Cation Distortion Isomerism in Three Five-co-ordinate Diethylenetriamine(di-2-pyridylamine)copper(II) Complexes

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The crystal structures of three [Cu(dien)(bipyam)]$X_2 \cdot nH_2O$ (dien = diethylenetriamine, bipyam = di-2-pyridylamine) complexes have been determined by *X*-ray crystallographic methods, where X = Cl^-, *n* = 2 (1); X = ClO_4^-, *n* = 1 (2); and X = NO_3^-, *n* = 0 (3). All three crystallise in the monoclinic space group $P2_1/c$ with *Z* = 4; in (1) *a* = 7.78(2), *b* = 9.75(3), *c* = 28.01(5) Å, and β = 115.0(5)°; in (2) *a* = 15.683(5), *b* = 7.621(5), *c* = 21.044(9) Å, and β = 121.42(2)°; and in (3) *a* = 12.201(5), *b* = 16.052(6), *c* = 9.851(4) Å, and β = 90.76(2)°. All three structures were solved by heavy-atom techniques and successive Fourier syntheses; all three complexes involve a distorted five-co-ordinate CuN_5 chromophore, whose stereochemistry ranges from distorted square pyramidal in (1), through an intermediate geometry in (2), to a distorted trigonal-bipyramidal stereochemistry in (3). The three stereochemistries represent individual structures in the pathway of the Berry twist and represent cation distortion isomers of the [Cu(dien)(bipyam)]$^{2+}$ cation. The angular changes in the CuN_5 stereochemistry are parallelled in the electronic reflectance spectra of the three complexes and in the calculated crystal-field energy level of the copper(II) ion.

A WEALTH of *X*-ray crystallographic data [1,2] has established the existence of the five-co-ordinate square-based pyramidal and trigonal-bipyramidal stereochemistries for the copper(II) ion, especially in mixed-ligand complexes.[3,4] Within the square-pyramidal stereochemistry the differences in the mean in-plane bond lengths, R_S, and the mean out-of-plane bond lengths, R_L, are consistent [1] with the non-spherical symmetry of the copper(II) ion (prolate ellipsoid); the recent correlation [2,5] of R_S and R_L, with the tetragonality ($T = R_S/R_L$), has established that the tetragonality is variable [2] (within certain limits) and that consequently the eccentricity of the prolate ellipsoid of the copper(II) ion is variable. The term ' plasticity ' [5] has been introduced to describe this situation and the occurrence of distortion isomers of copper(II) complexes. This term can be extended to apply to cation or anion distortion isomers and the present paper reports the crystal structure of three cation distortion isomers [6] of the [Cu(dien)(bipyam)]$^{2+}$ cation [dien = diethylenetriamine or bis(2-aminoethyl)amine and bipyam = di-2-pyridylamine] as its $Cl_2 \cdot 2H_2O$, $[ClO_4]_2 \cdot H_2O$, and $[NO_3]_2$ salts, along with their electronic and magnetic properties.

EXPERIMENTAL

Preparation.—All three complexes were prepared [7] by dissolving $CuX_2 \cdot xH_2O$ (6 mmol) [X = Cl in (1), ClO_4 in (2), and NO_3^- in (3)] in hot methanol (10 cm^3) and adding to bipyam (1 g, 6 mmol) and dien (0.7 cm^3, 6 mmol) in hot methanol (40 cm^3); the hot solution was filtered and allowed to stand [Found for (1): C, 37.6; H, 5.70; N, 19.0. $C_{14}H_{26}Cl_2CuN_6O_2$ requires C, 37.8; H, 5.70; N, 18.9%. Found for (2): C, 30.3; H, 4.40; N, 15.6. $C_{14}H_{24}Cl_2CuN_6O_9$ requires C, 30.3; H, 4.40; N, 15.1%. Found for (3): C, 36.5; H, 4.80; N, 25.2. $C_{14}H_{22}CuN_8O_6$ requires C, 36.2; H, 4.95; N, 25.1%].

Crystal Data.—The crystal and refinement data for (1), (2), and (3) are summarised in Table 1; for all three complexes the preliminary unit-cell data were determined from precession photographs and for (2) and (3) refined on a Philips PW 1 100 four-circle diffractometer. The intensities for (1) were collected photographically by the equi-inclination Weissenberg technique using five-film packs and estimated by the S.R.C. Microdensitometer Service (Rutherford Laboratory). The intensities for (2) and (3) were collected on the diffractometer with graphite-monochromatised Mo-K_α radiation. A θ—2θ scan mode was used and reflections with $3.0 < \theta < 30°$ in one quadrant were examined. A constant scan speed of 0.05° s^{-1} was used with a variable scan width of (0.7 + 0.1 tan θ)°, with an acceptance criterion $I > 2.5\sigma(I)$, Lorentz and polarisation corrections were applied, but none for absorption or extinction.

