$(CO)_{10}$, although not statistically significant, is in accord with the aforementioned π acceptor capabilities of the mercury atom. Within each $Mn(CO)_5$ group, the average $C_{ax}\cdots C_{eq}$ nonbonding distance is 2.712 Å. This value is slightly longer than the corresponding value of 2.64 Å observed in $Mn_2(CO)_{10}$[41] but is in agreement with the greater angular distortion and greater metal-carbon bond lengths present in $Hg[Mn(CO)_5]_2$.

The mean C-O distance of 1.154 (10) Å agrees well with the value of 1.156 Å in $Mn_2(CO)_{10}$ and also with values observed in other transition metal carbonyls. There is no significant difference between the axial and equatorial C-O distances in this compound, which is consistent with the known insensitivity of the C-O bond length to changes in bond order in the range 2-3. The Mn-C-O angles have an average value of 178°; thus there is no significant distortion from linearity due to intermolecular packing forces and/or electronic effects. The closest intermolecular contacts (Table III) of range 3.1-3.4 Å indicate no abnormal intermolecular forces.[69]

Acknowledgment.—The authors are indebted to Professors L. F. Dahl and P. M. Treichel for many helpful comments and criticisms and for financial support. We are also grateful to Dr. J. J. Benedict, who supplied the crystals used in this study, and to Mrs. A. Aylesworth for technical assistance. Support by the National Science Foundation is gratefully acknowledged (grants to L. F. Dahl (GP-4919X) and P. M. Treichel (GP-17207)). The use of the UNIVAC 1108 computer at the Madison Academic Computing Center was made possible through partial support from the National Science Foundation and the Wisconsin Alumni Research Foundation administered by the University Research Committee.

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[69] NOTE ADDED IN PROOF.—Since acceptance of this article, a short paper has appeared by W. Clegg and P. J. Wheatly [*J. Chem. Soc. A*, 3572 (1971)] on the crystal structure of $Hg[Mn(CO)_5]_2$. As expected, their results which were obtained with film data are not quite so precise as ours which utilized diffractometry data. However, it is gratifying that a comparison of the molecular parameters shows no corresponding values deviating by more than three standard deviations. It is noteworthy that the value of the Hg-Mn bond length quoted in both the abstract and text of their paper is incorrect but that their correct value is listed in their Table 3.

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Out-of-Plane Interactions in Parallel-Planar Copper(II) Dimers. The Structure and Magnetic Properties of Dibromobis(2-methylpyridine)copper(II)

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The crystal and molecular structure of dibromobis(2-methylpyridine)copper(II), $Cu(NC_6H_7)_2Br_2$, has been determined from three-dimensional single-crystal X-ray data collected by counter methods on an automatic diffractometer. The material crystallizes in space group C_i^1-$P\bar{1}$ of the triclinic system with two formula units in a cell of dimensions a = 8.777 (5), b = 11.738 (13), and c = 8.494 (5) Å; α = 74.75 (7), β = 60.73 (4), and γ = 70.52 (7)°. The observed and calculated densities are 1.90 (2) and 1.904 g cm^{-3}, respectively. Least-squares refinement of the structure has led to an R factor (on F) of 0.044 for 1481 independent reflections having $F^2 > 3\sigma(F^2)$. The structure consists of weakly bound bromine-bridged dimers, the bridging Cu-Br separation being 3.872 (5) Å. The coordination about the copper is tetragonal pyramidal, with two trans bromine atoms and two nitrogen atoms in the basal plane and the bridging bromine atom axial. The Cu-Cu separation in the dimer is 4.926 (6) Å. The structure is very similar to that of the corresponding dichloro complex. Despite the weakness of the bridging of the dimer the complex exhibits an antiferromagnetic transition with a Neél temperature of 4.5°K.

