Na_2S_5 were determined at various temperatures.

5. ESCA work on the polysulfides provides conclusive evidence of the unbranched chain structure of the polysulfide linkage.

Registry No. K_2S_3, 37488-75-8; Na_2S_3, 37488-76-9; Na_2S_6, 37188-08-2; K_2S_6, 37188-07-1; Na_2S_5, 37488-74-0; Na_2S_4, 37488-78-1; Na_2S_2, 22868-13-9.

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Exchange Interactions in Polynuclear Transition Metal Complexes. Structural Properties of Cesium Tribromocuprate(II), $CsCuBr_3$, a Strongly Coupled Copper(II) System

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The crystal structure of the antiferromagnetic (μ_{eff} 0.11 BM at 23°) compound cesium tribromocuprate(II), $CsCuBr_3$, has been determined from three dimensional X-ray (Mo Kα) counter data. The compound crystallizes in the orthorhombic system, space group $C222_1$ ($D_2{}^5$), with $a = 12.776$ (2) Å, $b = 7.666$ (2) Å, $c = 12.653$ (4) Å (23°), $\rho_c = 4.67$, $\rho_o = 4.52$ (4) g/cm^3, $V = 1239.2$ Å^3, $Z = 8$. Full-matrix-least-squares refinement based on 842 unique reflections gave final discrepancy factors of $R_1 = 0.069$ and $R_2 = 0.074$ on F. The structure contains facial-bridged $[Cu_2Br_9]^{5-}$ dimers, which share corners with six other dimers in a three-dimensional network. A comparison of the structures of $CsCuBr_3$ and $CsCuCl_3$ and a consideration of the Goodenough-Kanamori rules strongly suggests that spin coupling through one of the linear Cu-Br-Cu bridge groups is responsible for the low magnetic susceptibility observed for the compound at room temperature. A reexamination of the structure of Cs_2CuBr_4, cesium tetrabromocuprate(II), using three-dimensional counter data, is also reported. The details of the structure are in substantial agreement with those reported previously (B. Morosin and E. C. Lingafelter, *Acta Crystallogr.*, **13**, 807 (1960)), although there are some differences in the copper-bromine bond lengths. Least-squares refinement based on 634 unique reflections gave final discrepancy factors of $R_1 = 0.079$ and $R_2 = 0.069$. The space group is *Pnma* ($D_{2h}{}^{16}$) with $a = 10.168$ (4), $b = 7.954$ (3), $c = 12.914$ (5) Å, $\rho_c = 4.12$, $\rho_o = 4.02$ (6) g/cm^3, $V = 1044.4$ Å^3.

Introduction

Kato, Jonassen, and Fanning[1] have noted that, in many cases, copper(II) complexes containing the bromide ion have magnetic moments lower than those of the corresponding chloride complexes. Inoue, Kishita, and Kubo[2] recently investigated the magnetic susceptibilities of $KCuBr_3$ and $CsCuBr_3$ and found that $KCuBr_3$ is isostructural with $KCuCl_3$[3] with μ_{eff} equal to 1.52 and 0.83 BM at room and liquid nitrogen temperatures, respectively. $CsCuBr_3$ was reported to have only a very slight paramagnetism and it was concluded that the unpaired electrons of the copper atoms are almost completely coupled. The unusual magnetic behavior of this copper(II) complex suggested that a complete structural study of $CsCuBr_3$ would be of considerable interest. In this paper, we present the results of a single-crystal analysis of $CsCuBr_3$ and a reexamination of the crystal structure of Cs_2CuBr_4.

Experimental Section

Crystal Preparation. Both $CsCuBr_3$ and Cs_2CuBr_4 are obtained as products when aqueous solutions 2 *M* in $CuBr_2$ and 1 *M* in $CsBr_3$ are mixed together. Since both $CsCuBr_3$ and Cs_2CuBr_4 are dark red and since recrystallization of $CsCuBr_3$ from water results in disproportionation according to the reaction

$$3CsCuBr_3 \xrightarrow{H_2O} Cs_2CuBr_4 + CsCuBr_3 + CuBr_2$$

the separation and identification of $CsCuBr_3$ is difficult. The composition and crystal habit (see below) of Cs_2CuBr_4 were first identified by single-crystal X-ray photographs. $CsCuBr_3$ was then separated mechanically from Cs_2CuBr_4 under a microscope. Both $CsCuBr_3$ and Cs_2CuBr_4 appear to be air stable.

Anal. Calcd for $CsCuBr_3$: Cu, 14.54; Br, 54.98. Found: Cu, 13.94; Br, 54.56.

