Crystal Structure † and Electronic Properties of Bis(2,2′-bipyridyl)-cyanocopper(II) Nitrate Dihydrate: A Correlation of the In-plane Angular Distortion with the Splitting of the Electronic Spectrum

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The crystal structure of the title compound $[Cu(bipy)_2(CN)][NO_3]\cdot 2H_2O$ has been determined by *X*-ray analysis. It crystallises in the monoclinic space group, $P2_1/n$ with $a = 9.263(3)$, $b = 24.678(4)$, $c = 10.123(3)$ Å, $\beta = 109.83(8)°$, and $Z = 4$. The five-co-ordinate CuN_2N_2C chromophore has a distorted trigonal-bipyramidal stereochemistry related to a regular trigonal-bipyramidal stereochemistry by distortion towards square pyramidal. The cyanide ion is bonded to the copper atom in the trigonal plane, *via* the carbon atom at a distance of 1.974(5) Å. The three in-plane trigonal angles of 138.0, 126.5, and 95.4° show considerable distortion from 120°, and are considered responsible for the splitting in the twin-peaked electronic reflectance spectrum (12 820 and 14 920 cm^{-1}).

The crystal structure[1] of $[Cu(phen)_2(CN)][NO_3]\cdot H_2O$ (1) (phen = 1,10-phenanthroline) involves a basic trigonal-bipyramidal CuN_4C chromophore with almost equivalent bonding of the phen ligands, with near equivalent ($\approx C_2$) angular distortion from trigonal, 132.4, 129.0, and 98.6°, respectively, and which yields an asymmetric single peak at 13 070 cm^{-1} in the electronic reflectance spectrum. The observation of a twin-peaked electronic reflectance spectrum for $[Cu(bipy)_2(CN)][NO_3]\cdot 2H_2O$ (2) (bipy = 2,2′-bipyridyl) suggests the presence of a square-pyramidal distorted trigonal-bipyramidal stereochemistry[2,3] for the CuN_4C chromophore. In order to confirm this the single-crystal *X*-ray structure of complex (2) has been determined and the electronic properties of (1) and (2) are used to suggest 'an electronic criterion of stereochemistry' to distinguish[4] the stereochemistries in these two complexes, which could then be used to predict the structure of complexes of unknown crystal structure.

Experimental

Preparation.—Complex (2) was prepared by standard methods[1-3] as dark blue diamond-shaped crystals (Found: C, 49.95; H, 4.05; N, 16.4. $C_{21}H_{20}CuN_6O_5$ requires C, 50.45; H, 4.0; N, 16.8%). Complex (1) was prepared by the literature method[1] and characterised by microanalysis.

Crystallography.—*Crystal data.* $C_{21}H_{20}CuN_6O_5$, $M = 499.54$, Monoclinic, $a = 9.263(3)$, $b = 24.678(4)$, $c = 10.123(3)$ Å, $\beta = 109.83(8)°$, $U = 2\,172.82$ Å^3, $D_m = 1.52 \pm 0.02$ g cm^{-3}, $Z = 4$, $D_c = 1.53$ g cm^{-3}, $F(000) = 1\,043.96$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 10.07 cm^{-1}, space group $P2_1/n$, $0k0$, k even; $h0l$, $h + l$ even.

Data collection was carried out as described previously[5] on a flat diamond-shaped crystal developed on the [101] face and elongated parallel to the b axis with dimensions 0.2 × 0.3 × 0.1 mm. 3 684 Reflections were retained with $3.0 < \theta < 30°$ and $I > 2.5\sigma(I)$. The refinement converged when the shift-to-error ratio of any parameter was less than 0.007 with a refined weighting scheme, $w = k/\sigma^2(F_o + gF_o^2)$, where the final k and g were 0.724 and 0.006 24, respectively. The final R and R' values were 0.0420 and 0.0508, with a maximum residual electron density of 0.357 e Å^{-3}. All calculations were carried out with the SHELX 76 and XANADU (G. M. Sheldrick), PLUTO (S. Motherwell), and XPUB (R. Taylor) systems of programs[6] on an IBM 370/138 computer.

The final atomic co-ordinates are given in Table 1, selected bond lengths and bond angles in Table 2, Figure 1 illustrates the molecular structure of (2) and the atom-numbering scheme used, and Figure 2 shows the molecular packing in the unit cell viewed down the b axis.