Introduction

There has been considerable interest in recent years in the role of out-of-plane copper-ligand interactions between parallel-planar copper(II) dimers.[1,2] One such system of potential importance is that formed by copper(II) halides with pyridine and substituted pyridines. The crystal structures of $Cu(py)_2Cl_2$[3] and $Cu(py)_2Br_2$[4] show distorted octahedral coordination around the copper atom with two halogen and two nitrogen atoms lying in the basal plane around the copper atom and two halogen atoms from neighboring molecules occupying the axial sites. On the basis of infrared spectroscopic measurements several possible structures have been proposed for the complexes $Cu(\alpha\text{-pic})_2X_2$ (where α-pic = α-picoline (2-methylpyridine) and X = Cl or Br). These include square planar,[5] where the α-methyl group completely blocks the axial sites, and five- or six-coordinate,[6] where the α-methyl group blocks only one or none of the axial coordination sites, respectively. The spectroscopic data of both groups[5,6] of authors, however, are in agreement in showing that the bromo series of complexes of pyridine and substituted pyridines exhibits a completely different trend than the chloro series. Thus, the copper-bromide asymmetric stretching frequencies of $Cu(\alpha\text{-pic})_2Br_2$ (233 cm^{-1}), $Cu(\gamma\text{-pic})_2Br_2$ (255), $Cu(2,6\text{-lut})_2Br_2$ (233), and $Cu(2,4,6\text{-coll})_2Br_2$ (228) (coll = collidine) are lower than or equal to that of $Cu(py)_2Br_2$ (255), whereas the copper-chloride asymmetric stretching frequencies

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[1] B. J. Hathaway and A. A. G. Tomlinson, *Coord. Chem. Rev.*, **5**, 1 (1970).
[2] W. E. Hatfield, *Inorg. Chem.*, **11**, 216 (1972).
[3] J. D. Dunitz, *Acta Crystallogr.*, **10**, 307 (1957).
[4] V. Kupcik and S. Durovic, *Czech. J. Phys.*, **10**, 182 (1960).
[5] M. Goldstein, E. F. Mooney, A. Anderson, and H. A. Gebbie, *Spectrochim. Acta*, **21**, 105 (1965).
[6] J. R. Allen, D. H. Brown, R. H. Nuttall, and D. W. A. Sharp, *J. Chem. Soc., A*, 1031 (1966).

of the corresponding chloride complexes (308, 292, 305, 296 cm^{-1}) are all higher than that of the Cu(py)$_2$Cl$_2$ (287 cm^{-1}). Hence, the spectroscopic data suggest that the structures of the dichloro and dibromo complexes may be quite different. Our recent low-temperature magnetic data,[7] however, suggest that the structures of these two complexes are very similar. The structure of Cu(α-pic)$_2$Cl$_2$ has been reported by Duckworth and Stephenson;[8] the apparent inconsistency between the spectral and magnetic data prompted us to examine the structure of the dibromo complex, which we report here.

Experimental Section

The compound dibromobis(2-methylpyridine)copper(II) was prepared by the reaction of copper(II) bromide with excess 2-methylpyridine in hot methanol[9] and was recrystallized as blue triclinic needles from absolute methanol. Weissenberg and precession photographs of a crystal mounted along the needle axis showed no symmetry. The crystal system was, therefore, taken as triclinic, space group $P1$ or $P\bar{1}$; the latter space group was confirmed by structure analysis. The unit-cell dimensions were obtained from a computer-controlled FACS-I Picker automatic diffractometer by accurately centering, at a takeoff angle of 0.5°, ten general reflections and refining them by the least-squares procedure of Busing and Levy.[10] Their values, at 22°, and the estimated standard deviations (in parentheses) as obtained from the inverse of the least-squares matrix are a = 8.777 (5), b = 11.738 (13), c = 8.494 (5) Å; α = 74.75 (7), β = 60.73 (4), γ = 70.52 (7)°. The radiation used was Mo Kα (λ_{α_1} 0.7093 Å). The density of 1.904 g cm^{-3} calculated for two formula units in the cell is in good agreement with 1.90 g cm^{-3} obtained by flotation in a solution of carbon tetrachloride and 1,2-dibromoethane. Hence no crystallographic symmetry need be imposed on monomeric species in the cell.