Magnetic Susceptibility Measurements. The room-temperature magnetic susceptibility measurements were made on a standard Gouy apparatus with a Sartorius Model 2604 balance and an Alpha Al-7500 electromagnet with 4-in. diameter pole faces. A 1.9-cm pole gap was used for all measurements. A glass sample tube having a diameter of 8 mm and a sample length of 14.25 cm was suspended below the balance in a Plexiglas chamber to eliminate air-currents. Temperatures were read from a thermometer placed in this chamber; $HgCo(NCS)_4$ was used as a standard to "calibrate" the balance.[4]

Data Collection and Solution of the Structures. Intensity data were measured on an automated Picker four-circle X-ray diffractometer which utilized monochromatic Mo Kα radiation (oriented graphite crystal monochromator) for data collection. A symmetrical 2θ scan was taken about the position calculated for Kα_1 with stationary-crystal, stationary-counter background counts of 10 sec being made at the beginning and the end of the scan range. The scan range was 1.5° plus an increment determined by the wavelength dispersion. Copper foil attenuators of various thicknesses were automatically inserted in front of the counter aperture whenever the counting rate exceeded 10,000 counts/sec. Observed reflections were defined by the criterion $I_{obsd} > 3\sigma_c(I)$ where $\sigma_c = [I_c + 0.25(t_c/t_b)^2 (B_1 + B_2)]^{1/2}$, I_c is the total integrated counts, t_c/t_b is the ratio of the time spent counting the peak intensity to the time spent counting the background intensities, and B_1 and B_2 are back-

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[1] M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, **64**, 99 (1964).

[2] M. Inoue, M. Kishita, and M. Kubo, *Inorg. Chem.*, **6**, 900 (1967).

[3] R. D. Willett, C. Dwiggins, Jr., R. F. Kruh, and R. E. Rundle, *J. Chem. Phys.*, **38**, 2429 (1963).

[4] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

Table I. Positional Parameters for $CsCuBr_3$

Atom	x	y	z
Cs(1)	0.3255 (2)	0	0
Cs(2)	0	0.0139 (4)	$^1/_4$
Cu	0.1559 (2)	0.5046 (5)	0.1287 (2)
Br(1)	0.3025 (3)	$^1/_2$	0
Br(2)	0.0747 (2)	0.2641 (3)	0.0295 (2)
Br(3)	0	0.5291 (5)	$^1/_4$
Br(4)	0.2607 (3)	0.2614 (5)	0.2762 (3)

Table II. Individual Thermal Parameters for $CsCuBr_3$

	β_{11}[a]	β_{22}	β_{33}	β_{12}[b]	β_{13}	β_{23}
Cs(1)	0.0033 (2)	0.0092 (6)	0.0045 (3)	0	0	−0.0009 (3)
Cs(2)	0.0042 (2)	0.0136 (6)	0.0040 (2)	0	0.0004 (1)	0
Cu	0.0044 (2)	0.0084 (7)	0.0033 (3)	0.0009 (5)	0.0006 (2)	0.0002 (3)
Br(1)	0.0008 (2)	0.0116 (9)	0.0018 (3)	0	0	−0.0002 (4)
Br(2)	0.0034 (2)	0.0044 (5)	0.0018 (1)	0.0022 (3)	−0.0000 (1)	−0.0015 (3)
Br(3)	0.0024 (2)	0.0006 (7)	0.0060 (4)	0	0.0009 (3)	0
Br(4)	0.0057 (3)	0.0260 (9)	0.0080 (3)	−0.0059 (5)	−0.0003 (2)	−0.0100 (5)

[a] The form of the thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Restrictions on the temperature parameters: (i) for Cs(1) and Br(1), $\beta_{12} = \beta_{13} = 0$; (ii) for Cs(2) and Br(3), $\beta_{12} = \beta_{23} = 0$.

ground counts. The raw intensities were corrected for background, Lorentz, and polarization effects ($(\cos^2 2\theta_m + \cos^2 2\theta)/(1 + \cos^2 2\theta_m)$, where θ_m and θ are the Bragg angles of the monochromator crystal and specimen crystal, respectively), and absorption. Weights ($1/\sigma^2(F)$) were chosen from a Hughes scheme:[5] $F_o \leqslant 4F_{min}$, $\sigma(F_o) = 4F_{min}/F_o$; $F_o > 4F_{min}$, $\sigma(F_o) = F_o/4F_{min}$, where F_{min} was taken as the magnitude of the minimum observed reflection. The scattering factors for Cs^+, Cu^{2+}, and Br^- were taken from the compilation of Hanson and Pohler.[6] Anomalous dispersion corrections ($\Delta f'$ and $\Delta f''$) for all atoms were taken from the compilation of Cromer[7] and applied to the calculated structure amplitudes.

