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The Crystal and Molecular Structure of Dibromo(2-(2-aminoethyl)pyridine)copper(II)

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The crystal and molecular structure of dibromo(2-(2-aminoethyl)pyridine)copper(II), $CuBr_2(C_7N_2H_{10})$, has been determined from three-dimensional X-ray data collected by counter methods. The material crystallizes in space group D_{2h}^{15}-*Pbca* of the orthorhombic system with eight formula units in a cell of dimensions $a = 8.861$ (7), $b = 19.896$ (16), and $c = 11.269$ (9) Å. The observed and calculated densities are 2.28 and 2.309 g cm^{-3}, respectively. Least-squares refinement of the structure has led to a final value of the conventional *R* factor (on *F*) of 0.039 for 1371 independent reflections having $F^2 > 3\sigma(F^2)$. The complex consists of infinite Cu–Br–Cu chains which are joined by doubly bridged Cu–Br–Cu–Br linkages, where the bromine atoms involved in these pairwise linkages are not involved in the chain propagation. Both types of bromine bridges are asymmetric, the Cu–Br separations in the chains being 2.388 (2) and 3.569 (2) Å while those in the pairwise interactions are 2.413 (2) and 3.706 (3) Å. The geometry of the pairwise linkages is unusual in that the angle at the copper atoms is obtuse, and this causes the Cu–Cu separation to be only 4.006 (3) Å. The antiferromagnetic exchange observed for the complex is explained by this weakly bridged aggregation.

Introduction

A complex of formulation $Cu(AEP)Br_2$ (where AEP is 2-(2-aminoethyl)pyridine) was first reported by Uhlig and Maaser,[1] and these authors suggested that the complex consisted of bromine-bridged, five-coordinate copper dimers. In view of our recent magnetic and crystallographic studies on bridged copper dimers,[2-6] we felt that it was essential to examine the molecular structure of this complex, especially since there were, to our knowledge, no published structural data on bromine-bridged copper dimers.[7] This lack of structural data has hindered our attempts to explore further the nature of the magnetic exchange mechanism in coupled copper(II) systems.

Collection and Reduction of the X-Ray Data

Attempts to prepare the complex by the method of Uhlig and Maaser[1] proved unsuccessful, the only product obtained being the blue monomeric complex $Cu(AEP)_2Br_2$. The green, crystalline material was prepared by adding a few drops of 2-(2-aminoethyl)pyridine to a concentrated solution of cupric bromide in absolute methanol. The fine, green precipitate which formed immediately was dissolved in hot absolute methanol; well-formed green plates crystallized from this solution on cooling. *Anal.* Calcd for $CuBr_2C_7N_2H_{10}$: C, 24.33; H, 2.92; N, 8.11. Found:[8] C, 24.40; H, 2.90; N, 8.08.

On the basis of precession and Weissenberg photography, the crystals were assigned to the orthorhombic system. The observed systematic absences are *hk*0 for *h* odd, *h*0*l* for *l* odd, and 0*kl* for *k* odd, which strongly suggests that the space group is D_{2h}^{15}-*Pbca*, a unique space group. The cell constants, obtained by the least-squares procedure described below, are $a = 8.861$ (7), $b = 19.896$ (16), and $c = 11.269$ (9) Å. The observations were made at 25° with the wavelength assumed as λ(Mo Kα_1) 0.7093 Å. A density of 2.309 g cm^{-3} calculated for eight monomeric formula units agrees well with the value of 2.28 (3) g cm^{-3} obtained by flotation in dibromoethane–diiodomethane solution. Hence, no crystallographic symmetry need be imposed on monomeric species in the cell.

Diffraction data were collected from a hexagonal-plate crystal in which the hexagonal faces were (010) and ($0\bar{1}0$) and the edges were ($\bar{1}01$), (001), (101), ($10\bar{1}$), ($00\bar{1}$), and ($\bar{1}0\bar{1}$). The separations between opposite pairs of faces were as follows: ($\bar{1}01$) and ($10\bar{1}$), 0.056 cm; (101) and ($\bar{1}0\bar{1}$), 0.045 cm; (001) and ($00\bar{1}$), 0.045 cm; (010) and ($0\bar{1}0$), 0.017 cm. The crystal was mounted on a glass fiber normal to the ($\bar{1}01$) planes, and in this orientation intensity data were collected at room temperature on a Picker four-circle automatic diffractometer using Mo Kα radiation. The mosaicity of the crystal was examined by means of the narrow-source, open-counter, ω-scan technique; the width at half-height for a typical strong reflection was found to be approximately 0.08°, which is acceptably low.[9] Twelve reflections from the crystal were accurately centered through a narrow vertical slit at a takeoff angle of 0.5°. These observations formed the basis for the least-squares refinement of cell parameters and orientation, which was effected using the logic documented by Busing and Levy[10] in the PDP-8/L computer.

