Crystal Structure and Electronic Properties of Bis(2,2'-bipyridyl)-thiocyanatocopper(II) Tetrafluoroborate

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The crystal structure of the title compound, $[\mathrm{Cu(bipy)_2(NCS)}][\mathrm{BF_4}]$ (1) (bipy = 2,2'-bipyridyl), has been determined by *X*-ray analysis. It crystallises in the monoclinic space group *C*2/*c* with a = 12.791(3), b = 24.641(4), c = 15.456(3) Å, β = 107.4(1)°, and Z = 8. The five-co-ordinate $\mathrm{CuN_2N'_2N''}$ chromophore has a distorted bipyramidal stereochemistry related to a regular trigonal-bipyramidal stereochemistry by a distortion towards square pyramidal. The single-crystal e.s.r. spectra involve rhombic g values, R = 1.21 $[(g_2 - g_1)/(g_3 - g_2)$ where $g_1 < g_2 < g_3]$, and cannot be used to distinguish between a d_{z^2} or $d_{x^2-y^2}$ ground state, but the direction of the highest g value establishes that it correlates with the elongated Cu–N direction of the square-pyramidal distortion of the $\mathrm{CuN_2N'_2N''}$ chromophore. This, together with the twin-peaked electronic reflectance spectra (11 170 and 14 120 cm^{-1}), suggests that the structure of (1) is best described as square-pyramidal distorted trigonal bipyramidal.

THE ability of the thiocyanate ion to co-ordinate to the copper(II) ion in a series [1,2] of $[\mathrm{Cu(bipy)_2(NCS)}]\mathrm{Y}$ type complexes (bipy = 2,2'-bipyridyl) has been known for some time, with the i.r. spectra [2] suggesting that the co-ordination is *via* the nitrogen atom. The structure of the $[\mathrm{Cu(bipy)_2(NCS)}]^+$ cation was earlier suggested to be distorted trigonal bipyramidal [1,2] by analogy with the known structure [3] of $[\mathrm{Cu(bipy)_2I}]\mathrm{I}$, but the possibility of a *cis*-distorted octahedral structure was not ruled out, especially as the electronic spectra [2] involved two peaks of comparable intensity [4] in the region 10 000—15 000 cm^{-1}, as also observed in the *cis*-distorted octahedral structure of $[\mathrm{Cu(bipy)_2(ONO)}][\mathrm{NO_3}]$.[5] The method of bonding of the thiocyanate ion to give a *cis*-distorted octahedral structure was not made clear [2] and a suggestion [6] that a Cu(μ-NCS)(μ-SCN)Cu bridging unit was involved even in the $[\mathrm{Cu(bipy)_2(NCS)}][\mathrm{NCS}]$ complex, has further complicated the situation. The recent realisation that the $[\mathrm{Cu(bipy)_2Cl}]^+$ cation [7] can exist in a series of cation distortion isomers,[8] ranging from a near regular trigonal-bipyramidal $\mathrm{CuN_4Cl}$ chromophore to a square-pyramidal distorted trigonal bipyramid and related by the structural pathways [9] of Figure 1, suggests that the $[\mathrm{Cu(bipy)_2(NCS)}]^+$ cation may also form a range of cation distortion isomers characterised by a range of $\mathrm{CuN_2N'_2N''}$ chromophore geometries.

For this reason the *X*-ray crystal structure of $[\mathrm{Cu(bipy)_2(NCS)}][\mathrm{BF_4}]$ (1) has been determined, along with its e.s.r. and electronic spectra, and these are now reported.

EXPERIMENTAL

Preparation.—Complex (1) was prepared by standard methods [2] as emerald green crystals (Found: C, 48.0; H, 3.50; N, 13.15. $\mathrm{C_{21}H_{16}BCuF_4N_5S}$ requires C, 48.4; H, 3.10; N, 13.45%).

