(17)	O(11)	0.228 1(5)	0.397 3(10)	−0.308 2(16)
O(4)	0.123 5(5)	0.187 1(8)	0.103 7(14)	O(12)	0.252 0(5)	0.262 2(9)	−0.276 1(15)
C(14)	0.098 6(9)	0.099 0(14)	0.114 4(22)	C(44)	0.227 8(10)	0.218 3(15)	−0.399 7(24)
C(15)	0.034 5(5)	0.122 0(9)	0.196 7(15)	C(45)	0.169 0(5)	0.173 5(9)	−0.356 6(15)
C(16)	0.026 3(5)	0.153 8(9)	0.337 6(15)	C(46)	0.134 0(5)	0.200 4(9)	−0.229 7(15)
C(17)	−0.032 2(5)	0.174 4(9)	0.407 5(15)	C(47)	0.080 9(5)	0.157 4(9)	−0.202 3(15)
C(18)	−0.082 4(5)	0.163 2(9)	0.336 3(15)	C(48)	0.062 8(5)	0.087 3(9)	−0.301 7(15)
C(19)	−0.074 2(5)	0.131 4(9)	0.195 4(15)	C(49)	0.097 8(5)	0.060 4(9)	−0.428 6(15)
C(20)	−0.015 7(5)	0.110 8(9)	0.125 6(15)	C(50)	0.150 9(5)	0.103 4(9)	−0.456 0(15)
O(5)	0.377 0(4)	0.508 1(8)	0.164 1(13)	O(13)	0.145 6(5)	0.579 4(8)	0.375 9(12)
O(6)	0.366 0(4)	0.589 2(9)	0.373 5(14)	O(14)	0.202 5(5)	0.700 0(9)	0.425 9(15)
C(21)	0.362 3(8)	0.580 8(13)	0.254 5(23)	C(51)	0.185 9(9)	0.624 8(14)	0.437 2(19)
C(22)	0.338 0(9)	0.655 8(15)	0.197 0(22)	C(52)	0.219 0(8)	0.572 9(12)	0.525 3(19)
N(4)	0.320 3(6)	0.733 0(11)	0.301 8(20)	N(8)	0.268 1(6)	0.626 7(10)	0.589 9(16)
C(23)	0.363 4(11)	0.790 4(15)	0.358 1(24)	C(53)	0.257 6(10)	0.678 7(14)	0.705 2(24)
O(7)	0.417 7(6)	0.784 9(9)	0.299 7(15)	O(15)	0.211 1(6)	0.690 7(10)	0.790 7(15)
O(8)	0.343 9(6)	0.850 7(10)	0.467 8(17)	O(16)	0.307 4(5)	0.728 3(9)	0.740 2(15)
C(24)	0.381 6(10)	0.924 6(16)	0.518 5(24)	C(54)	0.303 9(9)	0.789 3(15)	0.873 5(23)
C(25)	0.384 2(9)	0.987 1(10)	0.422 5(16)	C(55)	0.286 6(7)	0.882 7(8)	0.867 8(17)
C(26)	0.329 9(9)	1.021 9(10)	0.394 7(16)	C(56)	0.250 1(7)	0.899 0(8)	0.773 5(17)
C(27)	0.331 2(9)	1.082 3(10)	0.311 9(16)	C(57)	0.231 4(7)	0.986 8(8)	0.776 6(17)
C(28)	0.386 7(9)	1.107 8(10)	0.256 8(16)	C(58)	0.249 1(7)	1.058 3(8)	0.874 1(17)
C(29)	0.440 9(9)	1.073 1(10)	0.284 5(16)	C(59)	0.285 6(7)	1.042 0(8)	0.968 5(17)
C(30)	0.439 7(9)	1.012 7(10)	0.367 4(16)	C(60)	0.304 4(7)	0.954 2(8)	0.965 4(17)
O(17)	0.417 5(6)	0.296 0(12)	0.091 1(19)	O(18)	0.127 9(5)	0.758 9(9)	0.282 9(13)
C(61)	0.458 4(12)	0.252 8(18)	−0.028 5(28)	C(64)	0.154 9(12)	0.807 3(18)	0.188 1(27)
C(62)	0.437 6(14)	0.165 8(22)	−0.117 4(34)	C(65)	0.193 5(13)	0.882 8(19)	0.261 1(29)
C(63)	0.520 0(13)	0.225 1(19)	0.024 3(30)	C(66)	0.104 5(16)	0.856 4(24)	0.141 2(37)

* Phenyl rings [C(15)—C(20), C(25)—C(30), C(45)—C(50), C(55)—C(60)] were treated as rigid groups of D_{6h} idealized geometry and C–C distances of 1.395 Å.

radiation, are reported in Table 1. During the total data collection, a decrease in the intensities of standard reflections of about 10% was observed, and an appropriate correction was applied. All data were corrected for Lorentz and polarization effects, but not for absorption in view of the small crystal size and absorption coefficient. The reflections having $I > 2\sigma(I)$ were denoted observed and used in the structure determination.