A. $CsCuBr_3$. Cs_2CuBr_4 crystals were found to crystallize in a prismatic microblock shape, while the majority of $CsCuBr_3$ crystals were obtained in a long prismatic habit. The long prismatic crystals of $CsCuBr_3$ were demonstrated to be twinned by Weissenberg and precession techniques. A single crystal was finally found which was shaped like an irregular cone with a hole in the bottom of the cone. Since further search for an untwinned crystal was not successful, this crystal was mounted and used for subsequent data collection. The cone was 0.44 mm in height with a base diameter of 0.32 mm. A preliminary X-ray investigation suggested that the crystal system was hexagonal with Laue symmetry $6/m$; however, a careful comparison of absorption corrected intensities from symmetry-related reflections showed that the crystal system was pseudohexagonal and actually orthorhombic. The crystal was mounted on the diffractometer so that the Φ axis of the diffractometer was coincident with the orthorhombic [210] direction. Systematic absences for the orthorhombic indexing as determined from precession and Weissenberg photographs were hkl, $h + k \neq 2n$; and $00l$, $l \neq 2n$ so that the space group was uniquely indicated to be $C222_1$. The orthorhombic lattice constants and standard deviations obtained by a least-squares fit to the angular setting of 12 reflections are a = 12.776 (3) Å, b = 7.666 (2) Å, c = 12.653 (4) Å, and V = 1239.25 Å^3 (25°, λ(Mo Kα) 0.71069 Å). The calculated density of 4.67 g/cm^3 for 8 $CsCuBr_3$ units/unit cell can be compared with the observed density of 4.52 (4) g/cm^3.

Two symmetry-related sets of intensities, which gave a total of 3368 reflections (including a check on the systematic absences due to face centering), were measured. A total of 842 unique reflections was available for the structural analysis after excluding systematic absences. Since the linear absorption coefficient was large (μ = 298.45 cm^{-1}) and the crystal was an odd shape, the absorption correction is very important (see below).

The $CsCuBr_3$ structure was solved by Patterson and Fourier techniques. Two bromine atoms and the cesium atom were found from the Patterson map and subsequent Fourier[8] maps revealed the remaining atoms. Several cycles of least-squares refinement,[9] varying one scale factor, and isotropic thermal parameters converged at R_1 = 0.190. A difference Fourier map was calculated and did not show any peaks with electron density greater than 1.4 e/Å^3. This confirmed that the model was correct and that there were no solvent molecules in the crystal structure. Twenty-one faces were defined in order to determine the path lengths of the X-ray beam for different crystal orientations and absorption corrections were then made on the two symmetry sets of data using the program ORABS2. These two symmetry sets of data were averaged to give 842 unique reflections, of which 32 were judged as unobserved. Further least-squares refinement, varying one scale factor, the positional and isotropic temperature parameters, based on the averaged data set, reduced R_1 to 0.131. The weighting scheme described above and the real and imaginary anomalous dispersion corrections[7] for cesium, copper, and bromine atoms were then applied. Three further cycles of isotropic refinement gave

$$R_1 = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|} = 0.245$$

$$R_2 = (\Sigma w(F_o - F_c)^2/\Sigma wF_o^2)^{1/2} = 0.111$$

Introduction of anisotropic thermal parameters for all atoms and four subsequent least-squares refinements (one scale factor, positional and thermal parameters) gave as final discrepancy indices[10] R_2 = 0.069 excluding unobserved reflections and R_2 = 0.074 including unobserved reflections.

The estimated standard deviation of an observation of unit weight (ERF) given by $[\Sigma w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$ (where NO is the number of observations and NV is the number of variables) was 4.01 and is probably high due to systematic errors in the absorption corrections. The background on the final difference Fourier map did not exceed 0.9 e/Å^3. The positional and thermal parameters derived from the last cycle of least-squares refinement are presented in Tables I and II along with their estimated standard deviations.

B. Cs_2CuBr_4. Precession and Weissenberg photographs showed that the Cs_2CuBr_4 crystal system is orthorhombic with absences $0kl$, $k + l \neq 2n$; and $hk0$, $h \neq 2n$. These absences are consistent with the orthorhombic space groups $Pnma$ (D_{2h}^{16}) (centric) and $Pn2_1a$ (C_{2v}^9) (acentric). Lattice constants and standard deviations obtained from a least-squares fit to the angular settings of 12 reflections which were carefully centered on the diffractometer are a = 10.168 (4) Å, b = 7.954 (3) Å, c = 12.914 (5) Å, and V = 1044.4 Å^3 (25°, λ(Mo Kα) 0.71069 Å). The calculated density is 4.12 g/cm^3 for 4 Cs_2CuBr_4 units/unit cell and the averaged observed density measured by the pycnometric method using bromobenzene is 4.02 (6) g/cm^3.

A crystal was ground into a sphere of mean diameter 0.3 mm by a modification of Bond's method[11] and mounted along [210] in a glass capillary. The sample crystal was oriented so that the c^* axis was offset by approximately 1° from the Φ axis of the diffractometer. A takeoff angle of 1.51° was found to give approximately 80% of

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(5) For a discussion of the appropriateness of this choice, see S. C. Abrahams, *Acta Crystallogr., Sect. A*, **25**, 165 (1969), and included references.

(6) H. P. Hanson and R. F. Pohler, *Acta Crystallogr.*, **21**, 435 (1966).

(7) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

(8) J. Gvildys, "A Two- and Three-Dimensional Fourier Summation Program," Argonne National Laboratory, Argonne, Ill., 1968.