Electronic Properties.—These were recorded as described previously.[7] The electronic reflectance spectra of complexes (1) and (2) are shown in Figure 3(*a*); the former involves an asymmetric single peak at 13 070 cm^{-1}, and the latter consists of two equally intense peaks, only just resolved, at 12 820 and 14 920 cm^{-1} (Table 4). The polycrystalline e.s.r. spectrum of complex (2) involves an isotropic spectrum, 2.098, with no evidence of a high g value; at the temperature of liquid nitrogen a high g value of 2.22 is just resolved, Figure 3(*b*). The spectrum of complex (1) is rhombic with g values of 2.018, 2.120, and 2.210 at the temperature of liquid nitrogen. The single-crystal g values for complex (2) are 2.031, 2.102 and 2.205; those for (1) are 2.023, 2.109, and 2.231. In complex (2) the lowest g value of 2.031 is parallel to the unique crystallographic b axis, but as the CuN_4C chromophore is misaligned[7] with respect to the b axis the crystal g values do not equate with the local molecular g values. In the triclinic space group[1] of complex (1), the crystal g values equate with the local molecular g values; g_1 correlates with the N(1)–N(3) direction, g_2 with Cu–C(21), and g_3 with N(2)–N(4), Table 3, and not with Cu–N(4).

Results and Discussion

Crystal Structure.—The crystal structure of complex (2) consists of discrete $[Cu(bipy)_2(CN)]^+$ cations, NO_3^- anions, and two molecules of water in the unit cell. There are no unusual bond lengths or angles in the bipy ligands[8] and the nitrate anion[9] involves reasonable N–O bond distances, mean 1.241(4) Å, and angles, mean 120.0(3)°. Both the cation and anion are in general positions with no evidence of semico-ordination[10] to the copper atom by the nitrate or water molecules (Figure 2) with the planes of the N(1)–N(2) bipy ligand and the nitrate ions stacked parallel to the a^*b lattice plane.

A referee has pointed out that both water molecules, O(4)

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† *Supplementary data available* (No. SUP 23457, 29 pp.): H-atom co-ordinates, thermal parameters, complete bond lengths and angles, least-squares planes, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Atomic co-ordinates (× 10^4) of $[Cu(bipy)_2(CN)][NO_3]\cdot 2H_2O$ with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Cu	5 674(1)	3 710(1)	4 154(1)
N(1)	4 812(3)	2 965(1)	4 068(3)
C(1)	3 297(4)	2 856(1)	3 624(3)
C(2)	2 753(5)	2 337(2)	3 627(4)
C(3)	3 805(6)	1 915(2)	4 083(4)
C(4)	5 357(5)	2 029(1)	4 546(4)
C(5)	5 843(4)	2 563(1)	4 538(3)
C(6)	7 474(4)	2 732(1)	5 048(3)
C(7)	8 688(5)	2 375(2)	5 518(4)
C(8)	10 174(5)	2 578(2)	6 003(4)
C(9)	10 390(4)	3 128(2)	6 042(4)
C(10)	9 127(4)	3 464(2)	5 552(4)
N(2)	7 701(3)	3 272(1)	5 053(3)
N(3)	6 707(3)	4 437(1)	4 566(2)
C(11)	7 293(4)	4 687(1)	3 664(3)
C(12)	8 027(4)	5 184(1)	3 985(4)
C(13)	8 163(4)	5 425(1)	5 243(4)
C(14)	7 559(3)	5 166(1)	6 159(3)
C(15)	6 832(3)	4 674(1)	5 794(3)
C(16)	6 122(3)	4 372(1)	6 687(3)
C(17)	6 206(4)	4 542(1)	8 022(3)
C(18)	5 542(5)	4 231(2)	8 787(4)
C(19)	4 789(5)	3 762(1)	8 211(4)
C(20)	4 745(4)	3 613(1)	6 877(3)
N(4)	5 378(3)	3 913(1)	6 124(2)
C(21)	4 306(4)	3 919(1)	2 260(3)
N(5)	3 503(4)	4 033(1)	1 162(3)
O(4)	805(4)	4 387(1)	8 832(3)
O(5)	4 297(4)	502(1)	5 939(4)
N(6)	3 879(4)	1 749(1)	7 275(3)
O(1)	3 995(4)	2 244(1)	7 382(3)
O(2)	2 626(3)	1 524(1)	6 842(3)
O(3)	5 071(3)	1 455(1)	7 589(3)

