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# A Novel Halogen-Bridged System: Synthesis and Structures of Dibromo[2-(2-aminomethyl)pyridine]copper(II) and Dibromo(2-methyl-1,2-diaminopropane)copper(II)

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The complex dibromo[2-(2-aminomethyl)pyridine]copper(II), $CuC_6H_8N_2Br_2$, has been synthesized, and the crystal structures of this complex and of dibromo(2-methyl-1,2-diaminopropane)copper(II), $CuC_4H_{12}N_2Br_2$, have been determined. The aminomethylpyridine complex crystallizes in the monoclinic space group $P2_1/m$, with two formula units in a cell of dimensions $a = 8.222$ (15), $b = 6.372$ (13), $c = 9.883$ (18) Å, and $\beta = 116.3$ (1)°, with observed and calculated densities of 2.51 and 2.43 g cm$^{-3}$, respectively. The structure has been refined by full-matrix least-squares methods to a final value of the conventional $R$ factor (on $F$) of 0.046 based on 763 independent observations. The diaminopropane complex crystallizes in the orthorhombic space group $Pnma$, with four formula units in a cell of dimensions $a = 20.276$ (28), $b = 6.208$ (3), and $c = 7.058$ (3) Å and observed and calculated densities of 2.33 and 2.330 g cm$^{-3}$, respectively. The structure has been refined to a final value of $R$ of 0.039 based on 669 intensities. In both complexes, the formula unit is constrained to lie in a crystallographic mirror plane, which is the $ac$ plane in both cases. For the 2-methyl-1,2-diaminopropane complex, this brings about a disorder of three of the four carbon atoms. Both structures consist of infinite dibromo-bridged chains, in which one bromide ligand serves to propagate the chain in both directions while the other is not involved in the chain; thus, one bromide is coordinated to three copper atoms while the other is coordinated to only one. This form of chain is unique. The geometry about each copper center is distorted octahedral, with two cis nitrogen atoms and two bromides in the plane and the weaker chain-propagating bromide interactions out of the plane. The Cu–Cu separations in the two chains are 3.737 (6) and 3.866 (2) Å for the aminomethylpyridine and diaminopropane complexes, respectively, with associated Cu–Br–Cu bridging angles of 80.77 (4) and 87.56 (3)°, respectively.

## Introduction

There has been considerable recent research activity in the structural and magnetic chemistry of complexes of the general formulation $CuLX_2$ (where L is a bidentate ligand) or $CuA_2X_2$ (where A is unidentate). Complexes of these general types show an amazingly wide variety of geometries, including doubly bridged dimeric structures with tetrahedral,[2,3] trigonal-bipyramidal,[4-7] and tetragonal-pyramidal[8-14] geometry at copper, doubly bridged chains,[15-19] singly bridged chains,[20,21] complex polymeric aggregates involving both dimeric and chain interactions,[22,23] tetramers,[24] and simple monomers.[25,26]

While our principal interest in these complexes has been in attempting to correlate their magnetic properties with their precise molecular structures,[27] at present we are hampered by the availability of too few data for any given structural type to allow any meaningful correlations. The class of complexes for which the most data are available is the tetragonal-pyramidal dimeric type.[8-14] The observation of this geometry for both the *N,N,N′,N′*-tetramethylethylenediamine (tmen) and *N,N*-dimethylethylenediamine (dmen) complexes[11,13,14] suggested to us that the 2-methyl-1,2-diaminopropane complexes might also exhibit this structure. Moreover, the existence of dimeric interactions in some complexes of 2-(2-aminoethyl)pyridine[20,22,23] indicated that the methyl analogue, 2-(2-aminomethyl)pyridine, was worthy of study for the same reason. The synthesis and unit cell constants of the 2-methyl-1,2-diaminopropane bromide have been reported by other workers;[28] we here report the synthesis of the aminomethylpyridine bromide and the structural characterization of these two complexes, which exhibit similar bridging geometries but which are different from any previously reported structural type.

## Experimental Section

**Dibromo[2-(2-aminomethyl)pyridine]copper(II).** The complex was prepared by the dropwise addition of a small quantity of 2-(2-aminomethyl)pyridine to a solution of 0.20 g (0.001 mol) of anhydrous copper(II) bromide in 30 mL of absolute methanol. The fine green precipitate which formed immediately was redissolved in hot methanol; green, platelike crystals formed on cooling. Anal. Calcd for $C_6H_8Br_2CuN_2$: C, 21.74; H, 2.44. Found: C, 22.4; H, 2.49.

