

## Single-crystal Structure and Electronic Properties of Bis[hydrotris-(pyrazol-1-yl)borato]copper(II)

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The single-crystal structure of  $[\text{Cu}\{\text{BH}(\text{N}_2\text{C}_3\text{H}_3)_3\}_2]$  has been determined by X-ray crystallography. The triclinic unit cell, space group  $P\bar{1}$ , with  $a = 10.309(2)$ ,  $b = 13.794(3)$ ,  $c = 11.677(3)$  Å,  $\alpha = 127.39(2)$ ,  $\beta = 88.46(2)$ , and  $\gamma = 116.63(2)^\circ$ , has two independent molecules with the copper(II) atoms at centres of symmetry. The tris-(pyrazolyl)borate ligands are tridentate to yield an elongated rhombic octahedral  $\text{CuN}_6$  chromophore involving a marked distortion away from the trigonal symmetry of the free tripod ligands. The two independent  $\text{CuN}_6$  chromophores have significantly different Cu–N bond lengths which yield tetragonalities ( $R_s/R_l$ ) of 0.792 and 0.866, respectively. The polycrystalline electronic properties are shown to be consistent with the restricted tetragonal distortion of the  $\text{CuN}_6$  chromophore imposed by the bite of the hydrotris(pyrazolyl)borate ligand. The relative tetragonalities of the two chromophores suggest that while  $\text{Cu}(1)\text{N}_6$  involves a static stereochemistry, that of  $\text{Cu}(2)\text{N}_6$  involves some fluxional behaviour as suggested by an analysis of the root-mean-square displacements of the  $\text{CuN}_6$  chromophores.

PRELIMINARY data on the preparation and electronic spectra of  $[\text{Cu}\{\text{BH}(\text{N}_2\text{C}_3\text{H}_3)_3\}_2]$  included a single peak in the electronic spectra at  $16\,100\text{ cm}^{-1}$  which could be consistent with a compressed tetrahedral  $\text{CuN}_4$  chromophore<sup>1,2</sup> rather than a  $\text{CuN}_6$  chromophore as suggested by the stoichiometry of the complex.<sup>2</sup> Since the tetrahedral  $\text{CuN}_4$  chromophore is not very common in copper(II) complexes<sup>3,4</sup> but has been reported<sup>5</sup> in  $[\text{Cu}\{\text{GaMe}_2(\text{N}_2\text{C}_5\text{H}_7)\}_2]$  and as the structure<sup>6</sup> of the copper(I) complex  $[\{\text{Cu}^{\text{I}}[\text{BH}(\text{N}_2\text{C}_3\text{H}_3)_3\}_2]$  has been shown to involve a centrosymmetric bridged dimer with a distorted tetrahedral  $\text{Cu}^{\text{I}}\text{N}_4$  chromophore, the crystal structure of  $[\text{Cu}\{\text{BH}(\text{N}_2\text{C}_3\text{H}_3)_3\}_2]$  is now reported, along with its more detailed electronic properties.

### EXPERIMENTAL

The original crystals of  $[\text{Cu}\{\text{BH}(\text{N}_2\text{C}_3\text{H}_3)_3\}_2]$  (provided by Drs. F. J. Lalor and K. Dignam, University College, Cork) were subject to crystal twinning, but recrystallisation from acetonitrile produced crystals free from twinning and suitable for data collection.

*Crystal Data.*— $\text{C}_{18}\text{H}_{20}\text{B}_2\text{CuN}_{12}$ ,  $M = 489.16$ , Triclinic,  $a = 10.309(2)$ ,  $b = 13.794(3)$ ,  $c = 11.677(3)$  Å,  $\alpha = 127.39(2)$ ,  $\beta = 88.46(2)$ ,  $\gamma = 116.32(2)^\circ$ ,  $U = 1\,106.72$  Å<sup>3</sup>,  $D_m(\text{floatation}) = 1.450 \pm 0.02\text{ g cm}^{-3}$ ,  $Z = 2$ ,  $D_c = 1.468\text{ g cm}^{-3}$ ,  $F(000) = 498.0$ , Mo- $K\alpha$  radiation,  $\lambda = 0.710\,69$  Å,  $\mu(\text{Mo-}K\alpha) = 9.66\text{ cm}^{-1}$ , space group  $P\bar{1}$  no systematic absences.