Crystal Data.—$\mathrm{C_{21}H_{16}BCuF_4N_5S}$, M = 520.41, Monoclinic, a = 12.791(3), b = 24.641(4), c = 15.456(3) Å, β = 107.4(1)°, U = 4 648.54 Å^3, D_m = 1.52 ± 0.02 g cm^{-3}, Z = 8, D_c = 1.49 g cm^{-3}, $F(000)$ = 2 103.92, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 10.34 cm^{-1}, space

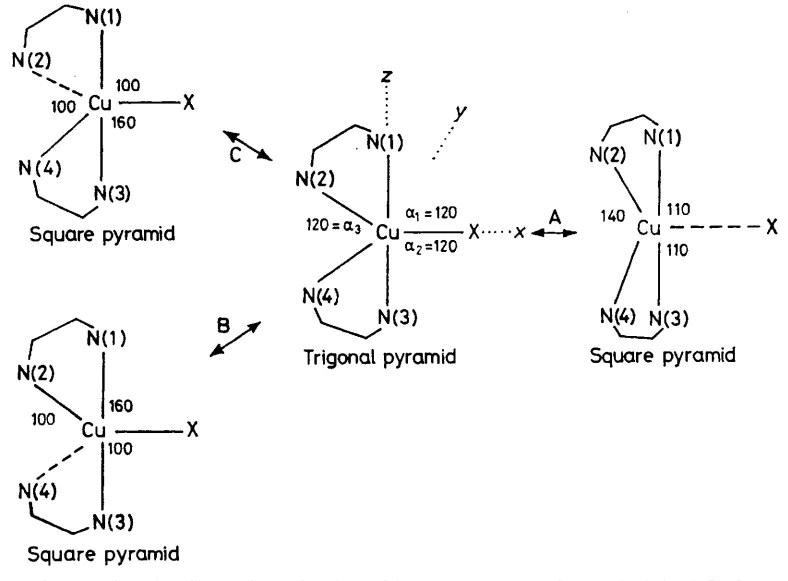

FIGURE 1 Structural pathways for the distortion of a $\mathrm{CuN_4X}$ chromophore of the $[\mathrm{Cu(bipy)_2X}]\mathrm{Y}$ complexes, from trigonal bipyramid to square pyramid involving three alternative routes; angles (°)

group *C2/c* from systematic absences;[10] *0k0*, *k* even; *h0l*, *l* even, *hkl*, *h* + *k* even.

Data collection was carried out as described previously.[11] 2 938 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 0.01, with a refined weighting scheme, $w = k/[\sigma^2(F_o) + g(F_o)^2]$, where the final values of *k* and *g* were 1.000 and 0.0124 respectively. The final *R* values were $R = 0.0691$ and $R' = 0.0757$ with a maximum residual electron density of 1.16 e $Å^{-3}$ associated with two peaks along the two-fold axis. All calculations were carried out with the SHELX-76[12] and XANADU (G. M. Sheldrick), PLUTO (S. Motherwell), and XPUB (R. Taylor) systems of programs on an IBM 370/138 computer.

The final atomic co-ordinates are given in Table 1, some selected bond lengths and bond angles in Table 2, and some mean plane data in Table 3. The final structure factors, anisotropic thermal parameters, the calculated hydrogen-atom positions, full bond-length and -angle data, and detailed mean-plane data are given in Supplementary Publication No. SUP 23099(24 pp.).* Figure 2 illustrates the structure of (1) and the atom-numbering scheme used.

TABLE 1

Atomic co-ordinates ($\times 10^4$) of $[Cu(bipy)_2(NCS)][BF_4]$ with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*
Cu	2 142(1)	794	918(1)
N(1)	2 224(4)	−12(2)	1 032(3)
C(1)	3 074(5)	−318(3)	979(5)
C(2)	3 082(6)	−871(3)	1 056(5)
C(3)	2 218(6)	−1 122(3)	1 198(6)
C(4)	1 323(6)	−819(2)	1 251(5)
C(5)	1 349(5)	−261(2)	1 161(4)
C(6)	457(5)	102(2)	1 199(4)
C(7)	−508(5)	−83(3)	1 345(5)
C(8)	−1 303(6)	286(4)	1 373(5)
C(9)	−1 111(6)	820(3)	1 287(5)
C(10)	−143(5)	983(3)	1 157(5)
N(2)	627(4)	636(2)	1 089(3)
N(3)	1 982(4)	1 593(2)	886(4)
C(11)	1 357(6)	1 863(3)	180(5)
C(12)	1 211(7)	2 427(3)	195(6)
C(13)	1 743(8)	2 691(3)	946(7)
C(14)	2 382(7)	2 420(3)	1 710(6)
C(15)	2 490(5)	1 869(2)	1 651(5)
C(16)	3 149(5)	1 527(2)	2 419(4)
C(17)	3 701(7)	1 739(3)	3 272(5)
C(18)	4 239(6)	1 377(3)	3 945(5)
C(19)	4 282(6)	824(3)	3 744(5)
C(20)	3 712(5)	653(3)	2 883(5)
N(4)	3 160(4)	994(2)	2 234(3)
N(5)	2 809(5)	797(2)	−75(4)
C(21)	3 270(5)	778(2)	−600(4)
S(1)	3 922(2)	760(1)	−1 350(1)
B(1)	5 000	3 271(5)	2 500
F(1)	4 176(4)	3 585(2)	1 991(3)
F(2)	4 634(5)	2 962(2)	3 094(4)