The intensity data were collected from two crystals, both of whose mosaicities were checked by the usual method.[11] Both were triclinic needles with the following developed faces: (100), ($\bar{1}$00), (010), (0$\bar{1}$0), (001), (001). The distances between the parallel faces, in the order described above, were 0.49, 0.22, and 0.19 mm for the first crystal and 0.64, 0.11, and 0.21 mm for the second crystal. The crystals were mounted on glass fibers along the needle axis (the a axis) and the arcs of the eucentric goniometer head were adjusted so that neither the a nor the a^* axis of the crystal was parallel to the ϕ axis of the instrument, thus avoiding multiple reflections.[12] A FACS-I Picker automatic diffractometer with molybdenum X-ray tube was used for all data collection. Reasonable monochromaticity of the Mo Kα beam was obtained by interposing a 0.003 in. thick niobium foil between the crystal and the counter. A further monochromatization was achieved through a pulse height analyzer which was set for approximately a 90% window centered on the Mo Kα peak. The takeoff angle for the first crystal was 2.0° and for the second crystal 1.2°; at these angles the peak intensity of a typical strong reflection was approximately 90% of the maximum value as a function of takeoff angle. The receiving aperture size, selected to minimize the extraneous background, was 4.0 mm high by 4.0 mm wide and was positioned about 32 cm from the crystal. The data were collected by the θ–2θ scan technique at a scan rate of 2°/min for the first and 1°/min for the second crystal. The scan range for the first crystal was −0.75° from the Kα_1 peak to +0.75° deg from the Kα_2 peak. The corresponding values for the second crystal were −1.0 to +1.0°. Stationary-background counts of 10 sec were taken at each end of the scan. Attenuators of Cu foil were automatically inserted when the intensity of the diffracted beam exceeded 7000 counts/sec at any time during the scan.[13] The intensities of three standard reflections, measured after every 100 reflections, remained essentially constant throughout the data collection. Intensity data were collected for reflections having $2\theta \leq 52°$. There were very few reflections with intensities above background beyond 52°. A total of 1481 reflections were found to have intensities greater than three times their estimated standard deviations.

The data were processed separately for both crystals. The measured intensities were corrected for background and assigned standard deviations according to the formula[13]

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

as described by Corfield, *et al.*[14] The term p, which is included to prevent the very strong reflections from being given too high a weight,[15] was assigned a value of 0.04 for both crystals since their mosaicities were quite small. The values of I and $\sigma(I)$ were corrected for Lorentz and polarization as well as for absorption effects. The linear absorption coefficient for the compound is 74.7 cm^{-1} for Mo Kα radiation. The transmission coefficients were found to range from 0.225 to 0.344 for the first crystal and from 0.162 to 0.470 for the second.[16]

Structure Solution and Refinement

The positions of the one Cu and the two Br atoms in the asymmetric unit were derived readily from an unsharpened three-dimensional Patterson function. One cycle of full-matrix least-squares refinement on these parameters assuming variable isotropic temperature factors yielded values for the usual disagreement factors $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2)^{1/2}$ of 0.295 and 0.351, respectively. A difference Fourier map calculated at this stage showed all the nonhydrogen atoms unambiguously. Two cycles of refinement on positional and individual isotropic temperative parameters of all the nonhydrogen atoms gave R_1 = 0.202 and R_2 = 0.226. Another three cycles of refinement with anisotropic temperature factors for all atoms reduced R_1 to 0.092 and R_2 to 0.120. At this point absorption corrections were made to both the data sets and three cycles of refinement carried out on this data set gave R_1 = 0.061 and R_2 = 0.083. A difference Fourier synthesis was now calculated in order to locate the hydrogen atoms. Although there were peaks in this difference map near positions expected for the hyrogen atoms, it was considered more accurate to put the hydrogens attached to the picoline rings in their idealized positions assuming a C–H bond length of 0.95 Å[17] and those attached to the methyl groups in positions found in the difference map. Two more cycles of refinement keeping the hydrogen atom parameters fixed and varying all others yielded the final disagreement factors R_1 = 0.044 and R_2 = 0.051. There were no parameter shifts in the last cycle of refinement greater than the corresponding estimated standard deviation. The final difference Fourier map was featureless.