Solution and Refinement of the Structure.—The space group $P\bar{1}$ was assumed and confirmed by the structure analysis. The structure was solved by conventional Patterson and Fourier methods and refined isotropically by full-matrix least-squares calculations to $R = 0.159$ and $R' = 0.168$ ($w = 1.0$).* The structure was further refined with anisotropic thermal parameters for the Cu, O, and N atoms, and with the phenyl rings treated as rigid groups of D_{6h} idealized geometry (C–C 1.395 Å); because of the large number of atomic parameters, the atoms were subdivided into two groups, which were refined in alternate cycles. The model converged with $R = 0.095$ and $R' = 0.103$ [$w = 1/\sigma^2(F)$], with changes in parameters in the last cycle being 0.1σ or less. The weighting scheme showed no trend of $\Sigma w\Delta^2$ *vs.* $|F_o|$, sin θ, or Miller indices. The highest peaks (~0.7 e Å^{-3}) in a final difference-Fourier map appeared in positions consistent with those expected for hydrogen atoms, but none of these was included in the structure factor calculations. An attempt to refine the model in the non-centric space group $P1$ provided no significant improvement, and hence the poor agreement factor

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* The quantity minimized during the refinement was $\Sigma w(|F_o| - |F_c|)^2$, where w is the weighting factor. The unweighted and weighted residuals are defined as follows: $R = (\Sigma|F_o| - |F_c|)/\Sigma|F_o|$; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