Preliminary unit-cell dimensions and space-group data were obtained from oscillation and Weissenberg photographs and refined on a Hilger and Watts four-circle diffractometer; the diffractometer was also used for data collection. 3 609 Reflections with  $I > 3\sigma(I)$  in the range  $0 < 2\theta < 55^\circ$  were considered observed and used in the subsequent refinement. No account was taken of anomalous dispersion except for the copper atom and no corrections were made for secondary extinction or absorption effects. Data reduction and crystallographic calculations were carried out on an IBM 370/138 computer (University College Cork) using the SHELX-76 set of crystallography programs. Atomic scattering factors were used as published.<sup>7</sup> The co-ordinates of the metal atoms were determined from a three-

† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

dimensional Patterson synthesis as occupying the centres of symmetry at 0.0, 0.0, 0.0 and 0.0, 0.5, 0.0 respectively; subsequent Fourier synthesis was used to develop the two independent copper(II) chromophores and to locate all the non-hydrogen atoms. Least-squares refinement with isotropic temperature factors gave  $R = 0.104$ ; anisotropic temperature factors were then included and the position of the hydrogen atoms were calculated with fixed C–H and B–H bond lengths of 1.08 Å and fixed temperature factors of 0.07 Å<sup>2</sup> and floated on the associated carbon or boron atom positions. A refined weighting scheme was used, where  $w = k/[\sigma^2(F_o) + g(F_o)^{31}]$  and the final values of  $k$  and  $g$  were 1.727 7 and  $6.29 \times 10^{-4}$  respectively. The refinement was continued until the shift-to-error ratio of any parameter was less than 0.02 and yielded  $R = 0.043\,9$  and  $R' = 0.047\,9$ , with a highest residual electron density of  $0.63\text{ e Å}^{-3}$ . The structure factors, anisotropic temperature factors, and calculated hydrogen atomic co-ordinates are in Supplementary Publication No. SUP 22551 (25 pp.).† The final atomic co-ordinates are given in Table 1, the bond lengths in Table 2, and the bond angles in Table 3. Table 4 gives some relevant mean planes and Figure 1 gives an ORTEP diagram ‡ of the molecular structures of the two independent copper(II) chromophores (including the thermal ellipsoids) and the atomic numbering system used.

*Electronic Properties.*—These were recorded as previously described.<sup>8,9</sup> The electronic reflectance spectrum of  $[\text{Cu}\{\text{BH}(\text{N}_2\text{C}_3\text{H}_3)_3\}_2]$  gave a main band at  $16\,400\text{ cm}^{-1}$  with a clearly resolved shoulder at  $10\,400\text{ cm}^{-1}$ . The polycrystalline e.s.r. spectrum yielded an anisotropic signal with resolved nuclear hyperfine structure and yielded the approximate  $g$  values  $g_{\perp} = 2.065$ ,  $g_{\parallel} = 2.223$ , and  $A_{\parallel} = 140\text{ G}$ .§ While these data are suggestive of an axially elongated  $\text{CuN}_6$  chromophore<sup>2,3</sup> (particularly the high  $A$  value), they only relate to crystal  $g$  factors and it is not possible to relate these to the local molecular  $g$  factors when two independent  $\text{CuN}_6$  chromophores misaligned by  $69^\circ$  are present in the unit cell. No significant temperature effect on the e.s.r. spectrum was observed.

### RESULTS AND DISCUSSION

*Crystal Structure.*—The structure involves two independent centrosymmetric  $[\text{Cu}\{\text{BH}(\text{N}_2\text{C}_3\text{H}_3)_3\}_2]$  units,

‡ The authors are indebted to a referee for providing the ORTEP diagram of Figure 1.

§ Throughout this paper:  $1\text{ G} = 10^{-4}\text{ T}$ .