Intensity data were collected at a takeoff angle of 1.4°; at this angle the peak intensity of a typical strong reflection is approximately 90% as a function of takeoff angle. The receiving aperture size, selected to minimize extraneous background, was 4.0×4.0 mm and was positioned 32 cm from the crystal. The data were collected by the θ–2θ scan technique at a scan rate of 1°/min. Allowance was made for the presence of both Kα_1 and Kα_2 radiations, the peaks being scanned from $-0.5°$ in 2θ below the calculated Kα_1 peak position to $+0.5°$ in 2θ above the calculated Kα_2 peak position. Stationary-counter, stationary-crystal background counts of 10 sec were taken at each end of the scan. The Mo Kα beam was filtered through 3.0-mil Nb foil after diffraction from the crystal. Attenuators were inserted automatically when the intensity of the diffracted beam exceeded about 7000 counts/sec during the scan; the attenuators were Cu foils, their thickness being chosen to give attenuator factors of approximately 2.3. These attenuator factors were determined by the method which we have previously described.[11] The pulse height analyzer was set for approximately a 90% window centered on the Mo Kα peak.

A unique data set having $2\theta < 55°$ was gathered; a total of 2733 independent intensities were recorded. The intensities of three standard reflections, measured after every 100 reflections, remained essentially constant throughout the run, showing only the deviations from the mean predicted from counting statistics. There were very few reflections above background at values of $2\theta > 55°$.

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[1] E. Uhlig and M. Maaser, *Z. Anorg. Allg. Chem.*, **322**, 25 (1963).

[2] D. J. Hodgson, P. K. Hale, and W. E. Hatfield, *Inorg. Chem.*, **10**, 1061 (1971).

[3] J. A. Barnes, W. E. Hatfield, and D. J. Hodgson, *Chem. Phys. Lett.*, **7**, 374 (1970).

[4] J. A. Barnes, W. E. Hatfield, and D. J. Hodgson, *Chem. Commun.*, 1593 (1970).

[5] D. Y. Jeter, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chim. Acta*, **5**, 257 (1971).

[6] W. E. Hatfield, *Inorg. Chem.*, **11**, 216 (1972).

[7] We have recently solved the structure of $Cu(pic)_2Br_2$ (pic = 2-methylpyridine), which is, in fact, a bromine-bridged copper dimer: P. Singh and D. J. Hodgson, presented at the 23rd Southeastern Regional Meeting of the American Chemical Society, Nashville, Tenn., Nov 4–5, 1971, Paper 47.

[8] Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

[9] T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957.

[10] W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **22**, 457 (1967).

[11] D. J. Hodgson and J. A. Ibers, *Acta Crystallogr., Sect. B*, **25**, 469 (1969).

Data processing was carried out as described by Corfield, *et al.*[12] After correction for background, the intensities were assigned standard deviations according to the formula[12]

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

and the value of p was selected as 0.05 since the mosaicity of the crystal was quite small. This term in the expression is used to prevent extremely high weight being given to very strong reflections.[13] The values of I and $\sigma(I)$ were corrected for Lorentz-polarization effects and for absorption factors. The absorption coefficient for this compound for Mo Kα radiation is 106.1 cm^{-1}, and for the sample chosen the transmission coefficients evaluated by numerical integration were found to range from 0.047 to 0.205.[14] Of the 2733 independent reflections, 1371 were greater than 3 times their estimated standard deviations.

Solution and Refinement of Structure

The positions of copper and the two bromine atoms were determined from a three-dimensional Patterson function. 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 $\Sigma w(|F_o| - |F_c|)^2$; the weights w were taken as $4F_o^2/\sigma^2(F_o^2)$. In all calculations of F_c the atomic scattering factors for Cu and Br were taken from Cromer and Waber,[15] that for H was taken from Stewart, Davidson, and Simpson,[16] and those for C and N were taken from the tabulation of Ibers.[17] The effects of anomalous dispersion were included in calculations of F_c,[18] the values of $\Delta f'$ and $\Delta f''$ being taken from the tabulation of Cromer.[19] Only the 1371 independent intensities which were greater than 3 times their estimated standard deviations were used in the refinement of the structure.

