Contribution from the William Rand Kenan Jr. Laboratories of Chemistry,
The University of North Carolina, Chapel Hill, North Carolina 27514

Structure of Bis[2-(2-aminoethyl)pyridine]copper(II) Iodide

VICKI C. COPELAND and DEREK J. HODGSON*

Received February 6, 1973

The crystal and molecular structure of bis[2-(2-aminoethyl)pyridine]copper(II) iodide, $[Cu(C_7N_2H_{10})_2]I_2$ has been determined from three-dimensional X-ray data collected by counter methods. The material crystallizes in space group $C_{2h}{}^5$-$P2_1/c$ of the monoclinic system with two formula units in a cell of dimensions a = 8.304 (1), b = 14.311 (2), c = 7.677 (2) Å, and β = 108.07 (1)°. The observed and calculated densities are 2.11 (3) and 2.150 g cm^{-3}, respectively. The structure has been refined by least-squares methods to a final value of the R factor (on F) of 0.029 for 2239 independent reflections having $F^2 > 3\sigma(F^2)$. The complex consists of four-coordinated $[Cu(C_7N_2H_{10})_2]^{2+}$ cations which are well separated from discrete I^- anions. The copper atom lies on an inversion center and the geometry at the copper atom is square planar. Hence, the structure of this complex is in contrast to the five-coordinate geometry found for the bromo analog.

Introduction

The preparations of complexes of formulation $Cu(AEP)_2X_2$ and $Cu(AEP)X_2$, where X is a halogen and AEP is 2-(2-aminoethyl)pyridine, were first reported by Uhlig and Maaser,[1] and it was assumed by these workers that the former complexes were monomeric, with six-coordination at the copper atoms while the latter were dimeric and five-coordinated. Our recent structural[2] and magnetic[3] investigations of $Cu(AEP)Br_2$, however, have shown that this complex is best described as a six-coordinate polymer, containing both Cu–Br–Cu chain interactions and Cu–Br–Cu–Br pairwise (dimeric) linkages; all of these interactions are weak, the chain propagating Cu–Br distance being 3.569 Å while the dimeric Cu–Br separation is 3.706 Å.

We have also recently reported[4] the structure of $Cu(AEP)_2Br_2$ and found that the complex consists of monomeric, five-coordinated $[Cu(AEP)_2Br]^+$ cations and discrete Br^- anions. This ionic species is not unique, since a similar result had been reported[5] earlier for the structure of $Cu(bipy)_2I_2$ (where bipy is 2,2′-bipyridine). The corresponding nitrite complex, $[Cu(bipy)_2(ONO)]NO_3$, however, has been shown[6] to be six-coordinated, with the NO_2 group occupying two cis positions in the octahedron. Hathaway and coworkers[7] have inferred from electronic and epr spectra that several different structures obtain for complexes of the types $Cu(bipy)_2X_2$ and $Cu(bipy)_2XY$, depending on the size and coordinating properties of the anions X and Y. McWhinnie and coworkers[8,9] have reached similar conclusions, again based on spectroscopic data, for the complexes $Cu(dipyam)_2X_2$ (where dipyam is 2,2′-dipyridylamine). These workers suggest that the complexes $Cu(dipyam)_2X_2$, where X is Cl, Br, or I, all have different geometries at the copper atom; the iodo complex is suggested to be square pyramidal, the bromo complex octahedral, and the chloro complex trigonal bipyramidal.

The AEP complexes, clearly, provide an opportunity to test these concepts concerning the relationship between the geometry at copper and the nature of the anion. Hence, we have undertaken a complete, three-dimensional structural investigation of the iodo complex of formulation $Cu(AEP)_2I_2$; we report the results of this analysis here.