The least-squares refinements were carried out on F, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$, and the weights w were taken as $w = 4F_o^2/\sigma^2(F_o)^2$. The atomic scattering factors for Cu and Br were taken from Cromer and Waber,[18] for C and N from Ibers,[19] and for H from Stewart, Davidson, and Simpson.[20] Anomalous dispersion corrections to the Cu and Br scattering factors were taken from Cromer.[21]

Examination of the final values of $|F_o|$ and $|F_c|$ suggests to us that no correction for secondary extinction is necessary. The value of R_2 showed no dependence on $|F_o|$ or on sin θ, which suggests that our choice of p = 0.04 is essentially correct.

The positional parameters and their estimated standard deviations as obtained from the inverse of the least-squares matrix are given in Table I. The thermal parameters and their esd's are

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

(8) V. F. Duckworth and N. C. Stephenson, *Acta Crystallogr., Sect. B*, **25**, 1795 (1969).

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

(17) The use of this shortened value has been discussed elsewhere: D. J. Hodgson, P. K. Hale, and W. E. Hatfield, *Inorg. Chem.*, **10**, 1061 (1971).

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

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TABLE I

FINAL POSITIONAL PARAMETERS, WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

	x/a	y/b	z/c
Cu	0.09767 (13)	−0.22352 (9)	0.04890 (13)
Br1	−0.16789 (11)	−0.08609 (8)	0.24279 (11)
Br2	0.36650 (11)	−0.34861 (9)	−0.15899 (12)
N1	0.2312 (8)	−0.2173 (6)	0.1781 (8)
N2	−0.0394 (9)	−0.2398 (6)	−0.0690 (9)
C1	0.2527 (10)	−0.3052 (8)	0.3075 (10)
C2	0.3450 (11)	−0.2941 (9)	0.3980 (11)
C3	0.4093 (12)	−0.1955 (9)	0.3551 (12)
C4	0.3899 (14)	−0.1117 (10)	0.2242 (12)
C5	0.2997 (11)	−0.1218 (8)	0.1352 (11)
C6	0.1737 (13)	−0.4112 (9)	0.3552 (13)
C7	−0.0201 (11)	−0.1701 (8)	−0.2288 (12)
C8	−0.1134 (12)	−0.1727 (9)	−0.3179 (11)
C9	−0.2273 (11)	−0.2463 (9)	−0.2476 (12)
C10	−0.2474 (11)	−0.3190 (9)	−0.0874 (14)
C11	−0.1483 (10)	−0.3170 (8)	0.0024 (11)
C12	−0.1587 (13)	−0.3971 (9)	0.1734 (12)
H2[a]	0.3618	−0.3540	0.4898
H3	0.4741	−0.1871	0.4187
H4	0.4373	−0.0456	0.1940
H5	0.2852	−0.0613	0.0443
H7	0.0582	−0.1189	−0.2784
H8	−0.0998	−0.1234	−0.4278
H9	−0.2918	−0.2496	−0.3089
H10	−0.3238	−0.3699	−0.0347
H61	0.0705	−0.3947	0.4125
H62	0.2259	−0.4740	0.4141
H63	0.1981	−0.4361	0.2489
H121	−0.0545	−0.4365	0.1770
H122	−0.2194	−0.3333	0.2600
H123	−0.2240	−0.4580	0.2235

[a] All hydrogen atoms, except those belonging to the two methyl groups, were placed in their calculated positions 0.95 Å from the attached carbon atom. The methyl hydrogens were found from a difference Fourier. The hydrogen positions were not varied.