Weissenberg and precession photographs indicated that the crystals belonged to the monoclinic system, the observed systematic absences of $0k0$ for $k$ odd being consistent with the space groups $P2_1$ and $P2_1/m$. The cell constants, determined by least-squares methods, are $a = 8.222$ (15), $b = 6.372$ (13), $c = 9.883$ (18) Å, and $\beta = 116.3$ (1)°; these observations were made at 21 °C with Mo K$\alpha$ radiation with $\lambda$(Mo K$\alpha$) assumed as 0.7093 Å. A density of 2.51 g cm$^{-3}$ obtained by flotation in benzene/bromoform mixtures is in tolerable agreement with the value of 2.43 g cm$^{-3}$ calculated for two formula units per cell. Hence, in the centrosymmetric space group $P2_1/m$, all atoms, except the amine hydrogen atoms, would be constrained to lie in the mirror plane at $y = {}^1/_4$. Our experience suggested to us (incorrectly) that this was not probable, and so initial refinements were carried out in space group $P2_1$; at a late stage of the refinement, we were able to demonstrate that the centrosymmetric choice $P2_1/m$ is, indeed, the correct one (vide infra).

Diffraction data were collected on a platelike crystal having faces $(10\bar{1})$, $(\bar{1}01)$, (001), $(00\bar{1})$, (010), and $(0\bar{1}0)$. The separations between opposite pairs of faces were as follows: $(10\bar{1})$ to $(\bar{1}01)$, 0.0014 cm; (001) to $(00\bar{1})$, 0.0084 cm; and (010) to $(0\bar{1}0)$, 0.059 cm. The crystal was mounted on a glass fiber parallel to the $b$ axis, and data were collected on a Picker four-circle automatic diffractometer using Mo K$\alpha$ radiation. The takeoff angle was 1.2°; at this angle the peak intensity of a typical strong reflection was approximately 95% of its maximum value. A total of 1307 reflections were examined by the $\theta$–$2\theta$ scan technique at a scan rate of ${}^1/_2$°/min. Allowance was made for the presence of both K$\alpha_1$ and K$\alpha_2$ radiations, the peaks being scanned from −0.7° in $2\theta$ below the calculated K$\alpha_1$ peak position to +0.7° in $2\theta$ above the calculated K$\alpha_2$ peak position. Stationary-counter, stationary-crystal background counts of 20 s were taken at each end of the scan.

A unique data set having $2\theta < 55°$ was gathered. There were few reflections above background at values of $2\theta > 55°$. Throughout the data collection, the intensities of three standard reflections, measured every 100 reflections, remained essentially constant.

Data processing was carried out as described by Corfield et al.[29] After correction for background the intensities were assigned standard deviations according to the formula[29]

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

with the value of $p$ chosen to be 0.05. The values of $I$ and $\sigma(I)$ were corrected for Lorentz–polarization effects and for absorption factors. The absorption coefficient for the sample with Mo radiation is 117.74 cm$^{-1}$, and the transmission coefficients for the data crystal range from 0.16 to 0.76.[30] A total of 1232 reflections were collected, of which 763 were independent data with $I > 3\sigma(I)$; only these data were used in the final refinement of the structure.

**Dibromo(2-methyl-1,2-diaminopropane)copper(II).** A sample of the compound was prepared by the method of Näsänen et al.,[28] and well-developed pale green crystals were grown from a methanol solution. A suitable crystal measuring 0.021 × 0.003 × 0.069 cm in the [100], [010], and [001] directions was used for space group assignment and intensity data collection. Weissenberg and precession photographs, taken with Cu K$\alpha$ and Mo K$\alpha$ radiations, demonstrated that the crystal belonged to the orthorhombic system, and systematic absences of $0kl$ for $k + l$ odd and $hk0$ for $h$ odd indicated the space groups $Pn2_1a$ or $Pnma$. The cell constants and their standard deviations were found to be $a$ = 20.276 (28), $b$ = 6.208 (3), and $c$ = 7.058 (3) Å; these results are consistent with the report of Näsänen et al.[28] By use of a mixture of benzene and bromoform, the density was measured as 2.33 g cm$^{-3}$, while the density calculated assuming four formula units per unit cell was 2.330 g cm$^{-3}$. Thus, for the crystal to be in the centrosymmetric space group, $Pnma$, the entire molecule would be constrained to lie in the mirror plane at $y = {}^1/_4$, with the exception of the two methyl groups and the hydrogen atoms, which would reflect into each other across the plane. Since it seemed unlikely that a five-membered aliphatic ring would be exactly planar, the space group was initially assumed to be $Pn2_1a$.

Diffraction data were collected using a Picker four-circle automatic diffractometer with Mo K$\alpha$ radiation of an assumed wavelength of 0.7093 Å. The crystal was mounted on a glass fiber parallel to the $b$ axis. Intensity data were collected at a takeoff angle of 1.3°, where the intensity of a typical strong reflection was approximately 90% of the maximum value as a function of takeoff angle. The receiving aperture was 5.0 mm high by 5.0 mm wide and was positioned 32 cm from the crystal. The data were collected by the $\theta$–$2\theta$ scan technique at a scan rate of 0.5°/min. To allow for the presence of both K$\alpha_1$ and K$\alpha_2$ radiations, the peaks were scanned from −1.0° in $2\theta$ below the calculated K$\alpha_1$ position to +1.0° in $2\theta$ above the calculated K$\alpha_2$ peak. Stationary-counter, stationary-crystal background counts of 20 s were taken at each end of the scan. The pulse height analyzer was set for approximately a 90% window centered on the K$\alpha$ peak.