Experimental Section

Dark olive green crystals of $Cu(AEP)_2I_2$ (AEP = 2-(2-aminoethyl)pyridine) were prepared by the method of Uhlig and Maaser,[1] and their identity was verified by elemental analysis.[10] Examination of the crystals by Weissenberg and precession photography indicated that they belong to the monoclinic system. The observed systematic absences of 0k0 for k odd and h0l for l odd are consistent with a space group assignment of $C_{2h}{}^5$-$P2_1/c$. The cell constants, obtained by the least-squares procedure of Busing and Levy,[11] are a = 8.304 (1), b = 14.311 (2), c = 7.677 (2) Å, and β = 108.07 (1)°. A density of 2.150 g cm^{-3} calculated for two formula units in the cell is in acceptable agreement with the value of 2.11 (3) g cm^{-3} obtained by flotation in dibromoethane–dichloromethane solution. Hence, in space group $P2_1/c$, the copper ions are constrained to lie on a crystallographic inversion center.

Diffraction data were collected from a parallelpiped crystal with faces $(\bar{1}10)$, $(1\bar{1}0)$, (010), $(0\bar{1}0)$, (001), and $(00\bar{1})$. The separations between opposite pairs of these faces were as follows: $(\bar{1}10)$ and $(1\bar{1}0)$, 0.007 cm; (010) and $(0\bar{1}0)$, 0.014 cm; (001) and $(00\bar{1})$, 0.112 cm. The crystal was mounted on a glass fiber roughly normal to the (001) planes, and data were collected on a Picker four-circle automatic diffractometer using niobium-filtered (0.0015 in.) Mo Kα radiation in the manner described previously.[12] The data were collected at a scan rate of 1°/min, and the peaks were scanned from 0.75° in 2θ below the calculated Kα_1 peak position to 0.75° above the calculated Kα_2 peak position. Data were collected out to a value of 2θ(Mo Kα_1) = 60°, 2918 independent intensities being recorded; there were very few reflections above background at values of $2\theta > 58°$.

The data were processed by the method of Corfield, Doedens, and Ibers[13] using our program DATPROC.[14] After background corrections were applied, the intensities were assigned standard deviations $\sigma(I)$ as[15]

$$\sigma(I) = [C + 0.25(t_s/t_b)^2(B_H + B_L) + p^2I^2]^{1/2}$$

where the symbols have their usual meanings[12,13] and p was chosen as 0.05. An absorption correction was applied to the data;[16] the linear absorption coefficient μ for these atoms and Mo Kα radiation is 49.04 cm^{-1}, and for the sample used the transmission coefficients were found to lie in the range 0.480–0.753. Of the 2918 independent intensities, 2239 were greater than 3 times their assigned standard deviations.

---

(1) E. Uhlig and M. Maaser, *Z. Anorg. Allg. Chem.*, 322, 25 (1963).
(2) V. C. Copeland, P. Singh, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, 11, 1826 (1972).
(3) D. Y. Jeter, W. E. Hatfield, and D. J. Hodgson, *J. Phys. Chem.*, 76, 2707 (1972).
(4) P. Singh, V. C. Copeland, W. E. Hatfield, and D. J. Hodgson, *J. Phys. Chem.*, 76, 2887 (1972).
(5) G. A. Barclay, B. F. Hoskins, and C. H. L. Kennard, *J. Chem. Soc.*, 5691 (1963).
(6) F. S. Stephens and I. M. Procter, *J. Chem. Soc. A*, 1248 (1969).
(7) B. J. Hathaway, I. M. Procter, R. C. Slade, and A. A. G. Tomlinson, *J. Chem. Soc. A*, 2219 (1969).
(8) W. R. McWhinnie, *J. Chem. Soc.*, 5165 (1964).
(9) J. C. Lancaster, W. R. McWhinnie, and P. L. Welham, *J. Chem. Soc. A*, 1742 (1971).
(10) Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.
(11) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, 22, 457 (1967).
(12) D. J. Hodgson, P. K. Hale, and W. E. Hatfield, *Inorg. Chem.*, 10, 1061 (1971).
(13) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 6, 197 (1967).
(14) J. T. Veal and D. J. Hodgson, *Inorg. Chem.*, 11, 1420 (1972).
(15) W. R. Busing and H. A. Levy, *J. Chem. Phys.*, 26, 563 (1957).
(16) For a description of the programs used in this analysis, see ref 4.

