Crystal Structure of Bis(2-aminoethyl)amine(di-2-pyridylamine)zinc(II) Nitrate and the Electronic Properties of the Copper(II)-doped System

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The crystal structure of the title compound [Zn(dien)(bipyam)][NO_3]$_2$ has been determined by *X*-ray crystallographic analysis using photographic data. The complex crystallises in the monoclinic space group $P2_1/c$, with $a = 12.34(5)$, $b = 16.26(5)$, $c = 9.92(5)$ Å, $\beta = 92.0(5)°$, and $Z = 4$. The zinc(II) ion is five-co-ordinate with a distorted trigonal-bipyramidal stereochemistry, the mean out-of-plane and in-plane Zn–N bond distances being 2.20 and 2.09 Å respectively. The e.s.r. and electronic spectra of 1% copper-doped [Zn(dien)(bipyam)][NO_3]$_2$ have been determined using polycrystalline samples and single-crystal techniques and the results interpreted to suggest that the stereochemistry of the doped CuN_5 chromophore corresponds closely to that observed in the isomorphous [Cu(dien)(bipyam)][NO_3]$_2$ complex, rather than to the stereochemistry of the ZnN_5 chromophore of the host lattice. Caution is expressed over the use of the Zn–N distances and N–Zn–N angles to describe the stereochemistry of the CuN_x chromophore when doped into isomorphous zinc(II) complexes as host lattices and the use of the electronic reflectance spectra of copper(II)-doped zinc(II) complexes as a criterion for comparable stereochemistries is advocated. A comparison of the *g* and *A* factors and one-electron orbital energies is made with other very distorted copper(II) systems.

A WEALTH of *X*-ray crystallographic data[1,2] has established the existence of the five-co-ordinate square-pyramidal and trigonal-bipyramidal stereochemistries for the copper(II) ion, particularly for mixed-ligand complexes.[3,4] The geometry involved is intermediate between the regular geometries due to the flexible stereochemistry of the copper(II) ion (the ' Plasticity Effect '[5]) and has allowed the isolation of a series of cation-distortion isomers[6] of the bis(2-aminoethyl)amine(di-2-pyridylamine)copper(II) cations, whose structures vary from distorted square pyramidal to distorted trigonal pyramidal, related by the Berry twist mechanism.[7] A correlation was suggested[6] between the electronic reflectance spectra of these complexes and the stereochemistry of the CuN_5 chromophore, but owing to the gross distortions present it was not possible to define the electronic ground states due to the problem of defining the local molecular axes and to the misalignment present in the monoclinic crystals involved.[8] In order to obtain more information on the electronic properties of the [Cu(dien)(bipyam)]$^{2+}$ ion [dien = bis(2-aminoethyl)amine (diethylenetriamine), bipyam = di-2-pyridylamine], the crystal structure of [Zn(dien)(bipyam)][NO_3]$_2$ has been determined and the single-crystal electronic properties of the copper(II)-doped complex are reported.

EXPERIMENTAL

Preparation.—The salt Zn[NO_3]$_2$·$6H_2O$ (1.9 g, 6 mmol) was dissolved in a solution of hot methanol (10 cm^3) and water (30 cm^3) and added to a hot solution containing bipyam (1.3 g, 7.6 mmol) and dien (0.75 cm^3, 6.9 mmol) in methanol (40 cm^3); the resulting solution was filtered and allowed to stand (Found: C, 36.4; H, 4.8; N, 24.7. $C_{14}H_{22}N_8O_6Zn$ requires C, 36.2; H, 4.8; N, 24.2%). The copper(II)-doped crystals of [Zn(dien)(bipyam)][NO_3]$_2$ were obtained similarly using a stoicheiometric amount of Cu[NO_3]$_2$·$3H_2O$.

Crystal Data.—$C_{14}H_{22}N_8O_6Zn$, $M = 463.8$, Monoclinic, $a = 12.34(5)$, $b = 16.26(5)$, $c = 9.92(5)$ Å, $\beta = 92.0(5)°$, $U = 1\,989.22$ Å^3, $D_m = 1.60$ g cm^{-3} (by flotation), $Z = 4$, $D_c = 1.55(5)$ g cm^{-3}, $F(000) = 988.0$, space group, $P2_1/c$ (C^5_{2h}, no. 14), Cu-K_α radiation, $\lambda = 1.541\,8$ Å, $\mu = 20.48$ cm^{-1}.

The unit-cell parameters were determined from precession photographs and the intensities were estimated photometrically using the S.R.C. Microdensitometer Service (Harwell) from multiple-film equi-inclination Weissenberg photographs for the layers *hk*0—*hk*8 and *h*11—*h*21 using Cu-K_α radiation. Lorentz and polarisation corrections, but no corrections for absorption or extinction, were applied. Complex neutral scattering factors[9] were used and the copper atom was corrected for anomalous dispersion. All calculations were carried out on the I.B.M. 370/138 computer (University College, Cork) using the SHELX-76 crystallography programs.

Structure Determination.—The structure was solved using three-dimensional Patterson and Fourier techniques until all the non-hydrogen atoms had been located. The structure was refined using full-matrix least squares, minimising the function $\Sigma w|F_o| - |F_c|^2$, until the final shift/estimated standard deviation was <0.07. Anisotropic temperature factors were refined for the zinc atom, the six nitrogen atoms of the cation, and all the atoms of the nitrate ions. Calculated hydrogen positions were used, with a fixed C–H and N–H bond distance of 1.08 Å and a fixed temperature factor of 0.07 Å^2, and floated on the associated C or N atoms. A refined weighting scheme was used, with the final form $w = 1.0/[\sigma^2(F) + 0.033\,8F^2]$ and a final R value of 0.070 7 was obtained using 1 589 unique reflections with a final maximum residual electron density of 0.58 e Å^{-3}.