TABLE 1

Atom co-ordinates \* ( $\times 10^4$ ) for  $[\text{Cu}\{\text{BH}(\text{N}_2\text{C}_3\text{H}_3)_2\}_2]$ 

Atom	$x/a$	$y/b$	$z/c$
Cu(1)	0	0	0
N(1)	521(3)	-1 505(2)	-1 369(2)
N(2)	1 868(3)	-1 121(3)	-1 648(2)
C(1)	1 943(3)	-2 301(3)	-2 601(3)
C(2)	634(9)	-3 462(3)	-2 936(3)
C(3)	-225(3)	-2 920(3)	-2 152(3)
N(3)	2 209(2)	1 422(2)	1 361(2)
N(4)	3 361(2)	1 473(3)	775(3)
C(4)	4 735(3)	2 492(3)	1 932(3)
C(5)	4 470(3)	3 113(3)	3 294(3)
C(6)	2 881(3)	2 413(3)	2 888(3)
N(5)	849(3)	555(3)	-1 691(3)
N(6)	2 281(3)	777(3)	-1 699(3)
C(7)	2 781(4)	1 175(3)	-2 509(3)
C(8)	1 670(4)	1 222(3)	-3 044(3)
C(9)	495(4)	824(3)	-2 512(3)
B(1)	3 014(3)	443(3)	-978(3)
Cu(2)	0	5 000	0
N(7)	1 629(3)	7 206(2)	1 290(2)
N(8)	2 380(2)	8 076(2)	2 821(2)
C(10)	3 353(3)	9 454(3)	3 437(3)
C(11)	3 241(3)	9 486(3)	2 287(3)
C(12)	2 159(3)	8 063(3)	985(3)
N(9)	1 982(3)	5 210(3)	1 264(3)
N(10)	2 590(3)	6 356(2)	2 817(2)
C(13)	3 766(3)	6 455(3)	3 440(3)
C(14)	3 945(4)	5 366(3)	2 293(8)
C(15)	2 814(3)	4 627(3)	966(3)
N(11)	-707(2)	5 543(2)	1 796(2)
N(12)	328(2)	6 630(2)	3 260(2)
C(16)	-438(3)	6 889(3)	4 248(3)
C(17)	-1 986(3)	5 957(3)	3 440(3)
C(18)	-2 103(3)	5 134(3)	1 902(3)
B(2)	2 070(3)	7 422(3)	3 566(3)

\* Estimated standard deviations are in parentheses.

TABLE 2

Bond lengths (Å)

N(1)-Cu(1)	2.018(3)	N(3)-Cu(1)	1.991(2)
N(5)-Cu(1)	2.528(4)	N(2)-N(1)	1.357(4)
C(3)-N(1)	1.328(4)	C(1)-N(2)	1.343(5)
B(1)-N(2)	1.541(5)	C(2)-C(1)	1.367(5)
C(3)-C(2)	1.378(5)	N(4)-N(3)	1.350(4)
C(6)-N(3)	1.337(3)	C(4)-N(4)	1.349(3)
B(1)-N(4)	1.545(4)	C(5)-C(4)	1.367(5)
C(6)-C(5)	1.381(4)	N(6)-N(5)	1.367(4)
C(9)-N(5)	1.328(7)	C(7)-N(6)	1.347(6)
B(1)-N(6)	1.519(7)	C(8)-C(7)	1.364(7)
C(9)-C(8)	1.391(5)	N(7)-Cu(2)	2.082(2)
N(9)-Cu(2)	2.356(4)	N(11)-Cu(2)	1.998(2)
N(8)-N(7)	1.368(3)	C(12)-N(7)	1.322(6)
C(10)-N(8)	1.343(4)	B(2)-N(8)	1.535(6)
C(11)-C(10)	1.379(6)	C(12)-C(11)	1.382(3)
N(10)-N(9)	1.369(3)	C(15)-N(9)	1.328(6)
C(13)-N(10)	1.339(5)	B(2)-N(10)	1.527(5)
C(14)-C(13)	1.370(5)	C(15)-C(14)	1.384(5)
N(12)-N(11)	1.363(2)	C(18)-N(11)	1.323(4)
C(16)-N(12)	1.336(8)	B(2)-N(12)	1.533(4)
C(17)-C(16)	1.363(3)	C(18)-C(17)	1.394(4)

Figure 1, each copper atom being involved in six-coordination by the nitrogen atoms of six separate pyrazolyl rings. Each hydrotris(pyrazol-1-yl)borato-ligand is involved in three-co-ordination as a tripod ligand,<sup>10</sup> but each ligand involves serious distortion (Figure 2) from the three-fold symmetry of the free ligand. The  $\text{CuN}_6$  chromophores of both independent  $[\text{Cu}\{\text{BH}(\text{N}_2\text{C}_3\text{H}_2)_2\}_2]$  units involve an elongated rhombic octahedral stereochemistry, but with significant differences in the bond lengths involved (Table 2) which result in a clear difference in the resulting tetragonalities<sup>11</sup>  $T$ , of 0.792