(9) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, a Fortran Crystallographic Least-Squares Program," U. S. Atomic Energy Commission Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(10) Listings 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-73-441.

(11) W. L. Bond, *Rev. Sci. Instrum.*, **22**, 344 (1951).

Table III. Positional and Isotropic Thermal Parameters for Cs_2CuBr_4

	x	y	z	B,[a] Å^2
Cs(1)	0.1290 (4)[a]	$^1/_4$	0.1058 (4)[a]	3.7
	0.1267 (4)		0.1055 (4)	
Cs(2)	0.0049 (4)[a]	$^1/_4$	0.6694 (4)[a]	3.0
	0.0057 (4)		0.6706 (3)	
Cu	0.2311 (7)[a]	$^1/_4$	0.4187 (7)[a]	2.0
	0.2286 (6)		0.4200 (5)	
Br(1)	0.0010 (6)[a]	$^1/_4$	0.3819 (6)[a]	3.3
	0.0072 (7)		0.3798 (5)	
Br(2)	0.3440 (6)[a]	$^1/_4$	0.5797 (6)[a]	3.1
	0.3413 (6)		0.5778 (5)	
Br(3)	0.2960 (6)[a]	0.5138 (6)[a]	0.3546 (6)[a]	4.0
	0.2949 (4)	0.5151 (6)	0.3540 (4)	

[a] Taken from Morosin and Lingafelter.[12]

Table IV. Individual Anisotropic Thermal Parameters of Atoms in Cs_2CuBr_4

	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{23}	β_{13}
Cs(1)	0.0053 (5)	0.0158 (10)	0.0099 (5)	0	0.0001 (4)	0
Cs(2)	0.0064 (5)	0.0094 (10)	0.0064 (4)	0	−0.0008 (4)	0
Cu	0.0073 (9)	0.0008 (21)	0.0065 (8)	0	−0.0000 (8)	0
Br(1)	0.0098 (9)	0.0171 (20)	0.0022 (7)	0	−0.0022 (7)	0
Br(2)	0.0093 (9)	0.0241 (19)	0.0011 (4)	0	0.0007 (5)	0
Br(3)	0.0132 (7)	0.0147 (9)	0.0111 (5)	0.0005 (6)	0.0007 (4)	0.0016 (5)

[a] The form of the thermal ellipsoid is that given in Table I. The restrictions for all atoms except Br(3) are that $\beta_{12} = \beta_{13} = 0.0$.

the maximum intensity obtainable from the variation of intensity of a reflection with takeoff angle. A typical full-width at half-height measurement for an ω scan of a resolved $K\alpha_1$ peak was 0.11°, indicating a satisfactorily low mosaic spread. The intensities of two standard reflections, measured after every 50 reflections, showed no significant variation with time. A total of 2188 intensities was collected in the octants hkl and $\bar{h}\bar{k}\bar{l}$, and averaged to yield an independent set of 1118 intensities of which 634 were judged to be observed and were used in the structure refinement. The similarity of the observed lattice constants to those reported for Cs_2CuBr_4 by Morosin and Lingafelter[12] was initially ignored and the symbolic addition procedure for sign determination was used to solve the structure (assuming space group *Pnma*). By successive assignment of the origin and two symbolic signs, 81 reflections with $|E|$ greater than 1.650 were assigned signs. An E map[8] based on these 81 signed reflections clearly showed five peaks on the mirror plane at $y = {}^1/_4$ and one peak at $y = 0$. One of the peaks at $y = {}^1/_4$ had four nearest neighbor peaks with bond distances in the neighborhood of 2.5 Å. This peak was assumed to be due to a copper atom and the adjacent four atoms were taken as bromine atoms. The remaining peaks were assigned as cesium atoms. A trial model based on these assignments gave an R_1 index of $R_1 = 0.245$. The true chemical formula was thereby confirmed to be Cs_2CuBr_4 instead of $CsCuBr_3$. At this stage, the real and imaginary anomalous dispersion corrections[7] for all atoms were applied. Least-squares refinement[9] (one scale factor, the positional and isotropic temperature parameters) led to an R_1 index of 0.090 after four cycles. Three more cycles of anisotropic refinement[10] gave the final discrepancy factors $R_1 = 0.079$ and $R_2 = 0.069$. The final atomic positions and individual anisotropic temperature factors are listed in Tables III and IV and compared to Morosin and Lingafelter's earlier film data results.[12]

Results and Discussion

$CsCuBr_3$. $CsCuBr_3$ is a unique example of the complexes $CsMX_3$ (M = divalent first-row transition metal cation; $X^- = Cl^-$ or Br^-) in that it has a *three-dimensional* infinite network of $Cu_2Br_9^{5-}$ dimeric units. Each dimer is composed of two face-shared distorted octahedra with copper atoms at the centers and bromine atoms at the corners (Figure 1 and Table V). In contrast to the structure of $CsCuCl_3$[13] in which a face-shared arrangement of $Cu_2Cl_9^{5-}$ groups is repeated indefinitely in one direction, each of the six terminal bromine atoms in a dimer unit of $Cu_2Br_9^{3-}$ acts as a linear bridge (Cu-Br-Cu angles of 171.5 (2) and 167.6 (2)°) to another dimeric unit (Figure 2).