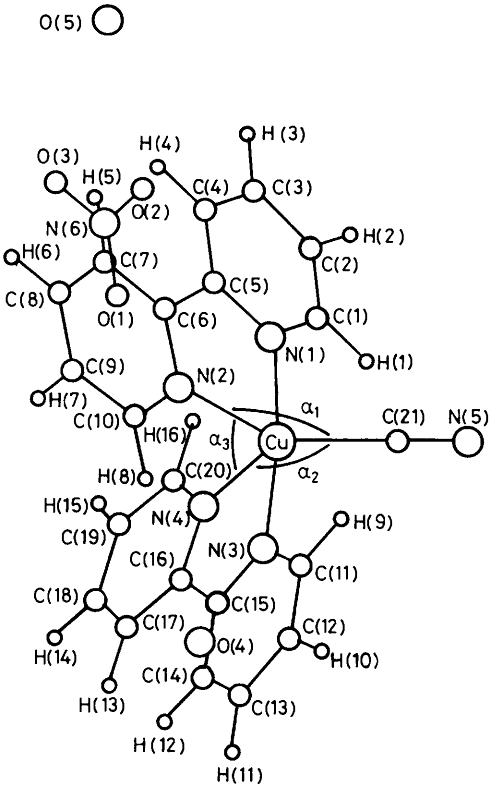

Figure 1. Molecular structure of $[Cu(bipy)_2(CN)][NO_3]\cdot 2H_2O$ showing the atom numbering and angle notations used

and O(5), are involved in a rather unusual quadrilateral hydrogen bonding to their symmetry-related molecules through the centres of symmetry at $0\,\tfrac{1}{2}\,0$ and $\tfrac{1}{2}\,0\,\tfrac{1}{2}$, respectively, with non-bonding distances of 2.93 and 2.78 Å, respectively. The i.r. spectrum of complex (2) shows a rather broad peak at 3 325 cm^{-1} with a broad shoulder at 3 220 cm^{-1} which may be consistent with significant hydrogen bonding, but as the hydrogen atoms involve calculated positions this hydrogen bond is not well defined. Neither water molecule makes any significant non-bonding contacts with the remainder of the atoms in the structure.

The stereochemistry of the $[Cu(bipy)_2(CN)]^+$ cation of (2) is clearly five-co-ordinate with the cyanide group bonding *via* its carbon atom to give a basically trigonal-bipyramidal $CuN_2N'_2C$ chromophore, Figure 1. The out-of-plane bond lengths Cu–N(1) and Cu–N(3) are significantly different, 1.996(4) and 2.008(4) Å [mean 2.002(4) Å], and are significantly shorter than the two in-plane distances Cu–N(2) and Cu–N(4), 2.088(4) and 2.161(5) Å, respectively (mean 2.125 Å), a difference >0.1 Å as previously reported[11] for trigonal-bipyramidal copper(II). The two in-plane Cu–N distances are themselves significantly different (0.073 Å), with the Cu–N(4) distance [2.161(5) Å] being the longest Cu-bipy distance. The cyanide ion co-ordinates in-plane to the copper atom *via* the carbon atom at a distance of 1.974(5) Å. None of the out-of-the-trigonal-plane bond angles is unusual,[12] 90 ± 10°, with the bites of the bipy ligands comparable at 79.4 ± 0.8°. The individual pyridine rings of the bipy ligands are reasonably planar, root-mean-square deviations being less than 0.0087 Å, with the separate bipy ligands involving angles of twist of 5.5 and 3.4°, respectively, both less than the values (up to 11°) previously observed[10] for co-ordinated bipy. The mean planes of the bipy ligands are inclined at 86.5° to each other. The N(1)–Cu–N(3) angle, α_8, of 170.9(1)° (Table 2) is almost linear, with the N(1) and N(3) atoms bent away from the Cu–CN bond, and the α_4 and α_5 angles, 94.7(2) and 94.2(2)°, respectively, are greater than 90°, indicative of a trigonal[13] rather than a tetrahedral twist to the CuN_4 chromophore of the N(1)—N(4) atoms. Within the trigonal-plane