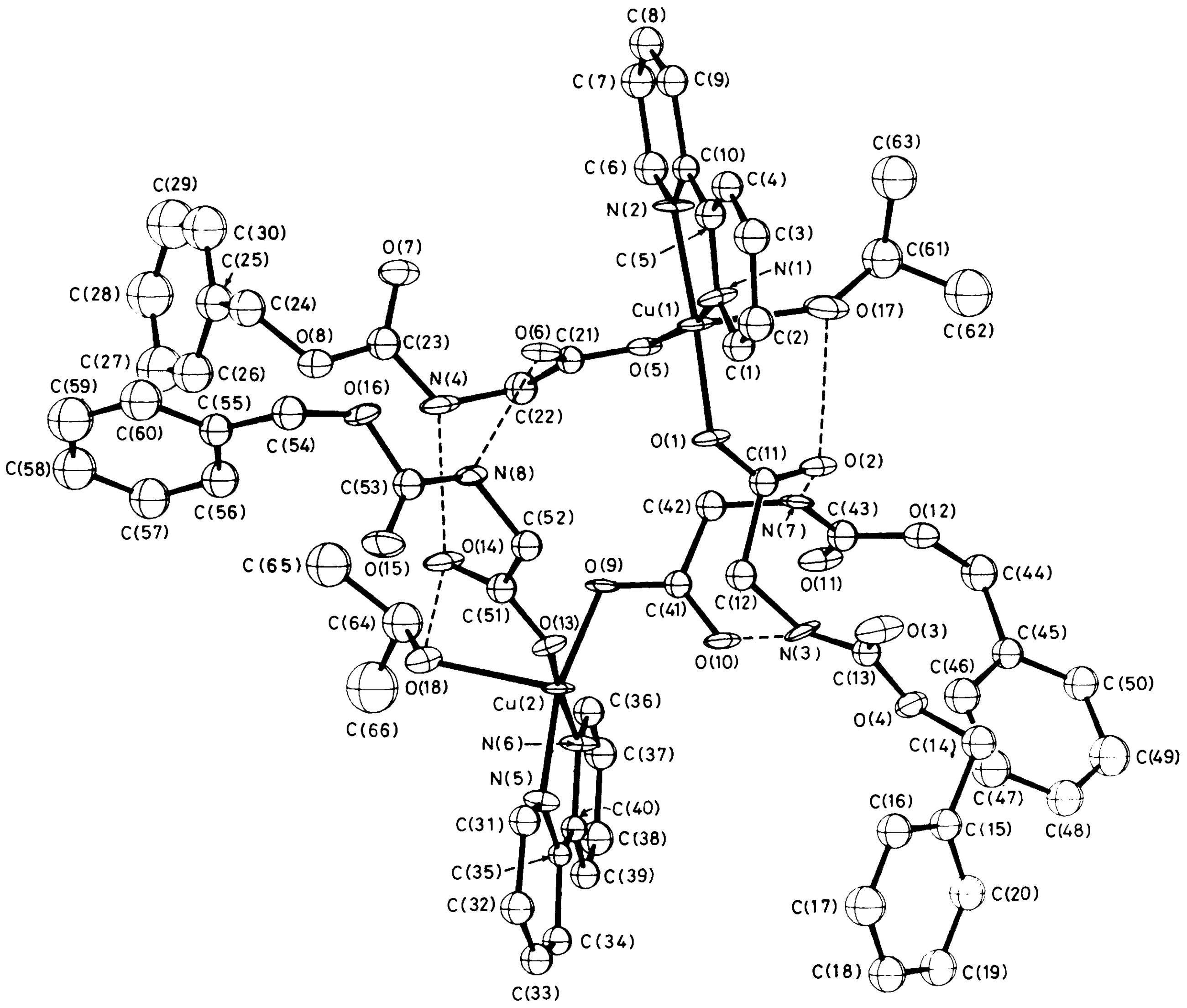

Figure 1. ORTEP view of the complex showing the atom numbering and thermal motion ellipsoids (25%). Hydrogen bonds are represented as dashed lines

was interpreted as due to the poor quality of the diffraction data.

Complex neutral-atom scattering factors [7] were employed throughout; major calculations were carried out on a Cyber 7600 computer, using the SHELX 76 program package [8] and the ORTEP plotting program.[9] The final atomic co-ordinates are reported in Table 2.

Results and Discussion

Interatomic distances and angles involving Cu atoms are given in Table 3, with atoms labelled as in Figure 1. The mean bond distances and bond angles for the four crystallographically independent bglyO ligands are reported in Figure 2. A packing diagram is shown in Figure 3.

The structure consists of two crystallographically independent, but chemically equivalent, Cu(bglyO)$_2$(bipy)(Pr^{i}OH) molecules, which are linked in dimeric units by four hydrogen-bonding interactions. Each Cu atom displays slightly distorted square-pyramidal five-co-ordination, arising from ligation by a bipy molecule (bidentate, through its N atoms) and two bglyO ions (unidentate, through the α-carboxylate O atoms) in the equatorial plane, and by a Pr^{i}OH molecule in an apical position. As expected for a square-pyramidal structure,[10] the metal atoms are displaced from the mean plane through their four basal atoms by 0.172 and 0.171 Å, respectively, toward the axial O atom. Both basal co-ordination planes show small tetrahedral distortions, with atomic deviations from the best-fit planes within ±0.081 Å. In both complex

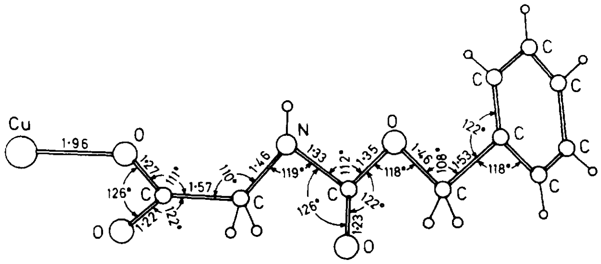

Figure 2. Average bond lengths (Å) and bond angles (°) for the four independently determined bglyO ligands