Table 1 lists the final atomic co-ordinates, Table 2 the bond distances and angles, and Figure 1 shows the molecular structure and atom-numbering scheme. The structure-factor tables, the calculated hydrogen-atom co-ordinates, the isotropic and anisotropic temperature factors, some selected non-bonded distances, and some relevant mean planes are in Supplementary Publication No. SUP 22709 (19 pp.).†

Physical Methods.—The e.s.r. and electronic spectra were determined as previously described.[1,10] Figure 2(*a*) shows

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† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

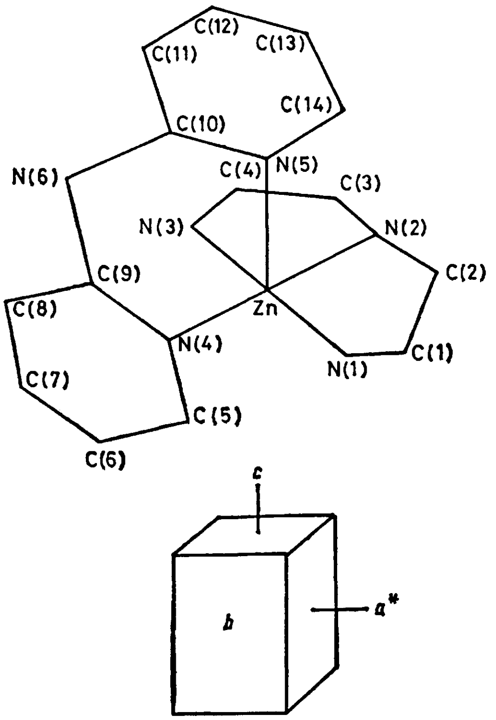

FIGURE 1 Local molecular structure and atom-numbering scheme (*a*) and crystal morphology (*b*) of [Zn(dien)(bipyam)]-$[NO_3]_2$

the polycrystalline e.s.r. spectrum of 1% copper-doped [Zn(dien)(bipyam)]$[NO_3]_2$, Figure 2(*b*)—(*d*) the single-crystal e.s.r. spectra, Figure 3 the electronic reflectance spectra over the concentration range 1—100%, and Figure 4 the polarised single-crystal electronic spectrum.

TABLE 1

Atomic co-ordinates (× 10^4) for [Zn(dien)(bipyam)]$[NO_3]_2$ with estimated standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Zn	2 780(1)	4 528(1)	3 274(1)
N(1)	3 863(6)	3 685(5)	4 180(6)
N(2)	4 188(5)	4 698(4)	1 918(6)
N(3)	1 955(6)	4 359(4)	1 431(7)
N(4)	1 555(6)	4 113(4)	4 603(6)
N(5)	2 580(6)	5 716(4)	4 011(7)
N(6)	1 608(7)	5 317(5)	5 938(7)
C(1)	4 986(8)	3 879(6)	3 774(8)
C(2)	4 966(8)	4 015(5)	2 292(8)
C(3)	3 717(7)	4 653(5)	517(8)
C(4)	2 748(7)	4 058(5)	447(8)
C(5)	1 211(7)	3 321(5)	4 418(9)
C(6)	613(8)	2 897(7)	5 343(9)
C(7)	349(9)	3 317(6)	6 494(10)
C(8)	670(9)	4 134(7)	6 697(10)
C(9)	1 270(7)	4 509(6)	5 706(9)
C(10)	2 097(7)	5 907(5)	5 175(8)
C(11)	2 075(8)	6 744(6)	5 641(9)
C(12)	2 542(7)	7 356(6)	4 921(9)
C(13)	3 028(8)	7 155(6)	3 731(10)
C(14)	3 035(7)	6 353(6)	3 301(9)
N(7)	4 139(8)	3 340(5)	7 692(8)
O(1)	4 826(7)	3 166(5)	8 574(7)
O(2)	4 173(7)	4 037(5)	7 132(6)
O(3)	3 404(7)	2 842(5)	7 340(9)
N(8)	−929(7)	4 046(4)	815(8)
O(4)	8 131(7)	4 287(5)	1 039(8)
O(5)	9 662(5)	3 794(4)	1 781(6)
O(6)	9 406(7)	4 013(5)	−347(7)

TABLE 2

Bond lengths (Å) and angles (°) for [Zn(dien)(bipyam)]-$[NO_3]_2$ with estimated standard deviations in parentheses

