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## Crystal Structure and Magnetic Susceptibility of $\text{Cu}_2\text{Br}_4(\text{C}_5\text{H}_5\text{N})_2$ , Di- $\mu$ -bromo-bis[bromo(pyridine)copper(II)]. A One-Dimensional Chain of Dimers

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$\text{Cu}_2\text{Br}_4(\text{C}_5\text{H}_5\text{N})_2$ , di- $\mu$ -bromo-bis[bromo(pyridine)copper(II)], crystallizes in the space group  $C\bar{1}$ ,  $Z = 2$ , with lattice constants  $a = 17.902(21)$  Å,  $b = 3.978(4)$  Å,  $c = 10.776(16)$  Å,  $\alpha = 86.89(11)^\circ$ ,  $\beta = 101.94(10)^\circ$ , and  $\gamma = 93.28(8)^\circ$ . Intensity data were collected on a Picker diffractometer using a  $\theta$ - $2\theta$  scan technique and refined by a least-squares technique to a final conventional  $R$  value of 0.083. The centrosymmetric binuclear molecules stack above each other along the crystallographic  $b$  axis. Within each dimer, copper-bromide distances range from 2.412(4) to 2.464(6) Å while interdimer distances are 2.928(4) and 3.331(4) Å. The pyridine ring is not coplanar with the  $\text{Cu}_2\text{Br}_4$  plane but is twisted at an angle of  $54^\circ$  from the dimer plane to allow efficient packing of the pyridine rings. The magnetic susceptibility, measured from 2.8 to 231 K, reaches a maximum slightly above 10 K. The susceptibility data are interpreted in terms of a model for an Ising chain of Heisenberg dimers. Both the intradimer- and interdimer-exchange constants are  $-11$  cm $^{-1}$ . The weak antiferromagnetic intradimer coupling is contrasted to the strong antiferromagnetic interaction in the  $\text{Cu}_2\text{Br}_6^{2-}$  ion in  $\text{KCuBr}_3$  ( $2J = -135$  cm $^{-1}$ ). The trans effect of the pyridine reduces the electron density at the bridging bromides, producing a much weaker exchange interaction.

### Introduction

The halide complexes have enjoyed a long and colorful history in inorganic chemistry. The idiosyncrasies of copper chloride complexes are well documented and have been recently reviewed by Smith.<sup>1</sup> On the other hand, very little structural information is available on copper bromide salts. It is often assumed that they will be isomorphous to the corresponding chlorides. However, since the observed geometries are a delicate balance between crystal field effects, ligand-ligand repulsion, and crystal packing, it is not surprising to find that the assumed isomorphism does not always hold. There is a similar dearth of information on magnetic interaction in copper(II) bromides. For these reasons, we are pursuing structural and magnetic studies on a variety of copper bromide complexes.

The copper bromide-pyridine (py) system was first explored in detail by Harris and Sinn.<sup>2</sup> The salt  $\text{CuBr}_2 \cdot 2\text{py}$  had been known for a considerable length of time.<sup>3</sup> Magnetic investigations have been made by Jeter and Hatfield.<sup>4</sup> Although unable to prepare the desired  $\text{CuBr}_2 \cdot \text{py}$ , Harris and Sinn isolated a tetrameric species. The correct identity of this species was established as  $\text{Cu}_4\text{Br}_6\text{O}(\text{py})_4$  by a later crystallographic investigation.<sup>5</sup> During the course of that investigation, we readily obtained dark orange-brown crystals which gave the correct analysis for  $\text{CuBr}_2 \cdot \text{py}$ . In this paper, we present a structural and magnetic investigation of the orange-brown compound, which has a molecular formula of  $\text{Cu}_2\text{Br}_4(\text{py})_2$ .