Table 3. Interatomic distances (Å) and angles (°) involving the Cu atoms

Cu(1)–N(1)	1.98(2)	Cu(2)–N(5)	2.02(1)	Cu(1)–O(5)	1.97(1)	Cu(2)–O(13)	1.93(1)
Cu(1)–N(2)	2.01(1)	Cu(2)–N(6)	2.00(2)	Cu(1)–O(17)	2.27(2)	Cu(2)–O(18)	2.34(1)
Cu(1)–O(1)	1.96(1)	Cu(2)–O(9)	1.96(1)	Cu(1) · · · O(6)	2.62(1)	Cu(2) · · · O(10)	2.84(1)
N(1)–Cu(1)–N(2)	82.6(6)	N(5)–Cu(2)–N(6)	83.1(6)	N(2)–Cu(1) · · · O(6)	89.6(5)	N(6)–Cu(2) · · · O(10)	81.7(5)
N(1)–Cu(1)–O(1)	90.3(6)	N(5)–Cu(2)–O(9)	166.1(5)	O(1)–Cu(1)–O(5)	92.4(5)	O(9)–Cu(2)–O(13)	91.9(5)
N(1)–Cu(1)–O(5)	165.1(5)	N(5)–Cu(2)–O(13)	91.5(6)	O(1)–Cu(1)–O(17)	99.5(6)	O(9)–Cu(2)–O(18)	94.9(5)
N(1)–Cu(1)–O(17)	95.0(7)	N(5)–Cu(2)–O(18)	98.1(5)	O(1)–Cu(1) · · · O(6)	88.5(4)	O(9)–Cu(2) · · · O(10)	50.7(5)
N(1)–Cu(1) · · · O(6)	110.7(5)	N(5)–Cu(2) · · · O(10)	115.6(5)	O(5)–Cu(1)–O(17)	99.5(6)	O(13)–Cu(2)–O(18)	94.9(5)
N(2)–Cu(1)–O(1)	171.5(6)	N(6)–Cu(2)–O(9)	92.0(5)	O(5)–Cu(1) · · · O(6)	54.8(5)	O(13)–Cu(2) · · · O(10)	95.2(5)
N(2)–Cu(1)–O(5)	93.3(6)	N(6)–Cu(2)–O(13)	171.9(6)	O(17)–Cu(1) · · · O(6)	154.2(6)	O(18)–Cu(2) · · · O(10)	144.3(6)
N(2)–Cu(1)–O(17)	92.1(5)	N(6)–Cu(2)–O(18)	91.8(6)				

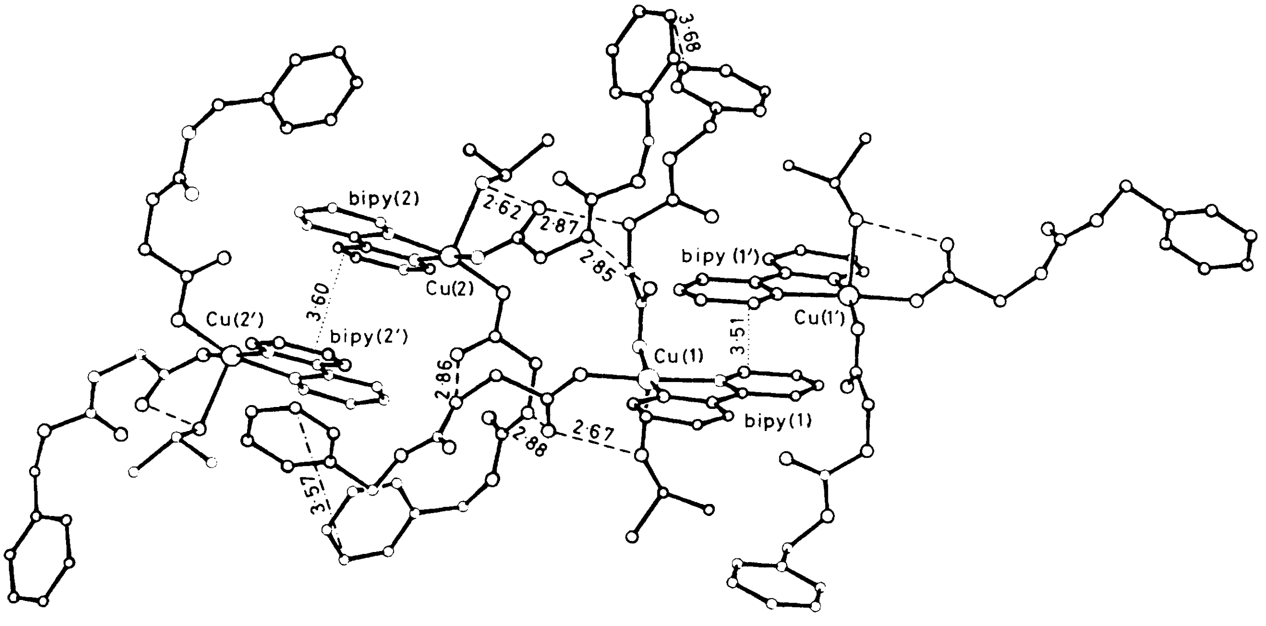

Figure 3. The molecular packing as viewed (approximately) down the *z* axis. Hydrogen bonds (— — —), intermolecular stacking (· · · ·), and hydrophobic interactions (— · — · —) (between molecular units related by unit-cell translations along the *z* axis) are shown

molecules the closest approaches to the sixth octahedral position around the Cu atoms (2.62 and 2.84 Å, respectively) are due to the other α-carboxylate O atoms, which we consider to be outside the metal co-ordination sphere, mainly on the basis of their interatomic angles (see Table 3). The dimensions of the two co-ordination polyhedra do not differ significantly from each other, or from those previously reported for many small peptide or amino acid complexes of copper(II).[11–14]