Initially, the three 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 $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2)^{1/2}$ were 0.255 and 0.357, respectively. A difference Fourier synthesis revealed the locations of all remaining nonhydrogen atoms, and two further cycles of least-squares refinement with variable anisotropic thermal parameters assigned to all atoms yielded values of $R_1 = 0.104$ and $R_2 = 0.131$. A similar calculation, run after the absorption correction had been applied, gave $R_1 = 0.049$ and $R_2 = 0.074$; this substantial improvement in the refinement is to be expected for a crystal with such a high absorption coefficient (*vide supra*). The ten hydrogen atoms were unambiguously located in a difference Fourier map computed at this stage, and two further least-squares cycles were calculated in which the nonhydrogen atoms were assigned anisotropic thermal parameters and the hydrogen atoms were assigned isotropic thermal parameters; also all positional and thermal parameters (including those of the hydrogen atoms) were refined. This reduced the values of the agreement factors to 0.039 and 0.045; the substantial improvement in R_2 caused by the introduction of these extra 40 variables is significant at any meaningful confidence level.[20] A final difference Fourier synthesis showed no peak higher than 0.7 e Å^{-3}, the peak height of an average carbon atom in this analysis being 4 e Å^{-3}.

In the last cycle of least-squares refinement, no atomic parameter experienced a shift as great as its estimated standard deviation, which is taken as evidence that the refinement had converged. The value of R_2 showed no dependence on sin θ or on $|F_o|$, which indicates that our choice of $p = 0.05$ is essentially correct. Examination of the final values of $|F_o|$ and $|F_c|$ suggested to us that no correction for secondary extinction is necessary, and the application of a correction of the type described by Zachariasen[21] led to a value for the extinction coefficient which did not differ significantly from zero.

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. The mean-square amplitudes of vibration, U_{ij}, calculated from the thermal parameters, are listed in Table III. A table of observed and calculated structure amplitudes is available.[22]

TABLE I

POSITIONAL PARAMETERS FOR $Cu(C_7N_2H_{10})Br_2$

Atom	x	y	z
Cu	0.06002 (9)[a]	0.06612 (4)	0.12544 (8)
Br(1)	−0.00783 (9)	0.04575 (4)	−0.19711 (7)
Br(2)	−0.20100 (8)	0.09600 (4)	0.12516 (6)
N(1)	0.1263 (7)	0.1633 (3)	0.1237 (5)
N(2)	0.2630 (7)	0.0329 (3)	0.0783 (6)
C(1)	0.2338 (8)	0.1861 (3)	0.0521 (5)
C(2)	0.2827 (10)	0.2518 (4)	0.0589 (7)
C(3)	0.2193 (10)	0.2949 (4)	0.1407 (8)
C(4)	0.1122 (10)	0.2707 (3)	0.2154 (7)
C(5)	0.0680 (9)	0.2052 (4)	0.2049 (7)
C(6)	0.3030 (9)	0.1371 (4)	−0.0344 (6)
C(7)	0.3750 (9)	0.0779 (4)	0.0272 (7)
H(2)[b]	0.383 (12)	0.270 (5)	0.000 (8)
H(3)	0.243 (14)	0.333 (7)	0.146 (12)
H(4)	0.075 (9)	0.293 (4)	0.276 (7)
H(5)	−0.005 (7)	0.190 (3)	0.258 (6)
H(61)	0.219 (10)	0.113 (4)	−0.091 (7)
H(62)	0.379 (12)	0.162 (5)	−0.080 (10)
H(71)	0.442 (12)	0.094 (6)	0.081 (10)
H(72)	0.443 (12)	0.059 (5)	−0.031 (9)
H(N1)	0.288 (8)	0.010 (4)	0.142 (6)
H(N2)	0.256 (12)	−0.008 (6)	0.049 (8)

[a] The numbers in parentheses here and elsewhere in this paper refer to the estimated standard deviation in the least significant digit. [b] The H atoms are numbered with reference to the C or N atom to which they are bonded. Thus, H(4) is attached to C(4), H(61) is attached to C(6), and H(N1) and H(N2) are attached to N(2).