N(1)–Zn	2.096(9)	N(2)–Zn–N(1)	80.9(3)
N(2)–Zn	2.252(9)	N(3)–Zn–N(1)	125.2(4)
N(3)–Zn	2.079(9)	N(3)–Zn–N(2)	81.7(4)
N(4)–Zn	2.148(9)	N(4)–Zn–N(1)	89.0(4)
N(5)–Zn	2.082(9)	N(4)–Zn–N(2)	168.3(2)
C(1)–N(1)	1.491(13)	N(4)–Zn–N(3)	99.5(4)
C(2)–C(1)	1.486(13)	N(5)–Zn–N(1)	122.5(4)
N(2)–C(2)	1.506(13)	N(5)–Zn–N(2)	101.5(3)
C(3)–N(2)	1.490(11)	N(5)–Zn–N(3)	111.8(4)
C(4)–C(3)	1.538(14)	N(5)–Zn–N(4)	88.9(4)
N(3)–C(4)	1.489(12)	C(1)–N(1)–Zn	109.3(6)
C(5)–N(4)	1.367(12)	C(2)–C(1)–N(1)	108.4(8)
C(9)–N(4)	1.327(12)	N(2)–C(2)–C(1)	110.0(8)
C(6)–C(5)	1.381(14)	C(2)–N(2)–Zn	105.1(6)
C(7)–C(6)	1.380(15)	C(3)–N(2)–Zn	105.5(6)
C(8)–C(7)	1.399(16)	C(3)–N(2)–C(2)	114.7(7)
C(9)–C(8)	1.391(15)	C(4)–C(3)–N(2)	110.5(7)
N(6)–C(9)	1.396(13)	N(3)–C(4)–C(3)	106.9(8)
C(10)–N(6)	1.375(12)	C(4)–N(3)–Zn	107.9(6)
C(11)–C(10)	1.438(13)	C(5)–N(4)–Zn	115.8(6)
N(5)–C(10)	1.354(12)	C(9)–N(4)–Zn	124.5(7)
C(12)–C(11)	1.363(14)	C(9)–N(4)–C(5)	118.5(8)
C(13)–C(12)	1.381(14)	C(6)–C(5)–N(4)	123.5(9)
C(14)–C(13)	1.372(15)	C(7)–C(6)–C(5)	116.7(10)
N(5)–C(14)	1.383(13)	C(8)–C(7)–C(6)	121.0(11)
O(1)–N(7)	1.230(13)	C(9)–C(8)–C(7)	117.9(10)
O(2)–N(7)	1.263(12)	C(8)–C(9)–N(4)	122.3(10)
O(3)–N(7)	1.256(13)	N(6)–C(9)–N(4)	120.4(9)
O(4)–N(8)	1.252(13)	N(6)–C(9)–C(8)	117.3(9)
O(5)–N(8)	1.253(11)	C(10)–N(6)–C(9)	134.5(7)
O(6)–N(8)	1.238(11)	C(11)–C(10)–N(6)	118.0(8)
		N(5)–C(10)–N(6)	121.6(8)
		N(5)–C(10)–C(11)	120.4(8)
		C(12)–C(11)–C(10)	120.6(9)
		C(13)–C(12)–C(11)	118.7(10)
		C(14)–C(13)–C(12)	119.9(10)
		N(5)–C(14)–C(13)	123.1(9)
		C(10)–N(5)–Zn	125.0(6)
		C(14)–N(5)–Zn	117.7(7)
		C(14)–N(5)–C(10)	117.4(8)
		O(2)–N(7)–O(1)	119.1(10)
		O(3)–N(7)–O(1)	121.5(10)
		O(3)–N(7)–O(2)	119.4(10)
		O(5)–N(8)–O(4)	119.0(9)
		O(6)–N(8)–O(4)	121.3(9)
		O(6)–N(8)–O(5)	119.6(9)

RESULTS AND DISCUSSION

Crystal Structure.—The structure of [Zn(dien)(bipyam)]$[NO_3]_2$ consists of discrete $[Zn(dien)(bipyam)]^{2+}$ cations and nitrate anions. There are no unusual features in either the bond lengths or bond angles of the nitrate ions [11] or in the organic ligands [12] present. The zinc(II) ion involves a distorted five-co-ordinate geometry with no evidence of co-ordination by a sixth ligand. The ZnN_5 chromophore is best described as having a distorted trigonal-bipyramidal stereochemistry since the N(2)–Zn–N(4) angle is almost linear, 168.3°, and the N(1)–Zn–N(5), N(5)–Zn–N(3), and N(1)–Zn–N(3) angles, 122.5, 111.8, and 125.2° respectively, are near 120°. In addition, the two axial Zn–N bonds are significantly longer (mean 2.20 Å) than the three in-plane Zn–N bonds (mean 2.09 Å), as previously found for the trigonal-bipyramidal zinc(II) chromophore of tris(2-dimethylaminoethyl)-aminezinc(II) bromide,[13] namely 2.19 and 2.11 Å respectively.

It is of interest to compare the structure of [Zn(dien)(bipyam)]$[NO_3]_2$ with that of the corresponding [Cu-