All three structures were solved by Patterson and Fourier techniques and refined by blocked-matrix least squares with anisotropic temperature factors for all the non-hydrogen atoms in (2) and (3), but only for the copper and chlorine atoms in (1). The positions of the hydrogen atoms were calculated geometrically assuming C–H and N–H = 1.08 Å and a fixed temperature factor of 0.07 Å^2 and floated on the associated carbon or nitrogen atom. The refinement converged when the ratio of the maximum shift to estimated standard deviation was 0.07 in (1), 0.06 in (2), and 0.02 in (3) using a refined weighting scheme $w = k/[\sigma^2(F_o) + g(F_o)^2]$. See Table 1 for the final values of *k* and *g*. Complex neutral scattering factors were used [8] for the non-hydrogen atoms and those for the heavy atoms were corrected for anomalous dispersion. All calculations were carried out using the programs SHELX-76 [9] and XANADU, G. M. Sheldrick; PLUTO, S. Motherwell; and XPUB, R. Taylor, on an IBM 370/138 computer. The final non-hydrogen atomic co-ordinates are given in Table 2, selected bond distances and bond angles in Table 3, some mean planes in Table 4, and some selected non-bonding distances in Figure 3. Figure 1 illustrates the local molecular structure and atom-numbering scheme used in all these complexes. The list of final structure factors, calculated hydrogen atomic co-ordinates, anisotropic temperature factors, the full list of bond lengths and bond angles, and some selected non-bonding distances are in Supplementary Publication No. SUP 23039 (60 pp.).†

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† For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.

TABLE 1

Crystal and refinement data for [Cu(dien)(bipyam)]X_2

X	(1) $Cl^-\cdot H_2O$	(2) $ClO_4^-\cdot 0.5H_2O$	(3) NO_3^-
M	444.71	554.8	461.54
Stoicheiometry	$C_{14}H_{26}Cl_2CuN_6O_2$	$C_{14}H_{24}Cl_2CuN_6O_9$	$C_{14}H_{22}CuN_8O_6$
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a(Å)	7.78(2)	15.683(5)	12.201(5)
b(Å)	9.75(3)	7.621(5)	16.052(6)
c(Å)	28.01(5)	21.044(9)	9.851(4)
β(°)	115.0(5)	121.42(2)	90.76(2)
U(Å^3)	1 925.63	2 146.38	1 929.15
Z	4	4	4
D_m(flotation) (g cm^{-3})	1.53(4)	1.88(4)	1.63(4)
D_c (g cm^{-3})	1.50	1.72	1.59
Radiation	Cu-K_α	Mo-K_α	Mo-K_α
F(000)	916.0	1 140.0	955.96
μ(cm^{-1})	41.34	12.52	11.38
No. unique reflections	1 146	3 011	3 580
Data used	all	all	3 440
No. varied parameters	117	290	265
R ($= \Sigma\Delta/\Sigma\|F_o\|$)	0.066 9	0.047 5	0.065 4
R' ($= \Sigma\Delta w^{\frac{1}{2}}/\Sigma\|F_o\|w^{\frac{1}{2}}$)	0.069 7	0.051 5	0.065 4
k	1.0	1.077 6	1.0
g	0.056 5	0.000 504	0.007 15
Max. final shift-to-error ratio	0.07	0.06	0.02
Residual electron density (e Å^{-3})	0.67	0.58	1.19 (0.58)
No. atoms anisotropic	3	32	29

