

Acta Cryst. (1975). B31, 632

Structure refinements on dichloro- and dibromobis(pyridine)copper(II).* By B. MOROSIN, *Sandia Laboratories, Albuquerque, N.M. 87115, U.S.A.*

(Received 23 September 1974; accepted 24 October 1974)

Parameters on the structures of dichloro- and dibromobis(pyridine)copper(II) have been refined by the least-squares method using 1270 and 1373 Mo $K\alpha$ intensity data respectively. The two structurally closely related materials crystallize in space group $P2_1/n$ with lattice constants $a=16.967$, $b=8.5596$, $c=3.8479$ Å and $\beta=91.98^\circ$ for the chloride compound and $a=8.424$, $b=17.599$, $c=4.0504$ Å and $\beta=97.12^\circ$ for the bromide. The structures consist of infinite linear chains parallel to c in which the copper coordination is distorted octahedral (Cu-Cl 2.298 and 3.026 Å; Cu-N 2.004 Å; Cu-Br 2.451 and 3.240 Å; Cu-N 2.013 Å) with the centers of the nearest chains separated by over 8.5 Å; closest contacts between such polymeric chains consist of 3.759 and 3.891 Å C-C contacts and 3.687, 3.785 and 3.837 Å C-Cl contacts in the chloride, and 3.810 and 3.845 Å C-C contacts and 3.840, 3.964 and 4.009 Å C-Br contacts in the bromide.

Introduction

Dichlorobis(pyridine)copper(II), $\text{Cu}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_2$, commonly referred to as copper dipyridine chloride and abbreviated CPC, is one of the best quasi-one-dimensional linear-chain spin $\frac{1}{2}$ systems thus far discovered and, hence, its magnetic properties have received much attention (Duffy, Venneman, Strandburg & Richards, 1974). Interestingly the magnetic properties of the corresponding bromide compound CPB, though similar (Jeter & Hatfield, 1972), show some important differences, probably because of larger spin-orbit contribution found in materials containing Cu-Br bonds. Early structure studies on both CPC (Dunitz, 1957) and CPB (Kupčik & Āurovič, 1960) consisted of projected data, visually estimated along two directions; no attempt to assign a definite value for the precision of the final parameters was made. Detailed structure refinements on these important materials are reported in this communication.

Experimental details and results

Both CPC and CPB grow as fragile, needle-like prisms with mechanical properties governed by the structure of the materials, *i.e.* chemically bonded polymeric $-\text{MX}_2-$ chains held together by weak van der Waals interactions between chains. Hence, careless handling results in a bent or strained specimen; furthermore, attempts to cleave crystals perpendicular to the direction of these chains usually result in ends which are frayed and close inspection usually reveals the presence of collinear fibres. Etching with water was successful in reducing specimen length to about 0.2 mm for intensity-data crystals. The other difficulty concerns twinning; however, with first-level Weissenberg photographs and perseverance, crystals suitable for X-ray and magnetic measurements were obtained.

Lattice parameters determined on a Picker diffractometer with Mo $K\alpha$ radiation were $a=8.424$ (2), $b=17.599$ (9), $c=4.0504$ (8) Å, $\beta=97.12$ (2)°, and $a=16.967$ (3), $b=8.5596$ (4), $c=3.8479$ (7) Å, $\beta=91.98$ (2)° for CPB and CPC, respectively. The θ - 2θ scan technique and a scintillation detector employing pulse-height discrimination were used to measure the Mo $K\alpha$ intensity data to $55^\circ 2\theta$. Of 1270 intensities measured on CPC, 1063 intensities were greater than 3σ where $\sigma=(N_{sc}+K^2N_b)^{1/2}$ and N_{sc} , N_b and K are the total scan count, background counts and the time ratio

of the scan to background, respectively; on CPB a complete hemisphere of measured intensities yielded 1055 observed and 318 'less than' intensities. Scattering factors were taken from Table 3.3.1A of *International Tables for X-ray Crystallography* (1962) and for hydrogen from Stewart, Davidson & Simpson (1965) and dispersion corrections were taken from Table 3.3.2C of *International Tables for X-ray Crystallography* (1962). Initial parameters were taken from Dunitz (1957) for CPC and from Kupčik & Āurovič (1960) for CPB and intensity data subjected to least-squares refinement using isotropic thermal parameters. The function $w(F_o - F_c)^2$ was minimized with $w=1/\sigma^2$. The difference Fourier syntheses clearly showed the positions of hydrogen atoms about the pyridine ring. The positional parameters for hydrogen were included with fixed isotropic thermal parameters in subsequent refinement cycles in which ani-