The six copper-bromine bond lengths can be conveniently placed into two groups: "equatorial" bonds of 2.456 (4), 2.482 (4), 2.522 (3), and 2.541 (5) Å and "axial" bonds of 2.868 (4) and 2.959 (5) Å. The difference between the average axial Cu-Br bond distance and the average equatorial Cu-Br bond distance is 0.41 Å, which is less than in $CsCuCl_3$, where the axial Cu-Cl bond distance is 2.78 Å and the equatorial bond distances are 2.28 and 2.35 Å. The average equatorial Cu-Br distance (2.50 ± 0.044 Å) is larger than that observed in $CuBr_2$[14] (2.40 Å) and the shortest Cu-Br distance in five-coordinate $Cu^{II}Br$ complexes.[15] The average axial Cu-Br distance (2.914 ± 0.045 Å) is considerably shorter than that in $CuBr_2$[14] (3.18 Å) or dibromobis(2-methylpyridine)copper(II)[15] (3.87 Å). The copper-copper distance in a dimer is 3.257 (5) Å, which is 0.21 Å shorter than the copper-copper distance in the close-packed $CuBr_2$ crystal.

Table V. Bond Distances and Angles for $CsCuBr_3$

Bond Distances, Å

Cu-Br(2)	2.460 (4)	Cu-Br(3)	2.522 (2)	Cu-Br(2)′	2.868 (3)
Cu-Br(1)	2.482 (3)	Cu-Br(4)′	2.541 (4)	Cu-Br(4)	2.959 (4)

Bond Angles, Deg

Br(1)-Cu-Br(2)	88.45 (12)	Br(1)-Cu-Br(2)′	79.86 (10)
Br(1)-Cu-Br(3)	175.17 (18)	Br(1)-Cu-Br(4)	93.62 (11)
Br(1)-Cu-Br(4)′	90.32 (13)	Br(2)-Cu-Br(2)′	87.38 (11)
Br(2)-Cu-Br(3)	91.89 (13)	Br(2)-Cu-Br(4)	92.31 (14)
Br(2)-Cu-Br(4)′	177.46 (32)	Br(2)′-Cu-Br(3)	95.34 (11)
Br(2)′-Cu-Br(4)	173.48 (20)	Br(2)′-Cu-Br(4)′	90.20 (14)
Br(3)-Cu-Br(4)	91.17 (12)	Br(3)-Cu-Br(4)′	89.14 (14)
Br(4)-Cu-Br(4)′	89.97 (8)	Cu-Br(1)-Cu′	82.02 (16)
Cu-Br(2)-Cu′	74.94 (12)	Cu-Br(2)′-Cu′	74.94 (10)
Cu-Br(3)-Cu(a)	171.46 (24)	Cu-Br(4)-Cu(b)	167.60 (18)
Cu-Br(4)′-Cu(c)	167.60 (18)		

Within a dimer, three bromine atoms bridge two copper atoms with Cu(dimer 1)-Br-Cu(dimer 1) angles of approximately 80° (see Table V). The Br-Br distances in the terminal bromine triangles of a dimer are 3.553, 3.899, and 3.927 (4) Å, while Br-Br distances in the bromine triangle which bridges two Cu atoms are 3.447 (3), 3.447 (3), and 3.680 (2) Å. The distances between bromine atoms in the two adjacent triangles can be divided into a group with distances of 3.980 (3) and 3.991 (2) Å and another group with smaller distances of 3.562 (4) and 3.580 (3) Å. (See Table VI.) The cesium atoms are in close-packed dodecahedral holes (Table VII). There are six bromine atoms adjacent to a cesium atom in a plane with three bromine atoms above and three below.

It is appropriate at this point to examine the magnetic properties of $CsCuBr_3$ and their relation, if any, to the structural features described above.

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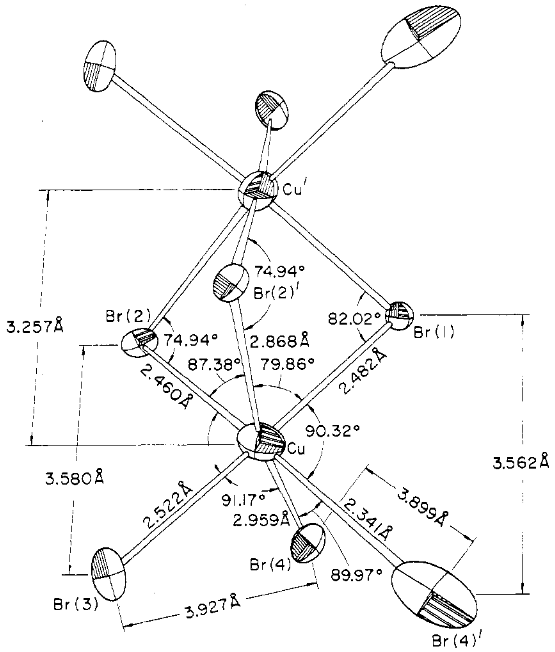
(12) B. Morosin and E. C. Lingafelter, *Acta Crystallogr.*, **13**, 807 (1960).