TABLE 2

Selected bond lengths (Å) and angles (°) for $[Cu(bipy)_2(NCS)][BF_4]$ with estimated standard deviations in parentheses

Cu–N(1)	1.993(7)	N(1)–Cu–N(2) (α_6)	80.1(3)
Cu–N(2)	2.069(7)	N(1)–Cu–N(3) (α_8)	174.7(2)
Cu–N(3)	1.980(7)	N(1)–Cu–N(4) (α_{10})	98.4(3)
Cu–N(4)	2.120(6)	N(1)–Cu–N(5) (α_4)	92.8(3)
Cu–N(5)	1.967(9)	N(3)–Cu–N(2) (α_9)	95.6(3)
N(5)–C(21)	1.137(11)	N(3)–Cu–N(4) (α_7)	79.7(3)
C(21)–S(1)	1.618(10)	N(3)–Cu–N(5) (α_5)	92.4(3)
B(1)–F(1)	1.353(9)	N(2)–Cu–N(4) (α_3)	104.6(3)
B(1)–F(2)	1.378(10)	N(2)–Cu–N(5) (α_1)	137.9(2)
		N(4)–Cu–N(5) (α_2)	117.5(3)
		Cu–N(5)–C(21)	174.2(5)
		N(5)–C(21)–S(1)	179.1(5)
		F(1)–B(1)–F(2)	110.0(4)

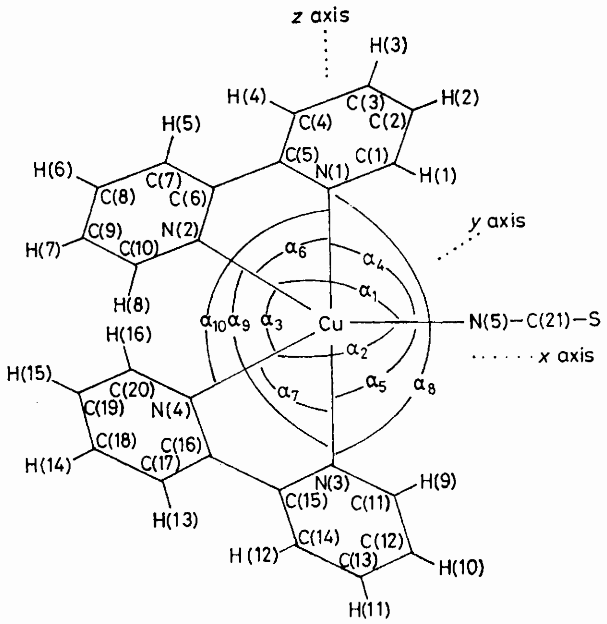

FIGURE 2 Molecular structure of the $[Cu(bipy)_2(NCS)]^+$ cation, showing the atom numbering and angle notation used

