

## Crystal and Molecular Structure of Bis-[2-(2-aminoethyl)pyridine]-di-isothiocyanatocopper(II)

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The crystal and molecular structure of the title compound has been determined from three-dimensional X-ray diffractometer data. Crystals are monoclinic, space group  $P2_1/c$  with  $Z = 2$  in a cell of dimensions  $a = 8.398(5)$ ,  $b = 14.751(10)$ ,  $c = 7.834(5)$  Å, and  $\beta = 102.35(4)^\circ$ . The structure was refined by full-matrix least-squares techniques to  $R$  0.033 for 1536 independent observed reflections. The complex is a six-co-ordinated monomer with tetragonally distorted octahedral geometry at copper; four nitrogen atoms from two substituted pyridine ligands form the equatorial plane, while nitrogen atoms from the NCS groups occupy the axial sites. As expected the axial Cu-N bond lengths [2.593(3) Å] are considerably longer than the equatorial [2.022(2) and 2.061(2) Å]. The geometry at copper is different from that in either the analogous bromide or iodide complexes.

THE syntheses of a variety of complexes of the type  $[\text{Cu}(\text{aep})_2\text{X}_2]$  [ $\text{X} =$  halogen or pseudo-halogen,  $\text{aep} =$  2-(2-aminoethyl)pyridine] have been reported by Uhlig and Maaser,<sup>1</sup> who postulated that these complexes were monomeric with six-co-ordination at the copper atoms. Our more recent synthetic and structural work, however, has shown that while the complexes are monomeric, the co-ordination at copper in the solid state depends upon

the anion  $\text{X}$ .<sup>2-4</sup> Thus, when it is iodide the cation is the square-planar  $[\text{Cu}(\text{aep})_2]^{2+}$  unit,<sup>2</sup> when it is Br the copper is contained in the five-co-ordinated  $[\text{Cu}(\text{aep})_2\text{Br}]^+$  ion,<sup>3</sup> and when it is  $\text{ClO}_4$  the copper is six-co-ordinated<sup>4</sup> with the perchlorates 'semi-co-ordinated.'<sup>5</sup> A similar change in co-ordination with diverse anions has also been postulated for other copper complexes,<sup>6-8</sup> and demonstrated crystallographically for some.<sup>9-12</sup>

<sup>1</sup> E. Uhlig and M. Maaser, *Z. anorg. Chem.*, 1963, **322**, 25.

<sup>2</sup> V. C. Copeland and D. J. Hodgson, *Inorg. Chem.*, 1973, **12**, 2157.

<sup>3</sup> V. C. Copeland, P. Singh, W. E. Hatfield, and D. J. Hodgson, *J. Phys. Chem.*, 1972, **76**, 2887.

<sup>4</sup> D. L. Lewis and D. J. Hodgson, *Inorg. Chem.*, 1974, **13**, 143.

<sup>5</sup> D. S. Brown, J. D. Lee, B. G. A. Melson, B. J. Hathaway, I. M. Procter, and A. A. G. Tomlinson, *Chem. Comm.*, 1967, 369.

<sup>6</sup> B. J. Hathaway, I. M. Procter, R. C. Slade, and A. A. G. Tomlinson, *J. Chem. Soc. (A)*, 1969, 2219.

<sup>7</sup> W. R. McWhinnie, *J. Chem. Soc.*, 1964, 5165.

<sup>8</sup> J. C. Lancaster, W. R. McWhinnie, and P. L. Welham, *J. Chem. Soc. (A)*, 1971, 1742.

<sup>9</sup> J. E. Johnson, T. A. Beineke, and R. A. Jacobson, *J. Chem. Soc. (A)*, 1971, 1371.

<sup>10</sup> J. E. Johnson and R. A. Jacobson, *J.C.S. Dalton*, 1973, 580.

<sup>11</sup> M. Cannas, G. Carta, and G. Marongiu, *Chem. Comm.*, 1971, 673.

<sup>12</sup> G. D. Andreotti, L. Cavalca, and P. Sgarabotto, *Gazzetta*, 1971, **101**, 483.