Description of the Structure

The structure consists of infinite Cu–Br(2)–Cu–Br(2) chains which are joined by doubly bridged Cu–Br(1)–Cu–Br(1) interchain linkages; the polymeric nature of the complex is shown in Figure 1. The coordination polyhedron around the copper atoms is a tetragonally distorted octahedron, the basal plane being formed by two cis-nitrogen atoms and two bromine atoms and the inner coordination sphere being completed by two bromine atoms at much greater distances from the copper atom; a view of the coordination around a single copper atom is shown in Figure 2. The four "in-plane" ligands N(1), N(2), Br(1)′, and Br(2) are not coplanar. Br(1)′ and N(1), which are trans to each other, lie 0.31 and 0.36 Å, respectively, below the least-squares plane through the four ligands while Br(2) and N(2) are 0.30 and 0.38 Å, respectively, above this plane; the copper atom lies nearly in the plane, sitting 0.03 Å above it. This nonplanarity gives

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(12) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(13) W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957).

(14) In addition to various local programs, the programs for the IBM 360/75 used in this analysis were local modifications of Hamilton's GONO9 absorption correction program, Busing, Levy, and Martin's ORFLS least-squares and ORFFE function and error programs, Zalkin's FORDAP Fourier program, Ibers' PICKOUT processing program, and Doedens' RSCAN program.

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

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

(17) J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, Table 3.3.1A.

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

(19) D. T. Cromer, *ibid.*, **18**, 17 (1965).

(20) W. C. Hamilton, "Statistics in Physical Science," Ronald Press, New York, N. Y., p 157.

(21) W. H. Zachariasen, *Acta Crystallogr.*, **16**, 1139 (1963); *Acta Crystallogr., Sect. A*, **24**, 212 (1968).

(22) A listing of structure factor amplitudes 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, by referring to code number INORG-72-1826. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

TABLE II

THERMAL PARAMETERS FOR $Cu(C_7N_2H_{10})Br_2$

Atom	$\beta_{11}{}^a$ or B, Å^2	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.00817 (12)	0.00132 (2)	0.00698 (7)	0.00010 (8)	0.00147 (8)	0.00017 (3)
Br(1)	0.01136 (11)	0.00149 (2)	0.01083 (7)	−0.00026 (4)	0.00139 (8)	0.00070 (3)
Br(2)	0.00833 (9)	0.00196 (2)	0.00638 (5)	0.00033 (3)	0.00108 (6)	−0.00012 (3)
N(1)	0.0088 (7)	0.0014 (1)	0.0060 (4)	0.0000 (3)	−0.0006 (6)	0.0002 (2)
N(2)	0.0086 (8)	0.0016 (2)	0.0064 (5)	0.0005 (3)	−0.0009 (5)	−0.0001 (2)
C(1)	0.0075 (9)	0.0018 (2)	0.0047 (5)	0.0000 (3)	−0.0015 (6)	0.0008 (2)
C(2)	0.0141 (13)	0.0019 (2)	0.0078 (7)	−0.0011 (4)	0.0008 (8)	0.0006 (3)
C(3)	0.0146 (14)	0.0015 (2)	0.0104 (8)	−0.0012 (4)	−0.0032 (8)	0.0002 (3)
C(4)	0.0132 (12)	0.0014 (2)	0.0068 (7)	0.0002 (4)	−0.0019 (8)	−0.0007 (3)
C(5)	0.0100 (10)	0.0016 (2)	0.0070 (6)	0.0000 (4)	−0.0001 (7)	−0.0002 (3)
C(6)	0.0099 (11)	0.0026 (2)	0.0052 (6)	−0.0006 (4)	0.0022 (7)	0.0008 (3)
C(7)	0.0083 (10)	0.0021 (2)	0.0062 (6)	0.0000 (4)	0.0019 (7)	−0.0004 (3)
H(2)	6.1 (24)					
H(3)	9.9 (40)					
H(4)	2.9 (19)					
H(5)	2.3 (13)					
H(61)	3.6 (19)					
H(62)	6.8 (28)					
H(71)	2.1 (30)					
H(72)	5.1 (26)					
H(N1)	2.1 (16)					
H(N2)	5.9 (27)					