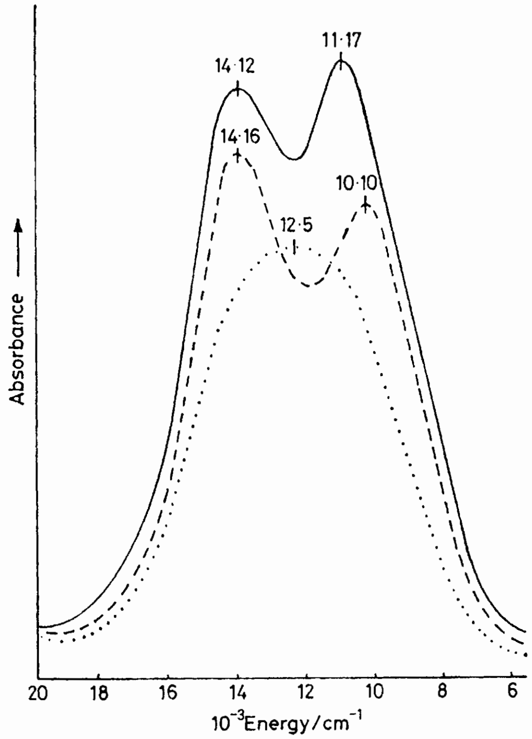

FIGURE 3 Electronic reflectance spectra of (*a*) $[Cu(bipy)_2(NCS)][BF_4]$ (——), (*b*) $[Cu(bipy)_2Cl][ClO_4]$ (— — —), and (*c*) $[Cu(bipy)_2Cl]Cl\cdot6H_2O$ (· · ·)

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

TABLE 3

Summary of mean planes

		r.m.s.d./Å
Plane (1):	N(1), C(1)—C(5)	0.004
Plane (2):	N(2), C(6)—C(10)	0.012
Plane (3):	N(1), C(1)—C(10), N(2)	0.012
Plane (4):	N(2), C(11)—C(15)	0.010
Plane (5):	N(4), C(16)—C(20)	0.013
Plane (6):	N(3), C(11)—C(20), N(4)	0.030
Plane (7):	N(1), N(2), N(3), N(4)	0.596
Plane (8):	N(1), N(2), N(3), N(5)	0.367

Dihedral angles (°) between planes: (1)—(2) 0.6; (4)—(5) 3.2; (3)—(6) 100.1

Electronic Properties.—These were recorded as previously described.[13] The electronic reflectance spectrum of (1) is shown in Figure 3, along with that of $[Cu(bipy)_2Cl][ClO_4]$ (2).[7] That of (1) consists of two equally intense peaks at 11 170 and 14 120 cm^{-1}. The single-crystal e.s.r. spectrum [13] of (1) yields the three crystal *g* values 2.011, 2.139, and 2.245; the lowest *g* value was measured parallel to the *b* axis and the intermediate and highest *g* values were measured in the *ac* plane. The intermediate *g* value, 2.139, makes an angle of 32.5° to the *c* axis.

RESULTS AND DISCUSSION

Crystal Structure.—The crystal structure of (1) consists of discrete $[Cu(bipy)_2(NCS)]^+$ cations and BF_4^- anions. There are no unusual bond lengths or bond angles [14] in the bipy ligands and the tetrafluoroborate [15] anion has reasonable B–F bond lengths, mean 1.366(10) Å, and bond angles, mean 111.1(4)°. Whereas the $[Cu(bipy)_2(NCS)]^+$ cation occupies a general crystallographic position, the boron of the BF_4^- anion occupies a special position on the crystallographic two-fold axis. While there was no serious residual electron density associated with this BF_4^- anion, the two peaks of highest residual electron density, 1.16 e $Å^{-3}$, were located on the alternative crystallographic two-fold axis, *ca*. 2.8 Å apart, with the next highest residual peak having less than 0.5 e $Å^{-3}$. Attempts to refine these two peaks as a disordered thiocyanate were not successful since they failed to locate a possible intermediate peak due to carbon, hence these residual two peaks were ignored. There was no evidence for semi-co-ordination [16] of the BF_4^- anion to the copper atom.