A unique data set having $3° \le 2\theta \le 57°$ was collected. There were few intensities greater than background at values of $2\theta > 57°$. A total of 1673 intensities was recorded. The intensities of three standard reflections, measured every 100 reflections, showed only the deviations from the mean predicted from counting statistics.

Data processing was carried out as described above. The absorption coefficient for this compound (Mo K$\alpha$ radiation) is 113.0 cm$^{-1}$ and the chosen crystal had transmission coefficients ranging from 45.22% to 88.34%. Of the 1673 reflections collected, 667 had $F^2 > 3\sigma(F^2)$; only these reflections were used in subsequent calculations.

## Solution and Refinement of the Structures

All least-squares refinements were carried out on $F$ minimizing the function $\sum w(|F_o| - |F_c|)^2$, with the weights $w$ defined as $4F_o/\sigma^2(F_o^2)$. In all calculations of $F_c$ the atomic scattering factors for all nonhydrogen atoms were taken from ref 31a and those for hydrogen were taken from Stewart, Davidson, and Simpson.[32] The effects of the anomalous dispersion of Cu and Br were included in $F_c$, the values of $\Delta f'$ and $\Delta f''$ being taken from ref 31b. The unweighted and weighted residuals are defined as $R_1 = \sum|(|F_o| - |F_c|)|/|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

**Dibromo[2-(2-aminomethyl)pyridine]copper(II).** The positions of the copper and two bromine atoms were determined from a three-dimensional Patterson function. Initial least-squares calculations were run in the noncentrosymmetric space group $P2_1$; refinement of these parameters led to values of $R_1$ and $R_2$ of 0.247 and 0.320, respectively. The carbon and nitrogen atoms were located in a subsequent difference Fourier summation, and isotropic least-squares refinement yielded $R_1$ = 0.138 and $R_2$ = 0.171; anisotropic refinement of the same positions (still in space group $P2_1$) gave $R_1$ = 0.046, $R_2$ = 0.056.

At this stage it was apparent that the $y$ coordinates of all atoms were virtually equal, which suggested that the space group might be $P2_1/m$; anisotropic refinement in the centrosymmetric space group, with all $y$ coordinates constrained to be 0.25, yielded $R_1$ = 0.047 and $R_2$ = 0.057. This small increase in the value of $R_2$ upon decreasing the number of variables from 99 to 67 is not statistically significant[33] and strongly suggests that the centrosymmetric space group $P2_1/m$ is the correct choice.

**Table I.** Positional Parameters (×10$^4$) for $Cu(C_6H_8N_2)Br_2$

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Cu | −913 (1) | 2500 | −1051 (1) |
| Br(1) | −3755 (1) | 2500 | −944 (1) |
| Br(2) | 740 (1) | 2500 | 1676 (1) |
| N(1) | −1873 (10) | 2500 | −3310 (9) |
| N(2) | 1490 (10) | 2500 | −1113 (8) |
| C(2) | −588 (14) | 2500 | −3796 (11) |
| C(3) | −1037 (16) | 2500 | −5319 (12) |
| C(4) | −2807 (19) | 2500 | −6378 (12) |
| C(5) | −4138 (17) | 2500 | −5873 (14) |
| C(6) | −3654 (16) | 2500 | −4340 (12) |
| C(7) | 1341 (15) | 2500 | −2607 (12) |
| H(3)[a] | −11 | 250 | −566 |
| H(4) | −313 | 250 | −744 |
| H(5) | −539 | 250 | −659 |
| H(6) | −460 | 250 | −399 |
| H(7) | 195 | 128 | −273 |
| H(N) | 215 | 128 | −060 |

[a] ×10$^3$ for hydrogen atoms, whose positions were not varied.