[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

MEAN-SQUARE AMPLITUDES OF VIBRATION (Å^2)

Atom	$U_{11}{}^a$ or U	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	0.03250	0.02646	0.04488	−0.00085	0.00742	−0.00189
Br(1)	0.04520	0.02978	0.06966	−0.00235	0.00705	0.00790
Br(2)	0.03315	0.03923	0.04104	0.00297	0.00545	−0.00134
N(1)	0.0350	0.0278	0.0385	0.0004	−0.0033	0.0021
N(2)	0.0340	0.0322	0.0412	0.0045	−0.0047	−0.0012
C(1)	0.0297	0.0369	0.0303	−0.0003	−0.0076	0.0086
C(2)	0.0562	0.0371	0.0505	−0.0098	0.0039	0.0068
C(3)	0.0580	0.0303	0.0672	−0.0104	−0.0161	0.0025
C(4)	0.0526	0.0272	0.0440	0.0021	−0.0096	−0.0078
C(5)	0.0398	0.0314	0.0451	−0.0003	−0.0006	−0.0026
C(6)	0.0393	0.0516	0.0337	−0.0056	0.0111	0.0088
C(7)	0.0328	0.0421	0.0401	−0.0007	0.0094	−0.0041
H(2)	0.077					
H(3)	0.126					
H(4)	0.037					
H(5)	0.030					
H(61)	0.046					
H(62)	0.086					
H(71)	0.027					
H(72)	0.064					
H(N1)	0.026					
H(N2)	0.075					

[a] The form of the anisotropic thermal ellipsoid is $\exp[-2\pi^2\cdot(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

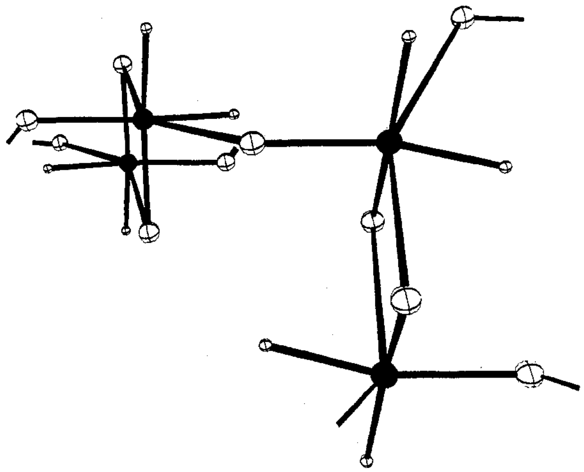

Figure 1.—View of the polymeric nature of $Cu(AEP)Br_2$. Cu atoms are shown as solid circles, N atoms as small open circles, and Br atoms as large open circles. The C and H atoms are omitted for clarity.

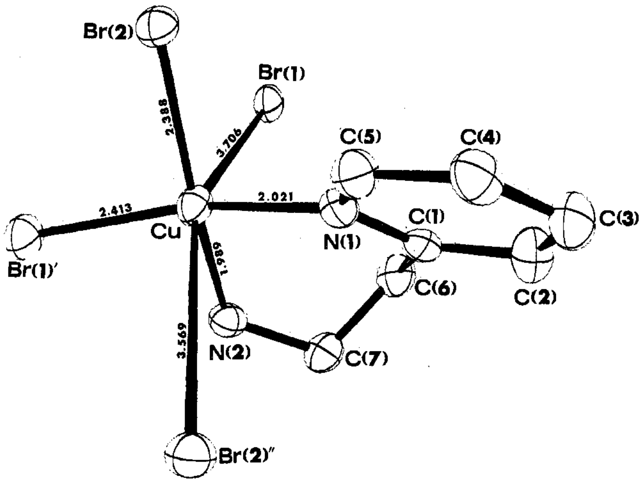

Figure 2.—View of the coordination around one Cu atom in $Cu(AEP)Br_2$. Atom Br(1)' is related to Br(1) by the inversion center; atom Br(2)'' is related to Br(2) by the *a* glide. The H atoms are omitted for clarity. Thermal ellipsoids are drawn at the 40% probability level.

rise to Br(1)'-Cu-N(1) and Br(2)-Cu-N(2) angles of 160.3 (2) and 163.4 (2)°, respectively, instead of the anticipated 180°. The angles subtended at the metal by ligands cis to each other, however, do not show such great deviations from 90° but lie in the range 87.5 (2)-93.0 (2)°. The internuclear separations and angles found in the complex are listed, along with their associated estimated standard deviations, in Table IV.