The stereochemistry of the $[Cu(bipy)_2(NCS)]^+$ cation of (1) is clearly five-co-ordinate with the thiocyanate group bonding to the copper atom through a terminal atom (as suggested by the i.r. spectra [2]) to give a five-co-ordinate $CuN_2N'_2N''$ chromophore. There is nothing unusual in this mode of bonding of the NCS^- ion, the anion is linear,[17] N(5)–C(21)–S(1) angle 179.1(5)°, with N(5)–C(21) and C(21)–S(1) bond distances of 1.137(11) and 1.618(10) Å respectively, in reasonable agreement with the structural data recently summarised for this anion.[17] The co-ordination of the NCS^- anion to the copper atom involves a significant deviation of the Cu–N(5)–C(21) angle, 174.2(5) °, from linearity.[17] The structure of the $CuN_2N'_2N''$ chromophore is basically trigonal bipyramidal, Figures 1 and 2. The out-of-plane bond lengths, Cu–N(1) and Cu–N(3), are not significantly different, mean 1.987(7) Å, but they are significantly different from the *two* in-plane Cu–bipy ligand distances Cu–N(2) and Cu–N(4), 2.069(7) and 2.120(6) Å respectively, mean 2.095(7) Å, a difference of *ca*. 0.1 Å, as previously reported for the trigonal-bipyramidal copper(II) ion.[11,18] In addition, the two in-plane Cu–N distances are significantly different, 0.051 Å, with the Cu–N(4) distance the greatest Cu–bipy ligand distance, 2.120(6) Å. The Cu–NCS distance of 1.967(9) Å then stands out as significantly shorter than the two other trigonal *in-plane* Cu–N distances (Table 2), and comparable to that of the two out-of-the plane distances, which might suggest that the in-plane Cu–NCS distance in a trigonal-bipyramidal CuN_2N_3 chromophore may be inherently shorter than the in-plane Cu–bipy distance, *cf*. the in-plane Cu–NCS distance of 1.92 Å in $[(H_3N)_2Cu(NCS)_3Ag]$.[19] Such an interpretation ignores the angular distortions about the Cu atom; none of the out-of-the plane N–Cu–N angles is unusual, all are 90 ± 10°, with the bites of the bipy ligands comparable at 79.9 ± 0.2°. The individual pyridine ligands are reasonably planar, Table 3, root-mean-square deviations (r.m.s.d.s) less than 0.013 Å, with the separate bipy ligands involving angles of twist of 0.6 and 3.2° respectively, both less than the values, up to 11°, previously observed [14] in this co-ordinated ligand. The mean planes of the bipy ligands are inclined at 100.1° to each other, an angle that is significantly greater than that of 30—60° in $[Cu(bipy)_2]^{2+}$ systems involving a distorted tetrahedral CuN_4 structure.[20] The N(1)–Cu–N(3) angle, α_8, of 174.7(2)° is almost linear, with the N(1) and N(3) atoms removed with respect to the Cu atom away from the N(5) atom, as indicated by the α_4 and α_5 angles [20] being greater than 90°, 92.8(3) and 92.4(3)° respectively, and justifying a trigonal rather than a tetrahedral twist to the CuN_4 chromophore of the N(1)—N(4) atoms. Within the trigonal *xy* plane, Figure 2, there are significant distortions of the α_1—α_3 angles from 120°; α_1 is significantly greater than 120°, 137.9(2)°, α_2 is slightly less 117.5(3)°, and α_3 is also significantly less, 104.6(3)°, and together they involve the $CuN_2N'_2N''$ chromophore in a significant distortion from a regular trigonal bipyramid. Equally significant, as the large α_1 angle lies opposite the longest in-plane Cu–N distance, that of 2.120(6) Å to N(4), the sense of this distortion could be considered to involve a square-pyramidal distortion of the regular trigonal CuN'_2N'' chromophore with elongation of the Cu–N(4) direction and α_1 representing the large basal angle. This type of distortion has already been recognised in the series of five cation distortion isomers of the $[Cu(bipy)_2Cl]^+$ cation,[7] whose extreme range of structures may be represented by the near regular trigonal-bipyramidal structure of $[Cu(bipy)_2Cl]Cl·6H_2O$,[21] (2), Figure 4(*a*), and the most square-pyramidal distorted trigonal-bipyramidal structure of $[Cu(bipy)_2Cl][ClO_4]$,[7] (3), Figure 4(*b*). The $CuN_2N'_2N''$ structure of (1) then corresponds to the extreme square-pyramidal distorted trigonal-bipyramidal structure of (3) along the structural pathway of Figure 1, *via* the route B (or its equivalent route C) distortion. In (1) the extent of the route B distortion is restricted by the bite of the N(3), N(4) bipy ligand (which has the largest twist angle of 3.2°) to a Cu–N(4) distance of 2.120(6) Å and an α_1 angle of 137.9(2)°. The relative shortness of the Cu–N(5) distance, 1.967(9) Å, see above, can then be understood, as the Cu–Cl bond distance of the route B distortion of the $[Cu(bipy)_2Cl]^+$ cation, decreased from 2.361(4) Å in the near regular trigonal structure to 2.263(3) Å in the square-pyramidal distorted structure. Consequently, the shortness of the Cu–N(5) bond distance in (1) is primarily an artifact of the route B distortion present and cannot necessarily be associated with the potentially π-bonding role of the thiocyanate ligand. Thus the square-pyramidal distorted trigonal-bipyramidal structure of (1) may be related to the more regular trigonal-bipyramidal $CuN_2N'_2N''$ chromophore by the structural pathway of Figure 1, resulting from a linear combination of the ν_3, ν_4, ν_7, and ν_8 normal modes of vibration of a trigonal-bipyramidal structure [Figure 3(*b*), ref. 7].