Such a series of compounds provides a means of correlating the electronic spectra and structures of monomeric copper complexes. McWhinnie and co-workers have attempted to deduce geometries about the copper ion for the series  $[\text{Cu}(\text{dipyam})_2\text{X}_2]$  (dipyam = 1,1'-dipyridylamine, X = Cl, Br, or I) based only on spectroscopic data. They have suggested that the bromo-complex is octahedral, the iodo-square-pyramidal, and the chloro-trigonal bipyramidal;<sup>7,8</sup> for the series  $[\text{Cu}(\text{bipy})_2\text{X}_2]$  and  $[\text{Cu}(\text{bipy})_2\text{XY}]$  (bipy = 2,2'-bipyridine), Hathaway and co-workers have used electronic and e.s.r. data to postulate geometries about the metal atom which they reported to be dependent on the size and co-ordinating properties of X and Y.<sup>6</sup> The structure of  $[\text{Cu}(\text{bipy})_2\text{I}_2]$ , for example, has been reported<sup>13</sup> and the geometry at the copper atom was found to be trigonal bipyramidal, which is comparable to that of  $[\text{Cu}(\text{aep})_2\text{Br}_2]$ .<sup>3</sup>

For the dipyam complexes, Jacobson has shown that in the perchlorate the metal is four-co-ordinate<sup>9</sup> whereas in the iodide it is five-co-ordinate.<sup>10</sup> These results are difficult to interpret since for the aep complexes the co-ordination number at copper apparently increases as the size of the ligating atom decreases,<sup>4</sup> while for these dipyam complexes the trend is reversed. Moreover, the electronic spectra of  $[\text{Cu}(\text{bipy})_2\text{I}]$  and  $[\text{Cu}(\text{dipyam})_2\text{I}]$  are quite different, despite their structural similarity.

In an attempt to test our conjecture<sup>4</sup> (*vide supra*) that there is a correlation between co-ordination number at copper and ligating atom size, and also to provide a further member of the series for eventual spectroscopic correlation, we have undertaken a three-dimensional structural investigation of the thiocyanate complex,  $[\text{Cu}(\text{aep})_2(\text{SCN})_2]$ .

#### EXPERIMENTAL

Dark blue crystals of  $[\text{Cu}(\text{aep})_2(\text{NCS})_2]$  were prepared by the method of Uhlig and Maaser.<sup>1</sup> The first product obtained from a solution prepared as suggested by these workers (but diluted to three times the volume) were green plate-like crystals whose formulation is  $\text{Cu}(\text{aep})(\text{NCS})_2$  and whose properties are currently under investigation; after two crops of this green material had been removed by filtration, blue crystals of  $[\text{Cu}(\text{aep})_2(\text{NCS})_2]$  were formed and subjected to elemental analysis.

*Crystal Data.*— $\text{C}_{18}\text{H}_{20}\text{CuN}_6\text{S}_2$ ,  $M = 424.0$ , Monoclinic,  $a = 8.398(5)$ ,  $b = 14.751(10)$ ,  $c = 7.834(5)$  Å,  $\beta = 102.35(4)^\circ$ ,  $D_c = 1.486$ ,  $Z = 2$ ,  $D_m = 1.49(3)$ ,  $U = 948.0$  Å<sup>3</sup>. Space group  $P2_1/c$ . Mo- $K_\alpha$  radiation,  $\lambda = 0.7107$  Å;  $\mu(\text{Mo-}K_\alpha) = 14.2$  cm<sup>-1</sup>.

The cell constants were determined by least-squares methods.<sup>14</sup> With two molecules in the unit cell, the copper

<sup>13</sup> G. A. Barclay, B. F. Hoskins, and C. H. L. Kennard, *J. Chem. Soc.*, 1963, 5691.

<sup>14</sup> W. R. Busing and H. A. Levy, *Acta Cryst.*, 1967, **22**, 457.

<sup>15</sup> D. L. Lewis and D. J. Hodgson, *Inorg. Chem.*, 1973, **12**, 1682.

<sup>16</sup> P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 197.

<sup>17</sup> W. R. Busing and H. A. Levy, *J. Chem. Phys.*, 1957, **26**, 563.

<sup>18</sup> D. J. Hodgson, P. K. Hale, and W. E. Hatfield, *Inorg. Chem.*, 1971, **10**, 1061.

<sup>19</sup> S. A. Goldfield and K. N. Raymond, *Inorg. Chem.*, 1971, **10**, 2604.

atoms are constrained to lie on a crystallographic inversion centre.