(13) A. W. Schlueter, R. A. Jacobson, and R. E. Rundle, *Inorg. Chem.*, **5**, 277 (1966).

(14) L. Helmholz, *J. Amer. Chem. Soc.*, **69**, 886 (1947).

(15) A summary of Cu-Br bond distances is given by P. Singh, D. Y. Jeter, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, **11**, 1657 (1972).



Figrue 1. A perspective view of the $[Cu_2Br_9]$ dimer unit in $CsCuBr_3$. Br(4) is related to Br(4)' by the transformation $^1/_2 - y, ^1/_2 + y, ^1/_2 - z$. Br(2) is related to Br(2)' by the symmetry x, y, z. The second relation also holds for Cu and Cu'.

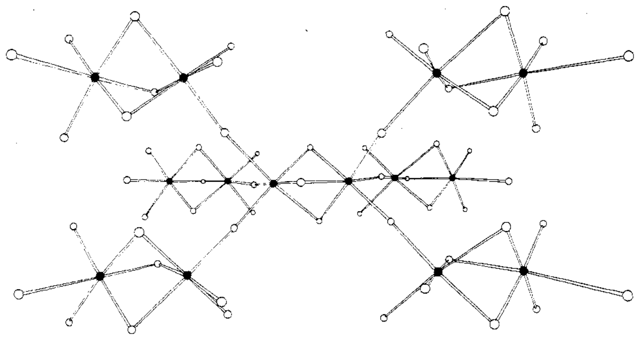


Figure 2. A perspective view normal to the [001] direction of the neighbor dimer units around a $[Cu_2Br_9]$ dimer unit in $CsCuBr_3$.

Table VI. Selected Nonbonded Distances for $CsCuBr_3$

Near Neighbor Distances within a Dimer Unit, Å			
Cu-Cu'	3.257 (5)	Br(3)-Br(4)	3.553 (3)
Br(1)-Br(2)	3.447 (3)	Br(4)-Br(4)'	3.899 (1)
Br(1)-Br(2)'	3.680 (2)	Br(1)-Br(4)'	3.562 (4)
Br(3)-Br(4)	3.927 (4)	Br(2)-Br(4)	3.580 (3)
Br(2)-Br(2)'	3.680 (2)	Br(2)'-Br(3)	3.991 (2)
		Br(1)-Br(4)	3.980 (3)
Near Neighbor Distances between Adjacent Dimer Units,[a] Å			
Br(1)-Br(2)(d)	4.041 (3)	Cu-Cu(b)(c)	5.465 (2)
Br(2)-Br(2)(e)	4.118 (4)	Cu-Cu(d)(e)	7.450 (5)
Cu-Cu(a)	5.029 (5)		

[a] (a), (b), and (c) are dimer units joined with the parent dimer unit through terminal bromine atoms; (d) and (e) are dimer units which parallel the parent dimer unit along the crystallographic *c* axis.

Table VII. Selected Cs-Br Distances in $CsCuBr_3$ (Å)

Cs(1)-Br(1)	3.844 (0)	Cs(2)-Br(1)(a)	4.048 (2)
Cs(1)-Br(2)	3.809 (2)	Cs(2)-Br(2)	3.518 (3)
Cs(1)-Br(2)(d)	3.680 (2)	Cs(2)-Br(2)(f)	4.238 (3)
Cs(1)-Br(3)(d)	3.876 (1)	Cs(2)-Br(3)	3.949 (5)
Cs(1)-Br(4)	3.547 (3)	Cs(2)-Br(4)	3.848 (3)
Cs(1)-Br(4)''[a]	4.112 (3)	Cs(2)-Br(4)(b)	3.633 (3)

[a] Br(4)'' is the Br(4) atom at the other terminus of the original dimer unit.

Only a slight paramagnetism, $\chi_A = 0.14 \times 10^{-3}$ cgs emu, has been observed for $CsCuBr_3$ in the temperature range of 80-300°K. We have repeated these measurements and found a value of -0.16×10^{-6} cgs emu/g for the magnetic susceptibility of $CsCuBr_3$ at room temperature (23°). After correction for the diamagnetic contribution (in cgs emu) of all ions (Cu^{2+}, -11×10^{-6}; Br^-, -36×10^{-6}; Cs^+, -31×10^{-6}), a small paramagnetic susceptibility, $\chi_A = 0.80 \times 10^{-4}$ cgs emu, was obtained for the molar susceptibility. Using $\mu = 2.83(\chi_A - (N\alpha)T)^{1/2}$, where N stands for the temperature-independent paramagnetism (assumed to be equal to 60×10^{-6} cgs emu for Cu(II)), the effective magnetic moment per copper atom is 0.11 BM. This value, like that reported earlier, is not experimentally different from zero and agrees with the earlier conclusion that the unpaired electrons of the copper atoms are completely coupled.