**Table II.** Thermal Parameters ($U_{ij}$ in A$^2$) for $Cu(C_6H_8N_2)Br_2$[a]

| Atom | $U_{11}$[b] | $U_{22}$ | $U_{33}$ | $U_{13}$ |
|---|---|---|---|---|
| Cu | 264 (6) | 480 (8) | 371 (6) | 145 (5) |
| Br(1) | 307 (5) | 905 (10) | 598 (7) | 239 (5) |
| Br(2) | 408 (6) | 493 (6) | 366 (5) | 144 (4) |
| N(1) | 260 (39) | 413 (46) | 387 (42) | 104 (34) |
| N(2) | 284 (40) | 488 (50) | 367 (42) | 142 (34) |
| C(2) | 405 (57) | 528 (66) | 441 (57) | 238 (48) |
| C(3) | 590 (73) | 692 (82) | 388 (57) | 229 (56) |
| C(4) | 716 (82) | 772 (90) | 370 (60) | 197 (58) |
| C(5) | 453 (67) | 887 (99) | 448 (64) | −75 (54) |
| C(6) | 398 (59) | 635 (78) | 535 (68) | 112 (49) |
| C(7) | 319 (54) | 1237 (99) | 328 (53) | 134 (45) |

| Atom | $U$ | Atom | $U$ | Atom | $U$ |
|---|---|---|---|---|---|
| H(3) | 736 | H(5) | 757 | H(7) | 698 |
| H(4) | 737 | H(6) | 501 | H(N) | 527 |

[a] Anisotropic thermal parameters are ×10$^4$; isotropic thermal parameters are ×10$^4$. [b] The form of the anisotropic thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{13}hla^*c^*)]$.

The hydrogen atoms were located in a subsequent difference Fourier summation, but attempts to refine their positions led to unrerasonable shifts. Consequently, the hydrogen atoms were placed in positions calculated on the basis of trigonal geometry at the pyridine carbon atoms and tetrahedral geometry at the methylene carbon and amine nitrogen atoms, with C–H and N–H bond lengths of 0.95 and 0.90 Å, respectively;[34] the hydrogen atoms were assigned fixed isotropic thermal parameters which were computed by adding 1.5 Å$^2$ to the value of the isotropic thermal parameter of the carbon or nitrogen atom to which they are attached in the last isotropic least-squares calculation. Least-squares refinement of this model led to values of 0.046 and 0.052 for $R_1$ and $R_2$, respectively.

Examination of the values of $|F_c|$ and $|F_o|$ suggested to us that no correction for secondary extinction is necessary, and none was applied. In the final cycle of least-squares refinement, there were 763 observations and 67 variables, a reflection to variable ratio of 11:4:1. In this final cycle, no parameter underwent a shift of more than 0.005$\sigma$, which is taken as evidence of convergence. The value of $R_2$ shows no unusual dependence on $|F_o|$ or on sin $\theta$, which suggests that our weighting scheme is adequate. A final difference Fourier showed several peaks higher than 1.2 e Å$^{-3}$, but these are in chemically meaningless positions and are probably due to some error in crystal measurement for this highly absorbing sample. The positional and thermal parameters derived from the final cycle, along with their standard deviations as estimated from the inverse matrix, are presented in Tables I and II. A compilation of observed and calculated structure amplitudes is available.[35]

Table III. Positional Parameters (X $10^4$) for $Cu(C_4H_{12}N_2)Br_2$

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Cu | −179.2 (6) | 2500 | 1550 (2) |
| Br(1) | 910.5 (5) | 2500 | 2970 (2) |
| Br(2) | 254.5 (6) | 2500 | −1667 (2) |
| N(1) | −684 (4) | 2500 | 4012 (13) |
| N(2) | −1088 (4) | 2500 | 391 (12) |
| C(1) | −1359 (6) | 3270 (28) | 3621 (19) |
| C(2) | −1645 (5) | 2500 | 1833 (16) |
| C(3)[a] | −1876 (8) | 32 (28) | 2038 (28) |
| C(4)[a] | −2211 (7) | 3850 (39) | 1173 (27) |
| H1N1 | 488 | 3385 | 4865 |
| H2N1 | −700 | 1157 | 4508 |
| H1N2 | −1131 | 1316 | −352 |
| H2N2 | −1131 | 3684 | −352 |
| H1C1 | −1636 | 2805 | 4629 |
| H2C1 | −1347 | 4795 | 3587 |

[a] Disordered carbon atoms with multiplicity of 0.5.

Table IV. Thermal Parameters (X $10^4$) for $Cu(C_4H_{12}N_2)Br_2$

| Atom | $\beta_{11}$[a] | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| Cu | 12.4 (3) | 425 (7) | 102 (3) | 0.0 | 0.1 (7) | 0.0 |
| Br(1) | 14.1 (3) | 455 (6) | 153 (3) | 0.0 | 9.5 (7) | 0.0 |
| Br(2) | 17.5 (3) | 363 (5) | 110 (2) | 0.0 | 6.6 (6) | 0.0 |
| N(1) | 17 (2) | 370 (43) | 121 (19) | 0.0 | 0 (5) | 0.0 |
| N(2) | 12 (2) | 414 (42) | 106 (17) | 0.0 | 5 (5) | 0.0 |
| C(1) | 15 (3) | 352 (100) | 129 (27) | −4 (12) | 10 (7) | −48 (34) |
| C(2) | 12 (2) | 360 (50) | 141 (23) | 0.0 | 10 (6) | 0.0 |
| C(3) | 23 (4) | 110 (48) | 295 (46) | 31 (14) | 9 (13) | 2 (52) |
| C(4) | 19 (4) | 377 (73) | 253 (44) | 42 (16) | 2 (11) | 2 (54) |