Diffraction data were collected from a parallelepiped crystal with faces (0 $\bar{1}1$ ), (0 $1\bar{1}$ ), (011), (0 $\bar{1}\bar{1}$ ), (100), and ( $\bar{1}00$ ). The separations between the opposite pairs of these faces were: (0 $\bar{1}1$ ) and (0 $1\bar{1}$ ), 0.306 mm; (011) and (0 $\bar{1}\bar{1}$ ), 0.333 mm; (100) and ( $\bar{1}00$ ), 0.200 mm. The crystal was mounted on a glass fibre roughly normal to the (100) planes, and data were collected on a Picker four-circle automatic diffractometer using a highly-oriented graphite monochromator and Mo- $K_\alpha$  radiation as described elsewhere.<sup>15</sup> Data were collected by the  $\theta$ - $2\theta$  scan technique at a scan rate of  $1^\circ$  min<sup>-1</sup>, and the peaks were scanned from  $0.75^\circ$  in  $2\theta$  below the calculated  $K_{\alpha 1}$  peak position to  $0.75^\circ$  above the calculated  $K_{\alpha 2}$  peak position. Data were collected out at a value of  $2\theta(\text{Mo-}K_{\alpha 1})$   $55^\circ$ , 2277 independent intensities being recorded; there were very few reflections above background at values of  $2\theta > 55^\circ$ .

The data were processed by the method of ref. 16. After background corrections were applied the intensities were assigned<sup>17</sup> standard deviations  $\sigma(I)$ , where  $\sigma(I) = [C + 0.25(I_s/I_b)^2(B_{II} + B_L) + p^2I^2]^{1/2}$  where the symbols have their usual meanings<sup>18</sup> and  $p$  was chosen as 0.05. The values of  $I$  and  $\sigma(I)$  were corrected for Lorentz and polarization effects.<sup>19</sup> No correction for absorption was made. Of 2277 independent intensities recorded, 1536 had  $I > 3\sigma(I)$  and were used in the refinement of the structure.

The locations of the copper and sulphur atoms were obtained from examination of a three-dimensional Patterson function,<sup>20</sup> and two cycles of least-squares refinement were run on these positions. All least-squares refinements in this analysis were carried out on  $F$ , the function minimized being  $\sum w(|F_o| - |F_c|)^2$  and the weights  $w$  being taken as  $4F_o^2/\sigma^2(F_o^2)$ . In all calculations of  $F_c$  the atomic scattering factors for copper and sulphur were taken from ref. 21, that for hydrogen from ref. 22, and those for carbon and nitrogen from ref. 23. The effects of the anomalous dispersion of copper were included in calculations of  $F_c$ ,<sup>24</sup> the values of  $\Delta f'$  and  $\Delta f''$  for copper being taken from ref. 25.

Initially, the two atoms were assigned variable isotropic thermal parameters. After two cycles of least-squares refinement  $R$  was 0.456 and  $R'$  0.524 ( $R' = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o^2)]^{1/2}$ ). The remaining atoms, including the hydrogen atoms, were located in subsequent difference-Fourier maps. Two further cycles of least-squares refinement gave  $R$  0.034 and  $R'$  0.049 with the non-hydrogen atoms being assigned variable anisotropic and hydrogen atoms variable isotropic thermal parameters.

Examination of the values of  $|F_o|$  and  $|F_c|$  suggested that the data were suffering from secondary extinction, and a correction of the type described by Zachariasen<sup>26</sup> led to a value for the extinction coefficient of  $5.2(3) \times 10^{-8}$ . Examination of the values of  $R'$  showed a dependence on  $\sin \theta$ ,

<sup>20</sup> In addition to various local programs for the IBM 370/165, the programs used were local modification of J. A. Ibers' NUCLS least-squares program, W. R. Busing, K. O. Martin, and H. A. Levy's ORFEE function and error program, W. T. L. Robinson's FOURIER program, C. K. Johnson's ORTEP plotting program, and R. J. Doedens RSCAN program.

<sup>21</sup> D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

<sup>22</sup> R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

<sup>23</sup> 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, Table 3.3 1A.

<sup>24</sup> J. A. Ibers and W. C. Hamilton, *Acta Cryst.*, 1964, **17**, 781.

<sup>25</sup> D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

<sup>26</sup> W. H. Zachariasen, *Acta Cryst.*, 1968, **A24**, 212.

which suggested that our weighting scheme was inappropriate. The weights were modified by dividing the weights  $w$  for data with  $2\theta < 22.5^\circ$  by 1.56 and those for data with  $30^\circ \geq 2\theta > 22.5^\circ$  by 1.14. Final values are  $R$  0.033 and  $R'$  0.044. A final difference-Fourier map showed no peak  $> 0.3 \text{ e}\text{\AA}^{-3}$ , the peak height of a typical carbon atom in this synthesis being *ca.*  $9 \text{ e}\text{\AA}^{-3}$ . In the last cycle of least-squares refinement the greatest shift in an atomic parameter was  $0.37\sigma$ . Final positional and thermal parameters are given in Tables 1 and 2, and observed and calculated structure