TABLE 2

Fractional atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

	(1)				(2)			(3)		
	x/a	*y/b*	*z/c*	*U*	*x/a*	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*
Cu	2 000(3)	1 451(2)	1 297(1)		2 227	1 033(1)	2 375	2 848	4 450	3 273
N(1)	1 535(16)	2 014(14)	1 914(5)	38(3)	3 058(3)	2 482(5)	2 088(2)	3 950(3)	3 740(2)	4 323(3)
N(2)	3 954(16)	182(12)	1 810(5)	34(3)	1 726(3)	−184(5)	1 387(2)	4 130(2)	4 640(2)	1 985(3)
N(3)	2 148(16)	223(13)	733(5)	34(3)	882(3)	252(6)	2 226(2)	1 941(3)	4 355(2)	1 498(3)
N(4)	−456(15)	2 249(12)	789(4)	27(2)	2 477(3)	2 573(5)	3 221(2)	1 671(3)	4 070(2)	4 538(3)
N(5)	3 483(14)	3 178(11)	1 198(4)	26(2)	3 303(3)	−851(4)	3 151(2)	2 580(3)	5 702(2)	3 938(3)
N(6)	675(16)	4 502(12)	745(5)	35(3)	3 265(3)	380(5)	4 164(2)	1 659(4)	5 274(2)	5 920(4)
C(1)	2 963(22)	1 330(17)	2 385(7)	50(3)	3 011(4)	1 653(6)	1 439(3)	5 062(3)	3 907(3)	3 799(4)
C(2)	3 409(21)	−40(17)	2 241(6)	42(3)	1 962(4)	937(6)	931(3)	4 971(3)	3 990(3)	2 293(4)
C(3)	4 022(21)	−1 068(15)	1 509(6)	37(3)	644(4)	−587(6)	1 041(3)	3 708(3)	4 623(3)	567(4)
C(4)	3 887(21)	−622(17)	984(7)	45(3)	474(4)	−1 143(6)	1 654(3)	2 719(3)	4 064(3)	462(4)
C(5)	−1 973(20)	1 368(18)	624(6)	41(3)	2 104(4)	4 223(6)	3 037(3)	1 322(4)	3 274(3)	4 337(5)
C(6)	−3 741(20)	1 803(15)	313(6)	38(3)	2 075(4)	5 362(6)	3 522(3)	687(4)	2 853(3)	5 237(5)
C(7)	−3 988(22)	3 122(17)	133(7)	43(3)	2 465(4)	4 804(6)	4 256(3)	358(4)	3 275(3)	6 395(5)
C(8)	−2 496(19)	4 001(15)	270(6)	31(3)	2 852(4)	3 155(6)	4 455(3)	687(4)	4 080(3)	6 619(5)
C(9)	−680(17)	3 531(15)	618(5)	26(3)	2 864(3)	2 054(5)	3 925(2)	1 353(3)	4 463(3)	5 647(4)
C(10)	2 618(19)	4 360(16)	991(6)	30(3)	3 607(3)	−864(5)	3 877(2)	2 112(3)	5 889(2)	5 116(4)
C(11)	3 659(21)	5 572(17)	1 005(6)	41(3)	4 241(4)	−2 148(6)	4 364(2)	2 058(3)	6 709(3)	5 621(4)
C(12)	5 598(20)	5 526(17)	1 230(6)	42(3)	4 587(4)	−3 426(6)	4 102(3)	2 496(4)	7 343(3)	4 871(5)
C(13)	6 522(23)	4 289(18)	1 433(7)	51(3)	4 315(3)	−3 406(6)	3 359(3)	2 968(4)	7 159(3)	3 620(5)
C(14)	5 424(20)	3 153(17)	1 414(6)	40(3)	3 689(3)	−2 088(6)	2 918(2)	2 982(3)	6 347(2)	3 199(4)
Cl(1)	899(6)	2 343(4)	−336(2)		670(1)	−832(2)	4 130(1)			
Cl(2)	−1 744(7)	435(5)	2 890(2)		4 234(1)	6 569(2)	1 246(1)			
N(7)								4 195(3)	1 668(2)	2 798(4)
N(8)								957(3)	9 056(2)	4 189(3)
O(1)	858(17)	2 821(14)	3 540(5)	68(3)	1 010(6)	718(7)	4 476(4)	3 447(3)	2 137(2)	2 399(5)
O(2)	1 677(16)	5 297(12)	3 185(5)	58(3)	−343(4)	−990(8)	3 878(5)	4 295(3)	963(2)	2 254(3)
O(3)					1 172(4)	−2 257(6)	4 603(3)	4 850(4)	1 872(3)	3 702(4)
O(4)					690(7)	−963(10)	3 509(4)	1 893(3)	9 327(3)	3 931(4)
O(5)					4 598(4)	5 887(6)	1 968(2)	374(3)	8 823(2)	3 210(3)
O(6)					5 031(3)	7 397(6)	1 219(2)	626(4)	9 026(2)	5 360(3)
O(7)					3 860(4)	5 171(5)	726(2)			
O(8)					3 469(4)	7 803(6)	1 064(3)			
O(9)					1 954(3)	5 820(5)	1 241(2)			

TABLE 3

Selected bond lengths (Å) and bond angles (°), with estimated standard deviations in parentheses

	(1)	(2)	(3)
N(1)–Cu	1.988(14)	2.025(7)	2.035(5)
N(2)–Cu	2.015(14)	2.024(6)	2.050(5)
N(3)–Cu	2.024(14)	2.051(7)	2.062(5)
N(4)–Cu	1.995(13)	1.994(6)	2.009(5)
N(5)–Cu	2.125(13)	2.169(5)	2.142(5)
N(2)–Cu–N(1)	84.8(6)	84.8(3)	83.9(2)
N(3)–Cu–N(1)	159.0(5)	151.9(1)	137.2(1)
N(3)–Cu–N(2)	85.3(6)	83.8(3)	83.8(2)
N(4)–Cu–N(1)	92.4(6)	95.0(3)	89.3(2)
N(4)–Cu–N(2)	162.6(5)	167.8(1)	170.7(1)
N(4)–Cu–N(3)	91.6(6)	90.9(3)	97.1(2)
N(5)–Cu–N(1)	101.8(6)	102.5(3)	118.2(2)
N(5)–Cu–N(2)	107.0(5)	101.8(2)	99.8(2)
N(5)–Cu–N(3)	98.8(6)	104.9(3)	104.2(2)
N(5)–Cu–N(4)	90.4(5)	90.2(3)	88.9(2)