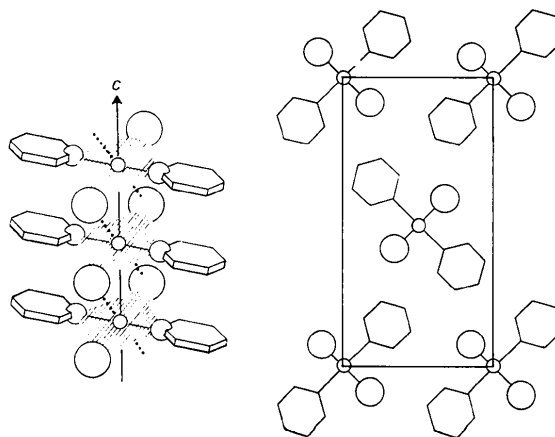


Fig. 1. Schematic representation of the crystal structure of CPC and CPB. On the left are illustrated the chains, formed by sharing of halide ions, which parallel the c axis in both compounds. The pyridine ligand is tipped away from the plane through the nitrogen and closer halide ions. On the right the structure in projection (along c) is illustrated. The large circles represent halide ions, the small, copper ions. No labels are given; for CPC, the long direction of the cell corresponds to $a \sin \beta$ (b for CPB) while the short direction corresponds to b ($a \sin \beta$ for CPB). No shading of bonds to indicate elevation is shown since there would be a reversal in direction for the face-centered chain when CPC is compared with CPB.

* This work was supported by the U.S. Atomic Energy Commission.

sotropic thermal parameters for the remaining atoms were used. Final residual values, $R = \sum |F_o| - |F_c| / \sum |F_o|$ were 0.052 and 0.035 for CPC and CPB, respectively.* These positional and thermal parameters are given in Table 1 and the corresponding interatomic separations in Table 2. The computations were performed with the X-RAY 72 System (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

In these compounds, the copper coordination is distorted octahedral, consisting of four closer atoms (two pyridine N and two halide ions with Cu-N of 2.004 Å and Cu-Cl of 2.298 Å in CPC and Cu-N of 2.013 Å and Cu-Br of 2.451 Å in CPB and two more distant halide ions (Cu-Cl 3.026 Å; Cu-Br 3.240 Å). The halide ions are shared by adjacent copper ions which results in chains which parallel the *c* axis (Fig. 1). Though both materials crystallize in space group $P2_1/n$, the structures are not isomorphous; however, they are quite similar. A comparison of positional parameters in Table 1 in which *x* and *y* for one compound

are interchanged clearly shows the similarity in projection of the two structures.

The Cu-N bond is essentially normal to the plane of the halide ions, as can be seen from the angles in Table 2; however, in the case of CPC, the copper atom definitely lies off the least-squares plane through the heavy atoms of the pyridine ligand. In CPC, the copper is found to be 0.072 Å away from the pyridine least-squares plane ($\sigma = 0.0015$ Å with maximum deviation 0.0024 Å); corresponding values in CPB are 0.020 Å above the plane for which $\sigma = 0.0078$ Å and the maximum deviation is 0.0099 Å. The angles between the least-squares plane through the pyridine and that through the nitrogen-nearest halide atoms (shaded in Fig. 1) are 58.2 and 58.7° for CPC and CPB, respectively. Because of the orientation of the pyridine ligand, some halide-light atom or light atom-light atom separations within the chain are shorter than the *c*-axis separation; these are given in Table 2(a) (*Intrachain separation*). The pyridine ligands appear to be distorted in the same manner, *i.e.* the C-N-C angles are less than 120° (118.1°), the adjacent N-C-C angles are larger than 120° with the average (1.380 Å) C-C bond length larger than the average (1.344 Å) N-C bond length. The unconstrained positional parameters for the hydrogen atoms resulted in an average 1.0 Å C-H separation [1.0-1.1 (1) Å range in CPC; 0.7-1.2 (1) Å in CPB].

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30748 (12 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Positional and thermal parameters*

U_{ij} are of the form $\exp(-2\pi^2 \sum U_{ij} h_i h_j a_i^* a_j^*)$ in units of 10^{-2}Å^2 .