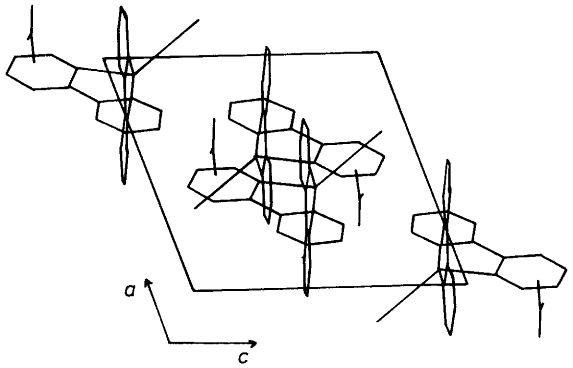

Figure 2. Molecular packing of $[Cu(bipy)_2(CN)][NO_3]\cdot 2H_2O$ viewed down the *b* axis

Table 2. Selected bond lengths (Å) and angles (°) for $[Cu(phen)_2(CN)][NO_3]\cdot H_2O$ (1) and $[Cu(bipy)_2(CN)][NO_3]\cdot 2H_2O$ (2) with estimated standard deviations in parentheses

	(1)	(2)		(1)	(2)
Cu-N(1)	2.001(10)	1.996(4)	C(21)-Cu-N(2) (α_1)	132.4(3)	138.0(1)
			C(21)-Cu-N(4) (α_2)	129.0(3)	126.5(2)
Cu-N(2)	2.102(6)	2.088(4)	N(2)-Cu-N(4) (α_3)	98.6(2)	95.4(2)
			C(21)-Cu-N(1) (α_4)	93.9(5)	94.7(2)
Cu-N(3)	2.014(10)	2.008(4)	C(21)-Cu-N(3) (α_5)	91.8(5)	94.2(2)
			N(1)-Cu-N(2) (α_6)	80.7(3)	80.2(2)
Cu-N(4)	2.123(6)	2.161(5)	N(3)-Cu-N(4) (α_7)	79.9(3)	78.6(2)
			N(1)-Cu-N(3) (α_8)	174.3(3)	170.9(1)
Cu-C(21)	1.935(10)	1.974(5)	N(1)-Cu-N(4) (α_9)	96.0(3)	94.5(2)
			N(3)-Cu-N(2) (α_{10})	95.9(3)	94.4(2)
N(5)-C(21)	1.161(5)	1.144(5)	N(5)-C(21)-Cu	174.3(3)	179.0(3)

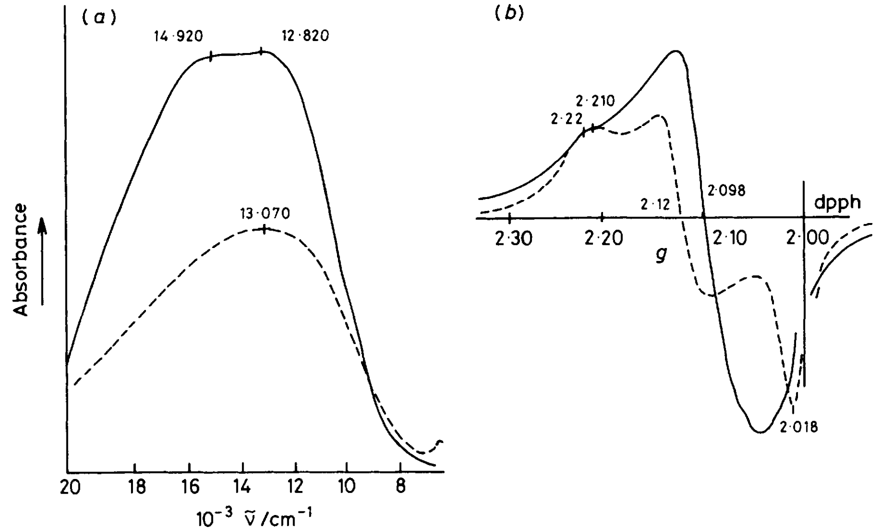

Figure 3. (a) Electronic reflectance and (b) polycrystalline e.s.r. spectra of $[Cu(bipy)_2(CN)][NO_3]\cdot 2H_2O$ (——) and $[Cu(phen)_2(CN)][NO_3]\cdot H_2O$ (— — —). dpph = Diphenylpicrylhydrazyl