TABLE 3

Bond angles ( $^\circ$ )

N(3)-Cu(1)-N(1)	88.7(1)	N(5)-Cu(1)-N(1)	80.3(1)
N(5)-Cu-N(3)	86.2(1)	N(2)-N(1)-Cu(1)	120.0(2)
C(3)-N(1)-Cu(1)	133.0(2)	C(3)-N(1)-N(2)	106.9(3)
C(1)-N(2)-N(1)	109.1(3)	B(1)-N(2)-N(1)	121.7(3)
B(1)-N(2)-C(1)	129.2(3)	C(3)-C(2)-C(1)	105.4(3)
C(2)-C(1)-N(2)	108.4(3)	C(2)-C(3)-N(1)	110.2(3)
N(4)-N(3)-Cu(1)	121.3(2)	C(6)-N(3)-Cu(1)	132.1(2)
C(6)-N(3)-N(4)	106.6(2)	C(4)-N(4)-N(3)	109.5(2)
B(1)-N(4)-C(1)	144.2(2)	C(9)-N(5)-N(6)	105.0(3)
C(7)-N(6)-N(5)	110.5(4)	B(1)-N(6)-N(5)	120.1(3)
B(1)-N(6)-C(7)	129.2(3)	C(9)-C(8)-C(7)	104.9(4)
C(8)-C(7)-N(6)	108.0(3)	C(8)-C(9)-N(5)	111.6(4)
N(4)-B(1)-N(2)	107.3(3)	N(6)-B(1)-N(2)	109.2(2)
N(6)-B(1)-N(8)	110.6(3)	N(11)-Cu(2)-N(7)	87.9(1)
N(9)-Cu(2)-N(7)	81.9(1)	N(8)-N(7)-Cu(2)	119.4(3)
N(11)-Cu(2)-N(9)	86.6(1)	C(12)-N(7)-N(8)	106.1(2)
C(12)-N(7)-Cu(2)	134.4(2)	B(2)-N(8)-N(7)	120.2(2)
C(10)-N(8)-N(7)	109.8(3)	C(12)-C(11)-C(10)	104.9(4)
B(2)-N(8)-C(10)	130.0(2)	C(11)-C(12)-N(7)	111.2(3)
C(11)-C(10)-N(8)	108.0(2)	C(15)-N(9)-Cu(2)	140.9(2)
N(10)-N(9)-Cu(2)	113.3(2)	C(13)-N(10)-N(9)	109.8(3)
C(15)-N(9)-N(10)	105.7(3)	B(2)-N(10)-C(13)	128.8(2)
B(2)-N(10)-N(9)	120.8(3)	C(14)-C(13)-N(10)	108.6(3)
C(15)-C(14)-C(13)	104.7(4)	N(12)-N(11)-Cu(2)	121.0(2)
C(14)-C(15)-N(9)	111.3(3)	C(18)-N(11)-N(12)	106.8(2)
C(18)-N(11)-Cu(2)	131.8(2)	B(2)-N(12)-N(11)	120.8(2)
C(16)-N(12)-N(11)	109.2(2)	C(18)-C(17)-C(16)	105.0(3)
B(2)-N(12)-C(16)	129.8(2)	C(17)-C(18)-N(11)	110.0(2)
C(17)-C(16)-N(12)	108.9(2)	N(12)-B(2)-N(8)	107.5(3)
N(10)-B(2)-N(8)	107.9(3)		
N(12)-B(2)-N(10)	110.7(2)		

TABLE 4

Equations of least-squares planes in the form  $lx + my + nz = p$ , where  $x$ ,  $y$ , and  $z$  are orthogonal axes. Deviations (Å) of relevant atoms from the planes are given in square brackets