TABLE 4

Equations of least-squares planes in the form $lX + mY + nZ = p$, where X, Y, and Z are a set of orthogonal axes. Deviations (Å) of relevant atoms from planes are given in square brackets

	l	m	n	p
(*a*) Complex (1)				
Plane (1): N(1), N(2), N(3), N(4) [root-mean-square (r.m.s.) deviation 0.020]				
	0.6110	0.7357	−0.2923	0.7113
[N(1) −0.020, N(2) 0.021, N(3) −0.020, N(4) 0.019, Cu 0.321]				
Plane (2): N(4), C(5)—C(9) (r.m.s. deviation 0.016)				
	−0.1601	0.2858	0.9448	2.8956
[N(4) 0.010, C(5) −0.025, C(6) 0.018, C(8) −0.018, C(9) 0.011]				
Plane (3): N(5), C(10)—C(14) (r.m.s. deviation 0.006)				
	0.0175	0.2462	0.9691	2.9425
[N(5) 0.005, C(10) −0.005, C(12) 0.009, C(13) −0.008]				
Angle between planes (2) and (3) is 10.5°. Angle between the Cu–N(5) direction and the perpendicular to plane (1) is 8.5°.				
(*b*) Complex (2)				
Plane (1): N(1), N(2), N(3), N(4) (r.m.s. deviation 0.131)				
	0.6237	−0.7318	0.2748	1.8174
[N(1) −0.129, N(2) 0.140, N(3) −0.133, N(4) 0.121, Cu 0.338]				
Plane (2): N(4), C(5)–C(9) (r.m.s. deviation 0.006)				
	0.8986	0.3514	−0.2627	2.4294
[N(4) −0.010, C(9) 0.010]				
Plane (3): N(5), C(10)—C(14) (r.m.s. deviation 0.013)				
	0.7865	0.5778	−0.2180	2.2674
[N(5) −0.022, C(10) 0.012, C(11) 0.005, C(12) −0.013, C(13) 0.003, C(14) 0.015]				
Angle between planes (2) and (3) is 14.7°. Angle between the Cu–N(5) direction and the perpendicular to plane (1) is 6.2°.				
(*c*) Complex (3)				
Plane (1): N(1), N(2), N(3), N(4) (r.m.s. deviation 0.290)				
	0.0044	0.9452	0.3265	7.3668
[N(1) −0.302, N(2) 0.311, N(3) −0.277, N(4) 0.268, Cu 0.437]				
Plane (2): N(4), C(5)—C(9) (r.m.s. deviation 0.0054)				
	0.8160	−0.3314	0.4737	1.5977
[C(5) −0.009, C(6) 0.008]				
Plane (3): C(10)—C(14), N(5) (r.m.s. deviation 0.008)				
	0.8853	−0.1243	0.4481	3.3549
[C(14) −0.010, N(5) 0.013, C(12) 0.008]				
Angle between planes (2) and (3) is 12.6°. Angle between the Cu–N(5) direction and the perpendicular to plane (1) is 9.1°.				