TABLE 1  
Atomic positional parameters

Atom	$x$	$y$	$z$
Cu	0	0	0
S	0.23796(9)	0.19099(5)	0.57849(9)
N(1)	-0.2039(2)	0.0489(1)	0.0760(2)
N(2)	0.0181(3)	0.1235(1)	-0.1069(3)
N(3)	0.1448(3)	0.0800(2)	0.2859(3)
C(1)	-0.3138(3)	0.1009(2)	-0.0312(3)
C(2)	-0.4468(3)	0.1369(2)	0.0229(4)
C(3)	-0.4686(4)	0.1201(2)	0.1884(4)
C(4)	-0.3564(4)	0.0674(2)	0.2978(4)
C(5)	-0.2258(3)	0.0342(2)	0.2384(3)
C(6)	-0.2840(3)	0.1189(2)	-0.2098(3)
C(7)	-0.1271(4)	0.1702(2)	-0.2051(5)
C(8)	0.1825(3)	0.1261(2)	0.4062(3)
H(2)	-0.512(4)	0.169(2)	-0.054(4)
H(3)	-0.445(5)	0.147(3)	0.220(5)
H(4)	-0.369(4)	0.054(2)	0.410(5)
H(5)	-0.152(4)	0.002(1)	0.309(4)
H(61)	-0.377(4)	0.347(2)	0.223(4)
H(62)	-0.277(4)	0.440(2)	0.239(4)
H(71)	-0.133(7)	0.267(4)	0.347(7)
H(72)	-0.112(6)	0.321(3)	0.181(7)
HN(1)	0.074(5)	0.152(3)	-0.016(5)
HN(2)	0.089(5)	0.125(3)	-0.167(5)

TABLE 2  
Thermal parameters

(a) Anisotropic parameters * ( $\times 10^4$ ; for Cu $\times 10^2$ )						
Atom	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Cu	1651(8)	496(3)	2392(10)	298(3)	1013(6)	419(3)
S	2352(14)	483(4)	2045(14)	-187(5)	331(10)	24(5)
N(1)	142(3)	42(1)	162(3)	7(1)	45(2)	6(1)
N(2)	179(4)	44(1)	188(4)	7(1)	59(3)	11(2)
N(3)	209(4)	81(2)	220(5)	-1(2)	29(3)	-14(2)
C(1)	131(3)	41(1)	151(4)	5(1)	25(3)	-2(2)
C(2)	146(4)	57(1)	230(5)	25(2)	43(4)	12(2)
C(3)	187(5)	65(2)	273(6)	18(2)	117(5)	-2(3)
C(4)	209(5)	62(1)	194(5)	-3(2)	98(4)	0(2)
C(5)	169(4)	49(1)	157(4)	6(2)	50(3)	14(2)
C(6)	178(4)	61(2)	147(4)	26(2)	17(3)	13(2)
C(7)	204(5)	66(2)	258(6)	26(2)	83(5)	60(3)
C(8)	118(3)	49(1)	177(4)	0(2)	39(3)	19(2)

(b) Isotropic parameters ( $\times 10^2$ )

Atom	$B/\text{\AA}^2$	Atom	$B/\text{\AA}^2$
H(2)	628(4)	H(62)	636(4)
H(3)	697(1)	H(71)	1041(9)
H(4)	577(4)	H(72)	918(8)
H(5)	463(5)	HN(1)	708(2)
H(61)	534(2)	HN(2)	658(12)

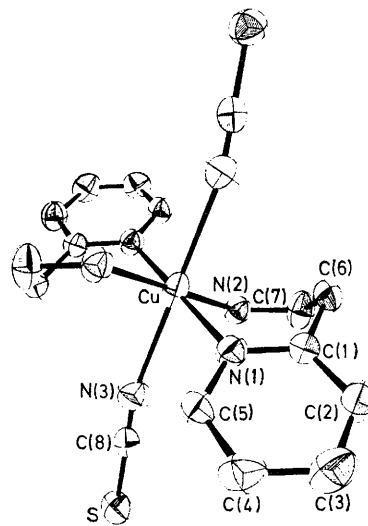
\* In the form:  $\exp[-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$ .

amplitudes are listed in Supplementary Publication No. SUP 21146 (11 pp., 1 microfiche).\*