### Experimental Section

The compound was prepared by slow evaporation of approximately equimolar quantities of  $\text{CuBr}_2$  and py in ethanol or propanol. Prolonged heating had to be avoided to keep from forming  $\text{Cu}_4\text{Br}_6\text{O}(\text{py})_4$ . The desired compound grew as long, fibrous needles. Any attempts to cut the crystal invariably caused the crystal to assume the appearance of a straw broom. Anal. Calcd: Cu, 21.01; Br, 52.84; N, 4.63; C, 19.86; H, 1.67. Found: Cu, 19.94; Br, 52.63; N, 4.09; C, 19.24; H, 1.60.

X-ray examination of the crystals showed no symmetry planes or axes, thus the crystal was assumed to be triclinic. A logical choice of axes, based on crystal morphology and selection of cell angles near  $90^\circ$ , leads to the choice of a  $C$ -centered cell with the needle axis chosen as the  $b$  axis. The samples examined invariably were polycrystalline. After much frustration, a crystal was mounted which showed only two major twin components. Because of the sparseness of the reciprocal lattice points due to the short needle axis, there were very few ac-

cidental overlaps of reciprocal lattice points from the two twins. Therefore, it was decided to collect a data set on the crystal. The crystal dimensions were  $0.052$  mm  $\times$   $0.084$  mm  $\times$   $0.34$  mm. The density, determined by flotation in a mixture of methylene bromide and methylene iodide was  $2.57$  g/cm $^3$ . The calculated density for  $Z = 4$  (monomeric units) is  $2.59$  g/cm $^3$ .

Crystallographic data were collected on an automated Picker diffractometer with Zr-filtered Mo  $K\alpha$  radiation. A  $\theta$ - $2\theta$  step scan was used with 20 steps/deg of 2.0 s duration and a scan width of 2.0 deg. Background counts were collected for 10 s before and after each scan. The standard deviation of each intensity was calculated by the relationship  $\sigma^2(I) = \text{TC} + \text{BC} + 0.03^2 I_0^2$  (all values were converted to an equivalent time scale), where TC = total counts, BC = background counts, and  $I_0 = \text{TC} - \text{BC}$ . A total of 1251 independent reflections were collected, of which 882 had  $F \geq 3\sigma(F)$ . Three standard reflections were monitored every 80 reflections. No systematic deviations from counting statistics were observed. Absorption corrections were made ( $\mu = 141$  cm $^{-1}$ ). Transmission factors ranged from 0.31 to 0.49. Crystallographic programs used were from a local program library<sup>6</sup> which included modified versions of ORFLS3,<sup>7</sup> ALFF,<sup>8</sup> ORFFE,<sup>9</sup> and ORTEP.<sup>10</sup> Atomic scattering factors, corrected for anomalous dispersion, were taken from ref 11.

Susceptibility measurements were made on a powder sample with an ac mutual inductance bridge<sup>12</sup> over the temperature range 1.5-240 K. The frequency used was 34 Hz with a field strength of 20 gauss. The out-of-phase component of the susceptibility,  $\chi''$ , was effectively zero over the whole temperature range, and so the reported values of the susceptibility are the in-phase component,  $\chi'$ .

The crystal structure was solved via the Patterson function, which gave the Cu and Br positions, and electron density maps, which gave

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Table I. Positional and Thermal Parameters for  $\text{CuBr}_2 \cdot \text{C}_5\text{H}_5\text{N}$ 

atom	x	y	z	$U_{11}^a$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Cu	0.5158 (2) <sup>b</sup>	0.8650 (8)	0.3490 (4)	0.0155 (16)	0.0311 (19)	0.0382 (22)	0.0224 (229)	0.0091 (91)	0.3516 (391)
Br(1)	0.4485 (2)	0.4557 (6)	0.2039 (3)	0.0202 (16)	0.0234 (14)	0.0461 (17)	0.1045 (299)	-0.0046 (91)	0.3760 (293)
Br(2)	0.5853 (2)	1.1969 (6)	0.5260 (3)	0.0140 (16)	0.0256 (20)	0.0393 (22)	0.1269 (224)	0.0046 (45)	0.3516 (293)
atom	x	y	z	$U, \text{\AA}^2$	atom	x	y	z	$U, \text{\AA}^2$
N	0.6046 (14)	0.9037 (56)	0.2629 (22)	3.03 (73) <sup>c</sup>	C(3)	0.7306 (18)	0.9016 (71)	0.1514 (26)	2.89 (85)
C(1)	0.5999 (16)	1.0027 (65)	0.1469 (25)	2.52 (83)	C(4)	0.7393 (15)	0.8060 (60)	0.2756 (23)	1.87 (74)
C(2)	0.6623 (16)	1.0164 (66)	0.0787 (25)	2.78 (87)	C(5)	0.6775 (16)	0.7886 (62)	0.3314 (24)	2.39 (82)