Solution and Refinement

The positions of the copper and iodine atoms were found in a three-dimensional Patterson function, and four cycles of least-squares refinement of these positions were run. All least-squares refinements in this analysis were carried out on F, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$ 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 Cu and I were taken from Cromer and Waber,[17] that for H was from Stewart, Davidson, and Simpson,[18] and those for C and N were from Ibers.[19] The effects of anomalous dispersion were included in calculations of F_c,[20] the values of $\Delta f'$ and $\Delta f''$ for I and Cu being taken from the tabulation of Cromer.[21] Only the 2239 independent intensities which were greater than 3 times their estimated standard deviations were used in the refinement of the structure.

Initially, the two atoms were assigned variable isotropic thermal parameters. After four cycles of least-squares refinement, using the data before they had been corrected for absorption effects, the usual agreement factors $R_1 = \Sigma \| F_o| - |F_c\| / \Sigma |F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/w(F_o)^2)^{1/2}$ were 0.243 and 0.337, respectively. A difference Fourier synthesis revealed the locations of the carbon and nitrogen atoms of the AEP ligand, and two cycles of least-squares refinement with variable isotropic thermal parameters assigned to all atoms gave values of 0.112 and 0.162 for R_1 and R_2, respectively. Two further cycles of least-squares refinement with variable anisotropic thermal parameters for all atoms gave values for R_1 and R_2 of 0.054 and 0.073. After the absorption correction had been applied (*vide supra*), two cycles of least-squares refinement gave $R_1 = 0.039$ and $R_2 = 0.062$. The positions of the hydrogen atoms were located unambiguously in a difference Fourier synthesis. In two further cycles of least-squares, the nonhydrogen atoms were assigned variable anisotropic thermal parameters and the hydrogen atoms were assigned variable isotropic thermal parameters, and all positional and thermal parameters (including the hydrogen parameters) were refined. This reduced the values of the agreement factors to 0.033 and 0.047.

Examination of the values of $|F_o|$ and $|F_c|$ suggested that a correction for secondary extinction was needed, and the application of a correction of the type described by Zachariasen[22] led to a value for the extinction coefficient of 2.5 (2) × 10^{-7}. The final values of R_1 and R_2 were 0.029 and 0.044, respectively. Examination of a final difference Fourier showed no peak greater than 0.5 e Å^{-3}, the peak height of a typical carbon atom in this synthesis being approximately 9 e Å^{-3}.

In the last cycle of least-squares refinement the greatest shift in an atomic parameter was 0.7 times its estimated standard deviation, which is taken as evidence that the refinement had converged; no nonhydrogen parameter experienced a shift as great as 0.1 times its estimated standard deviation. The value of R_2 showed no apparent dependence on either sin θ or $|F_o|$, which indicates that our choice of $p = 0.05$ is acceptable. The error in an observation of unit weight is 1.46.

The positional and thermal parameters derived from the last cycle of least-squares refinement, along with their associated standard deviations as estimated from the inverse matrix, are presented in Tables I and II. A list of structure factor amplitudes is available.[23]

Description of the Structure

The complex consists of monomeric, four-coordinate $[Cu(AEP)_2]^{2+}$ cations and discrete I^- anions. The coordination around the copper(II) ions is roughly square planar, and the geometry of the cation is shown in Figure 1. The inner coordination sphere is strictly planar as a result of the inversion center at the metal; similarly, the N(1)-Cu-N(1)′ and N(2)-Cu-N(2)′ angles are strictly linear. While 6 is probably the most common coordination number in copper(II) complexes, square-planar four-coordinate geometry is not uncommon. Thus, for example, the present structure may be compared to those of ethylenebis(guanidine)copper(II) chloride monohydrate,[24] bis(1-aminocyclopentanecarboxylato)copper(II),[25] bis(8-hydroxoquinolato)copper(II) bis(picryl azide),[26] bis(salicylaldiminato)copper(II),[27] bis(1-phenyl-1,3-butanedionato)copper(II),[28] and several other complexes.[29]