The magnetic susceptibility of $CsCuCl_3$ has been measured by Figgis and Harris[16] and a value of $\mu_{eff} = 1.95$ BM is reported at 300°K. Rioux and Gerstein[17] have investigated the low-temperature magnetic properties of $CsCuCl_3$ and found that the system exhibits a weak antiferromagnetic spin interaction between chains and only slightly stronger spin coupling within a chain. The susceptibility begins to deviate from Curie-Weiss behavior in the neighborhood of 55°K. Structurally, we note that the Cu-Cu distance of 3.257 (5) Å in $CsCuBr_3$ is relatively long for direct Cu-Cu exchange and is longer than the corresponding Cu-Cu distance in $CsCuCl_3$ of 3.062 (1) Å. We conclude, therefore, that the magnetic coupling in $CsCuBr_3$ is predominantly through the bromine bridges *via* a superexchange mechanism and we must therefore look at the structural differences in the halogen bridges for an explanation for the differences in the magnetic properties of $CsCuCl_3$ and $CsCuBr_3$. As indicated above,[1] magnetic susceptibility measurements suggest a greater tendency for antiferromagnetic coupling to occur in copper bromide than in copper chloride complexes. The difference, however, is ordinarily not large at room temperature. Some examples follow:[1,18] $CuBr_2$, $\mu_{eff} = 1.91$ BM, and $CuCl_2$, $\mu_{eff} = 1.97$ BM; $CuBr_2(py)_2$, $\mu_{eff} = 1.79$ BM, and $CuCl_2(py)_2$, $\mu_{eff} = 1.85$ BM; $KCuBr_3$, $\mu_{eff} = 1.52$ BM,[4] and $KCuCl_3$, $\mu_{eff} = 1.98$ BM. It does not seem likely that the exchange of bromine atoms for chlorine atoms alone is responsible for changing the magnetic moment from 1.95 BM for $CsCuCl_3$ to approximately zero for $CsCuBr_3$.

Spin coupling can occur both within a dimer and between dimeric units through the bridging bromine atoms. If we categorize the bridging bromine atoms according to the simple one-electron wave functions of a tetragonally quantized Cu^{2+} species, the results are as follows: $d_{x^2-y^2}$-Br(1)-$d_{x^2-y^2}$, 82.0°; d_{z^2}-Br(2)-$d_{x^2-y^2}$, 74.9°; $d_{x^2-y^2}$-Br(3)-$d_{x^2-y^2}$, 171.5°; $d_{x^2-y^2}$-Br(4)-d_{z^2}, 167.60°. A bridging arrangement corresponding to that observed for Br(1) and Br(2) in $CsCuBr_3$ is observed in $CsCuCl_3$[13] and is as follows: $d_{x^2-y^2}$-Cl(1)-$d_{x^2-y^2}$, 81.1°; d_{z^2}-Cl(2)-$d_{x^2-y^2}$, 73.8. The geometries of the face-shared portions of $CsCuBr_3$ and $CsCuCl_3$ are thus remarkably similar with corresponding bridge angles within 1.1° of each other. Since the magnetic moment of $CsCuCl_3$ shows no antiferromagnetic behavior to 55°K,[17,18] the diamagnetism of $CsCuBr_3$ must be primarily due to a strong antiferromagnetic coupling

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Table VIII. Comparison of Selected Bond Distances and Bond Angles in Cs_2CuBr_4, Cs_2CuCl_4, $[N(CH_3)_4]_2CuCl_4$, and $DPCuCl_4$ [a]

	Cs_2CuBr_4 (this study)	Cs_2CuBr_4 [12]	Cs_2CuCl_4 [21,22]	$[N(CH_3)_4]_2CuCl_4$ [22]	$DPCuCl_4$ [a]
		Bond Distances, Å			
Cu-X(1)	2.311 (10)	2.394 (8)	2.18 (2)	2.25	2.249 (1)
Cu-X(2)	2.337 (10)	2.380 (9)	2.25 (2)	2.22	2.244 (1)
Cu-X(3)	2.372 (6)	2.354 (9)	2.18 (2)	2.23	
X(1)-X(2)	4.252 (10)	4.333	3.92	4.00	3.459
X(1)-X(3)	3.622 (8)	3.686	3.39	3.60	3.485
X(2)-X(3)	3.608 (8)	3.624	3.46	3.56	
X(3)-X(3)'	4.217 (11)	4.202	3.83	4.52	
		Bond Angles, Deg			
X(1)-Cu-X(2)	132.32 (5)	130.4 (4)	124.9 (7)	130.6	129.18 (5)
X(1)-Cu-X(3)	101.31 (3)	101.9 (3)	102.9 (7)	101.8	101.85 (6) 100.66 (4)
X(2)-Cu-X(3)	100.02 (3)	99.9	102.5 (7)	99.5	99.23 (6)
X(3)-Cu-X(3)'	125.48 (5)	126.4	123.3 (7)	127.3	129.18 (5) 100.66 (4)

[a] *N,N'*-Dimethyl-4,4'-bipyridinium tetrachlorocuprate: J. H. Russell and S. C. Wallwork, *Acta Crystallogr., Sect. B*, **25**, 1691 (1969).