<sup>a</sup> Thermal parameters defined by  $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* \cos \gamma^* + 2U_{13}hla^*c^* \cos \beta^* + 2U_{23}klb^*c^* \cos \alpha^*)]$ . <sup>b</sup> Uncertainties given in parentheses. <sup>c</sup> Thermal parameters defined by  $T = \exp[-B(\sin^2 \theta)/\lambda^2]$ .

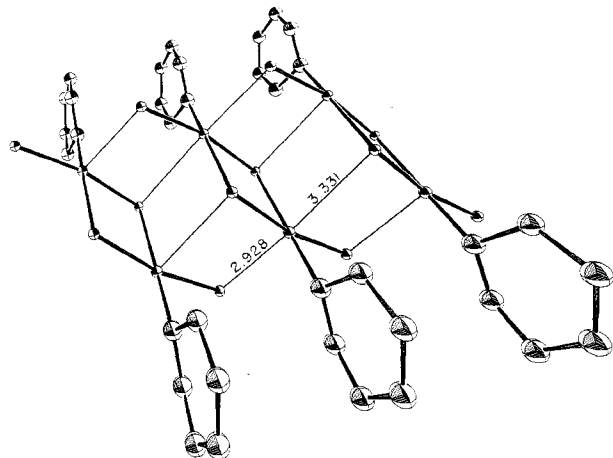


Figure 1. Illustration of the dimer packing to form linear chains parallel to the  $b$  axis.

the C and N positions. No attempt was made to locate the hydrogen atoms. The full-matrix least-squares refinement of  $F_o$  with weights,  $w_i = 1/\sigma^2(F_i)$ , proceeded to a final value of  $R_2 (= \sum w|F_o - F_c|^2 / \sum wF_o^2)^{1/2}$  of 0.092 and of  $R_1 (= \sum ||F_o| - |F_c|| / |F_o|)$  of 0.083 and a goodness of fit value of 2.45. This was extremely disappointing since the data set appeared to be of excellent quality. Equivalent reflections generally were in excellent agreement with each other. However, we have observed this frequently in  $\text{CuBr}_2$  salts. We believe it is due to the occurrence of photochemical reduction of the  $\text{Cu(II)}$  ion to  $\text{Cu(I)}$  in the crystal. Nevertheless, the basic structure is certainly correct, and the heavy-atom positional parameters cannot be far from their true values. Final positional parameters are given in Table I and interatomic distances and angles in Table II.

### Description of Structure

The structure consists of well-defined centrosymmetric  $\text{Cu}_2\text{Br}_4(\text{C}_5\text{H}_5\text{N})_2$  dimers which stack on top of one another to form linear chains as illustrated in Figure 1. The heavy-atom framework is essentially planar, but the pyridine rings are twisted  $54^\circ$  from the dimer plane, thus reducing the intradimer C-H...Br interactions. The bridging Cu-Br distances (2.456 and 2.464 Å) are approximately 0.05 Å longer than the terminal Cu-Br distance (2.412 Å). As anticipated, these distances are about 0.15 Å longer than in analogous chloride dimers. The bridging Cu-Br-Cu angle is  $95.5^\circ$ , again similar to that found in planar chloride dimers. The interdimer packing is closely related to that in  $\text{KCuCl}_3$ <sup>13</sup> and  $\text{CuCl}_2 \cdot \text{C}_5\text{H}_5\text{N}$ .<sup>14</sup> As such, both the fifth and sixth coordination sites of each copper atom are occupied, but the two interdimer Cu-Br distances are very different, 2.928 and 3.331 Å. Similar variations are observed in interdimer Cu-Cl distances in the two chloride salts. Specifically, the distances are 2.941 and 3.113 Å in  $\text{KCuCl}_3$  and 2.79 and 3.08 Å in  $\text{CuCl}_2 \cdot \text{CH}_3\text{CN}$ . The former distance is such that Br(1) just makes van der