	$l$	$m$	$n$	$p$
Plane (1):				
N(1), N(2), C(1)-C(3) (r.m.s. deviation = 0.0021)				
0.4509 -0.0564 0.8908 0.0234				
[C(2) + 0.0030, C(1) - 0.0026]				
Plane (2):				
N(3), N(4), C(4)-C(6) (r.m.s. deviation = 0.0012)				
0.0433 0.7929 -0.6079 0.0563				
[C(6) - 0.0016, N(3) 0.0014]				
Plane (3):				
N(5), N(6), C(7)-C(9) (r.m.s. deviation = 0.0016)				
0.4238 0.8696 0.2533 -0.1868				
[C(9) - 0.0022, C(8) 0.0021]				
Plane (4):				
N(7), N(8), C(10)-C(12) (r.m.s. deviation = 0.0012)				
-0.7275 0.6788 0.0996 3.2675				
[N(7) 0.0016, N(8) - 0.0014]				
Plane (5):				
N(9), N(10), C(13)-C(15) (r.m.s. deviation = 0.0013)				
0.6369 0.3079 -0.7067 4.5114				
[C(15) 0.0018, C(14) - 0.0015]				
Plane (6):				
N(11), N(12), C(16), -C(18) (r.m.s. deviation = 0.0033)				
0.0075 0.7966 -0.6045 6.6990				
[C(16) 0.0047, N(12) - 0.0042]				

Dihedral angle ( $^\circ$ ) between planes: 1-2 124.5; 1-3 68.4; 2-3 56.4; 4-5 109.0; 4-6 61.6; 5-6 47.4

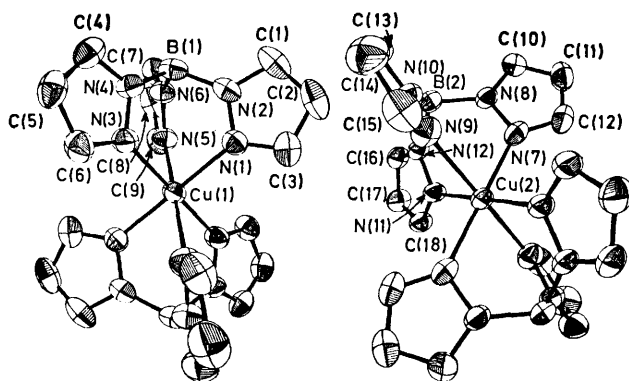


FIGURE 1 Molecular structure and atom-numbering system used for the two independent centrosymmetric chromophores of  $[\text{Cu}\{\text{BH}(\text{N}_2\text{C}_3\text{H}_3)_2\}_2]$ . Hydrogen atoms are not shown

and 0.866 for the Cu(1) and Cu(2) atoms respectively (where  $T = R_S$ , the mean in-plane Cu-N bond length divided by  $R_L$ , the mean out-of-plane Cu-N bond lengths). There is no obvious reason for this difference in tetragonality, which nicely reflects the plasticity<sup>12</sup> of the non-spherical symmetry of the  $d^9$  electron configuration of the copper(II) ion and generates two distortion isomers<sup>13</sup> of identical copper(II) chromophores in the same unit cell, but which may arise due to slight differences in the crystal-packing forces present.

All the bond lengths and angles in the hydrotris(pyrazol-1-yl)borate ligands are normal<sup>10</sup> (Tables 2 and 3), and correspond closely to those previously observed in the bis[hydrotris(pyrazol-1-yl)borato]cobalt(II) complex.<sup>10</sup> The least-squares planes of all six pyrazolyl five-membered rings are reasonably planar (Table 4), although it should be noted that the root-mean-square deviation of the N(11), N(12), C(16)—C(18) plane is slightly higher than that of the remaining five planes (see later). Due to the elongated rhombic octahedral stereochemistry of the  $\text{CuN}_6$  chromophores, the planes of the pyrazole rings associated with the elongation axes [N(5), N(6), C(7)—C(9)] are more distorted away from the approximate  $C_3$  axis than the other two pyrazolyl rings, N(1), N(2), C(1)—C(3) and N(3), N(5), C(4)—C(6) (Figure 2), this distortion being reflected in the divergence of the three angles of Figure 2 from  $120^\circ$ .