angles α_1—α_3 (Table 2) there are significant distortions from 120°: α_1, 138.0(1)°, and α_2, 126.5(2)°, are significantly greater than 120° and α_3, 95.4(2) °, is significantly less. The large α_1 angle lies opposite the longest in-plane Cu–N distance of 2.161(5) Å to N(4) and the sense of this distortion involves a square-pyramidal distortion of the regular trigonal $CuN_2N'_2C$ chromophore, with elongation of the Cu–N(4) direction and α_1 representing the large basal angle. This type of distortion has been recognised [2,3] previously, and the structure of complex (2) then corresponds to the extreme square-pyramidal distorted trigonal-bipyramidal structure, route B (ref. 2, Figure 4), with the N(1)—N(3) and C(21) atoms representing the basal plane and N(4) the fifth ligand direction. This sense of distortion may also be considered to arise from a linear combination of the ν_7 and ν_8 normal modes of vibration [ref. 2, Figure 5(a)] of a trigonal-bipyramidal $CuN_2N'_2C$ chromophore.

The relatively short Cu–C(21) distance of 1.974(5) Å can then be recognised [2] as an in-plane ligand distance, rather than a fifth-ligand distance. The cyanide–copper bond is almost linear, N(5)–C(21)–Cu 179.0(3)°, and the C(21)–N(5) distance of 1.144(5) Å is closely comparable to that previously observed [1] (1.14 ± 0.02 Å).

The structure of the $CuN_2N'_2C$ chromophore of complex (2) is closely comparable to that previously observed [1] in (1), Table 2, but there are significant differences: the Cu–C(21) distance in (2) is significantly longer (0.039 Å) at 1.974(5) Å, ΔN = [Cu–N(4) – Cu–N(2)] is greater [0.073 Å in (2) and 0.021 Å in (1)], the α_3 angle is 95.4° in (2) and 98.6° in (1), and $\alpha_1 - \alpha_2$ is 11.5° in (2) and 3.4° in (1). While individually these differences are small, together they represent a more unsymmetrical distortion from trigonal bipyramidal ($\approx C_2$) in complex (2) than in (1), such that (2) may be considered to represent a $CuN_2N'_2C$ chromophore structure further along the route B distortion (ref. 2, Figure 4) than in (1), which has *near* C_2 symmetry about the Cu–C(21) bond. Whether this difference is due to the differences in the type of chelate ligand present, where phen is strictly planar but the bipy ligands are twisted (mean 5.5°), is not clear, but $[Cu(phen)_2X]^+$ cations are generally more symmetrical [14-16] than the corresponding $[Cu(bipy)_2X]^+$ cations.[8] Nevertheless, the sense of distortion is not totally self-consistent as the Cu–C(21) distance is longer in (2) than in (1), whereas it is predicted to be shorter, if the decrease in the Cu–Cl bond distance in a series [2] of $[Cu(bipy)_2Cl]^+$ cations, with increasing distortion from trigonal, is the normal behaviour.

E.S.R. Spectra.—The polycrystalline e.s.r. spectrum of (2), Figure 3(b), yields only a broad near-isotropic spectrum, g = 2.098, with evidence of a high g value, 2.22, at low temperature. The single-crystal e.s.r. spectrum is more informative and yields three g values; namely 2.031, 2.102, and 2.205,

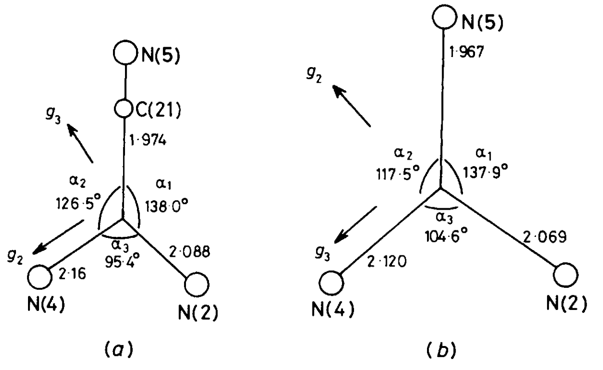

Figure 4. The in-plane Cu, N(2), N(4), X geometry and g directions of (*a*) $[Cu(bipy)_2(CN)][NO_3]\cdot 2H_2O$ and (*b*) $[Cu(bipy)_2(NCS)][BF_4]$