Table II. Bond Distances and Angles for  $\text{Cu}_2\text{Br}_4(\text{C}_5\text{H}_5\text{N})_2^a$ 

(a) Distances around the Copper Atom			
Cu-Br(1)	2.412 (4)	Cu-Br(2 <sup>b</sup> )	2.464 (6)
Cu-Br(1 <sup>a</sup> )	2.928 (4)	Cu-Br(2 <sup>c</sup> )	3.331 (4)
Cu-Br(2)	2.456 (5)	Cu-N	1.996 (27)
(b) Angles around the Copper Atom			
Br(1)-Cu-N	92.5 (7)	Br(1)-Cu-Br(2 <sup>c</sup> )	84.9 (1)
Br(1 <sup>a</sup> )-Cu-N	91.8 (6)	Br(2)-Cu-Br(2 <sup>b</sup> )	84.4 (2)
Br(2 <sup>b</sup> )-Cu-N	174.7 (6)	Br(2)-Cu-Br(1 <sup>a</sup> )	93.6 (1)
Br(2 <sup>c</sup> )-Cu-N	92.0 (6)	Br(2 <sup>c</sup> )-Cu-Br(1 <sup>a</sup> )	76.6 (2)
Br(1)-Cu-Br(2)	169.6 (2)	Br(2 <sup>b</sup> )-Cu-Br(1 <sup>a</sup> )	92.7 (1)
Br(1)-Cu-Br(2 <sup>b</sup> )	90.6 (2)	Br(2 <sup>b</sup> )-Cu-Br(2 <sup>c</sup> )	84.0 (1)
Br(1)-Cu-Br(1 <sup>a</sup> )	95.8 (2)		
(c) Distances and Angles in Ring			
N-C(1)	1.27 (4)	C(1)-N-C(5)	117.2 (26)
N-C(5)	1.45 (3)	N-C(1)-C(2)	125.6 (25)
C(1)-C(2)	1.46 (4)	C(1)-C(2)-C(3)	112.9 (24)
C(2)-C(3)	1.39 (4)	C(2)-C(3)-C(4)	124.1 (30)
C(3)-C(4)	1.35 (4)	C(3)-C(4)-C(5)	119.1 (25)
C(4)-C(5)	1.35 (4)	C(4)-C(5)-N	120.8 (23)
(d) Intradimer Distances and Angles			
Cu-Cu <sup>b</sup>	3.643 (9)	Br(2)-Br(2)	3.307 (6)
Cu-C(1)	2.903 (30)	Br(2)-C(5)	3.450 (30)
Cu-C(5)	2.978 (30)	Br(1)-Br(2 <sup>b</sup> )	3.466 (5)
Br(1)-N	3.198 (23)	Br(1)-C(1)	3.508 (28)
Br(2)-N	3.212 (25)	Cu-Br(2)-Cu <sup>b</sup>	95.5 (2)
(e) Interdimer Distances			
Br(1)-C(1 <sup>c</sup> )	3.511 (30)	C(1)-C(5 <sup>a</sup> )	3.832 (36)
Br(1)-N <sup>c</sup>	3.581 (24)	C(2)-C(4 <sup>a</sup> )	3.911 (35)

<sup>a</sup> Symmetry transformations: (a)  $x, 1 + y, z$ ; (b)  $1 - x, 2 - y, 1 - z$ ; (c)  $x, -1 + y, z$ .

Waals contact with the bridging bromine atoms on adjacent dimers. This produces a decided pyramidal distortion to the copper stereochemistry, trans N-Cu-Br(2) and Br(1)-Cu-Br(2) angles being 174.7 and  $169.6^\circ$ , respectively.