**Electronic Properties.**—The crystal  $g$  factors are consistent with the elongated rhombic octahedral stereochemistry of the two  $\text{CuN}_6$  chromophores present,<sup>2-4</sup> but it is not possible to relate them to the two separate independent sets of local molecular  $g$  factors in order to distinguish a  $d_{x^2-y^2}$  or  $d_{xy}$  type of approximate ground state for the  $\text{CuN}_6$  chromophores present. Since the tripod ligand imposes no serious chelate-ligand constraints between the two in-plane nitrogen atoms, it is most likely that an approximate  $d_{x^2-y^2}$  ground state<sup>2,4</sup> is appropriate. The electronic reflectance spectra are similar in appearance to the type of spectrum observed for the  $\text{CuN}_6$  chromophore in  $[\text{Cu}(\text{en})_3][\text{SO}_4]$ ,<sup>14</sup>  $[\text{Cu}$

$(\text{bipy})_3]\text{X}_2$ ,<sup>15</sup> and  $[\text{Cu}(\text{dien})_2]\text{X}_2$ <sup>16</sup> systems\* and significantly different to that observed for a compressed tetrahedral stereochemistry of a  $\text{CuN}_4$  chromophore as in  $[\text{Cu}(\text{bipyam})_2(\text{ClO}_4)_2]$ <sup>17</sup> (Table 5).

TABLE 5

Electronic reflectance spectra ( $10^3 \text{ cm}^{-1}$ ) of some octahedral  $\text{CuN}_6$  chromophores (a) and tetrahedral  $\text{CuN}_4$  chromophores (b)

Complex	Electronic spectra		
(a) Restricted elongated rhombic octahedral $\text{CuN}_6$			
$[\text{Cu}(\text{en})_3][\text{SO}_4]$	8.7		15.7
$[\text{Cu}(\text{bipy})_3][\text{ClO}_4)_2]$	8.7		15.4
$[\text{Cu}(\text{dien})_2]\text{Br}_2 \cdot \text{H}_2\text{O}$	8.8		15.4
(b) Compressed tetrahedral $\text{CuN}_4$			
$[\text{Cu}(\text{bipyam})_2(\text{ClO}_4)_2]$	10.4 (sh)	13.5 (sh)	15.7

The out-of-plane chelation of the tripod ligand then imposes a constraint<sup>16</sup> on the extent of elongation in the two Cu-N(5) and Cu-N(9) directions to give a restricted elongated tetragonal-octahedral stereochemistry as observed in other  $\text{CuN}_6$  systems<sup>2,5,16</sup> involving chelate nitrogen ligands. This comparison alone suggests that the two bands in the electronic spectrum of  $[\text{Cu}\{\text{BH}(\text{N}_2\text{C}_3\text{H}_3)_2\}_2]$  may be assigned by analogy as the  $d_{xz}$ ,  $d_{yz}$ ,  $d_{xy} \rightarrow d_{x^2-y^2}$  transition to the intense band at  $16\,400 \text{ cm}^{-1}$  and the  $d_{z^2} \rightarrow d_{x^2-y^2}$  transition to the band at  $10\,400 \text{ cm}^{-1}$ , but in the absence of good polarised single-crystal electronic spectra this assignment can only be tentative. Attempts to record such polarised spectra were unsuccessful in that the spectra only showed a change of intensity of the bands at  $16\,400$  and  $10\,400 \text{ cm}^{-1}$  rather than clear polarisation. This is not surprising in view of the

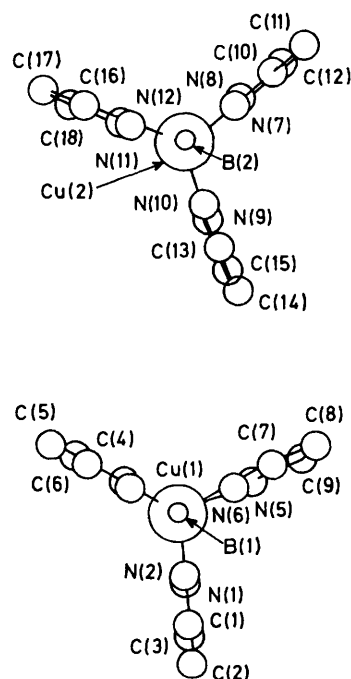


FIGURE 2 Projection down the B(1)—Cu(1) and B(2)—Cu(2) directions of the two independent chromophores of  $[\text{Cu}\{\text{BH}(\text{N}_2\text{C}_3\text{H}_3)_2\}_2]$

\* en = Ethylenediamine, bipy = 2,2'-bipyridyl, dien = diethylenetriamine, and bipyam = 2,2'-bipyridylamine.

presence of two independent  $\text{CuN}_6$  chromophores in the unit cell, the elongation axes of which are misaligned by *ca.*  $69^\circ$ .