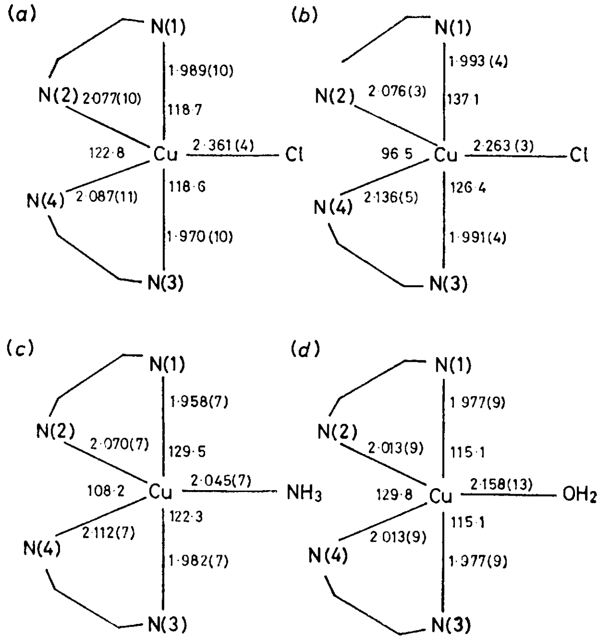

FIGURE 4 Molecular structures of (*a*) $[Cu(bipy)_2Cl]Cl\cdot6H_2O$, (2), (*b*) $[Cu(bipy)_2Cl][ClO_4]$, (3), (*c*) $[Cu(bipy)_2(NH_3)][BF_4]_2$, (4), and (*d*) $[Cu(bipy)_2(OH_2)][S_2O_6]$, (5); bond lengths (Å), angles (°)

Electronic Properties.—The polycrystalline e.s.r. spectrum of (1) yields a single *g* value of 2.09 and no evidence of a higher or lower *g* value. The single-crystal e.s.r. spectrum is more informative with rhombic *g* values of 2.011, 2.139, and 2.245. As the $CuN_2N'_2N''$ chromophore of (1) has its local molecular axes, Figure 2, approximately aligned, the N(1)–N(3) direction (the local molecular *z* direction) is approximately parallel (maximum misalignment 4.7°, Table 4) to the *b* axis direction, along which lies the lowest *g* factor of 2.011. The intermediate and highest *g* factors then lie in the *ac* plane, with the latter approximately parallel to the Cu–N(4) bond direction, Figure 5, which involves the greatest elongation, namely, 2.120(6) Å, with the intermediate *g* approximately parallel to the N(2)–N(5) direction. This is a little surprising since the Cu–N(5) bond, corresponding to the unique trigonal plane ligand, is relatively short, 1.967(9) Å, there is still a near trigonal angle of 117.5(3)° in the N(4)–Cu–N(5) angle, and the intermediate *g* value would have been anticipated to lie parallel to the Cu–N(5) direction.[22] Clearly, the elongation of the Cu–N(4) bond to 2.120 Å is sufficiently pronounced to determine the direction of the highest *g* factor in the trigonal plane, Figure 5. As the $CuN_2N'_2N''$ chromophore has a negligible misalignment (maximum 4.7°) the crystal *g* factors equate with the local molecular *g* factors and R $[(g_2 - g_1)/(g_3 - g_2)$ with $g_1 < g_2 < g_3] = 1.21$, which is so near 1.0 that it has no value in distinguishing a d_{z^2} ground state from a $d_{x^2-y^2}$ ground state.[13] Nevertheless, as the highest *g* factor lies parallel to the Cu–N(4) direction this suggests that a square-pyramidal distorted trigonal-bipyramid description is the more appropriate, and emphasises how important relatively small distortions of the bond lengths and bond angles of a regular trigonal-bipyramidal structure have to be to influence both the magnitudes and directions of the *g* factors in these distorted five-co-ordinate structures.