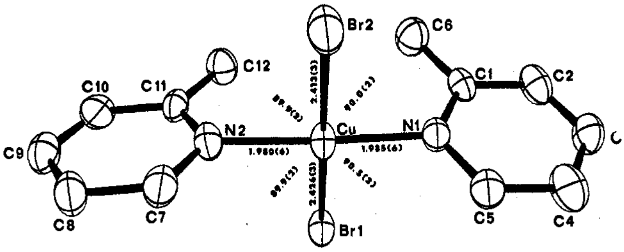

Figure 1.—View of one formula unit of $Cu(\alpha\text{-pic})_2Br_2$, demonstrating that atom Br2 is blocked by the carbon atoms C6 and C12. Hydrogen aroms are omitted for clarity. The thermal ellipsoids in all figures in this paper are drawn at the 40% probability level.

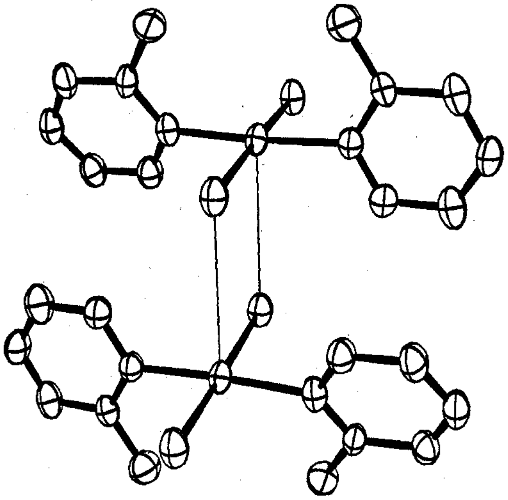

Figure 2.—View of one dimeric unit in $Cu(\alpha\text{-pic})_2Br_2$. The thin lines represent the weak interactions between Cu and Br1.

TABLE II

ANISOTROPIC THERMAL PARAMETERS, $\beta_{ij} \times 10^5$, FOR NONHYDROGEN ATOMS (Å²)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	1462 (19)	926 (10)	1484 (19)	−367 (11)	−871 (15)	−185 (11)
Br1	1593 (19)	1147 (11)	1869 (19)	−254 (11)	−894 (15)	−449 (11)
Br2	1579 (19)	1251 (12)	1952 (20)	−174 (11)	−946 (16)	−521 (12)
N1	1450 (132)	803 (68)	1625 (133)	−236 (77)	−849 (111)	−242 (78)
N2	1464 (134)	999 (74)	1639 (140)	−230 (83)	−861 (111)	−282 (82)
C1	1259 (160)	937 (94)	1406 (160)	−120 (95)	−768 (133)	−205 (98)
C2	1679 (192)	1344 (122)	1688 (181)	−138 (122)	−1105 (175)	−219 (119)
C3	1983 (205)	1243 (115)	1996 (199)	−389 (123)	−1155 (171)	−519 (124)
C4	2208 (226)	1447 (130)	1933 (209)	−301 (134)	−1347 (180)	−258 (134)
C5	1565 (182)	976 (101)	1959 (187)	−324 (112)	−894 (152)	−225 (111)
C6	2606 (240)	1088 (112)	2229 (209)	−450 (131)	−1393 (192)	−56 (121)
C7	1815 (191)	993 (100)	1899 (195)	−227 (110)	−1013 (158)	−413 (144)
C8	2080 (213)	1081 (99)	1762 (187)	−226 (117)	−1217 (172)	−299 (109)
C9	1657 (191)	1163 (111)	2089 (204)	−64 (117)	−1103 (164)	−603 (124)
C10	1399 (181)	1023 (104)	2938 (243)	98 (108)	−1221 (175)	−701 (131)
C11	1351 (166)	870 (89)	1801 (173)	−158 (98)	−876 (141)	−449 (102)
C12	2064 (209)	1036 (102)	2174 (208)	−590 (117)	−1039 (172)	21 (117)

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

given in Table II. A table of observed and calculated structure factors is available.[22]