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

**Dibromo(2-methyl-1,2-diaminopropane)copper(II).** The positions of the Cu and the two Br atoms were determined from a three-dimensional Patterson function. Three cycles of least-squares refinement in space group $Pn2_1a$ gave $R_1 = 0.258$ and $R_2 = 0.318$. Assuming the noncentrosymmetric space group $Pn2_1a$ the remaining nonhydrogen atoms were located; least-squares refinement of these parameters yields values of $R_1 = 0.169$ and $R_2 = 0.200$.

The absorption correction was then applied (vide supra) and after four further cycles of least-squares with anisotropic thermal parameters values of 0.041 and 0.056 were obtained for $R_1$ and $R_2$, respectively.

At this stage of the refinement, it was apparent that the structure was essentially planar but that (necessarily) the methyl carbon atoms and one methylene carbon atom were out of this plane. Examination of the thermal parameters $U_{ij}$ for those atoms showed that $U_{22}$, i.e., the amplitude of vibration perpendicular to the molecular plane, was abnormally large for all three of these atoms. Moreover, a difference Fourier summation computed at this stage revealed large amounts of residual electron density related to the out-of-plane carbon atoms but on the opposite side of the molecular plane. All of this evidence suggested that the molecule was disordered in the centrosymmetric space group, *Pnma*. Refinement of a 50/50 disordered model in both space groups also yielded values for $R_1$ and $R_2$ of 0.040 and 0.055, respectively. For both cases the nonmethyl hydrogen atoms were located in the Fourier map. Attempts to refine these hydrogen parameters were unsuccessful, so two further cycles of least-squares were run in which the hydrogen atoms were placed in fixed, calculated positions (vide supra) and assigned fixed isotropic thermal parameters of 6.0 Å$^2$. The values of $R_1$ and $R_2$ were 0.039 and 0.052 for the noncentrosymmetric and 0.039 and 0.050 for the centrosymmetric model. Attempts to locate the methyl hydrogen atoms were unsuccessful. The lower value of $R_2$, along with the more reasonable shape of the thermal ellipsoids, of the centrosymmetric refinement strongly suggests that the space group is *Pnma*.

In the final cycle of refinement, there were 64 varied parameters and 669 reflections, which gives a reflection to parameter ratio of 10:1. In the last cycle of least-squares, no parameter shifted by more than $0.2\sigma$, which indicated that the refinement had converged. Examination of the values of $|F_c|$ and $|F_o|$ suggested that no correction for secondary extinction was necessary. A final difference Fourier included three peaks above 0.5 e Å$^{-3}$, all of which were in the vicinity of the bromine atoms; this is again suggestive of some small error in our absorption correction. The positional and thermal parameters derived from the final least-squares cycle are tabulated in Tables III and IV; a listing of observed and calculated structure amplitudes is available.[35]

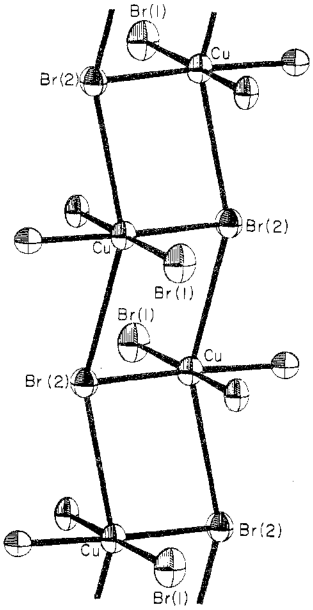

**Figure 1.** View of the bridging network in dibromo[2-(2-aminomethyl)pyridine]copper(II) and dibromo(2-methyl-1,2-diaminopropane)copper(II). The structure shown is the former complex, but the fundamental bridging geometry is the same for both complexes. The unlabeled atoms are nitrogen atoms.

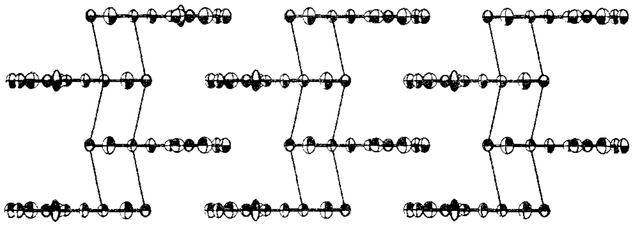

**Figure 2.** View of the packing of the planar formula units in the polymers. The structure shown is the aminomethylpyridine complex, viewed along the crystallographic *a** axis.