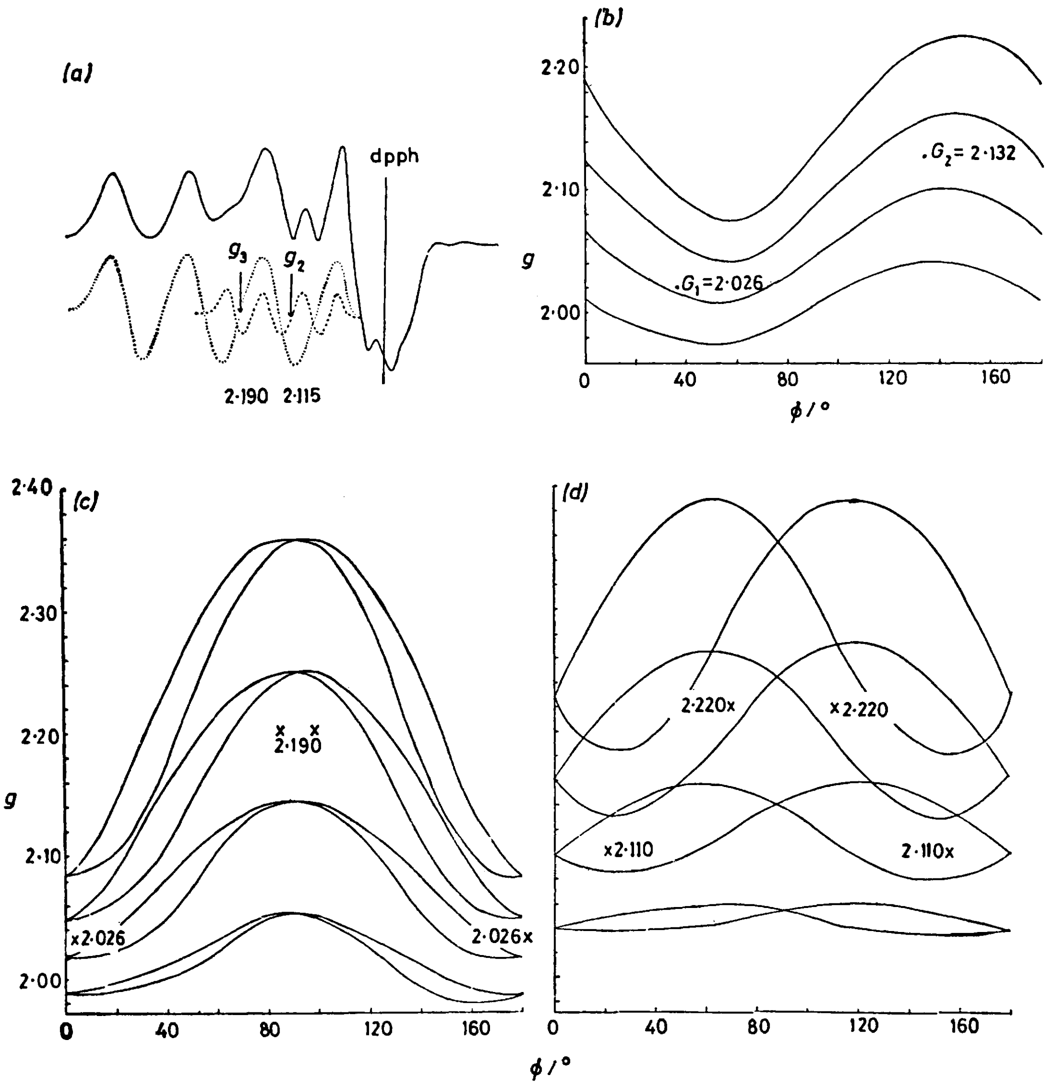

FIGURE 2 E.s.r. spectra of 1% copper-doped [Zn(dien)(bipyam)][NO_3]$_2$: (*a*) polycrystalline, showing hyperfine peaks as broken lines; (*b*)—(*d*) single-crystal, in the *ac*, (G_1,G_3), and (G_2,G_3) planes respectively. The rotation about the *b* axis in (*b*) defines the direction of the lowest and highest *g* factors G_1 and G_2, which in turn define the directions of rotation in (*c*) and (*d*). dpph = Diphenylpicrylhydrazyl

(dien)(bipyam)][NO_3]$_2$ complex, since these complexes[6] are as near isomorphous as two corresponding zinc(II) and copper(II) complexes can be (*a* = 12.20, *b* = 16.00, *c* = 9.85 Å, β = 91.00°, *Z* = 4, and space group $P2_1/c$). The MN_5 chromophores are both five-co-ordinate involving a distorted trigonal-bipyramidal stereochemistry but with significant differences in the local molecular stereochemistry, see Table 3 (I) and (II). In particular, the N(2)–M–N(4) direction involves the longest bond distances in the zinc complex, but the shortest ones in the copper complex, in which the Cu–N(5) is the longest bond distance. While the zinc complex has a reasonably trigonal Zn, N(1), N(3), N(5) plane (see SUP) that of the copper complex is much less regular.[14] This difference is particularly significant in view of the 'plasticity effect'[5] associated with the cation-distortion isomers of the [Cu(dien)(bipyam)]$^{2+}$ cation and illustrated by the structural data for the three copper(II) complexes of Table 3 (II)—(IV).

TABLE 3

Comparison of the local molecular chromophores of (I) [Zn(dien)(bipyam)][NO_3]$_2$, (II) [Cu(dien)(bipyam)][NO_3]$_2$, (III) [Cu(dien)(bipyam)][ClO_4]$_2$·H_2O, and (IV) [Cu(dien)(bipyam)]Cl_2·$2H_2O$

	(I)	(II)	(III)	(IV)
(*a*) Bond distances (Å)				
M–N(1)	2.10	2.03	2.03	1.99
M–N(2)	2.25	2.04	2.02	2.01
M–N(3)	2.08	2.07	2.05	2.02
M–N(4)	2.15	1.99	1.99	2.00
M–N(5)	2.08	2.15	2.17	2.126
(*b*) Bond angles (°)				
N(1)–M–N(3)	125.2	135.5	151.9	159.1
N(2)–M–N(4)	168.3	172.0	167.9	162.7
N(1)–M–N(5)	122.5	118.7	102.5	101.8
N(3)–M–N(5)	111.8	105.4	104.9	98.8

E.S.R. Spectra.—The polycrystalline e.s.r. spectrum [Figure 2(*a*)] is typically rhombic showing clear nuclear hyperfine splitting[15] of the two highest *g* factors but

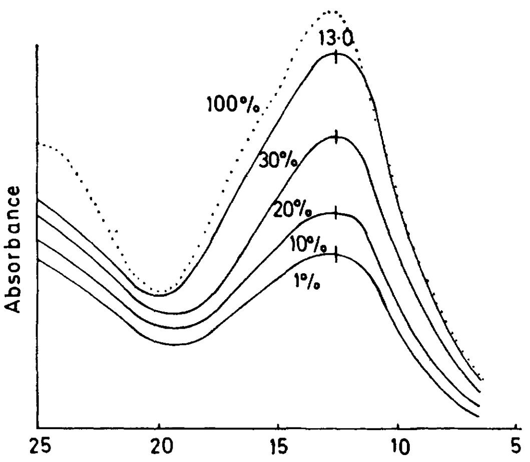

FIGURE 3 Electronic reflectance of copper-doped [Zn(dien)-(bipyam)][NO$_3$]$_2$ as a function of the copper concentration (%)