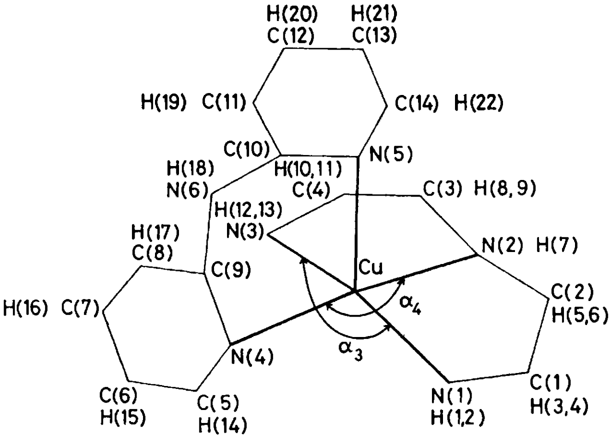

FIGURE 1 Schematic diagram of the chromophores with atom-labelling scheme

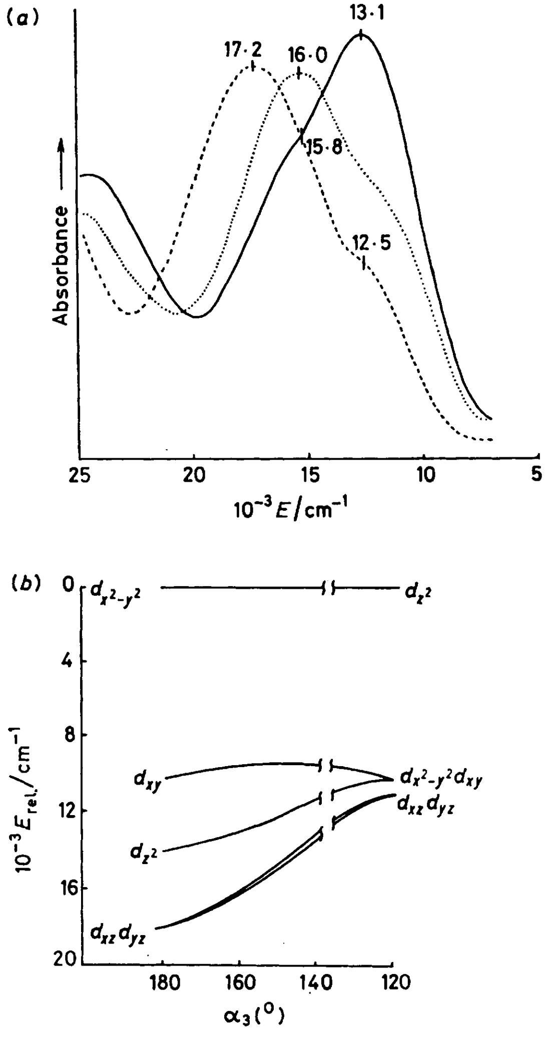

FIGURE 2 (*a*) The electronic diffuse reflectance spectra of the [Cu(dien)(bipyam)]X_2 complexes: X = $Cl^-\cdot H_2O$ (- - -); X = $ClO_4^-\cdot 0.5H_2O$ (···); X = NO_3^-(—). (*b*) The variation of the one-electron orbital levels with angular distortion N(1)–Cu–N(3) from 120° to 180° using a crystal-field model

Electronic Properties.—These were recorded as previously described.[1,10] Figure 2(*a*) reports the electronic reflectance spectra for all three complexes and Figure 2(*b*) some crystal-field calculations for the copper(II) ion in a regular trigonal-bipyramidal to square-pyramidal stereochemistry with variation in the α_3 angle of Figure 1 using a modified local molecular orbital program.[11]

DISCUSSION

Description of the Crystal Structures.—The structures of (1), (2), and (3) consist of discrete $[Cu(dien)(bipyam)]^{2+}$ cations and Cl^- anions in (1), ClO_4^- anions in (2), and NO_3^- anions in (3); in addition (1) has two molecules of water in the lattice and (2) has one molecule.

There are no unusual bond lengths or angles in the nitrate ions [12] of (3) and the perchlorate[13] ions of (2) are reasonably tetrahedral, 109 ± 6°; with equivalent Cl–O bond distances except for the Cl–O(4) distance of 1.329 (12) Å, which is significantly shorter, but this may result from the unusually high anisotropic temperature factors of the O(4) atom (see SUP 23039). The ClO_4^- ion showed some evidence of disorder, but attempts to represent this by a disordered perchlorate failed to improve the structure and both perchlorate anions were refined with high anisotropic temperature factors.[14] There was no evidence for semi-co-ordination [15] of the chloride or nitrate anion in (1) and (3) or of the water molecules in (1) and (2), but the O(2) atom in (2) does occupy a position 2.56(7) Å from the Cu atom, sufficiently close to be involved in weak semi-co-ordination to the copper atom.

The stereochemistry of the $[Cu(dien)(bipyam)]^{2+}$ cation is strictly five-co-ordinate in (1) and (3) with a CuN_5 chromophore, but in (2) the extra O(2) co-ordination gives a CuN_5O chromophore with a 4 + 1 + 1* stereochemistry.[16] In all three complexes a square-pyramidal CuN_5 chromophore is present, with the dien ligand occupying [17] three in-plane bonding positions and the bipyam bonding in the plane, N(4), and out of the plane, N(5), see Figure 1. There are no unusual bond distances or bond angles in the dien [17] or bipyam ligands [18] (Table 3 and SUP 23039) and the dien bonds have a planar,[19] rather than a bent conformation, as previously observed for the dien ligand when bonded to the copper(II) ion, see $[Cu(dien)(bipy)][NO_3]_2 \cdot 2H_2O$ [20] and $[Cu(dien)(phen)][NO_3]_2$ (bipy = 2,2'-bipyridyl, phen = 1,10-phenanthroline). The dien ligand [20] in (1) and (2) bonds with a symmetrical k'k' conformation, but unsymmetrically in (3), Figure 3. The individual pyridine rings of the bipyam ligands are reasonably planar, Table 4, however the pairs of rings are not coplanar, but inclined at angles of 10.5, 14.7, and 12.6° in (1), (2) and (3) respectively, Table 5. The CuN_5 chromophores involve four almost equivalent in-plane Cu–N distances, mean 2.00 Å, and a slightly longer Cu–N(5) bond distance, 2.125(13) Å in (1), 2.142(5) Å in (3), and 2.169(5) Å in (2), out-of-plane distances, which are comparable, Table 5, to the Cu–N(5) distance of 2.164(12) Å in $[Cu(dpt)(bipyam)][NO_3]_2$, where dpt = dipropylenetriamine or bis(3-aminopropyl)-amine, but are significantly different from complexes,[20,21] Table 5, where bipy or phen are involved in out of plane chelation 2.192(6)—2.224(20) Å. The difference in the Cu–N(5) bond distance of 0.05 Å, could be associated with the large angle of twist between the pyridine rings of the bipyam ligands in (1)—(3) of 10.5—14.7°, relative to the 0.0—2.15° in the phen and bipy ligands of (5)—(7),[20-21] but the relatively low angle of twist of the bipyam ligand of (4),[21] 4.3°, upsets this correlation.