Table I. Positional Parameters for $Cu(AEP)_2I_2$

	x	y	z
Cu	0.0	0.0	0.5
I	0.19652 (3)	0.13703 (2)	−0.09419 (3)
N(1)	−0.2116 (3)	0.0542 (2)	0.5397 (4)
N(2)	0.0255 (4)	0.1236 (2)	0.3853 (6)
C(1)	−0.3197 (3)	0.1073 (2)	0.4084 (4)
C(2)	−0.4586 (4)	0.1504 (2)	0.4386 (5)
C(3)	−0.4901 (5)	0.1373 (3)	0.6026 (6)
C(4)	−0.3814 (5)	0.0832 (3)	0.7334 (5)
C(5)	−0.2422 (5)	0.0441 (3)	0.6990 (5)
C(6)	−0.2855 (4)	0.1145 (2)	0.2295 (4)
C(7)	−0.1206 (5)	0.1645 (3)	0.2432 (6)
H(61)	−0.401 (5)	0.155 (3)	0.131 (6)
H(62)	−0.267 (7)	0.053 (4)	0.235 (8)
H(71)	−0.137 (6)	0.239 (4)	0.257 (7)
H(72)	−0.103 (6)	0.186 (4)	0.158 (8)
H(N(1))	0.06 (1)	0.161 (6)	0.53 (2)
H(N(2))	0.109 (9)	0.145 (4)	0.34 (1)
H(2)	−0.521 (5)	0.196 (3)	0.362 (6)
H(3)	−0.581 (7)	0.169 (4)	0.670 (8)
H(4)	−0.407 (6)	0.068 (3)	0.853 (7)
H(5)	−0.179 (6)	0.012 (3)	0.760 (7)

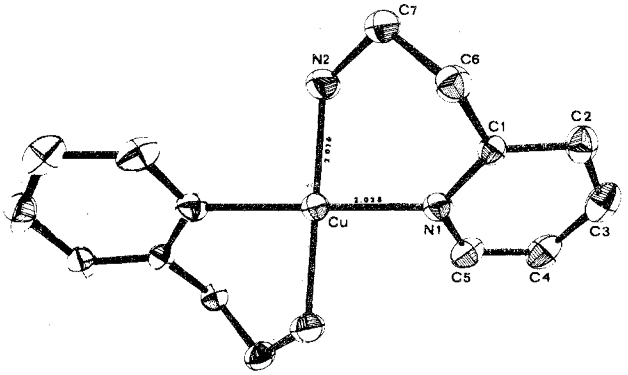

Figure 1. View of the $[Cu(C_7N_2H_{10})_2]^{2+}$ ion in $[Cu(C_7N_2H_{10})_2]I_2$. The hydrogen atoms have been omitted for clarity, and the thermal ellipsoids are drawn at the 40% probability level.

The internuclear separations and angles found in the complex are listed, along with their estimated standard deviations, in Table III. The Cu-N(1) bond length of 2.028 (3) Å is consistent with the values reported for a number of copper(II) complexes of pyridine and pyridine derivatives. Thus, while it is slightly longer than the values of 1.980 (6) and 1.985 (6) Å in dibromobis(2-methylpyridine)copper(II)[30] and somewhat shorter than the value of 2.16 (1) Å in 2-methylpyridinecopper(II) chloroacetate,[31] it is in good agreement

---

[17] D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, 18, 104 (1965).

[18] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

[19] J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, Table 3.3.1A.

[20] J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, 17, 781 (1964).

[21] D. T. Cromer, *Acta Crystallogr.*, 18, 17 (1965).

[22] W. H. Zachariasen, *Acta Crystallogr.*, 16, 1139 (1963); *Acta Crystallogr., Sect. A*, 24, 212 (1968); D. J. Hodgson and J. A. Ibers, *Acta Crystallogr., Sect. B*, 25, 469 (1969).