Description and Discussion

The structure of one formula unit of $Cu(\alpha\text{-pic})_2Br_2$ is shown in Figure 1, where the bond lengths and angles involving the central Cu atom are also indicated. The complex, however, consists of bromine-bridged dimeric units as shown in Figures 2 and 3. The Cu–Br1–Cu′–Br1′ moiety is strictly planar, there being a crystallographic inversion center in the middle of the dimer. The Cu–Cu′ separation is 4.926 (6) Å. The coordination polyhedron around the copper atoms is a distorted tetragonal pyramid with Br1, Br2, N1, and N2 in the basal plane and the bridging Br1 from another molecule occupying the fifth coordination site. The bridging interaction is rather weak, the out-of-plane Cu···Br distance being 3.872 (5) Å. The structure of this complex is very similar to that of the analogous chloride complex where a similar five-coordinate polyhedron

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(22) A listing of structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-1657. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

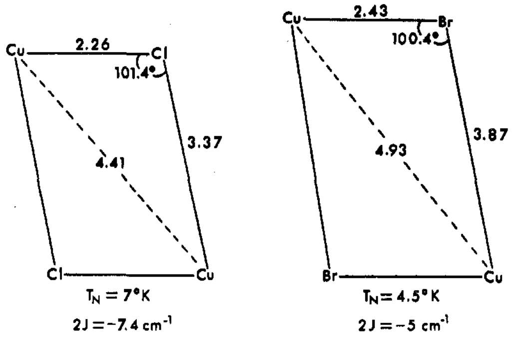

Figure 3.—A comparison of the bridged geometries and associated magnetic properties of dichloro- and dibromobis(2-methylpyridine)copper(II). Structural data for the dichloro complex are taken from ref 8.

about the copper atom was also found, with a large (3.37 Å) out-of-plane Cu···Cl distance.[8] It seems that the cis arrangement of the α-methyl groups on the two picoline rings, which leaves one axial site completely unblocked, is essential for five-coordination to copper in such compounds. Two examples where the arrangement of α-methyl groups is not cis and, therefore, the coordination about copper is only square-planar are the recent structures[23] of $Cu(2,3\text{-}Me_2py)_2X_2$, X = Cl or Br. In these structures both axial sites are completely blocked by the α-methyl groups which are trans to each other. It is interesting that the copper atom apparently prefers higher coordination over higher symmetry in the α-methylpyridine complexes but higher symmetry over higher coordination in the α,β-dimethylpyridine complexes. In the unsubstituted pyridine–copper complexes, $Cu(py)_2X_2$, X = Cl or Br, the copper atom achieves both high symmetry (C_i) and high coordination number (6).[3,4]

The internuclear distances and angles in the dimeric molecule, along with their associated estimated standard deviations, are presented in Table III. The two Cu–N bond lengths of 1.985 (6) and 1.980 (6) Å do not differ significantly. The two Cu–Br bond lengths, however, differ by 4 esd's and are, therefore, significantly different from each other, the longer one being to the bridging Br atom as expected. The four pairs of cis atoms in the basal plane around copper all form 90° angles at the copper atom to within the experimental error (3 esd's). The trans bromine atoms and the trans nitrogen atoms in the basal plane, however, form 176.2° angles at the Cu atom, thus differing significantly from 180°. This clearly implies nonplanarity of basal plane containing the copper atom. A least-squares plane through the five atoms Cu, Br1, Br2, N1, and N2 shows that the two bromine atoms are displaced from the plane by 0.07 Å each in the same direction while the two nitrogen atoms deviate by the same amount but in the opposite direction. The Cu atom is almost exactly in this plane, deviating from it by only 0.006 Å and in the same direction as the two nitrogens. Thus the slight distortion from square-planar arrangement of the two nitrogens and the two bromines is toward a tetrahedral coordination. The structure of this complex is, therefore, very similar to that of the analogous chloride complex.[8]

TABLE III

INTERNUCLEAR DISTANCES AND ANGLES[a]