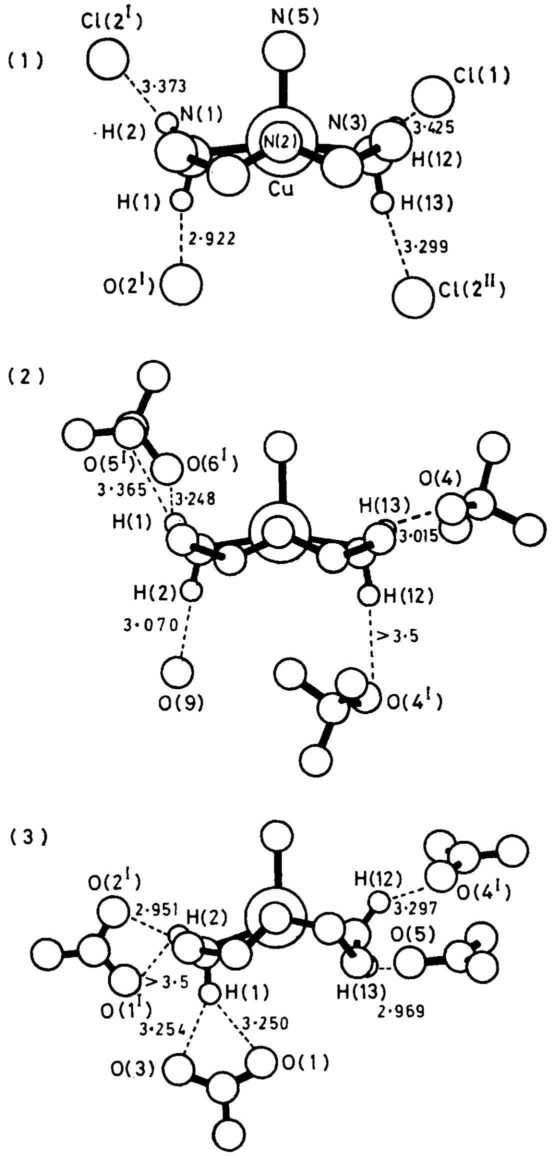

FIGURE 3 Conformation of the dien ligand as viewed along the Cu–N(2) bond. (1) X = $Cl^- \cdot H_2O$, (2) X = $ClO_4^- \cdot 0.5H_2O$, (3) X = NO_3^-

The difference in the Cu–N(5) distances is better associated with the difference in the bite distances, Table 5, in the out of the plane chelate ligands, which are 2.91—2.97 Å in the six-membered rings of the bipyam ligands compared with 2.65—2.69 Å in the five-membered rings of the bipy and phen ligands. Thus the large bite distances of the bipyam ligands not only generate near 90° N(4)–Cu–N(5) angles, compared with 77.7 ± 0.7° in the bipy and phen ligands, but surprisingly generate consistently shorter Cu–N(5) distances, of *ca.* 2.14 Å.

TABLE 5

The angle of twist between pyridine rings of bipyam, bipy, and phen ligands, the N(4)–N(5) bite distances, and Cu–N(5) distances in some [Cu(tridentate)(bidentate)] X_2 complexes

	Complex	Twist (°)	N(4)–N(5) (Å)	Cu–N(5) (Å)	N(4)–Cu–N(5) (°)
(1)	$[Cu(dien)(bipyam)]Cl_2 \cdot 2H_2O$	10.5	2.966(26)	2.125(13)	90.4(5)
(2)	$[Cu(dien)(bipyam)][ClO_4]_2 \cdot H_2O$	14.7	2.951(10)	2.169(5)	90.2(2)
(3)	$[Cu(dien)(bipyam)][NO_3]_2$	12.6	2.909(10)	2.142(5)	88.9(2)
(4)	$[Cu(dpt)(bipyam)][NO_3]_2$	4.3	2.949(24)	2.164(12)	89.2(6)
(5)	$[Cu(dpt)(bipy)][NO_3]_2$	2.2	2.651(22)	2.218(11)	77.0(4)
(6)	$[Cu(dien)(bipy)][NO_3]_2 \cdot 2H_2O$	1.3	2.661(12)	2.192(6)	78.4(2)
(7)	$[Cu(dien)(phen)][NO_3]_2$	0.0	2.692(40)	2.224(20)	77.8(8)

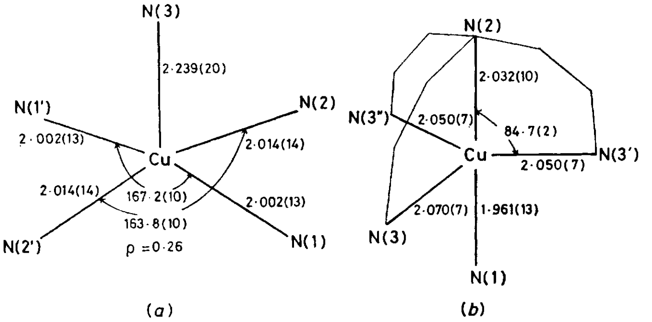

FIGURE 4 The molecular geometry (distances, Å; angles, °) of (*a*) $K[Cu(NH_3)_5][PF_6]_3$ and (*b*) $[Cu(tren)(NH_3)][ClO_4]_2$