Table V. Interatomic Distances (Å) in $Cu(C_6H_8N_2)Br_2$

| | | | |
|---|---|---|---|
| Cu–Cu | 3.737 (6) | C(2)–C(3) | 1.382 (14) |
| Cu–Br(1) | 2.385 (5) | C(3)–C(4) | 1.365 (16) |
| Cu–Br(2) | 2.422 (5) | C(4)–C(5) | 1.390 (19) |
| Cu–Br(2)′ | 3.260 (6) | C(5)–C(6) | 1.386 (16) |
| Cu–N(1) | 2.011 (9) | C(6)–N(1) | 1.364 (14) |
| Cu–N(2) | 2.003 (9) | C(2)–C(7) | 1.499 (14) |
| N(1)–C(2) | 1.340 (12) | C(7)–N(2) | 1.426 (13) |

## Description of the Structures

Both complexes are polymeric in the crystal. The coordination around each copper(II) center is the commonly observed[36] tetragonally elongated (4 + 2) octahedral. The four in-plane (short) bonds are to the two nitrogen atoms of the chelating ligand and to two cis bromide ligands, Br(1) and Br(2). The out-of-plane (long) bonds are to the basal Br(2) atoms of the copper atoms above and below. Views of this bridging network and the consequent infinite chain are shown in Figures 1 and 2. Since the copper and in-plane atoms in each structure lie on a crystallographic mirror plane, these five atoms are necessarily strictly coplanar. This polymeric structure in which one halide ligand is bound to three adjacent copper atoms while the other is terminal, observed for both of these complexes, is unique to our knowledge.

**Dibromo[2-(2-aminomethyl)pyridine]copper(II).** A view of a single formula unit of the complex is given in Figure 3, and

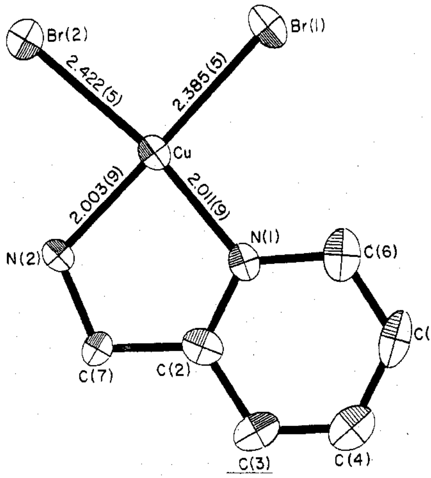

**Figure 3.** View of a single formula unit of dibromo[2-(2-aminomethyl)pyridine]copper(II). Thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms are omitted for clarity.

**Table VI.** Interatomic Angles (deg) in $Cu(C_6H_8N_2)Br_2$

| | | | |
|---|---|---|---|
| Cu-Br(2)-Cu | 80.77 (4) | Cu-N(1)-C(6) | 126.3 (7) |
| Br(1)-Cu-Br(2) | 91.6 (2) | Cu-N(1)-C(2) | 114.4 (6) |
| Br(1)-Cu-N(1) | 98.0 (3) | N(1)-C(2)-C(3) | 121.1 (9) |
| N(1)-Cu-N(2) | 82.8 (3) | C(2)-C(3)-C(4) | 121.0 (11) |
| N(2)-Cu-Br(2) | 87.6 (3) | C(3)-C(4)-C(5) | 117.8 (10) |
| N(1)-Cu-Br(2) | 170.4 (2) | C(4)-C(5)-C(6) | 120.1 (11) |
| N(2)-Cu-Br(1) | 179.3 (8) | C(5)-C(6)-N(1) | 120.7 (7) |
| Br(2)′-Cu-N(1) | 79.55 (5) | C(6)-N(1)-C(2) | 119.2 (9) |
| Br(2)′-Cu-N(2) | 82.42 (5) | N(1)-C(2)-C(7) | 116.6 (8) |
| Br(2)′-Cu-Br(1) | 97.71 (4) | C(3)-C(2)-C(7) | 122.3 (9) |
| Br(2)′-Cu-Br(2) | 99.23 (4) | C(2)-C(7)-N(2) | 112.8 (9) |
| Br(2)′-Cu-Br(2)″ | 155.50 (8) | C(7)-N(2)-Cu | 113.4 (6) |

the intramolecular distances and angles are listed in Tables V and VI, respectively. The in-plane Cu–Br bond lengths of 2.385 (5) and 2.422 (5) Å are normal;[7] as expected, the terminal Cu–Br(1) bond is shorter than the bond to the bridging Br(2) atom. The Cu–N bonds of 2.011 (9) and 2.003 (9) Å are also within the ranges normally observed for such bonds. The bond to the amine nitrogen atom is slightly the shorter; the same feature is observed in all six reported structures of copper(II) complexes of the related unsubstituted ligand 2-(2-aminoethyl)pyridine.[22,23,37–40] The chelating angle subtended at copper by the planar five-membered ring is 82.8 (3)°; this acute angle is within the range of 74–86° observed in complexes of 1,10-phenanthroline and 2,2′-bipyridine.[41–44] The N···N "bite" of 2.65 (1) Å in this complex is also, therefore, in the range found for these other five-membered, planar chelates. The geometry of the substituted pyridine ring is substantially similar to those in related complexes.[22,23,37–40]