(a) CPC

	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	0	0	0	2.50 (5)	2.13 (5)	4.37 (6)	-0.53 (4)	-0.87 (4)	0.57 (5)
Cl	0.07855 (8)	-0.1426 (2)	0.3812 (4)	3.08 (7)	2.63 (7)	3.93 (8)	0.08 (6)	-0.60 (6)	0.16 (6)
N	0.0800 (3)	0.1724 (6)	0.017 (1)	2.7 (2)	2.4 (2)	3.8 (3)	-0.2 (2)	-0.4 (2)	-0.1 (2)
C(1)	0.1555 (4)	0.1444 (8)	-0.066 (2)	2.9 (3)	3.2 (3)	4.8 (4)	-0.4 (3)	-0.3 (3)	0.0 (3)
C(2)	0.2123 (4)	0.2566 (9)	-0.048 (2)	3.8 (3)	4.8 (4)	4.3 (4)	-1.0 (3)	0.3 (3)	0.1 (3)
C(3)	0.1934 (4)	0.4061 (8)	0.063 (2)	4.8 (4)	3.3 (3)	4.7 (4)	-1.5 (3)	-0.1 (3)	0.4 (3)
C(4)	0.1166 (4)	0.4350 (8)	0.149 (2)	6.0 (4)	2.8 (3)	4.6 (4)	-0.3 (3)	-0.2 (3)	-0.8 (3)
C(5)	0.0612 (4)	0.3174 (7)	0.124 (2)	4.3 (3)	3.0 (3)	4.4 (4)	0.1 (3)	0.3 (3)	0.1 (3)
	<i>x</i>	<i>y</i>	<i>z</i>	U^*					
H(1)	0.161 (5)	0.03 (1)	-0.12 (2)	5.07					
H(2)	0.267 (6)	0.23 (1)	-0.12 (2)	5.07					
H(3)	0.238 (5)	0.50 (1)	0.09 (2)	5.07					
H(4)	0.100 (5)	0.54 (1)	0.27 (2)	5.07					
H(5)	0.002 (6)	0.34 (1)	0.12 (2)	5.07					

(b) CPB

	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	0	0	0	2.95 (6)	2.27 (5)	5.18 (7)	-0.75 (4)	-0.62 (5)	0.88 (4)
Br	-0.17029 (8)	0.07661 (3)	0.5930 (2)	3.28 (3)	2.78 (3)	3.76 (3)	0.16 (3)	0.22 (2)	0.51 (3)
N	0.1660 (6)	0.0829 (3)	0.040 (1)	3.0 (3)	2.4 (2)	4.2 (3)	-0.4 (2)	0.1 (2)	0.6 (2)
C(1)	0.1286 (8)	0.1527 (4)	0.136 (2)	3.9 (4)	2.5 (3)	5.3 (4)	-0.5 (3)	1.0 (3)	-0.1 (3)
C(2)	0.2391 (9)	0.2109 (4)	0.174 (2)	5.2 (4)	3.6 (3)	5.5 (5)	-0.7 (3)	1.6 (4)	-0.5 (3)
C(3)	0.3938 (9)	0.1969 (4)	0.103 (2)	4.5 (4)	3.9 (4)	5.6 (5)	-1.8 (3)	1.0 (3)	-0.1 (3)
C(4)	0.4319 (8)	0.1252 (4)	0.001 (2)	2.9 (3)	4.3 (4)	6.4 (5)	-0.2 (3)	0.7 (3)	0.3 (3)
C(5)	0.3155 (9)	0.0701 (4)	-0.023 (2)	3.8 (4)	3.9 (4)	5.5 (4)	-0.4 (3)	0.3 (3)	0.1 (3)
	<i>x</i>	<i>y</i>	<i>z</i>	U^*					
H(1)	0.00 (1)	0.171 (5)	0.20 (2)	5.07					
H(2)	0.21 (1)	0.273 (5)	0.29 (2)	5.07					
H(3)	0.49 (1)	0.232 (6)	0.08 (2)	5.07					
H(4)	0.55 (1)	0.116 (6)	-0.04 (2)	5.07					
H(5)	0.30 (1)	0.036 (6)	-0.09 (3)	5.07					

* Hydrogen thermal parameters were not refined.