While the out-of-plane Cu-Br distances of 3.569 and 3.706 Å are very long, the magnetic properties of this complex demonstrate conclusively that these weak interactions are significant. If the complex were viewed as a four-coordinate monomer it would be expected to obey the Curie-Weiss law, but the magnetic data deviate from Curie-Weiss behavior at low temperatures and indicate antiferromagnetic exchange interactions.[23] The low-temperature susceptibility data do not fit

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[23] D. Y. Jeter, W. E. Hatfield, and D. J. Hodgson, *J. Phys. Chem.*, in press.

TABLE IV

INTERNUCLEAR DISTANCES AND ANGLES IN $Cu(C_7N_2H_{10})Br_2$[a]

	Distance, Å		Angle, deg
Cu–Cu′	4.006 (3)	Br(1)′–Cu–Br(1)	101.33 (4)
Cu–Br(1)′	2.413 (2)	Br(1)′–Cu–Br(2)	92.55 (5)
Cu–Br(1)	3.706 (3)	Br(1)′–Cu–Br(2)″	90.22 (5)
Cu–Br(2)	2.388 (2)	Br(1)′–Cu–N(1)	160.3 (2)
Cu–Br(2)″	3.569 (2)	Br(1)′–Cu–N(2)	87.5 (2)
Cu–N(1)	2.021 (5)	Br(2)–Cu–Br(2)″	122.29 (5)
Cu–N(2)	1.989 (6)	Br(2)–Cu–Br(1)	82.46 (3)
N(1)–C(1)	1.328 (9)	Br(2)–Cu–N(1)	92.5 (2)
C(1)–C(2)	1.379 (10)	Br(2)–Cu–N(2)	163.4 (2)
C(2)–C(3)	1.379 (12)	Br(1)–Cu–Br(2)″	152.47 (4)
C(3)–C(4)	1.357 (12)	Br(1)–Cu–N(1)	98.2 (2)
C(4)–C(5)	1.366 (10)	Br(1)–Cu–N(2)	81.3 (2)
C(5)–N(1)	1.342 (9)	Br(2)″–Cu–N(1)	71.1 (2)
C(1)–C(6)	1.508 (10)	Br(2)″–Cu–N(2)	74.3 (2)
C(6)–C(7)	1.508 (11)	N(1)–Cu–N(2)	93.0 (2)
C(7)–N(2)	1.455 (10)	C(1)–N(1)–C(5)	118.6 (6)
C(2)–H(2)	1.17 (10)	N(1)–C(1)–C(2)	121.0 (7)
C(3)–H(3)	0.80 (14)	N(1)–C(1)–C(6)	117.6 (6)
C(4)–H(4)	0.88 (8)	C(2)–C(1)–C(6)	121.4 (7)
C(5)–H(5)	0.94 (7)	C(1)–C(2)–C(3)	120.0 (7)
C(6)–H(61)	1.10 (8)	C(2)–C(3)–C(4)	118.6 (7)
C(6)–H(62)	0.99 (11)	C(3)–C(4)–C(5)	119.0 (8)
C(7)–H(71)	0.91 (11)	C(4)–C(5)–N(1)	122.8 (7)
C(7)–H(72)	0.97 (11)	C(1)–C(6)–C(7)	112.3 (6)
N(2)–H(N1)	0.89 (7)	C(6)–C(7)–N(2)	111.9 (6)
N(2)–H(N2)	0.87 (11)		

[a] Atoms designated with a single prime are related to the reference atom by the inversion center; doubly primed atoms are related to the reference atom by the *a* glide perpendicular to *c*.

either the Van Vleck dimer equation[24] or the Ising chain model,[25] which implies that both the chain and pairwise pathways probably contribute to the antiferromagnetic exchange observed. It is noteworthy that exchange interactions involving Cu–Br separations which are greater than the bridging distances found here have been observed; in dibromobis(2-methylpyridine)copper(II) antiferromagnetic interactions occur,[5] and the out-of-plane Cu–Br distance is 3.872 Å.[7]