Atoms	Distance, Å	Atoms	Angle, deg
	$Cu(\alpha\text{-pic})_2Br_2$		
Cu–Br1	2.426 (3)	Br1–Cu–N1	90.5 (2)
Cu–Br2	2.413 (3)	Br2–Cu–N1	90.0 (2)
Cu–N1	1.985 (6)	Br1–Cu–N2	89.9 (2)
Cu–N2	1.980 (6)	Br_2–Cu–N2	89.9 (2)
N1–C1	1.337 (10)	Br_1–Cu–Br_2	176.2 (3)
N1–C5	1.331 (10)	N1-Cu–N2	176.2 (1)
C1–C2	1.412 (10)	Cu–N1–C1	122.1 (5)
C2–C3	1.343 (13)	Cu–N1–C5	118.8 (5)
C3–C4	1.316 (13)	C1–N1–C5	119.2 (6)
C4–C5	1.382 (11)	C1–N1–C5	119.2 (6)
C1–C6	1.494 (13)	N1–C1–C6	118.5 (7)
N2–C7	1.351 (11)	C2–C1–C6	122.0 (8)
N2–C11	1.350 (11)	N1–C1–C2	119.5 (8)
C7–C8	1.372 (11)	C2–C3–C4	120.2 (8)
C8–C9	1.350 (13)	C2–C3–C4	119.1 (8)
C9–C10	1.366 (13)	C3–C4–C5	121.1 (10)
C10–C11	1.418 (10)	C4–C5–N1	121.0 (8)
C11–C12	1.487 (12)	Cu–N2–C11	123.1 (5)
		Cu–N2–C7	117.3 (6)
		C7–N2–C11	119.6 (6)
		N2–C7–C8	121.5 (9)
		C7–C8–C9	120.4 (9)
		C8–C9–C10	119.3 (8)
	Dimer		
Cu---Cu′	4.926 (6)	Cu–Brl---Cu′	100.40 (9)
Cu---Br1′	3.872 (5)	Br1–Cu---Br1′	79.60 (9)
Br1---Br1′	4.182 (4)	C9–C10–C11	119.9 (9)
		C10–C11–C12	122.6 (9)
		N2–C11–C12	118.1 (7)
		N2–C11–C10	119.3 (8)

[a] Cu′ and Br1′ are related to Cu and Br1, respecively, by a center of inversion.

The two α-picoline moieties are separately planar; the one containing N1 has no atom removed from the least-squares plane by more than 0.01 Å and that containing N2 has no atom removed from it by more than 0.03 Å. The Cu atom is displaced from these planes by 0.05 and 0.09 Å, respectively. The two α-picolines are not coplanar, the dihedral angle between their planes being 17.2°. The CuN_2Br_2 plane is approximately at right angles to the two α-picoline planes, the dihedral angles being 82.2 and 99.1°, respectively.

The two Cu–Br bond lengths in this compound (2.413 and 2.426 Å) are comparable to the Cu–Br bond lengths found in dibromo[2-(2-aminoethyl)pyridine]-copper(II) (2.388 and 2.413 Å),[24a] where copper is bound to two bromine atoms, but are shorter than the Cu–Br bond in dibromobis[2-(2-aminoethyl)pyridine]copper(II) (2.703 Å)[24b] where the copper is bound to only one bromine atom and the complex is a cation. Similarly, the values found here are comparable to the values of 2.392 (2) and 2.40 Å found in dibromobis(2,3-dimethylpyridine)copper(II)[23] and in anhydrous copper(II) bromide.[25] The Cu–N distances of 1.980 (6) and 1.985 (6) Å are comparable to the values of 1.98 and 2.02 Å found in $Cu(\alpha\text{-pic})_2Cl_2$,[8] 2.021 Å in dibromo[2-(2-aminoethyl)pyridine]copper(II),[24a] and 2.02 Å found in $Cu(py)_2Cl_2$.[3]

The bond lengths and angles associated with the α-picoline ligand are all normal for such compounds. Thus, the mean of the four C–N bond lengths is 1.342 Å

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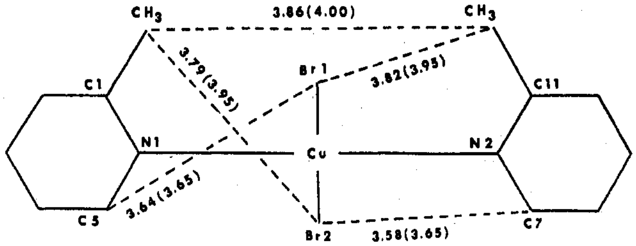

Figure 4.—Short, nonbonded contacts in Cu(α-pic)$_2$Br$_2$.