In (1), (2), and (3) there are significant differences in the angular distortion of the N(1)–Cu–N(3)(α_3) and N(2)–Cu–N(4) (α_4) angles of the CuN_5 chromophore, the former decreases 159.0(5), 151.9(1), and 137.2(1)° and the latter increases, 162.6(5), 167.8(1), and 170.7(1)° in the series. In (1) the values of α_3 and α_4 are almost equivalent 159.0 (5) and 162.6(5)° respectively, and are not too different from those of 165.5 $\pm$ 1.7° in the most regular square-pyramidal stereochemistry [22] of $K[Cu(NH_3)_5][PF_6]_3$, Figure 4 (*a*), where the angular distortions lift the copper(II) ion out of the plane of the N(1)–N(4) ligands by $\rho = 0.26$ Å, compared with a ρ of 0.32 Å in (1). In (1) the CuN_5 chromophore stereochemistry is the most regular square pyramidal, while in (2) and (3) there is an increasing angular distortion towards a trigonal-bipyramidal stereochemistry, with the N(2)–Cu–N(4) direction representing the trigonal axis which in (3) involves an α_4 angle of 170.7(1)° *i.e.* nearly linear, compared with the near trigonal angle, α_3, of 137.2(1)°. Consequently the stereochemistry of (3) is nearer to that of $[Cu(tren)(NH_3)][ClO_4]_2$ (tren = 2,2',2''-triaminotriethylamine), Figure 4(*b*), which involves the most regular σ-bonded trigonal-bipyramidal CuN_5 chromophore.[22] The angular distortion present in the three complexes (1), (2), and (3) represents a very significant distortion of the stereochemistry of the equivalent CuN_5 chromophores present involving differences of ($\alpha_4 - \alpha_3$) of 3.6(10), 15.9(2), and 33.5(2)° respectively, of the same $[Cu(dien)(bipyam)]^{2+}$ cation [ignoring the O(2) ligand in (2)]. Thus the three complexes represent a series of cation distortion isomers whose stereochemistries reflect the flexible stereochemistry [1,2] of the copper(II) ion or ' Plasticity Effect.'[5] Not only are the three stereochemistries different, but they are related by the change from a regular square-pyramidal stereochemistry towards that of a regular trigonal-bipyramidal stereochemistry, a change that follows the mechanistic pathway of the Berry twist,[23] in which a normal mode of vibration of the square pyramid, Figure 5, changes the stereochemistry to that of a trigonal bipyramid. The individual structures of (1), (2), and (3) then represent individual points in the structural profile [24-26] which are related by a mode of vibration of the CuN_5 chromophore. While the flexible stereochemistry of the d^9 configuration allows the different geometries to be attained, the precise geometry assumed must be determined by relatively weak lattice packing forces, such as hydrogen bonding and van der Waals forces. As the major difference in stereochemistry of the CuN_5 chromophore of (1), (2), and (3) is the α_3 angle, it is worth examining the hydrogen-bond involvement of the terminal N(1) and N(3) atoms of the dien ligand, Figure 3. No obvious pattern of hydrogen-bond contacts occurs which can account for the observed differences in the α_3 values of (1), (2), and (3).

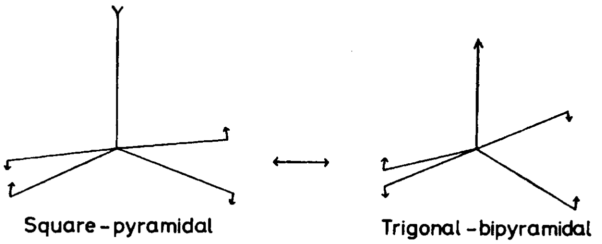

FIGURE 5 The forms of the Berry twist from a square-pyramidal to a trigonal-bipyramidal stereochemistry

One consequence of the trigonal distortion of the CuN_5 chromophore is the estimated standard deviation of the N(1)–N(4) planes, Table 4, which all involve N(1) and N(3) lying on one side of the plane, along with the Cu atom and N(2) and N(4) on the opposite side of the plane. Due to this lack of planarity, the copper atom lies well above this mean plane towards the N(5) atom, with deviations of 0.32, 0.34, and 0.44 Å for (1), (2), and (3), respectively; with the ρ value for (3) the largest, and all significantly greater than that of 0.26 Å in $K[Cu(NH_3)_5][PF_6]_3$.[22] Due to the out-of-plane bite of the bipyam ligand the Cu–N(5) directions are not at 90° to the N(1)–N(4) plane, but rather at an angle of 8.47(5), 6.24(2), and 9.09(2)° respectively, to the perpendicular to this plane in (1), (2), and (3) respectively. In the nearer square-pyramidal stereochemistry of (1) and (2) the N(1)–Cu–N(5) and N(3)–Cu–N(5) angles are comparable, *ca.* 100°, but in (3) there is a difference of 14°, possibly associated with the lower α_3 angle of (3), Table 3 and Figure 3.