In summary, there is little anomaly in the observed stereochemistry of this salt and it is concluded that the increase in ionic radius between  $\text{Cl}^-$  and  $\text{Br}^-$  has little steric consequence in square-planar copper bromide complexes.

### Magnetic Behavior

As can be seen from Figure 3, the compound exhibits definite, but weak, antiferromagnetic interactions. The high-temperature data ( $T > 61$  K) are quite accurately reproduced by the Curie-Weiss law, with  $C = 0.401$  (0.029) and  $\theta = -18.4$  (4.6). In the low-temperature region, the susceptibility reaches a maximum near 10 K. In order to account for this behavior, we modeled the susceptibility in several different ways on the basis of the structural characteristics of the salt. For completeness, this included (i) noninteracting dimers,<sup>15</sup> (ii) Heisenberg dimers corrected for mean field interactions,<sup>16</sup> (iii) 1-D Ising chain of spin  $1/2$  ions,<sup>17</sup> (iv) 1-D

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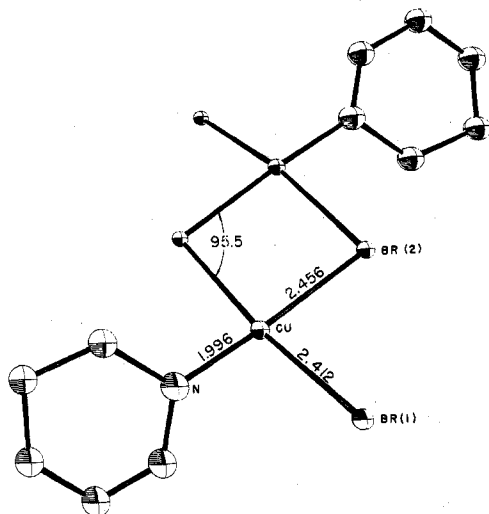


Figure 2. Illustration of the  $\text{Cu}_2\text{Br}_4(\text{py})_2$  dimer unit.

Table III. Exchange Parameters for Various Models in  $\text{cm}^{-1}$

model	$2J = \Delta E$	$2J'$	
		interdimer	interchain
(i) isolated dimer	-27.7 (6.3)		
(ii) dimer + mean field	-8.9 (1.1)	-25.0 (2.3)	
(iii) spin $1/2$ Ising chain	-22.1 (3.7)		
(iv) spin $1/2$ Heisenberg chain in classical limit	-25.7 (4.8)		
(v) spin $1/2$ Heisenberg chain + mean field	-18.3 (4.7)		-16.7 (5.5)
(vi) anisotropic Ising	-30.1 (2.4)		
(vii) Ising chain of dimers	-11.0 (3.7)	-11.0 (2.9)	

Heisenberg chain of spin  $1/2$  ions,<sup>18</sup> (v) 1-D Heisenberg chain with a mean field correction, (vi) anisotropic Ising chain of spin  $1/2$ ,<sup>19</sup> and (vii) Ising chain of Heisenberg dimers.<sup>12</sup> Neither the isolated dimer or 1-D Ising model gave reasonable fits to the data. The Ising model substantially underestimated the susceptibility in the region near the maximum. The 1-D Heisenberg model with the mean field correction fit the data quite well down to the maximum but slightly underestimated  $\chi$  at the maximum and overestimated  $\chi$  at very low temperatures. The Heisenberg dimer with mean field modifications gave a reasonable fit to the data; however, the mean field parameter was too large to be physically meaningful. The best fit over the complete temperature range was obtained with the model for an Ising chain of Heisenberg dimers. This reproduced the data to within 1%, except near the maximum in  $\chi$ , where the errors were in the neighborhood of 5%. The solid line in Figure 3 shows the fit for this model. The results for the various models are summarized in Table III. We concluded that the spins are antiferromagnetically coupled within and between the dimers, with an exchange coupling for each process being approximately  $11 \text{ cm}^{-1}$ . This model has been used to successfully treat linear chains of dimers where the interdimer coupling,  $2J'$ , is much less than the intradimer coupling,  $2J$ .<sup>20</sup> It is surprising, however, that it gives a superior fit in this situation, where  $2J \approx 2J'$ . This is probably more a result of the mathematics of the model, however, than the physics of the interactions. Neither the inter- nor intradimer coupling is expected to be pure Ising or Heisenberg exchange but will rather have some (perhaps substantial) anisotropic