While this is the only known example of a structure consisting of singly bromide-bridged asymmetric chains joined by doubly bromide-bridged asymmetric linkages, each part of it may be compared separately with known molecules. Singly bridged infinite Cu–Br–Cu chains have been shown to occur in anhydrous copper(II) bromide,[26] $CuBr_2$, in α-dibromodiamminecopper(II),[27] α-$Cu(NH_3)_2Br_2$, and in dibromobis(pyridine)copper(II),[28] $Cu(py)_2Br_2$. The Cu–Br(2) distance of 2.388 (2) Å found here for $Cu(AEP)Br_2$ is shorter than the values of 2.40, 2.46, and 2.54 Å found in $CuBr_2$, $Cu(py)_2Br_2$, and α-$Cu(NH_3)_2Br_2$, respectively, while the Cu–Br(2)″ separation of 3.569 (2) Å in $Cu(AEP)Br_2$ is much longer than the distances of 3.18, 3.19, and 3.08 Å in these three systems. Hence, it is apparent that the chain interactions in $Cu(AEP)Br_2$ are much less symmetric than in other systems studied, the Br atoms being relatively strongly bound to one copper atom and interacting only weakly with the adjacent atom, so that the Cu–Br(2) bond length of 2.388 (2) Å is normal for terminal Cu–Br bonds and is, in fact, shorter than the terminal, nonbridging Cu–Br distances of 2.450 (2) and 2.519 (2) Å in monomeric $CuBr_5^{3-}$.[29] The weakness of this Cu–Br(2)″ interaction accounts for the very low temperature (<5°K) at which the maximum of the magnetic susceptibility is observed in $Cu(AEP)Br_2$, as compared with values of 226°K in $CuBr_2$[30] and 36°K in $Cu(py)_2Br_2$.[31]

Doubly bridged, pairwise Cu–Br–Cu′–Br′ interactions occur in $CuBr_2$,[26] $Cu(pic)_2Br_2$,[7] and α-$Cu(NH_3)_2Br_2$,[27] and similar interactions involving chlorine instead of bromine bridges occur in the di-μ-chloro-bis(trichlorocuprate(II)) anion,[2] $Cu_2Cl_8^{4-}$, in anhydrous copper chloride,[32] $CuCl_2$, and in many other systems.[33] The Cu–Br(1)′ bond length of 2.413 (2) Å in $Cu(AEP)Br_2$ is similar to the values of 2.40, 2.42, and 2.54 Å found in $CuBr_2$, $Cu(pic)_2Br_2$, and α-$Cu(NH_3)_2Br_2$, respectively, while the Cu–Br(1) separation of 3.706 (3) Å is much longer than the distances of 2.40 and 3.08 Å in $CuBr_2$ and α-$Cu(NH_3)_2Br_2$ and is comparable with the value of 3.872 Å in $Cu(pic)_2Br_2$. The geometry of the Cu–Br(1)–Cu′–Br(1)′ moiety, however, is quite different from any with which we are familiar in that the Br(1)–Cu–Br(1)′ angle is obtuse (101.33 (4)°) and the Cu–Br(1)–Cu′ angle is acute (78.67 (4)°) whereas in the other systems, including the chloro-bridged systems, the angle subtended at the copper atom is acute while that at the bridging atom is obtuse. Hence, despite the long Cu–Br(1) distance, the Cu–Cu′ separation of 4.006 (3) Å in $Cu(AEP)Br_2$ is shorter than the value of 4.05 Å in α-$Cu(NH_3)_2Br_2$ and considerably shorter than the value of 4.93 Å in $Cu(pic)_2Br_2$. The Cu–Br(1)–Cu′–Br(1)′ moiety is strictly planar, there being a crystallographic inversion center in the middle of the four-membered ring.

There is no convincing evidence of hydrogen bonding in this structure. The only well-documented N–H···Br hydrogen bonds are those found in the various forms of ammonium bromide, in which the N···Br separation is in the range 3.45–3.47 Å and the N–H distance is 1.03 Å,[34–37] the H···Br contact being approximately 2.43 Å. It is noteworthy that the sum of the van der Waals radii of N and Br is 3.45 Å.[38] The only Br···N(2) contact which is shorter than 3.48 Å is a Br(1)···N(2) separation of 3.06 Å; the angles Br(1)···H(N1)–N(2) and Br(1)···H(N2)–N(2) of 99.3 and 94.6° which are associated with this contact preclude any hydrogen-bond formation,[39] and the Br(1)···H distances of 2.79 and 2.86 Å are not only much longer than the values in ammonium bromide but are actually longer than a Br(1)···H(61) (H(61) is a methylene hydrogen atom) separation of 2.69 Å found here. There is a Br(2)···H(N2)–N2 separation of 3.48 Å which subtends an angle of 153° at H(N2)