## DISCUSSION

The complex consists of monomeric six-co-ordinate  $[\text{Cu}(\text{aep})_2(\text{NCS})_2]$  units. The co-ordination around copper is a tetragonally distorted octahedron and the

geometry of the complex is shown in the Figure. Bond distances and angles and their estimated standard deviations are given in Tables 3 and 4. The equatorial plane is formed by the nitrogen atoms of the aep ligands with Cu-N(1) 2.061(2) and Cu-N(2) 2.022(2)  $\text{\AA}$ , well within the



View of the molecule, with thermal ellipsoids drawn at the 40% probability level; hydrogen atoms omitted for clarity

range (2.005–2.065  $\text{\AA}$ ) for the iodo-, bromo-, and perchlorate  $[\text{Cu}(\text{aep})_2\text{X}_2]$  complexes previously reported,<sup>2,4</sup> with the bond length to the pyridine nitrogen again longer than that involving the amine nitrogen atom.

TABLE 3

Bond distances ( $\text{\AA}$ )			
Cu-N(2)	2.022(2)	C(1)-C(6)	1.496(4)
Cu-N(1)	2.061(2)	C(3)-C(4)	1.371(5)
Cu-N(3)	2.593(3)	C(4)-C(5)	1.372(4)
S-C(8)	1.638(3)	C(6)-C(7)	1.513(5)
N(1)-C(5)	1.342(3)	C(7)-N(2)	1.468(4)
N(1)-C(1)	1.346(3)	C(8)-N(3)	1.151(4)
C(2)-C(3)	1.369(4)	C(1)-C(2)	1.384(3)
C(2)-H(2)	0.87(4)	C(4)-H(4)	0.93(3)
C(3)-H(3)	0.91(4)	C(5)-H(5)	0.87(3)
C(6)-H(61)	0.98(3)	C(7)-H(72)	0.94(5)
C(6)-H(62)	0.97(4)	N(2)-H(N1)	0.87(4)
C(7)-H(71)	1.01(5)	N(2)-H(N2)	0.84(4)

TABLE 4

Bond angles ( $^\circ$ )			
N(1)-Cu-N(2)	86.89(9)	C(2)-C(3)-C(4)	118.8(3)
N(2)-Cu-N(3)	83.4(1)	C(3)-C(4)-C(5)	118.8(3)
N(1)-Cu-N(3)	81.75(9)	C(4)-C(5)-N(1)	123.1(3)
C(1)-N(1)-Cu	121.3(1)	C(1)-C(6)-C(7)	112.6(2)
C(1)-N(1)-C(5)	118.1(2)	C(6)-C(7)-N(2)	113.6(2)
C(5)-N(1)-Cu	120.5(2)	C(7)-N(2)-Cu	120.8(2)
C(6)-C(1)-N(1)	117.1(2)	N(3)-C(8)-S	179.3(2)
C(2)-C(1)-C(6)	121.8(2)	Cu-N(3)-C(8)	166.6(2)
C(1)-C(2)-C(3)	120.1(3)	N(1)-C(1)-C(2)	121.2(2)

The N(1)-Cu-N(2) and N(1)-Cu-N(3) bond angles are 86.89(9) and 93.11(9) $^\circ$ , with planarity required by the inversion centre at copper. The value for the N(1)-Cu-N(2) angle is in good agreement with those obtained for

\* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

$\text{Cu}(\text{aep})_2\text{I}_2$  [88.8(1)°] and for  $[\text{Cu}(\text{aep})_2(\text{ClO}_4)_2]$  [86.54(7)°] but not with those for  $[\text{Cu}(\text{aep})(\text{OH})_2][\text{ClO}_4]_2$  [eaep = 2-(2-ethylaminoethyl)pyridine<sup>27</sup>] (92.7°),  $[\text{Cu}(\text{eaep})_2\text{Br}]\text{Br}$  (92.8°),<sup>2</sup> and  $\alpha$ - $[\text{Cu}(\text{dmaep})(\text{OH})_2(\text{ClO}_4)_2]$  [dmaep = 2-(2-dimethylaminoethyl)pyridine<sup>28</sup>] (96.3°). It has previously been noted that acute values of the aep 'bite' may be representative of preferred low-energy configurations of the ligands when steric constraints are not present and that there appeared to be an inverse correlation between anion contact volume and the co-ordination number of the copper atom.<sup>4</sup> For example, the largest anion iodide has for the copper atom a co-ordination number of four, the intermediate-sized bromide anion one of five, and the smallest oxygen (perchlorate) one of six. In the present case these observations seem to be correct in that, with nitrogen as the axially bound atom, the co-ordination number is six. However, the presence of the axial ligands does not cause the aep 'bite' to become obtuse.