**Fluxional Behaviour.**—The crystallographic analysis of  $[\text{Cu}\{\text{BH}(\text{N}_2\text{C}_3\text{H}_3)_2\}_2]$  indicates the presence of two distortion isomers<sup>12,13</sup> of the copper(II)  $\text{CuN}_6$  chromophores with no indication of the reason for the difference in tetragonality observed. Since the estimated standard deviations of the Cu–N bond lengths are low ( $<0.004 \text{ \AA}$ ), the crystal structure offers an opportunity to compare the geometries of two distortion isomers of comparable accuracy. The geometry of Cu(1), Figure 3(a), is not only more axially elongated than that of Cu(2) but involves a smaller rhombic distortion of the two in-plane Cu–N distances than those of Cu(2). These differences may be understood if the  $\text{CuN}_6$  chromophores present do not involve a static stereochemistry, but some temperature variability, or fluxional behaviour,<sup>18–20</sup> is present, in which the two chromophores differ in their degree of fluxional behaviour. The fluxional properties of the  $\text{CuO}_6$  chromophore were first demonstrated for the copper(II) ion doped into the zinc Tutton salts as a host lattice and suggested to explain the temperature variability of the *g* factors and *A* values. Fluxional effects also account for the changes observed<sup>21–23</sup> in the crystal structure of  $[\text{NH}_4]_2[\text{Cu}(\text{OH}_2)_6(\text{SO}_4)_2]$  at room and liquid-nitrogen temperatures [Figure 3(b)] in which the  $\text{CuO}_6$  chromophore becomes more elongated and axial with decreasing temperature.

A comparable explanation is thus available to describe the structural differences of the  $\text{CuN}_6$  chromophores of  $[\text{Cu}\{\text{BH}(\text{N}_2\text{C}_3\text{H}_3)_2\}_2]$ . That of Cu(1) is nearly axial with the lower tetragonality,  $T = 0.792$ , and may be represented (Figure 4) by the single potential well (I) with little or no thermal occupation of well (II). That of Cu(2) is much less axial, with a significantly higher tetragonality of 0.866, and may be represented by the potential well (I) with a significant thermal occupation of

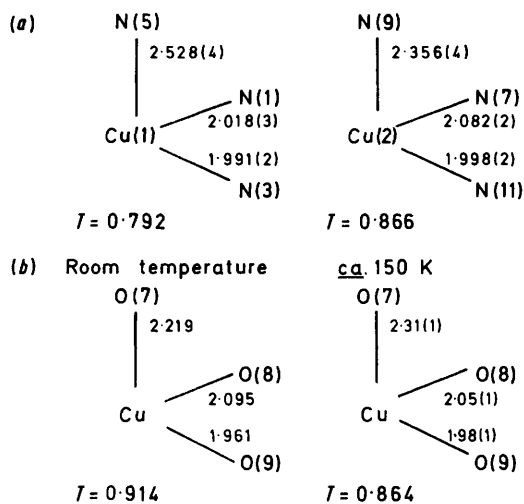


FIGURE 3 Local molecular structure of (a) the two independent chromophores of  $[\text{Cu}\{\text{BH}(\text{N}_2\text{C}_3\text{H}_3)_2\}_2]$ , (b)  $[\text{NH}_4]_2[\text{Cu}(\text{OH}_2)_6(\text{SO}_4)_2]$  at room temperature and at *ca.* 150 K

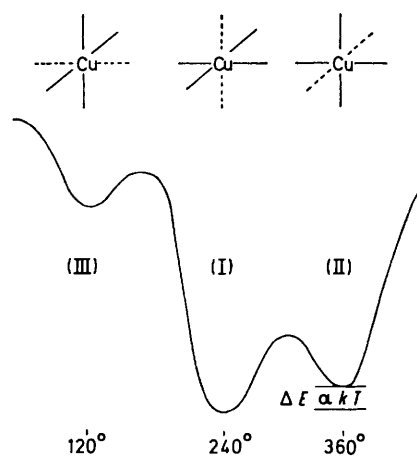


FIGURE 4 Potential-energy surface associated with the three elongated rhombic octahedral chromophores each misaligned by  $90^\circ$  and related by the original  $C_3$  axis of the parent regular octahedral chromophore