[23] A listing of structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-2157.

[24] N. R. Kunchur and M. Mathew, *Chem. Commun.*, 86 (1966).

[25] G. A. Barclay and F. S. Stephens, *J. Chem. Soc.*, 2027 (1963).

[26] A. S. Bailey and C. K. Prout, *J. Chem. Soc.*, 4867 (1965).

[27] E. N. Baker, D. Hall, and T. N. Waters, *J. Chem. Soc. A*, 680 (1966).

[28] P. K. Hon, C. E. Pfluger, and R. L. Belford, *Inorg. Chem.*, 5, 516 (1966).

[29] W. E. Hatfield and R. Whyman, *Transition Metal Chem.*, 5, 47 (1969).

[30] P. Singh, D. Y. Jeter, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, 11, 1657 (1972).

[31] G. Davey and F. S. Stephens, *J. Chem. Soc. A*, 2803 (1970).

Table II. Thermal Parameters for $Cu(AEP)_2I_2$

	$\beta_{11}{}^a$ or B, Å^2	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.00914 (8)	0.00394 (3)	0.0252 (2)	0.00177 (4)	0.00712 (9)	0.00458 (5)
I	0.01191 (5)	0.00385 (1)	0.01700 (6)	0.00044 (1)	0.00379 (3)	0.00028 (2)
N(1)	0.0093 (3)	0.0033 (1)	0.0142 (5)	0.0001 (2)	0.0027 (3)	0.0014 (2)
N(2)	0.0108 (4)	0.0039 (1)	0.0271 (9)	0.00001 (2)	0.0053 (5)	0.0037 (3)
C(1)	0.0076 (4)	0.0027 (1)	0.0108 (5)	−0.0002 (2)	0.0019 (3)	0.0001 (2)
C(2)	0.0102 (5)	0.0037 (1)	0.0170 (7)	0.0008 (2)	0.0042 (5)	−0.0007 (3)
C(3)	0.0119 (5)	0.0051 (2)	0.0183 (8)	−0.0004 (2)	0.0068 (5)	−0.0021 (3)
C(4)	0.0154 (6)	0.0060 (2)	0.0135 (6)	−0.0026 (3)	0.0061 (5)	−0.0017 (3)
C(5)	0.0112 (5)	0.0051 (2)	0.0137 (6)	−0.0008 (3)	0.0015 (4)	0.0023 (3)
C(6)	0.0109 (5)	0.0035 (1)	0.0120 (6)	0.0002 (2)	0.0029 (4)	−0.0000 (2)
C(7)	0.0124 (5)	0.0045 (2)	0.0181 (8)	0.0001 (2)	0.0057 (5)	0.0034 (3)
H(61)	3.2 (9)					
H(62)	7 (1)					
H(71)	5 (1)					
H(72)	5 (1)					
H(N(1))	12 (3)					
H(N(2))	7 (2)					
H(2)	2.9 (8)					
H(3)	5 (1)					
H(4)	5 (1)					
H(5)	3.6 (9)					

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table III. Internuclear Distances and Angles in $Cu(C_7N_2H_{10})_2{}^{2+}(I^-)_2$