Table IX. Comparison of Bond Lengths Corrected for Thermal Motion for Cs_2CuBr_4 (Å)

Bond	Uncorrected	Riding[24]	Independent[24]
Cu-Br(1)	2.311 (10)	2.295 (10)	2.351 (10)
Cu-Br(2)	2.337 (10)	2.357 (6)	2.422 (6)
Cu-Br(3)	2.372 (6)	2.322 (10)	2.372 (10)
Average	2.340 (9)	2.325 (9)	2.382 (9)

through Br(3) or Br(4). This point of view is also consistent with the interesting observation that there is a monotonic increase of the coupling constant, $2J$, with increasing Cu-X-Cu bridge angle ($X^- = OH^-$).[19] The extent of magnetic coupling, however, also involves the orbital occupancy. Taking the simple view of exchange described by Anderson,[20] coupling through Br(4) would involve an excited configuration which is the result of charge transfer from a bromine p orbital to the empty $d_{x^2-y^2}$ orbital of the Cu^{2+} ion. This, however, would leave a residual magnetic moment corresponding to one unpaired electron per two copper atoms. On the other hand, the Goodenough-Kanamori rules[20] and the arguments of Anderson[20] suggest large superexchange when two metal d orbitals, each with unpaired electrons, have lobes pointed directly toward a ligand and each other. We conclude, then, that the observed diamagnetism is primarily due to exchange through Br(3).

Cs_2CuBr_4. A comparison of selected bond lengths and bond angles from the two studies of Cs_2CuBr_4,[12] the Cs_2CuCl_4 structure,[21,22] and the $(N(CH_3)_4)_2CuCl_4$ structure[22] is shown in Table VIII. The structure of Cs_2CuBr_4 is similar to that of Cs_2CuCl_4 and Cs_2ZnBr_4.[23] The $CuBr_4{}^{2-}$ unit (Figure 3) possesses a distorted regular tetrahedral configuration about the copper. From Table VIII, the three copper to bromine distances are seen to be different, with the maximum difference between Cu-Br(1) and Cu-Br(3) being more than 6σ. Interestingly, Cu-Br bond lengths for the bromine atoms in the crystallographic mirror plane are shorter than the out-of-plane Cu-Br(3) bond length, in disagreement with the earlier study. The mean Cu-Br distance of 2.340 (9) Å is slightly shorter than the earlier value of Morosin and Lingafelter, 2.376 Å, and is shorter than the nearest copper-bromine distance in $CuBr_2$, 2.40 Å, where the bromine atoms are tetragonally bridged between two copper atoms. The bond lengths, corrected for thermal motion using the "riding" and "independent" models of Busing and Levy,[24] are compared in Table IX. The variation which is observed clearly demonstrates that caution is required in assigning a physically meaningful Cu-Br bond distance for this system. The angular distortions from T_d symmetry found in the $CuX_4{}^{2-}$ anion are relatively independent of the host lattice in the four unique systems in Table VIII, implying that the electronic properties of the Cu(II) ion and not crystal lattice forces are responsible for the observed $CuCl_4{}^{2-}$ geometry. The six X-Cu-X angles are of two types: large angles of 127.9 (2.6)° and smaller angles of 101.1 (1.2)°.

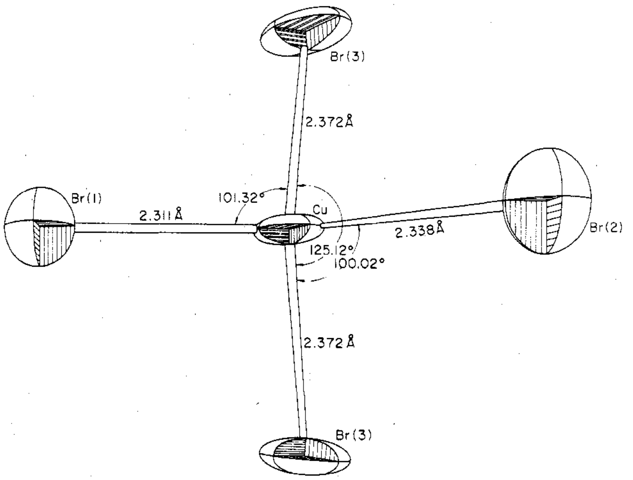

Figure 3. The coordination about the copper atom in Cs_2CuBr_4.

Registry No. $CsCuBr_3$, 37474-57-0; Cs_2CuBr_4, 35638-00-7.

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