TABLE 4

Angular directions (°) of the crystal *g* values and of some Cu–N and N–N directions measured with respect to the *a*,*b*, and *c* * directions for $[Cu(bipy)_2(NCS)][BF_4]$

	a	*b*	*c* *
g_1, 2.011	90.0	0.0	90.0
g_2, 2.139	30.1	90.0	139.9
g_3, 2.245	49.9	90.0	30.1
Cu–N(4)	54.1	76.5	39.1
Cu–N(5)	65.5	89.8	155.5
N(1)–N(3)	94.3	4.7	91.9
N(2)–N(5)	45.0	84.0	134.4

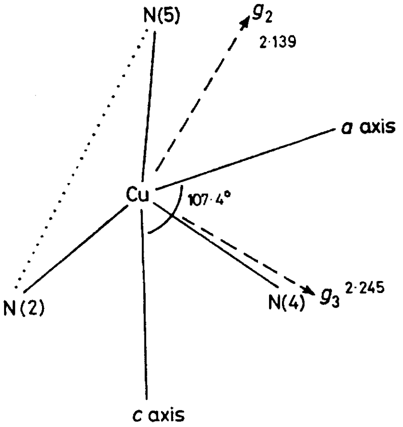

FIGURE 5 Projection of the CuN_5 chromophore of $[Cu(bipy)_2(NCS)][BF_4]$ down the *b* axis and the orientation of the crystal *g* factors

This behaviour contrasts with the behaviour of $[Cu(bipy)_2(NH_3)][BF_4]_2$,[22] (4), Figure 4(*c*), which has a comparable α_3 angle of 108.2° and an elongated Cu–N(4) distance of 2.112(7) Å, but a significantly smaller $\alpha_1 - \alpha_2$ angle of 7.2° [22.6 in (1), and 10.7° in (3)[7]], Figure 4(*b*), in both of which the intermediate *g* value is associated with the Cu–NH_3 direction in (4) and with the Cu–Cl direction in (3). As the Cu–N distances in (1), (3), and (4) are comparable, this difference in behaviour must be associated with the larger value of α_1 and in the difference $\alpha_1 - \alpha_2$. A comparable behaviour to that in (1) occurs[23] in $[Cu(bipy)_2(OH_2)][S_2O_6]$, (5), Figure 4(*d*), which distorts along the route A structural pathway of Figure 1, with a clear elongation of the Cu–OH_2 bond to 2.158(13) Å and α_3 lies above 120° at 129.8°; the highest *g* factor is associated with the Cu–OH_2 direction, which is unambiguously determined, as it lies along the *b* axis of this monoclinic system.

This rotation of the in-plane *g* factors has also been observed in the analogous six-co-ordinate *cis*-distorted octahedral $[Cu(bipy)_2(OXO)]Y$ systems,[11] where OXO = nitrite, acetate, or formate anions, which can also distort along a structural pathway, corresponding to Figure 1, to square-pyramidal *cis*-distorted octahedral (4 + 1 + 1 *), and in the distorted systems the highest *g* factor shows a significant rotation from its direction in the *cis*-distorted octahedral structure.

The electronic reflectance spectrum of (1) consists of two equally intense peaks at 11 170 and 14 120 cm^{-1}, a difference of 2 950 cm^{-1}. The spectrum compares[7] with that of (3), peaks at 10 100 and 14 160 cm^{-1}, but contrasts with the single peaks observed[22,23] in (2), (4), and (5) at 12 500, 12 300, and 12 450 cm^{-1} respectively. Thus the twin-peaked electronic spectrum of (1) and the directions of the local molecular *g* values are both consistent with a square-pyramidal distorted trigonal bipyramidal description of the structure of (1).

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