Atoms	Dist, Å	Atoms	Angle, deg
Cu–N(1)	2.028 (3)	N(1)–Cu–N(1)′	180
Cu–N(2)	2.016 (3)	N(2)–Cu–N(2)′	180
N(1)–C(1)	1.356 (4)	N(1)–Cu–N(2)	86.8 (1)
N(1)–C(5)	1.331 (5)	N(1)–Cu–N(2)′	93.2 (1)
N(2)–C(7)	1.479 (5)	C(1)–N(1)–C(5)	118.2 (3)
C(1)–C(2)	1.389 (4)	N(1)–C(1)–C(2)	121.1 (3)
C(2)–C(3)	1.374 (6)	N(1)–C(1)–C(6)	116.9 (3)
C(3)–C(4)	1.365 (6)	C(2)–C(1)–C(6)	121.9 (3)
C(4)–C(5)	1.381 (5)	C(1)–C(2)–C(3)	119.7 (3)
C(1)–C(6)	1.490 (4)	C(2)–C(3)–C(4)	118.8 (3)
C(6)–C(7)	1.520 (5)	C(3)–C(4)–C(5)	119.3 (3)
C(2)–H(2)	0.92 (4)	N(1)–C(5)–C(4)	122.8 (3)
C(3)–H(3)	1.14 (5)	C(1)–C(6)–C(7)	113.2 (3)
C(4)–H(4)	1.05 (5)	C(6)–C(7)–N(2)	112.3 (3)
C(5)–H(5)	0.73 (5)	H(N(1))–N(2)–C(7)	114 (4)
C(6)–H(61)	1.18 (4)	H(N(1))–N(2)–Cu	92 (4)
C(6)–H(62)	0.89 (5)	H(N(2))–N(2)–C(7)	96 (4)
C(7)–H(72)	0.79 (6)	H(N(2))–N(2)–C(7)	96 (4)
C(7)–H(71)	1.09 (5)	H(N(2))–N(2)–Cu	131 (4)
N(2)–H(N(1))	1.28 (9)	H(N(1))–N(2)–H(N(2))	104 (6)
N(2)–H(N(2))	0.93 (7)		

with the average value of 2.00 Å in dinitratobis(α-picoline)-copper(II)[32] and in dichlorobis(2-methylpyridine)copper(II) and the values of 2.021 (5) Å in $Cu(AEP)Br_2$, 2.022 (8) Å in dinitratobis(methyl-α-picolylamine)copper(II),[33] and 2.065 (3) Å in $[Cu(AEP)_2Br]Br$.[4] Similarly, the Cu-N(2) separation of 2.016 (3) Å is comparable with copper-amine bond lengths of 1.971 (2) and 1.984 (2) Å in carbonatodiammine-copper(II),[34] 1.989 (6) Å in $Cu(AEP)Br_2$,[2] 2.012 (9) and 2.017 (9) Å in selenatotetraamminecopper(II),[35] and 2.027 (4) Å in $[Cu(AEP)_2Br]$[4] and with values reported for many related systems all of which lie in the range of 1.97-2.07 Å.

The bite angle of the chelating AEP ligand in this structure is 86.8 (1)°. This is in marked contrast to the geometries of the AEP ligand in the other two complexes studied and to the geometries of 2-(2-ethylaminoethyl)pyridine (EAEP) in $[Cu(EAEP)OH]_2(ClO_4)_2$[36] and 2-(2-dimethylaminoethyl)-pyridine (DMAEP) in $[Cu(DMAEP)OH]_2(ClO_4)_2$;[37] in these four complexes the N-Cu-N "bite" falls in the range 92.7-96.3°; *i.e.*, all previous values have been obtuse whereas the present angle is acute. The present, four-coordinate complex, however, is presumably subject to less steric interaction than these five- and six-coordinate complexes; it may be, therefore, that in the absence of the steric influence of axial ligands the acute angle is of lower energy. Evidently, however, this angle can be readily deformed without severely straining the ligand. This apparent stereochemical nonrigidity of the six-membered chelate ring is in marked contrast to the rigidity of five-membered chelate rings like 2,2′-bipyridine (bipy) or ethylenediamine (en). Thus, in $[Cu(bipy)OH]_2(NO_3)_2$,[38] $[Cu(bipy)OH]_2SO_4 \cdot 5H_2O$,[39] $[Cu(bipy)_2I]I$,[5] $[Cu(bipy)_2NO_2]$-NO_3,[6] and $[Co(bipy)_2NO_3](OH)(NO_3) \cdot 4H_2O$[40] the N-M-N bites of the 2,2′-bipyridine ligand lie in the range 80-83.3°; the twenty-one independent N-M-N angles in $[Co(en)_3]$-$[Cu_2Cl_8]Cl_2 \cdot 2H_2O$,[12] $[Cr(en)_3][Cr(CN)_5NO] \cdot 2H_2O$,[41] $[Co(en)_3][CdCl_6]Cl_2 \cdot 2H_2O$,[14] $[Co(en)_3]_2(HPO_4)_3 \cdot 9H_2O$,[42] $[Ni(en)_3]SO_4$,[43] $[Cr(en)_3][Co(CN)_6] \cdot 6H_2O$,[44] and $[Cr(en)_3]$-$[Ni(CN)_5] \cdot 1.5H_2O$[45] are in the range 81.5-86.2°.