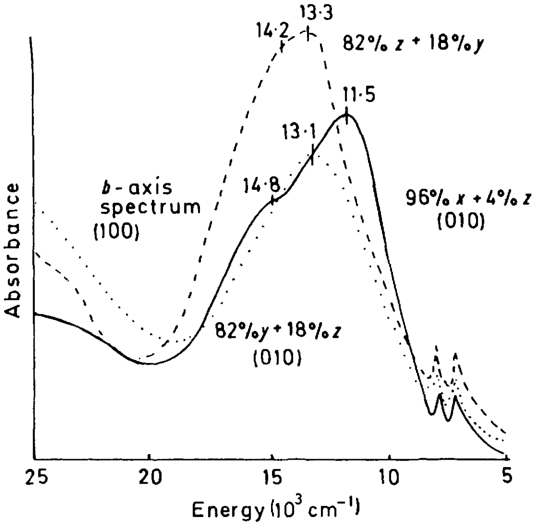

FIGURE 4 Polarised single-crystal electronic spectra of 10% copper-doped [Zn(dien)(bipyam)][NO$_3$]$_2$

TABLE 4

Crystal G factors and the local molecular g factors of 1% copper-doped [Zn(dien)(bipyam)][NO$_3$]$_3$ (*a*) and the crystal G factors of [Cu(dien)(bipyam)][NO$_3$]$_2$ (*b*)

	(*a*)	(*b*)
G_1	2.026	2.021
G_2	2.132	2.095
G_3	2.186	2.1786
g_1	2.026	
g_2	2.110	
g_3	2.220	
A_1 *	43.3	
A_2 *	66.2	
A_3 *	148.5	

* Values in 10^{-4} cm^{-1}.

TABLE 5

Direction cosines of the g factors of 1% copper-doped [Zn(dien)(bipyam)][NO$_3$]$_2$, Zn–N directions, and of the Cu–N directions in [Cu(dien)(bipyam)][NO$_3$]$_2$

	Direction cosines		
	a^*	b^*	c^*
g_1	−0.796	−0.087	0.599
g_2 approximate	0.576	−0.414	0.705
g_3	0.281	0.906	0.315
Zn–N(1)	0.6567	−0.5650	0.4995
Zn–N(4)	−0.7249	−0.3140	0.6131
Zn–N(5)	−0.1307	0.9273	0.3507
Cu–N(4)	−0.7331	−0.2836	0.6182
Cu–N(5)	−0.1552	0.9393	0.3060

The angle θ between two sets of direction cosines (l_1, m_1, n_1) and (l_2, m_2, n_2) is given by $\cos^{-1}\theta = (l_1l_2 + m_1m_2 + n_1n_2)$.

only an isotropic signal with evidence of hyperfine splitting for the lowest g. This spectrum showed no significant variation with temperature, thus ruling out any fluxional behaviour[16] associated with the doped-copper(II) stereochemistry. The single-crystal e.s.r. spectra [Figure 2(*b*)—(*d*)] show copper hyperfine splitting on all three g factors. The rotation about the b axis [Figure 2(*b*)] gave four hyperfine components in all directions and defined the two lowest *crystal* G factors, $G_1 = 2.026$ and $G_2 = 2.132$ in the ac plane (with G_1 making an angle of 54° to the c axis), with the highest crystal G factor, $G_3 = 2.186$, lying along the b axis. Figure 2(*c*) shows the rotation in the G_1,G_3 plane and Figure 2(*d*) that in the G_2,G_3 plane; in both rotations up to eight hyperfine components were observed, indicating the presence of the two misaligned chromophores[8] of a monoclinic system. In the G_1,G_3 plane the angle of misalignment is $2\alpha = 20°$, while in the G_2,G_3 plane $2\alpha = 50°$. Table 4 lists the crystal G factors, the local molecular g and A factors, and the crystal G factors of [Cu(dien)(bipyam][NO$_3$]$_2$ for comparison.[14] The local molecular g factors are very rhombic with $(g_2 - g_1)/(g_3 - g_2) = 0.763$, which suggests a ground-state intermediate between a pure $d_{x^2-y^2}$ and a d_{z^2} ground state with only a slight preference for the former. The order of magnitude of the A values with $A_3 \gg A_2 > A_1$ also suggests[17] an approximately $d_{x^2-y^2}$ ground state for the doped CuN$_5$ chromophore rather than an approximately d_{z^2} ground state, for which the largest A value is associated with the lowest g value.[18] With such a rhombic component to the g values and a very distorted stereochemistry, it is impossible to predict the direction of the local molecular axes. Table 5 lists the direction cosines of the local molecular g factors for one of the CuN$_5$ chromophores of 1% copper-doped [Zn(dien)(bipyam)]-[NO$_3$]$_2$ along with those of selected Zn–N directions and also those of the Cu–N directions of [Cu(dien)(bipyam)]-[NO$_3$]$_2$ as the unit-cell dimensions of the zinc and copper complex differ very little. Figure 5 illustrates the relationship[8] between the local molecular g factors and the Cu–N directions of 1% copper-doped [Zn(dien)-(bipyam)][NO$_3$]$_2$. While there is only a 12° discrepancy between the g directions and the Zn–N(4) directions, there is a much larger discrepancy within the trigonal plane Cu, N(1), N(2), N(3). Nevertheless, the lowest g factor, 2.026, does correspond to the approximate trigonal axis and the highest, 2.220, does correspond to the elongation direction of the approximate square-pyramidal stereochemistry (notwithstanding a 25.3°

deviation) in 1% copper-doped [Zn(dien)(bipyam)]-$[NO_3]_2$. These directions are those predicted for the *g* factors from the distortions of the stereochemistry of the pure copper(II) complex and contrast with the distortions in the pure zinc(II) complex, where the longest Zn–N bonds lie along the trigonal axes and there is no significant difference between the Zn–N(5), Zn–N(1), and Zn–N(3) directions of the trigonal plane. This implies that from an e.s.r. point of view the stereochemistry of the CuN_5 chromophore of 1% copper-doped [Zn(dien)-(bipyam)]$[NO_3]_2$ corresponds to that of the pure copper complex rather than to that of the ZnN_5 chromophore of the pure zinc complex. This conclusion is supported by the values of the *crystal* *g* factors of the doped system (G_1, G_2, and G_3) and the crystal *G* factors (not the resolved local molecular *g* factors) of [Cu(dien)(bipyam)]$[NO_3]_2$ (Table 4).[14]