The Cu–Cu separation in the chain is 3.737 (6) Å, the out-of-plane Cu–Br(2)′ distance and associated Cu–Br(2)′–Cu angle being 3.260 (6) Å and 80.77 (4)°, respectively. This Cu–Cu separation is relatively short but is within the range of 3.570 (3) to 4.926 (6) Å observed[7,12–14] in dibromo-bridged copper(II) dimers and is shorter than the value of 4.050 (1) Å in $Cu(py)_2Br_2$.[45] The Cu–Br(2)′ distance is comparable to those in the polymeric systems[19,45] $Cu(py)_2Br_2$ and $\alpha$-$Cu(NH_3)Br_2$ and in $CuBr_2$ itself.[46] The bridging angle of 80.77 (4)°, however, is smaller than the values in these comparable dimers and polymers, which range from 83.7 to 100.4°. It is this very acute Cu–Br–Cu angle which leads to the relatively small Cu–Cu separation.

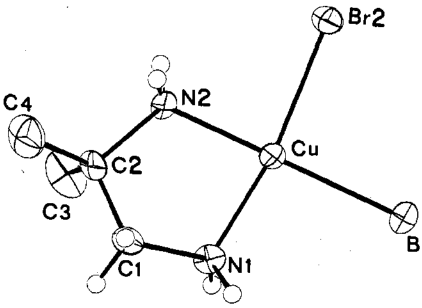

**Figure 4.** View of a single formula unit of dibromo(2-methyl-1,2-diaminopropane)copper(II). Only one of the two disordered positions of atoms C(1), C(3), and C(4) is shown. Hydrogen atoms are omitted for clarity.

**Table VII.** Selected Internuclear Distances (Å) in Dibromo(2-methyl-1,2-diaminopropane)copper(II)

| | | | |
|---|---|---|---|
| Cu-Br(2) | 2.435 (2) | C(1)-C(2) | 1.470 (17) |
| Cu-Br(1) | 2.426 (4) | C(2)-C(3) | 1.609 (17) |
| Cu-Br(2)′ | 3.109 (2) | C(2)-C(4) | 1.497 (18) |
| Cu-N(1) | 2.017 (9) | N(2)-C(2) | 1.521 (13) |
| Cu-N(2) | 2.016 (8) | Cu-Cu′ | 3.866 (2) |
| N(1)-C(1) | 1.475 (16) | | |

**Table VIII.** Selected Angles (deg) in Dibromo(2-methyl-1,2-diaminopropane)copper(II)

| | | | |
|---|---|---|---|
| Br(1)-Cu-N(2) | 179.5 (21) | Br(1)-Cu-Br(2)′ | 91.93 (3) |
| Br(2)-Cu-N(1) | 170.7 (3) | Br(1)-Cu-Br(2)″ | 91.93 (3) |
| Br(2)′-Cu-Br(2)″ | 173.60 (10) | Cu-Br(2)-Cu′ | 87.56 (3) |
| N(1)-Cu-Br(1) | 96.1 (3) | Cu′-Br(2)-Cu″ | 173.60 (10) |
| N(1)-Cu-N(2) | 83.4 (4) | Cu-N(1)-C(1) | 108.0 (7) |
| N(1)-Cu-Br(2)′ | 87.26 (4) | Cu-N(2)-C(2) | 114.1 (6) |
| N(1)-Cu-Br(2)″ | 87.26 (4) | N(1)-C(1)-C(2) | 114.9 (11) |
| N(2)-Cu-Br(2) | 87.2 (3) | C(1)-C(2)-N(2) | 106.3 (8) |
| N(2)-Cu-Br(2)′ | 88.05 (4) | C(1)-C(2)-C(3) | 110.4 (11) |
| N(2)-Cu-Br(2)″ | 88.05 (4) | C(1)-C(2)-C(4) | 112.9 (10) |
| Br(2)-Cu-Br(1) | 93.24 (8) | N(2)-C(2)-C(3) | 106.0 (7) |
| Br(2)-Cu-Br(2)′ | 92.44 (3) | N(2)-C(2)-C(4) | 111.2 (9) |
| Br(2)-Cu-Br(2)″ | 92.44 (3) | C(3)-C(2)-C(4) | 109.7 (13) |

There is no convincing evidence for any hydrogen bonding in this structure. The N–H···Br hydrogen bonds in the various forms of ammonium bromide all involve N···Br separations of less than 3.50 Å and H···Br distances of approximately 2.43 Å;[47–50] it is noteworthy that the sum of the van der Waals radii of N and Br is approximately 3.45 Å.[51] In the present structure, the shortest N(2)···Br(1) contact is 3.795 (7) Å, with associated H···Br distance and N–H···Br angle of 2.85 Å and 174°, respectively.