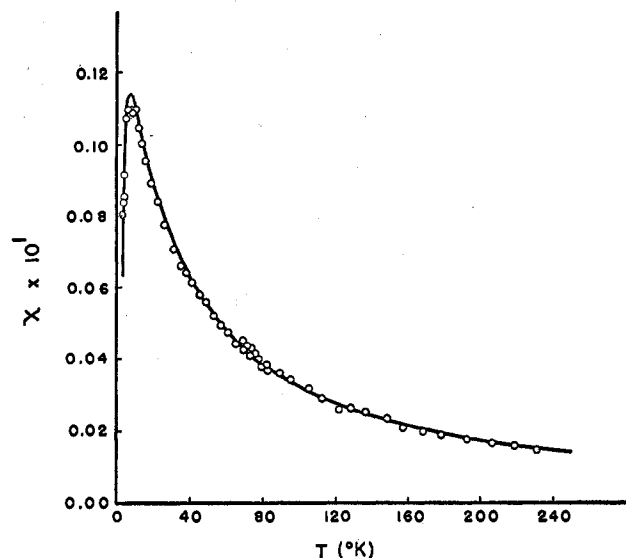


Figure 3. A plot of the molar susceptibility  $\chi$  vs.  $T$  for  $\text{Cu}_2\text{Br}_4(\text{py})_2$ . The Ising chain of Heisenberg dimers model fit is shown as a solid line.

character to it. Thus, a model which incorporates both types of interactions, even if it partitions it incorrectly, could be expected to give a better fit than either model on the basis of limiting cases.

The data analysis for this salt illustrates the problem in attempting to extract several magnetic parameters from susceptibility data. We found that the data could be reproduced quite accurately by several different models and that it was necessary to use physical intuition to decide which were reasonable models for the system.

### Discussion

The role of structural and electronic properties in determining the strength of exchange interactions is of interest. It has been shown that the coupling varies linearly with bridging angle in planar hydroxy-bridged copper dimers<sup>21</sup> and that it varies monotonically with distortion of the copper coordination sphere in other copper dimers.<sup>22</sup> In this case, we observe the role that the nature of the nonbridging ligands plays in determining these interactions by comparing  $\text{CuBr}_2\cdot\text{py}$  and  $\text{KCuBr}_3$ . Since  $\text{KCuBr}_3$  is isostructural with  $\text{KCuCl}_3$ , the Cu-Br-Cu bridging angles and the distortions of the  $\text{Cu}^{2+}$  coordination sphere should be nearly the same in  $\text{CuBr}_2\cdot\text{py}$  and  $\text{KCuBr}_3$ . Nonetheless, the exchange constants are dramatically different,  $2J = -11 \text{ cm}^{-1}$  for  $\text{CuBr}_2\cdot\text{py}$  and  $2J = -135 \text{ cm}^{-1}$  for  $\text{KCuBr}_3$ .<sup>23</sup> The difference in exchange coupling must be related to the greater electron-withdrawing nature of the pyridine ligand as compared with the bromide ion. This would be expected to decrease the unpaired electron density at the trans bromide ion, particularly in the Br 4s orbital. Since this orbital provides the principal antiferromagnetic pathway, the lower exchange coupling is not surprising. We anticipate it should be possible to tune the strength of the exchange coupling in  $\text{CuBr}_2\cdot\text{L}$  complexes by varying the electron-withdrawing capability of L.

Registry No.  $\text{Cu}_2\text{Br}_4(\text{C}_5\text{H}_5\text{N})_2$ , 73505-51-8.

**Supplementary Material Available:** A listing of observed and calculated structure factor amplitudes (3 pages). Ordering information is given on any current masthead page.

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