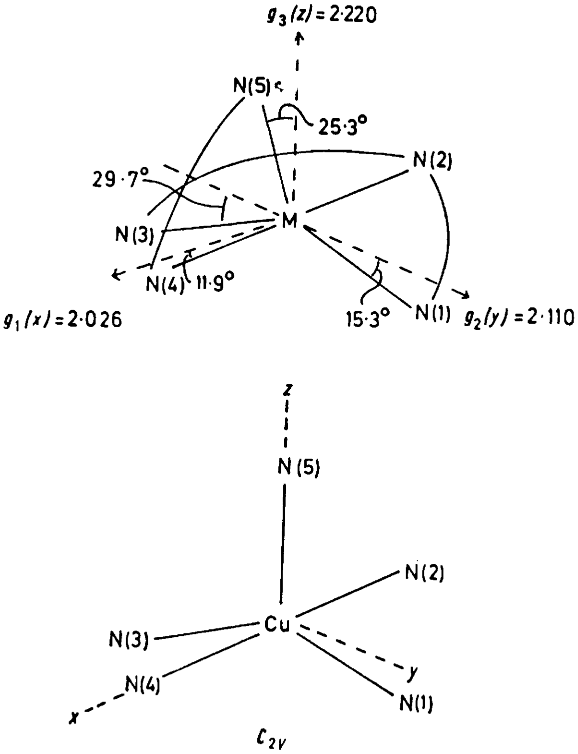

FIGURE 5 Relationship between the molecular *g* ellipsoid of 1% copper-doped [Zn(dien)(bipyam)]$[NO_3]_2$ and the chromophore stereochemistry (copper)

The local molecular *g* and *A* factors (Table 6) agree well with previous data for distorted five-co-ordinate copper(II) complexes[15] doped in zinc host lattices. All three doped systems give comparable rhombic *g* and *A* factors, with the highest *A* factor associated with the highest *g* factors,[17] as is usual for systems corresponding to an approximately $d_{x^2-y^2}$ ground state and in contrast to systems with an approximate d_{z^2} ground state where the highest *A* factor is associated with the lowest *g* factor.[18] In all three complexes the intermediate and lowest *A* factors are comparable in value and significantly higher (*ca.* 40×10^{-4}—70×10^{-4} cm^{-1}) than those observed in axially elongated CuN_6 chromophores ($<30 \times 10^{-4}$ cm^{-1}). The *g* factors of copper-doped [Zn(dien)(bipyam)]$[NO_3]_2$ and [Zn(Mesal)] (Mesal = *N*-methylsalicylideneiminate) are clearly rhombic with *R* values of 0.763 and 1.00 respectively, consistent with the very distorted CuN_5 stereochemistry of the former system. The *R* value for copper-doped [Zn(salmhpn) [salmhpn = *NN'*-4-methyl-4-azaheptane-1,7-diylbis-(salicylideneiminate)] is much higher (0.188) suggesting a much more axially elongated CuN_3O_2 stereochemistry in this system, consistent with the high energy of the band maximum (14 000 cm^{-1}) for this system. For these reasons the ground state of copper-doped [Zn(dien)-(bipyam)]$[NO_3]_2$ will be presumed to be dominated by the $d_{x^2-y^2}$ orbital and the stereochemistry to involve a very distorted square-pyramid, with a ground-state expression $\cos\beta|x^2 - y^2> + \sin\beta|z^2>$ where $\beta = -22.5°$ as defined in ref. 15 for an approximate C_{2v} symmetry.

TABLE 6

The *g* and *A* factors (10^{-4} cm^{-1}) for two distorted square-pyramidal copper(II) complexes doped in the corresponding zinc(II) complex *

	[Zn(Mesal)]	[Zn(salmhpn)]
g_x	2.02	2.04
g_y	2.13	2.07
g_z	2.25	2.23
R	1.0	0.188
A_x	47	66
A_y	65	38
A_z	131	150

* See ref. 15.

Electronic Spectra.—The electronic reflectance spectra of 1—100% copper-doped [Zn(dien)(bipyam)]$[NO_3]_2$ consist of a broad band at 13 000 cm^{-1} with a slight shoulder at *ca.* 15 000 cm^{-1}, Figure 3, which is independent of the copper(II) concentration over the *whole* concentration range. Thus, in this system the electronic spectrum suggests that the CuN_5 chromophore assumes a stereochemistry that is independent of that of the zinc-host lattice and corresponds much more closely to that of the CuN_5 chromophore of the pure copper(II) complex. Consequently, the electronic properties of the CuN_5 chromophore will be determined by the Cu–N distances and N–Cu–N angles of the pure copper(II) complex and not by the Zn–N distances and N–Zn–N angles of the pure zinc(II) complex as has been suggested recently.[15]