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and has a Br···H(N2) separation of 2.68 Å, but we do not believe that this is a hydrogen bond since Br···N contacts of considerably less than 3.48 Å which do not involve hydrogen bonding are quite common in systems of this type. Thus, there is a Br(2)···N(1) (N(1) is the pyridine nitrogen atom) separation of 3.195 Å in this molecule, and there are Br···N contacts of 3.101 (9) and 3.105 (9) Å in dibromobis(2,3-dimethylpyridine)copper(II).[40]

The Cu-N bond lengths are consistent with those found in related systems. Hence, the Cu–N(1) distance of 2.021 (5) Å is similar to the values of 1.98 (1) and 2.02 (1) Å in dichlorobis(2-methylpyridine)copper(II),[41] 1.989 (6) Å in *trans*-bis[(chloroacetato)(2-methylpyridine)]copper(II),[42] 1.99 Å in dibromobis(pyridine)copper(II),[28] 2.02 Å in dichlorobis(pyridine)copper(II),[43] and 2.161 (10) Å in 2-methylpyridinecopper(II) chloroacetate.[44] Similarly, the Cu–N(2) separation of 1.989 (6) Å is comparable to the values of 1.971 (2) and 1.984 (2) Å in carbonatodiamminecopper(II),[45] 2.012 (9) and 2.017 (9) Å in selenatotetraamminecopper(II),[46] 2.031 (6) and 2.032 (6) Å in sulfatotetraamminecopper(II),[46] and in other copper–amine systems. The pyridine ring is planar, with no atom deviating from the least-squares plane by more than 0.012 Å. The bond lengths and angles in the ring and in the exocyclic aminoethyl group are similar to those found in other pyridine and substituted-pyridine complexes.[41–44]

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The Crystal and Molecular Structure of Hexakis(2-imidazolidinone)cadmium(II) Perchlorate

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The crystal and molecular structure of hexakis(2-imidazolidinone)cadmium(II) perchlorate has been determined by a single-crystal X-ray diffraction study using diffractometer data. The title compound crystallizes in the space group $P\bar{1}$ with one molecule in a unit cell with dimensions a = 11.298 (1) Å, b = 12.299 (1) Å, c = 6.377 (1) Å, α = 96.20 (1)°, β = 94.61 (1)°, and γ = 114.29 (1)°. The structure was solved by the heavy-atom method and refined by block-diagonal least squares to a final value of the conventional reliability index (R) of 0.046 for the 2364 statistically significant reflections. The ethyleneurea ligands are coordinated through the carbonyl oxygen and form a distorted octahedron about the cadmium with Cd–O distances of 2.348 (5), 2.282 (4), and 2.239 (4) Å and with O–Cd–O angles ranging from 86.1 to 93.9°. An extensive pattern of hydrogen bonding between the amide nitrogens and the carbonyl oxygens of adjacent ethyleneurea groups is observed.

Introduction

The coordination chemistry of ureido compounds has received considerable attention in recent years. Ureas (or any amide-type compound) possess two potential sites for coordination, the carbonyl oxygen and the amide nitrogen. Although Neubauer and Kerner reported the first urea complex in 1857,[2a] it was not until 100 years later that Penland and coworkers[2b] used infrared spectroscopy to predict the mode of bonding (*i.e.*, nitrogen to metal or oxygen to metal) in a series of urea complexes. Since that time, many references in the literature have suggested that the mode of bonding can be deduced from the position of the carbonyl stretching frequency of the complex relative to that of the free ligand.[3–5] A shift of the carbonyl absorption to lower frequency is presumed to indicate oxygen to metal bonding, while a shift to higher frequency would indicate nitrogen to metal bonding. For example, based on infrared spectral data, Penland and coworkers postulated oxygen to metal bonding in urea complexes of Cr(III), Fe(III), Zn(II), and Cu(II) and nitrogen to metal bonding with Pt(II) and Pd(II). Costamagna and Levitus[6] used similar arguments to demonstrate oxygen to metal bonding in a series of cobalt complexes with N-substituted ureas. Madan and Denk[7] correlated

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