The pyridine ring is approximately planar, with no atom deviating from the least-squares plane by more than 0.013 Å. The geometry of the ring is similar to that reported for other substituted pyridines. Thus, we again observe a slight lengthening of the C-C bond which is adjacent to the exocyclic chain (C(1)-C(2)) relative to the other C-C bonds in the ring and a relatively short (1.490 (4) Å) exocyclic C-C bond between the ring α carbon atom (C(1)) and the side chain (C(6)). These effects are presumably the result of a drift of electron density from the ring to the side chain, thus imparting some partial π character to the C(1)-C(6) bond.[30]

---

(32) A. F. Cameron, D. W. Taylor, and R. H. Nuttall, *J. Chem. Soc., Dalton Trans.*, 58 (1972).

(33) N. A. Bailey and S. J. Bowler, *J. Chem. Soc. A*, 1763 (1971).

(34) M. H. Meyer, P. Singh, W. E. Hatfield, and D. J. Hodgson, *Acta Crystallogr., Sect. B*, **28**, 1607 (1972).

(35) B. Morosin, *Acta Crystallogr., Sect. B*, **25**, 19 (1969).

(36) D. L. Lewis, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, 11, 2216 (1972).

(37) D. L. Lewis and D. J. Hodgson, unpublished observations.

(38) R. J. Majeste and E. A. Meyers, *J. Phys. Chem.*, 74, 3497 (1970).

(39) A. T. Casey, B. F. Hoskins, and F. D. Whillans, *Chem. Commun.*, 904 (1970).

(40) C. W. Reimann, M. Zocchi, A. D. Mighell, and A. Santoro, *Acta Crystallogr., Sect. B*, 27, 2211 (1971).

(41) J. H. Enemark, M. S. Quinby, L. L. Reed, M. J. Stueck, and K. K. Walthers, *Inorg. Chem.*, 9, 2397 (1970).

(42) E. N. Duesler and K. N. Raymond, *Inorg. Chem.*, 10, 1486 (1971).

(43) Mazhar-Ul-Haque, C. N. Caughlan, and K. Emerson, *Inorg. Chem.*, 9, 2421 (1970).

(44) K. N. Raymond and J. A. Ibers, *Inorg. Chem.*, 7, 2333 (1968).

(45) K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, 7, 1362 (1968).

The ring angles are normal, falling in the range 118.2 (3)–122.8 (3)° with an average value of 120.0 (8)°.