**Dibromo(2-methyl-1,2-diaminopropane)copper(II).** A view of a single formula unit of the complex is shown in Figure 4; the figure shows only one of the two disordered models. The intramolecular distances and angles are given in Tables VII and VIII. The in-plane Cu–Br bond lengths of 2.425 (4) and 2.435 (2) Å are slightly longer than those in the aminomethylpyridine complex (vide supra) but are certainly normal, the shorter bond again being that to the terminal bromine atom, Br(1). The Cu–N distances of 2.016 (8) and 2.017 (9) Å are symmetric and comparable to the values found in other substituted ethylenediamine complexes. The geometry of the ligand is imprecise, of course, as a result of the disorder involving atoms C(1), C(3), and C(4); bond lengths and angles involving these atoms cannot be considered to be reliable estimates of these parameters. The conformation of the five-membered chelate ring is the envelope conformation, with Cu, N(1), C(2), and N(2) in the crystallographic mirror plane and C(1) disordered above and below this plane. The approximate out-of-plane distance of atom C(1) is 0.48 (2) Å. The chelating angle subtended by the substituted ethylenediamine ligand is 83.4 (4)°, with an associated N···N "bite" of 2.68 (1) Å; these values are very similar to those observed[14] in $[Cu(dmen)Cl_2]_2$ and $[Cu(dmen)Br_2]_2$ and not very different from those in the aminomethylpyridine complex (vide supra).

The Cu–Cu separation in the chain is 3.866 (2) Å, the out-of-plane Cu–Br(2)′ distance and Cu–Br(2)′–Cu angle

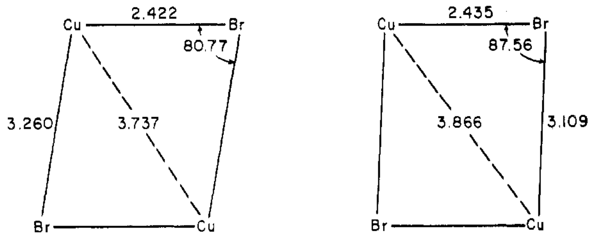

**Figure 5.** Comparison of the bridging geometries of dibromo[2-(2-aminomethyl)pyridine]copper(II) (left) and dibromo(2-methyl-1,2-diaminopropane)copper(II).

being 3.109 (2) Å and 87.56 (3)°, respectively. Hence, the out-of-plane Cu–Br interaction here is slightly stronger than that in the aminomethylpyridine complex (vide supra), but the larger bridging Cu–Br–Cu angle causes the resultant Cu–Cu separation to be greater in the present complex than in the aminomethylpyridine complex. As was noted above, these bridging parameters are within the ranges observed previously for other bromide-bridged complexes.

There is again no evidence for hydrogen bonding in this structure, the shortest intermolecular H···Br distance of 2.92 Å being even larger than that in the aminomethylpyridine complex.

## Discussion

The bridging geometries in these two similar chains are compared in Figure 5. While the two complexes exhibit fundamentally similar structures, the small differences revealed by examination of Figure 5 may have significant consequences. The much smaller bridging angle in the aminomethylpyridine complex brings about a greater distortion from pseudooctahedral geometry in that case, the trans Br(2)′–Cu–Br(2)′ angle being 155.50 (8)° while that in the 2-methyl-1,2-diaminopropane complex is 173.6 (1)°. More importantly, we would anticipate that, although the strengths of the out-of-plane interactions in the two complexes are similar, the magnitudes of the magnetic exchange in these two complexes will be greatly different. The nearly orthogonal bridge geometry in the diaminopropane complex would be expected to give rise to a very small value of $J$, the magnetic exchange parameter, for this complex; on the basis of the observed $J$ values for dimeric systems, it is entirely possible that $J$ will be positive (i.e. that the ground state will be the triplet state).[14,27,52] The bridging geometry in the aminomethylpyridine complex, however, would be expected to lead to a quite strongly antiferromagnetic interaction in this complex. While no magnetic data for these two complexes have been published, preliminary results for the diaminopropane complex are consistent with these expectations.[53]

The novel bridging geometry observed in these two complexes suggests to us that we (and others) are even further from being able to predict the geometries of complexes of the type $[Cu(L)X_2]$ than we previously realized. We shall continue to investigate this structurally prolific class of complexes.

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**Registry No.** $Cu(C_6H_8N_2)Br_2$, 63215-72-5; $Cu(C_4H_{12}N_2)Br_2$, 63180-97-2.

**Supplementary Material Available:** Listings of observed and calculated structure amplitudes for both complexes (9 pages). Ordering information is given on any current masthead page.

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