The polarised single-crystal electronic spectra of 1% copper-doped [Zn(dien)(bipyam)]$[NO_3]_2$ are shown in Figure 4. The spectra are measured parallel to the *b* axis and in the directions of polarisation in the *ac* plane as shown in Figure 6, directions that are nearly 45° misaligned to the directions of the crystal *G* factors in this plane.[8] This means that the measured spectra cannot be associated unambiguously with a local molecular direction or with the crystal *G* factors in this plane. Nevertheless, since the spectra show clear evidence of polarisation, they have been labelled as shown in Figure 6 (see later) using the molecular axes of Figure 5 with the percentage contribution due to the misalignment of CuN_5 chromophore in the monoclinic unit cell as indicated. The spectra show the presence of three clear electronic bands at 11 500, 13 100—13 500, and 14 200—14 800 cm^{-1} respectively. The spectrum measured parallel to the *b* axis is unique and symmetry-determined,[8] it has a maximum at 13 300 cm^{-1} with a clear shoulder at 14 200 cm^{-1}, and involves 82% *z* polarisation and 18% *y* polarisation. The most intense spectrum in the *ac* plane involves a band maximum at 11 550 cm^{-1} and a clear shoulder at 14 800 cm^{-1} and is 96% *x*- and 4% *z*-polarised while the second spectrum involves a single peak at 13 100 cm^{-1} and is 82% *y*- and 18% *z*-polarised. The alternative assignment of the two spectra in the *ac* plane reverses the associated polarisation above.

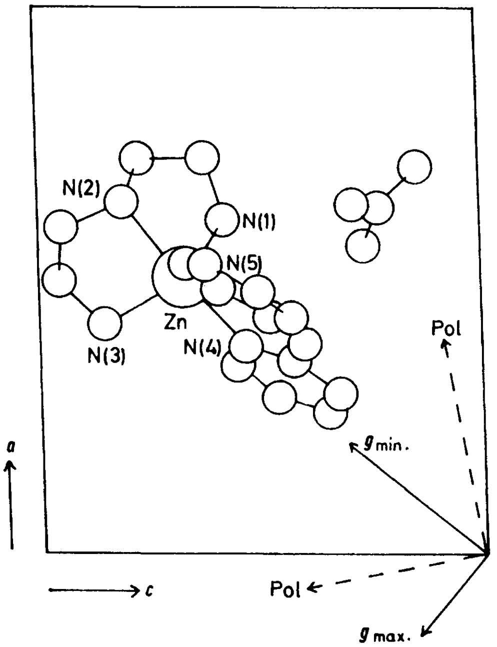

FIGURE 6 Projection of the unit cell of [Zn(dien)(bipyam)]-[NO$_3$]$_2$ down the *b* axis with the direction of the in-plane *g* factors and polarisation directions

In view of the marked polarisation the most appropriate effective symmetry is C_{2v} (Figure 5) and using the selection rules given previously[7] two assignments are possible using the alternative associations of the 010 face spectra in Figure 4. The two assignments only differ in the relative energies of the $d_{xz} \rightarrow d_{x^2-y^2}$ and $d_{yz} \rightarrow d_{x^2-y^2}$ transitions; in assignment A the former transition lies to lowest energy, while in B it is the $d_{yz}—d_{x^2-y^2}$ transition that lies to lowest energy. The assignment B is preferred since it is understandable in terms of the angular distortion, Table 3 (II), of the Cu–N(1) and Cu–N(3) bonds away from the *y* axis to give a N(1)–Cu–N(3) angle of *ca.* 135.6°, whereas the N(2)–Cu–N(4) angle is almost linear at 172° (Table 3). This assignment gives a one-electron orbital sequence $d_{x^2-y^2} > d_{yz} > d_{z^2} > d_{xz} > d_{xy}$ and is in reasonable agreement with the recent[15] calculation using the angular-overlap method in C_{2v} symmetry, except for a small reversal of the positions of the d_{z^2} and d_{yz} orbitals. This assignment is attractive in that it correlates well with the previous assignment[19] of [Cu(dien)(O$_2$CH)][O$_2$CH] which has a more square-pyramidal stereochemistry than [Cu(dien)(bipyam)][NO$_3$]$_2$ and was also in C_{2v} symmetry.

The assignment in C_{2v} symmetry also allows an alternative assignment of the reported[20] spectrum of [Cu(phen)$_2$(OH$_2$)][NO$_3$]$_2$ (phen = 1,10-phenanthroline) which was previously assigned in the higher symmetry of D_{3h}. This assignment (Table 7) is comparable to that of copper-doped [Zn(dien)(bipyam)][NO$_3$]$_2$ except for the energy of the $d_{xy} \rightarrow d_{x^2-y^2}$ transition, which is not observed. Both assignments enable the appearance in the reflectance spectra of a low-energy main peak with a high-energy shoulder to be understood in terms of the movement of the $d_{yz} \rightarrow d_{x^2-y^2}$ transition to lower energy as β (ref. 15, Figure 4) changes from 90 to 120°.

TABLE 7

Assignment of the polarised single-crystal spectra of 1% copper-doped [Zn(dien)(bipyam)][NO$_3$]$_2$ using the two alternative assignments of the *x*- and *y*-polarised spectra, and the assignment of the spectra of [Cu(dien)-(O$_2$CH)][O$_2$CH] and [Cu(phen)$_2$(OH$_2$)][NO$_3$]$_2$

	A	B
$d_{xz} \rightarrow d_{x^2-y^2}$	11.5	13.1
$d_{z^2} \rightarrow d_{x^2-y^2}$	13.3	13.3
$d_{yz} \rightarrow d_{x^2-y^2}$	13.1	11.5
$d_{xy} \rightarrow d_{x^2-y^2}$	14.2—14.8	14.2—14.8
	[Cu(dien)(O$_2$CH)][O$_2$CH]	[Cu(phen)$_2$(OH$_2$)][NO$_3$]$_2$
$d_{z^2} \rightarrow d_{x^2-y^2}$	11.5	12.0
$d_{xy} \rightarrow d_{x^2-y^2}$	14.2	Not observed
$d_{xz} \rightarrow d_{x^2-y^2}$	15.2	15.0
$d_{yz} \rightarrow d_{x^2-y^2}$	15.4	13.0