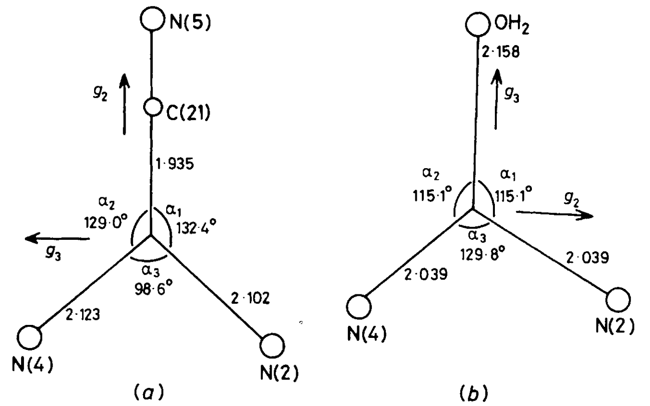

Figure 5. The in-plane Cu, N(2), N(4), X geometry and g directions of (*a*) $[Cu(phen)_2(CN)][NO_3]\cdot 2H_2O$ and (*b*) $[Cu(bipy)_2(OH_2)][S_2O_6]$

Table 3. Angular directions of the local molecular g values and some Cu–N, Cu–C, and N–N directions measured with respect to the a, b^*, and c^* directions for $[Cu(phen)_2(CN)][NO_3]\cdot H_2O$ (1)

	a	b^*	c^*
$g_1 = 2.023$	60	45	120
$g_2 = 2.109$	85	50	35
$g_3 = 2.231$	135	70	110
Cu–C(21)	96	44	47
Cu–N(4)	130	107	135
N(1)–N(3)	78	46	133
N(2)–N(4)	157	77	109

c^* is perpendicular to a in the ac plane and b^* is perpendicular to ac^*.

Table 4. Electronic reflectance spectra (cm^{-1}) of $[Cu(chelate)_2X]Y$ complexes, see Figure 3(*a*)

	Distorted square pyramidal		Distorted trigonal bipyramidal			
Complex	E_1	E_2	E	$\alpha_1 - \alpha_2$ [a] (°)	ΔE [b]	Ref.
$[Cu(bipy)_2(CN)][NO_3]\cdot 2H_2O$	12 820s [c]	14 920s [c]		11.5	2 100	This work
$[Cu(phen)_2(CN)][NO_3]\cdot H_2O$			13 070m [d]	3.4	—	This work
$[Cu(bipy)_2Cl][ClO_4]$	10 470s	13 240s		10.7	2 770	2
$[Cu(bipy)_2Cl]Cl\cdot 6H_2O$			12 500s [d]	0.1	—	2
$[Cu(bipy)_2(NCS)][BF_4]$	11 170s	14 120s		20.4	2 950	3
$[Cu(bipy)_2(OH_2)][S_2O_6]$			12 450s [d]	0.0	—	14, 17
$[Cu(bipy)_2(OH_2)][S_5O_6]$	10 075s	14 120s		38.7	4 045	14, 17
$[Cu(phen)_2(OH_2)][NO_3]_2$			12 500s [d]	0.0	—	14
$[Cu(phen)_2(OH_2)][BF_4]_2$			13 400s [d]	0.0	—	15

[a] α_1 = N(2)–Cu–X, α_2 = N(4)–Cu–X. [b] $E_2 - E_1$. [c] Only just resolved, Figure 3(*a*). [d] Asymmetric unresolved shoulder on high-frequency side, Figure 3(*a*).

but due to the square-pyramidal distorted trigonal-bipyramidal chromophore present, and the impossibility of predicting[7] the local molecular axes directions of the CuN_4C chromophore [which in any case are misaligned (10—25°) with respect to the two-fold crystallographic axis], it is not possible to determine the pure local g values from the above crystal g values. Nevertheless, the lowest g value, 2.031, lies parallel to the b axis and to the misaligned N(1)–N(3) directions ($2\alpha \approx 50°$), the intermediate value, 2.102, lies in the ac plane parallel to the projection of the two misaligned N(2)–N(3) directions ($2\alpha \approx 20°$) on the ac plane, and the highest value 2.205, lies in the ac plane parallel to the projection of the two misaligned Cu–N(4) directions ($2\alpha \approx 20°$) on the ac plane. While these are not strictly local molecular g values, they are consistent, $R = (g_2 - g_1)/(g_3 - g_2) = 1.47$, with a ground state intermediate between that of d_{z^2} and $d_{x^2-y^2}$ of a square-pyramidal distorted trigonal-bipyramidal CuN_4C chromophore. The directions of the intermediate and highest g values are different from those observed in $[Cu(bipy)_2(NCS)][BF_4]$ (3), where the highest g value lies approximately parallel to the long Cu–N(4), Figure 4(*b*), rather than to the approximate Cu–N(2) direction as in (2), Figure 4(*a*). This difference must arise from the greater value of $(\alpha_1 - \alpha_2)$ of 20.4° in (3) compared with a value of 11.5° in (2) and does emphasise the need to measure the directions of the in-plane g values in these distorted stereochemistries, as well as their magnitudes.