(σ = 0.011 Å) the variation from the mean being less than 1 esd. The mean C–N bond length for heterocyclic compounds quoted by Sutton[26] is 1.352 Å.

Although there are wide variations in the C–C bond lengths in the rings, it is evident that the bonds C1–C2 and C11–C10, which are adjacent to the exocyclic bond C1–CH$_3$, with lengths 1.412 (10) and 1.418 (10) Å, respectively, are slightly longer than the rest of them. A similar lengthening of the C–C bond adjacent to the side chain has been noted in all the α-aminoethylpyridine rings in their Cu(II) complexes recently studied in our laboratory.[24,27] The exocyclic bond between the α-carbon atom and the methyl group is quite short in both rings, the lengths being 1.487 and 1.494 Å. Both of these effects—shortening of the side-chain C–C bond and lengthening of the adjoining C–C ring bond—may be due to a drift of electrons from the ring C–C bond toward the exocyclic C–C bond, thus imparting to the latter some π-bond character. The other bonds in the α-picoline rings are normal. The angles in the picoline rings have normal values, the mean value for each ring being 120.0 (8)°.

The short nonbonded contacts in a molecule of Cu(α-pic)$_2$Br$_2$ are shown in Figure 4. It is obvious that the two picoline rings have twisted about the corresponding Cu–N bonds far enough so that their methyl groups interact rather strongly with the nearest bromine atoms, the contraction from the normal van der Waals distance being 0.13 Å for Br1---CH$_3$ and 0.16 Å for Br2---CH$_3$. This is also reflected in a shorter (3.86 Å) than normal (4.0 Å) methyl–methyl contact. The interaction between a bromine atom and its nearest ring atom is normal for Br1---C5 and only 0.07 Å shorter than normal for Br2---C7. The interactions between the bromine and the ring atoms are, therefore, not strong enough to distort the geometry of the rings, and, in fact, no distortion is found; both rings are found to be planar (*vide supra*). In Cu(α-pic)$_2$Cl$_2$[8] both α-picoline rings were found to be distorted, one with a short contact between a ring carbon atom and a chlorine atom (3.34 Å, van der Waals contact = 3.50 Å) being distorted slightly more than the other which had no such short contact.

Magnetic Properties

The magnetic susceptibilities of powdered samples of both Cu(α-pic)$_2$Br$_2$ and Cu(α-pic)$_2$Cl$_2$ were determined in the range 4.2–295°K, as described previously.[7] The data can be fitted to the Van Vleck equation[28] for pairs of exchange-coupled copper(II) ions, yielding a singlet–triplet splitting of 7.4 cm^{-1} for the dichloro complex and 5 cm^{-1} for the dibromo complex. These data are summarized in Figure 3, where the bridging geometries are also compared. The magnetic data reflect spin coupling between the copper(II) ions which is transmitted by a superexchange mechanism through the bridging halo ligands. The greater interaction in the dichloro complex is a consequence of the relatively shorter copper–halide bridging distance; the covalent radius of Cl is only about 0.15 Å smaller than that of Br,[29] while the Cu–Cl separation of 3.37 Å is 0.50 Å shorter than the Cu–Br distance of 3.872 Å. The marked similarity between the structures of these two complexes affords a unique example of the quantitative effects of relatively minor structural changes on the magnetic behavior of condensed copper(II) systems. The apparent inconsistency between the observed similarity of the two structures and the spectroscopic data merely reemphasizes the dangers inherent in attempting to predict molecular structures from vibrational spectroscopy.

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