Copper-doped Zinc.—Information on the stereochemistry of copper(II) complexes doped into the corresponding zinc(II) complex as a host lattice would be of value as much more electronic information[17] is available from the copper hyperfine structure of e.s.r. spectra of dilute copper(II) complexes. However, caution should be exercised when interpolating the copper(II) stereochemistry from the known structure of the zinc(II) complex. A number of situations can arise. (*i*) If the zinc(II) and copper(II) complexes do not have the same empirical formula then the zinc(II) stereochemistry provides *no* structural information on the copper(II) stereochemistry, *e.g.* [Zn(pys)$_2$]·4H$_2$O[21] and [Cu(pys)$_2$]·2H$_2$O (pys = pyridine-3-sulphonate).

(*ii*) If the complexes have the same empirical formula then two possibilities arise. (*a*) The complexes are not isomorphous in which case no information on the copper(II) stereochemistry is available from the zinc(II) stereochemistry, *e.g.* [Cu(O$_2$CCH$_2$OMe)$_2$]·2H$_2$O[22] and [Zn(O$_2$CCH$_2$OMe)$_2$]·2H$_2$O. (*b*) If the complexes are isomorphous then the stereochemistry of the zinc(II) and copper(II) chromophores will be *broadly* isostructural, *i.e.* four-, five-, and six-co-ordinate, but within each of these pairs of zinc and copper complexes there will be significant differences in the bond lengths and angles such that it will not be possible to infer the stereochemistry of the copper(II) chromophore from that of the zinc(II) analogue. The differences involved are nicely illustrated in the stereochemistries of the present $[Cu(dien)(bipyam)][NO_3]_2$ and $[Zn(dien)(bipyam)][NO_3]_2$ complexes, Table 3; further examples involving different co-ordination numbers are illustrated in Figure 7.

The best check of the stereochemistry of comparable copper(II) and copper(II)-doped zinc(II) complexes is in the comparability of their electronic properties; the most convenient to measure is that of the electronic reflectance spectra (as in Figure 3) but comparable crystal *G* factors are also useful. In the three pairs of complexes of Figure 6 the spectra of the copper(II) complexes are the same in the pure complex and in the zinc-doped systems over the whole concentration range [21-23] and indicate that the stereochemistry of the doped-copper(II) complex corresponds very closely to that of the pure complex, whereas in 1—40% copper-doped $[Zn(pys)_2]\cdot 4H_2O$ [21] the electronic spectra clearly differ from that of the non-isostructural $[Cu(pys)_2]\cdot 2H_2O$ complex. Thus, in these systems the copper(II) ion when doped into these zinc(II) complexes as a host lattice, while taking up the broad stereochemistry of the zinc(II) host lattice, will then distort the local chromophore stereochemistry in a way that relates to that present in the pure copper(II) complex involving significant differences in bond length (>0.1 Å) and bond angles (≈5°) due to the non-spherical symmetry of the copper(II) d^9 ion, relative to the more spherical symmetry of the zinc(II) d^{10} ion.

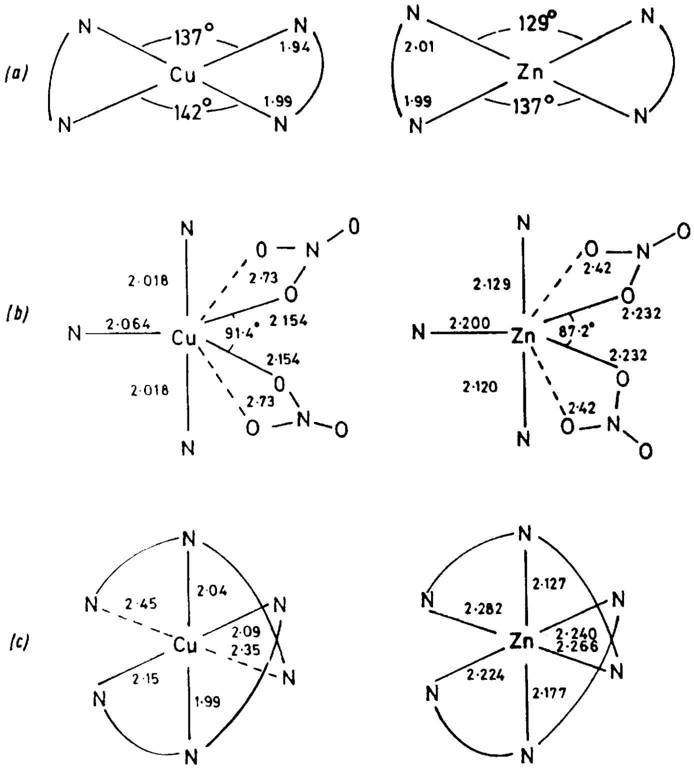

FIGURE 7 Local molecular structures of some 'isomorphous zinc(II) and copper(II) complexes: (*a*) $[M^{II}(bipyam)_2][ClO_4]_2$, compressed tetrahedral (ref. 23); (*b*) $[M^{II}(pyridine)_3(NO_3)_2]$, trigonal bipyramidal (ref. 24); (*c*) $[M^{II}(dien)_2]Br\cdot H_2O$, rhombic octahedral (ref. 25)

For this reason caution is advised in the use of Zn–L bond distances and L–Zn–L bond angles to predict the stereochemistry of the CuL_x species in copper(II)-doped zinc(II) complexes and the use of the electronic reflectance spectrum is recommended as the best criterion for comparable stereochemistries.

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