Table 2. *Interatomic separations (Å) and angles (°)*

(a) Intrachain separations

	CPC	CPB
Cu—X	2.299 (2)	2.451 (1)
Cu—X'	3.026 (2)	3.240 (1)
Cu—N	2.004 (5)	2.013 (5)
N—C(1)	1.353 (8)	1.339 (8)
N—C(5)	1.350 (8)	1.335 (9)
C(1)—C(2)	1.360 (10)	1.379 (10)
C(2)—C(3)	1.389 (10)	1.392 (11)
C(3)—C(4)	1.379 (10)	1.377 (11)
C(4)—C(5)	1.378 (10)	1.374 (10)
Cl—X	3.474 (7)	3.405 (6)
N—X	3.640 (5)	3.824 (6)
N—C(1)	3.719 (8)	3.840 (9)
C(3)—C(4)	3.717 (10)	3.829 (11)
C(2)—C(4)	3.765 (10)	3.844 (10)
C(2)—C(3)	3.657 (10)	3.831 (11)
C(1)—C(5)	3.756 (9)	3.857 (10)

(b) Shortest interchain separations

X—C(2)	3.687 (7)	3.840 (7)
X—C(4)	3.785 (7)	3.964 (7)
X—C(3)	3.890 (7)	4.021 (7)
C(1)—C(3)	3.759 (10)	3.924 (10)
C(1)—C(3)	3.837 (10)	3.810 (10)
C(2)—C(3)	3.965 (10)	
C(2)—C(3)	3.851 (10)	3.845 (10)
C(5)—C(5)	3.856 (9)	3.956 (10)
C(4)—C(5)	3.805 (10)	

(c) Angles

X—Cu—X'	91.52 (5)	90.36 (2)
X—Cu—N	90.4 (1)	90.1 (1)
X'—Cu—N	90.4 (1)	90.3 (2)
C(1)—N—C(5)	118.1 (5)	118.1 (6)
N—C(1)—C(2)	122.4 (9)	122.4 (6)
C(1)—C(2)—C(3)	119.8 (6)	118.8 (7)
C(2)—C(3)—C(4)	117.9 (6)	118.8 (7)
C(3)—C(4)—C(5)	120.1 (6)	118.5 (7)
N—C(5)—C(4)	121.7 (6)	123.4 (7)

Finally, a few remarks on the relationship of structural subtleties and magnetic studies are in order. Separations between chains may be important in understanding mag-

netic exchange interactions in these compounds and such contact separations shorter than 4.0 Å are listed in Table 2(b). Exchange interactions *via* paths involving such contacts can at best only be postulated. Nevertheless, Duffy, Venneman, Strandburg & Richards believe superexchanged paths between Cu ions (*via* the short Cu—Cl bond—pyridine ligand and its N—Cu bond) are the principal interactions governing the magnetic properties in CPC. The overall separations between the copper ions are fixed by the cell dimensions and symmetry. In CPC each Cu ion (at 0, 0, 0) is surrounded by 8 neighboring Cu ions on magnetically inequivalent chains at distances of 9.636 Å, at corners $\pm(a/2, b/2, c/2)$ and $\pm(a/2, -b/2, c/2)$, and 9.753 Å, at the alternate corners $\pm(a/2, b/2, -c/2)$ and $\pm(-a/2, b/2, c/2)$, and by 2 Cu ions on equivalent (simple translation along **b**) chains at 8.560 Å. A different set of corners of the approximate $17 \times 8 \times 4$ Å cell are involved in the case of CPB; but because of the cell edge interchange, these have the same coordinates as above. In this case, the quasi-body-centered copper is surrounded by neighbors on magnetically inequivalent chains at distances of 9.857 and 10.069 Å and by 2 Cu ions on equivalent (simple translation along **a**) chains at 8.424 Å.

References

- DUFFY, W. JR., VENNEMAN, J. E., STRANDBURG, D. L. & RICHARDS, P. M. (1974). *Phys. Rev.* **B9**, 2220–2227.
- DUNITZ, J. D. (1957). *Acta Cryst.* **10**, 307–313.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- JETER, D. Y. & HATFIELD, W. E. (1972). *J. Inorg. Nucl. Chem.* **34**, 3055–3060.
- KUPČÍK, V. & ĎUROVIČ, S. (1960). *Czech. J. Phys.* **10**, 182–190.
- STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). X-RAY 72, A System of Computer Codes for Crystallography, Technical Report TR-192, Univ. of Maryland.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.