The e.s.r. spectrum of (1) yields a rhombic set of g values, 2.023, 2.133, and 2.225, which equate with the local molecular g values as the space group is triclinic $P\bar{1}$, $R = 1.204$. The more accurate single-crystal g values, 2.023, 2.109, and 2.231, yield an R value of 1.41 which, although suggesting a $d_{x^2-y^2}$ ground state, is too near to 1.0 to be reliable. Table 3 gives the directions of the single-crystal g values measured with respect to the ac^* plane of the crystal along with the directions of the copper–ligand bonds. The lowest g value is parallel to the N(1)–N(3) direction, the intermediate g value to the Cu–C(21), and the highest value to the N(2)–N(4) direction, and *not* to the Cu–N(4), Figure 5(*a*). The directions of g_2 and g_3 are clearly rotated with respect to those observed in (2) and (3), Figure 4(*a*) and (*b*), but coincide with the approximate C_2 axis of the trigonal Cu, N(2), N(4), C(21) plane, and emphasise the near trigonal geometry of (1) compared with the square-pyramidal distorted structures of (2) and (3), Figure 4. This near trigonal symmetry of (1) is also reflected in the low ΔN value of 0.02 Å compared to the 0.07 Å in (2) and 0.0 in $[Cu(bipy)_2(OH_2)][S_2O_6]$ (4) where the copper ion lies on a C_2 crystallographic axis,[17] Figure 5(*b*). It is therefore of interest that the in-plane *g* values of (4) lie along and at right angles to the symmetry axis, Figure 5(*b*), but have their magnitudes reversed with respect to the elongation of the Cu–OH$_2$ distance (route B structural profile, ref. 2, Figure 4), and g_3 *coincides* with the C_2 axis.

Electronic Reflectance Spectra.—The twin-peaked electronic spectrum of (2), $\Delta E = 2\,100$ cm^{-1} [Figure 3(*a*)], is consistent [2] with the square-pyramidal distorted trigonal-bipyramidal CuN_4X chromophore present as previously observed for $[Cu(bipy)_2Cl][ClO_4]$ [2] and $[Cu(bipy)_2(OH_2)][S_5O_6]$,[18] see Table 4 for ΔE values. The relatively low ΔE value for (2) is consistent with the low $\alpha_1 - \alpha_2$ value of 11.5°. The single broad peak of (1), Figure 3(*a*), is then consistent with the more symmetrical ($\approx C_2$) trigonal CuN_4C chromophore present as previously observed for $[Cu(bipy)_2Cl]Cl\cdot6H_2O$,[2] $[Cu(bipy)_2(OH_2)][S_2O_6]$,[17] $[Cu(phen)_2(OH_2)][NO_3]_2$,[14] and $[Cu(phen)_2(OH_2)][BF_4]_2$,[15] Table 4. These data then suggest for $[Cu(chelate)_2X]Y$ complexes with an approximately trigonal-bipyramidal CuN_4X chromophore that the occurrence of two bands in the electronic spectra is a function of the asymmetry of the in-plane trigonal angles, $\alpha_1 - \alpha_2$ (Table 4). For $\alpha_1 - \alpha_2$ values near zero a single peak is observed, while for $\alpha_1 - \alpha_2 > 10°$ twin peaks are observed and the splitting in the electronic spectrum then increases with the value of $\alpha_1 - \alpha_2$ and suggests an 'electronic criterion of stereochemistry' to distinguish [4] these two structural situations for $[Cu(chelate)_2X]Y$ complexes with bipy- and phen-type ligands.

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