Electronic Properties.—The polycrystalline e.s.r. spectra of (1) and (2) were essentially isotropic, but with relatively low g values of 2.054 and 2.055 respectively, and no evidence for a higher g value, spectra that could only arise if partial resolution of copper hyperfine structure on the higher g factor occurs, which has so broadened the g factor that it was unobserved. Attempts to measure the single-crystal e.s.r. spectrum of (2) were so complicated by partially resolved copper hyperfine structure that it was not pursued, but lent some support to the interpretation of the polycrystalline spectra above. The polycrystalline e.s.r. spectrum of (3) is rhombic, 2.021, 2.095, and 2.179, with an R value of 0.894 [$R = (g_2 - g_1)/(g_3 - g_2)$] indicating a very intermediate set of g values. As the CuN_5 chromophore of (3) is misaligned [1] by 18.4° with respect to the Cu–N(5) and Cu–N(4) directions and in the absence of good single-crystal g values the crystal g values were not resolved into their local molecular g values; nevertheless, the lowest crystal g factor of 2.021 is almost pure and corresponds to the N(2)–Cu–N(4) direction. Any resolution of the two higher g values can only decrease the intermediate g value of 2.095 and increase the highest, 2.179, towards the extreme values observed in the copper-doped [Zn(dien)(bipyam)][NO_3]$_2$ system [27] of 2.026, 2.110, and 2.220 which yields an R value of 0.763 and which suggests a ground-state intermediate between $d_{x^2-y^2}$ and d_{z^2} with only a slight preference for the former.

The electronic reflectance spectra of (1), (2), and (3) are significantly different, Figure 2(*a*); (1) consists of a main peak at 17 200 cm^{-1} with a low-energy shoulder at *ca.* 12 000—13 000 cm^{-1}, while (3) has a clear maximum at 13 000 cm^{-1} with a poorly resolved high-energy shoulder at 15 800 cm^{-1}. These differences are also reflected in the different colours of the complexes, (1) is violet-blue, (2) is steel blue, and (3) is turquoise-green. These spectral changes parallel the changes observed in the more regular CuN_5 chromophores [22] of [Cu(tren)(NH_3)][ClO_4]$_2$ trigonal bipyramidal, and K[Cu(NH_3)$_5$][PF_6]$_3$ square pyramidal; the former has a maximum at 11 400 cm^{-1} with a high-energy shoulder at 15 200 cm^{-1} and the latter a maximum at 15 300 cm^{-1} with a low-energy shoulder at 11 000 cm^{-1} (Figure 2, ref. 22). In the electronic spectra of (1), (2), and (3) there is a clear shift in energy of the band maximum of 4 100 cm^{-1} in going from (1) to (3) along with a shift of the low-energy shoulder to a high-energy shoulder. This shift in the average energy of the three spectra is consistent with the shift in the relative energies from crystal-field calculations using the respective CuN_5 geometries and ignoring the effect of the O(2) atom in (2), Figure 2(*b*). Consequently, within this series of three cation distortion isomers the electronic reflectance spectra are most sensitive to the change in angular distortion of the CuN_5 chromophore stereochemistry and suggest that for this [Cu(dien)(bipyam)]$^{2+}$ cation there may be [28] an 'electronic criterion of stereochemistry' available in going from distorted square pyramidal to distorted trigonal bipyramidal for the same CuN_5 chromophore. Although, no polarised single-crystal electronic spectra were obtained for (1), (2), or (3), that for the 10% copper-doped [Zn(dien)(bipyam)][NO_3]$_2$ system [26] has been reported earlier. In view of the close correspondence of the crystal g factors for the 1% and 100% copper-doped complexes and the lack of variation in the electronic reflectance spectra over this concentration range (the non-co-operative Jahn–Teller [29] effect), the one-electron orbital sequence of the 10% copper-doped system, namely, $d_{x^2-y^2} > d_{z^2} > d_{xz}d_{yz}$ is also appropriate for (3). The one-electron energy levels, Table 6, are then closely comparable to those obtained for two other complexes of the copper(II) ion with distorted square-base pyramidal stereochemistries,[30,31] taking into account the different ligands involved and the different bond lengths and bond angles (see ref. 27 for discussion).

TABLE 6

The assignment of the one-electron energy levels (cm^{-1}) for (*a*) [Cu(dien)(bipyam)][NO_3]$_2$, (*b*) [Cu(dien)(O_2CH)][O_2CH], and (*c*) [Cu(phen)$_2$(OH_2)][NO_3]$_2$

	(*a*)	(*b*)	(*c*)
$d_{z^2} \rightarrow d_{x^2-y^2}$	13 100	11 500	12 000
$d_{xy} \rightarrow d_{x^2-y^2}$	14 200—14 800	14 200	Not observed
$d_{xz} \rightarrow d_{x^2-y^2}$	11 500	15 200	15 000
$d_{yz} \rightarrow d_{x^2-y^2}$	11 500	15 400	13 000

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