There is no convincing evidence of any N–H· · ·I hydrogen bonding in this system. The sum of the van der Waals radii of H and I is given by Bondi[46] as 3.18 Å and by Pauling[47] as 3.35 Å. The H(N(1))· · ·I separation of 2.72 Å observed here is significantly shorter than these values; using a more reasonable N(2)–H(N(1)) distance of 1.03 Å (instead of our observed value of 1.28 Å) we calculate an H(N(1))· · ·I separation of 2.92 Å, which is still significantly shorter than both Bondi's and Pauling's values. Hence, using the criterion of Hamilton and Ibers[48] that a hydrogen bond exists if both the A–H and H· · ·B (here A = N, B = I) separations are less than the sums of their van der Waals radii, one would conclude that there is a hydrogen bond between N(2) and I. But the N(2)· · ·I distance of 3.806 Å is considerably longer than the sum of the radii of these atoms (3.53 Å (Bondi) or 3.65 Å (Pauling)), whereas in NH_4I the N· · ·I separation of 3.63 Å is similar to this sum.[49] Similarly, in PH_4I the I· · ·H separation[50] is 2.868 (9) Å (smaller than the calculated value here) and the P· · ·I distance of 3.679 (4) Å is again less than the sum of the radii of P and I (3.78 Å (Bondi) or 4.05 Å (Pauling)). Moreover, in the present structure there are H· · ·I separations of 3.02 and 3.04 Å involving hydrogen atoms which are bonded to ring carbon atoms, so the real sum of van der Waals radii of H and I in this system cannot be greater than 3 Å, and, therefore, the calculated H· · ·I contact of 2.92 Å may not exceed this sum. Further evidence for our conclusion is that there is another N· · ·I separation in this structure which is shorter (3.693 *vs.* 3.806 Å) than the one under discussion, but this separation cannot involve hydrogen bonding since there is no hydrogen atom in this direction. While we do not suggest that the Hamilton and Ibers criterion is incorrect, we do note that its application is difficult because of an apparent inadequacy in the reported values of the van der Waals radius of hydrogen.

The geometry at the copper in this complex is in marked contrast to that found for the corresponding bromide.[4] In $Cu(AEP)_2Br_2$ one bromine atom is weakly coordinated to the metal, giving rise to the five-coordinated complex $[Cu(AEP)_2Br]Br$, whereas in $Cu(AEP)_2I_2$ neither iodide is coordinated. A calculation was made in order to determine what intramolecular contacts would result if the AEP ligands maintained their observed geometries and positions but the iodide ions were within bonding distance of the metal in apical positions. Using a normal Cu–I bond length of 2.68 Å,[5] we find that there would be I–C(6) contacts of 2.77 Å, which would be expected to cause severe steric strain. This calculation, therefore, explains why the iodide cannot be bonded to the copper atom in a trans octahedral arrangement if the cation retains its present geometry.

A similar calculation involving coordination of only one apical iodide and assuming C_{2v} geometry at copper (*i.e.*, assuming that C(6) and C(6)′ both lie below the basal plane and that the apical iodide is above the plane) leads to a different conclusion: the only severe interaction in this model would be an I–N(2) separation of 3.35 Å. This source of strain, moreover, would be relieved if the copper atom were to move out of the plane in the direction of the apical iodide, as is usually observed for tetragonal-pyramidal complexes,[45,51,52] and the Cu–I distance remained 2.68 Å. Hence, there is no apparent stereochemical reason for the complex to prefer four-coordination over five-coordination. It is noteworthy that in $Cu(bipy)_2I_2$ one iodide is coordinated,[5] leading to the five-coordinated complex $[Cu(bipy)_2I]I$ analogous to the bromo complex of AEP. On the basis of electronic spectroscopy,[8,9] McWhinnie and coworkers have suggested that $Cu(dipyam)_2I_2$ (dipyam = di(2-pyridyl)amine) is also five-coordinate but that $Cu(dipyam)_2Br_2$ is six-coordinate; unfortunately, no structural data on these complexes are available. The two AEP complexes, however, present an opportunity to examine further the relationship between the electronic spectra and structures of these chelated copper(II) complexes; these studies are presently being undertaken.

Registry No. $Cu(AEP)_2I_2$, 40544-41-0.

Acknowledgments. This research was supported by the Materials Research Center of the University of North Carolina under Grant GH-33632 from the National Science Foundation and by the National Science Foundation through Grant GP-10300.

---

(46) A. Bondi, *J. Phys. Chem.*, 68, 441 (1964).

(47) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

(48) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968, p 16.

(49) R. J. Havighurst, E. Mack, Jr., and F. C. Blake, *J. Amer. Chem. Soc.*, 46, 2368 (1924).

(50) A. Sequeira and W. C. Hamilton, *J. Chem. Phys.*, 47, 1818 (1967).

(51) D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, 8, 1282 (1969).

(52) D. S. Brown, F. W. B. Einstein, and D. G. Tuck, *Inorg. Chem.*, 8, 14 (1969).