well (II) in order to account for the higher observed tetragonality, and in which system  $\Delta E$  must be significantly less than  $200 \text{ cm}^{-1}$ . This suggestion would predict that the structure of the  $\text{CuN}_6$  chromophore of Cu(1) would show little variation with temperature while that of Cu(2) would show marked temperature variability as demonstrated for the structure of  $[\text{NH}_4]_2[\text{Cu}(\text{OH}_2)_6(\text{SO}_4)_2]$ .<sup>21</sup> It would be of interest to confirm these predictions by a low-temperature crystal-structure analysis of  $[\text{Cu}\{\text{BH}(\text{N}_2\text{C}_3\text{H}_3)_2\}_2]$  but unfortunately the number of parameters present would preclude this determination using the photographic low-temperature facilities available to the present authors.

Some evidence for the fluxional behaviour of the Cu(2)  $\text{N}_6$  chromophore, as opposed to the Cu(1)  $\text{N}_6$  chromophore, can be obtained from the anisotropic temperature factors<sup>20,24</sup> for both chromophores. The root-mean-square (r.m.s.) displacements ( $\text{\AA}$ ) calculated along the copper–nitrogen directions<sup>24</sup> and corrected for the displacements of the copper atom are given in Table 6. Significant displacements are observed, except for the Cu(1)–N(5) bond, where an exceptionally large contribution from the copper atom yields a negative result, suggestive of the presence of some systematic errors.<sup>25</sup> The r.m.s. displacements of the remaining donor atoms for Cu(1) are all  $<0.07 \text{ \AA}$ , a value that is comparable with values of  $0.05 \text{ \AA}$  obtained<sup>26</sup> for static systems and suggests a static  $\text{CuN}_6$  chromophore for the Cu(1) atom. By comparison, the shortest bond [Cu(2)–N(11)] of Cu(2) also shows a r.m.s. displacement of  $0.07 \text{ \AA}$

TABLE 6

Root-mean-square displacements ( $\text{\AA}$ ) of  $[\text{Cu}\{\text{BH}(\text{N}_2\text{C}_3\text{H}_3)_2\}_2]$ , along the defined bonding directions

	$U(\text{N})/\text{\AA}^2$	$U(\text{Cu})/\text{\AA}^2$	$\Delta U^{\frac{1}{2}}(\text{Cu-N})/\text{\AA}$
Cu(1)–N(1)	0.0389	0.0336	0.07(1)
Cu(1)–N(3)	0.0355	0.0337	0.04(1)
Cu(1)–N(5)	0.0479	0.0555	$<0.00$
Cu(2)–N(7)	0.0563	0.0348	0.15(1)
Cu(2)–N(9)	0.0557	0.0408	0.12(1)
Cu(2)–N(11)	0.0325	0.0277	0.07(1)

suggesting a static behaviour, but the intermediate and long bonds [Cu(2)-N(7) and Cu(2)-N(9)] show significantly larger thermal effects with r.m.s. displacements of 0.15 and 0.12 Å, respectively. The latter compare with values of 0.15 Å observed for cubic and trigonal systems which display a genuine dynamic Jahn-Teller effect.<sup>24,26</sup> This thermal analysis suggests greater apparent thermal averaging in the long and intermediate bonds of the Cu(2) chromophore, than for the short bond, consistent with the two-dimensional fluxional effect suggested above. The temperature effect on the local molecular *g* factors could yield some evidence for fluxional behaviour, but the failure to resolve the crystal *g* factors into the two independent sets of local molecular *g* factors prevented this approach, especially as there was no observable temperature effect on the polycrystalline e.s.r. spectrum. Equally, the effect of temperature could not be observed in the electronic reflectance spectra since the shorter time scale involved in *d-d* transitions (<10<sup>-13</sup> s) results in the observed electronic spectra representing the extrema of the fluxional system, *i.e.* the static elongated rhombic octahedral stereochemistry of the CuN<sub>6</sub> chromophore rather than the average CuN<sub>6</sub> stereochemistry. Under these circumstances no temperature effect on the electronic or e.s.r. spectra would be anticipated, despite the above suggestion of fluxional behaviour in the Cu(2) chromophore, since the effect would be too small to observe under these conditions.

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