Due to the relatively low precision of the present determination resulting from the marginal quality of available crystals, the dimensions of the organic ligands are only rather poorly defined. Given the magnitude of their estimated standard deviations, bond distances and angles appear to be normal.

The individual pyridine rings of the two independent bipy ligands, planar within ±0.030 Å, are twisted about the 2–2′ bond by 2.5 and 6.9°, respectively; these values are within the range (0—11°) previously reported for this co-ordinated ligand.[13–15]

Although individual bond distances and bond angles within the four crystallographically independent bglyO ligands show large deviations, their average values (see Figure 2) compare well with those reported for other benzyloxycarbonyl derivatives.[16–19]

The most significant feature of this structure appears to be its dimeric arrangement, due to four strong hydrogen-bonding interactions, which involve all the peptide groups and the unco-ordinated α-carboxylate O atoms of the bglyO ligands. The N · · · O distances range from 2.85 to 2.88 Å, and the N–H · · · O angles from 140 to 152°. Additional hydrogen bonds occur, within each complex molecule, between the apical propan-2-ol groups and α-carboxylate O atoms (O · · · O 2.67 and 2.62 Å, respectively).

One further interesting feature of the present structure is the crystal packing of these dimeric units, mainly determined by intermolecular ring-stacking interactions between bipy ligands, and by intermolecular hydrophobic interactions between phenyl groups of the bglyO moieties (see Figure 3). Such interactions, which enhance the stability of the mixed-ligand ternary complexes, have been observed in solution and in the solid state, but not many examples are as yet known.[3–6] The mean planes through equivalent bipy molecules (related by an inversion centre and hence parallel) are stacked by 3.51 and 3.60 Å, respectively, whereas the shortest interatomic stacking distances range from 3.56 to 3.76 Å for the bipy(1) · · · bipy(1′) interactions, and from 3.57 to 4.31 Å for bipy(2) · · · bipy(2′). The shortest interatomic separations between phenyl rings, which we have assumed as hydrophobic intermolecular

Table 4. Physical data[a] and room-temperature (298 K) magnetic, e.s.r., electronic, and i.r. data for $[Cu(bglyO)_2(bipy)(Pr^iOH)]$[b]

$g_{\parallel}$	2.273
$g_{\perp}$	2.089
$\mu_{eff.}$/B.M.	1.89
d–d transition, ν/cm^{-1}	15 300
ν(NH)/cm^{-1}	3 320ms
$\nu(OCO_{ester})_{asym}$/cm^{-1}	1 720vs
$\nu(OCO_{ester})_{sym}$/cm^{-1}	1 270s 1 240s
$\nu(OCO_{carboxylate})_{asym}$/cm^{-1}	1 615vs
$\nu(OCO_{carboxylate})_{sym}$/cm^{-1}	1 395s

[a] Temperature range for weight loss due to propan-2-ol, 353—402 K; decomposition temperature, 423 K. [b] Stretching and bending vibrations for the OH group of propan-2-ol appear at 3 370(sh), 950ms, and 820mw cm^{-1}.

interactions, are 3.57 and 3.68 Å, respectively, with dihedral angles between corresponding phenyl planes of 41.0 and 73.4°, respectively. Hydrophobic ligand–ligand interactions in ternary complexes have been previously reported to occur between aliphatic side chains or between aliphatic chains and aromatic rings, but not between two aromatic moieties.[3]

Its e.s.r. parameters and room-temperature electronic spectrum (Table 4) are similar to those of synthetic copper(II) peptides [20–22] or those of the ternary complexes having similar square-pyramidal structures.[23–26]

Of interest in the i.r. spectrum is the shift to lower energy of the symmetric carboxylate stretching vibration with respect to the frequencies found for the previously examined complexes,[2] in agreement with a monodentate carboxylate group coordination.[27]

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