The thiocyanate ligand is bonded to the metal through the nitrogen. The axial Cu-N(3) distance [2.593(3) Å] is, as is usual in six-co-ordinate copper(II) complexes,<sup>29</sup> considerably larger than the equatorial Cu-N separations, and is also greater than those found<sup>30</sup> for equatorial Cu-NCS bonds (1.98 Å) in  $[\text{Cu}(\text{NH}_3)_2(\text{NCS})_2]$  or for Cu-NCS bonds in the trigonal bipyramidal complexes  $[\text{Cu}(\text{tn})_2(\text{NCS})][\text{ClO}_4]$  [tn = bis-(2,3-diaminopropane)] (2.21 Å),<sup>11</sup> and  $[\text{Cu}(\text{tren})(\text{NCS})](\text{NCS})$  (1.95 Å).<sup>31</sup> The value is, however, very similar to that [2.517(7) Å] found<sup>32</sup> for axially co-ordinated isothiocyanate in  $[\text{Cu}(\text{dmen})_2(\text{NCS})_2]$  (dmen = *NN'*-dimethylethylenediamine). The N(3)-C(8) and C(8)-S distances [1.151(4) and 1.638(3) Å] are normal for *N*-bound thiocyanates.<sup>32</sup> The Cu-N(3)-C(8) angle [166.6(2)°] is much closer to linearity than that<sup>32</sup> in  $[\text{Cu}(\text{dmen})_2(\text{NCS})_2]$  (129°) or the corresponding Ni-N-C angle (140°) in  $[\text{Ni}(\text{en})_2(\text{NCS})_2]$ .<sup>33</sup> The N(3)-C(8)-S angle [179.3(2)°] is approximately linear. The Cu-N(3) bond is inclined at 81.8(1)° to the N(2)-Cu bond, *i.e.* the Cu...N(3) vector is not perpendicular to the equatorial plane. The direction of this deviation is such as to take N(3) away from the C(6) atom (*vide infra*); a similar distortion was also found in  $[\text{Cu}(\text{aep})_2(\text{ClO}_4)_2]$ .<sup>4</sup>

<sup>27</sup> D. L. Lewis, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, 1972, **11**, 2216.

<sup>28</sup> D. L. Lewis, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, 1974, **13**, 147.

<sup>29</sup> A. Santoro, A. D. Mighell, and C. W. Riemann, *Acta Cryst.*, 1970, **B26**, 979.

The geometry of the aep ligand is similar to that of other aminoethylpyridine moieties, with the chelating portion of the ligand again adopting the boat conformation. As Table 5 shows, the basal portion of the boat, which is

TABLE 5

Equations of least-squares planes, and deviations (Å) of relevant atoms from them

Plane (1): N(1), C(1)-(5)
$-0.4714x - 0.8184y - 0.5288z = 0.0786$
[N(1) 0.007, C(1) -0.001, C(2) -0.003, C(3) 0.001, C(4) 0.005, C(5) -0.009, C(6) -0.027, C(7) 1.276, N(2) -1.456, Cu -0.0079]
Plane (2): N(1), N(2), C(1), C(7)
$-0.0736x - 0.8265y - 0.5581z = -1.0677$
[N(1) 0.282, N(2) -0.005, C(5) -0.198, C(7) -0.0078, C(6) 0.664, Cu 1.068]

comprised of atoms N(1), C(5), C(7), and N(2), only poorly approximates to planarity with an average deviation from the best least-squares plane of 0.14 Å. The 'bow' and 'stern' of the boat are displaced from this plane by 0.664 [C(6)] and 1.068 Å (Cu); these deviations are very similar to those found in  $[\text{Cu}(\text{aep})_2\text{I}_2]$ <sup>2</sup> and  $[\text{Cu}(\text{aep})_2(\text{ClO}_4)_2]$ .<sup>4</sup>

The geometry at the copper established for this complex is quite different from that in either the corresponding iodide or bromide complexes; it is similar to that in the perchlorate, but the axial co-ordination in the present case (Cu-N 2.59 Å) is considerably stronger than that in the perchlorate (Cu-O 2.83 Å).<sup>4</sup> Hence, these four complexes present a unique opportunity to examine more closely the postulated relationships between the electronic and e.s.r. spectra and the structures of monomeric copper(II) complexes, which may lead to enhanced reliability of these spectroscopic methods as structural tools.

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