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Structure of Bis(4-methylpyridine)dichlorocopper(II): a Dislocated Linear Chain

WAYNE E. MARSH, EDWARD J. VALENTE and DEREK J. HODGSON*

Department of Chemistry, University of North Carolina, Chapel Hill, N.C. 27514, U.S.A.

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The crystal and molecular structure of bis(4-methylpyridine)dichlorocopper(II), $Cu(C_6H_7N)_2Cl_2$, *has been determined from three-dimensional photographic X-ray data obtained from a twinned and highly mosaic crystal. The complex crystallizes in space group* $P2_1/c$ *of the monoclinic system with two formula units in a cell of dimensions* a = *9.745(7),* b = *3.932(4),* c = *19.035(9) Å,* β = *111.8(2)°. The observed diffraction pattern, however, is nearly consistent with orthorhombic symmetry and the space group Cmma. The chain axis is parallel to the monoclinic crystallographic* b*-axis, and the twinning occurs perpendicular to this axis; the twinning causes dislocations in the chain by limiting the chain lengths to the sizes of the ordered crystal domains along the chain axis. The geometry at each copper atom is (4 + 2) tetragonally-elongated octahedral, the in-plane ligands being two* trans-*nitrogen atoms [Cu–N = 2.07(3) Å] and two* trans-*chlorine atoms [Cu–Cl = 2.35(1) Å]. The axial ligands are symmetry-related chlorine atoms, which are in-plane ligands of the adjacent copper atoms in the chain, the axial Cu–Cl and Cu–Cu′ distances being 3.19(1) and 3.932(4) Å, respectively. Each chain is very similar to that found in the analogous pyridine complex, but the arrangement of the chains in the crystal is more like that in the thiazole complex* $Cu(thz)_2Cl_2$.

Introduction

Complex compounds of the type CuX_2L_2 where L is pyridine or a substituted pyridine and X is halide are the subject of many structural, magnetic and spectroscopic studies [1–5]. These are aimed chiefly at gaining knowledge about the relationship between the structure and the properties of the complexes, particularly the magnetic interactions between copper atoms. Magnetic susceptibility measurements on bis(4-methylpyridine)dichlorocopper(II), $Cu(4\text{-}Mepy)_2Cl_2$, from 1.4 to 77 K are inconsistent with a linear chain structure as found in complexes like bis-pyridine- and bis(4-ethylpyridine)dichlorocopper(II) [1, 2, 4–6], and with the dimeric structure found in bis(2-methylpyridine)dichlorocopper(II) [7, 8]. A structural basis for these observations has not appeared; indeed [9], preliminary crystallographic information suggests a linear chain structure for $Cu(4\text{-}Mepy)_2Cl_2$. The specimens obtained by previous workers were invariably unsuitable for more detailed crystallographic analysis. It is also noteworthy that complexes of this general formulation may exist in more than one crystal form [10], and the 2-methylpyridine complex has recently been shown to exist as discrete monomers [11] as well as dimers [7]. Consequently, in order to increase our insight into the magnetic properties of the evidently anomalous 4-methylpyridine complex, we have undertaken a more complete structural study of $Cu(4\text{-}Mepy)_2Cl_2$; the results of this crystallographic study are presented herein.

Experimental

The complex was prepared by methods described previously [12, 13] in that an ethanol solution of 4-methylpyridine was added to an ethanol solution of $CuCl_2$ in a 2:1 mol ratio. A pasty substance precipitated, was collected and dried, and then recrystallized from dimethylformamide. Pale greenish-blue rods were so obtained. *Anal.* Calculated for $Cu(4\text{-}Mepy)_2Cl_2$: C, 44.94%; H, 4.40%; N, 8.74%. Found: C, 45.01%; H, 4.34%; N, 8.68%. Crystals were mounted along their long crystal axis, and photographic examination of many invariably showed large mosaicity (~5°) and splitting of reflections into two or more streaks. A crystal suitable for diffractometry could not be found. An individual crystal with only two apparent domains, as judged from the splitting of the reflection streaks, was aligned and used for data collection by integrated Weissenberg photography using multiple films and CuKα radiation with a Ni filter. The zero, first and second levels were

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*Author to whom correspondence should be addressed.

TABLE I. Fractional Coordinates of the Atoms with Estimated Standard Deviations in Parentheses.

Atom	x	y	z	B (A^2)
Cu	0	0	0	–
Cl	−0.176(1)	0.350(4)	−0.0886(6)	–
N1	0.129(4)	−0.004(11)	−0.066(2)	2.4(8)
C2	0.279(6)	0.135(14)	−0.031(3)	3.6(12)
C3	0.366(6)	0.144(14)	−0.078(3)	3.8(12)
C4	0.306(6)	0.028(16)	−0.154(3)	3.9(11)
C5	0.161(5)	−0.113(12)	−0.182(2)	1.9(9)
C6	0.070(5)	−0.121(13)	−0.141(2)	2.2(10)
C7	0.404(6)	0.077(15)	−0.204(3)	4.1(12)

Anisotropic Librations for Cu and Cl ($\times 10^3$)[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	13(2)	68(12)	3(5)	9(4)	4(8)	5(2)
Cl	12(2)	39(15)	2(5)	9(4)	0(8)	3(2)

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

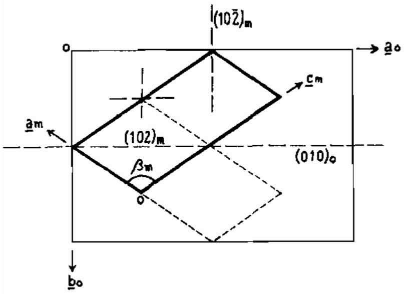

Fig. 1. The twinning model is diagrammed. The darkened outline represents the ordered monoclinic cell seen in projection down the *b* axis. The pseudo-mirror planes (– – –) result from twinning of the monoclinic cell with the cell (------) related to it by near superposition of *a* on −*c*, generating the *pseudo*orthorhombic cell shown in light outline. Relevant planes and axes are indicated with subscripts *m* and *o* referring to the monoclinic and *pseudo*orthorhombic cells, respectively.

recorded and then visually estimated with the aid of a graded series of diffuse point exposures (relative intensity scale 0 to 40). The apparent space group of the twinned crystal was Cmma on the basis of systematic absences (h + k = 2n for hkl, h = 2n for hk0) with *a* ~ 31.5 Å, *b* ~ 21.5 Å, and *c* = 3.932(4) Å. The short cell axis was parallel to the long crystal axis, and the repeat distance was measured from oscillation photographs. This space group assignment was suspect, however, because the reflections at higher θ values on the upper-level photographs straddled, rather than lay upon, the festoons; adjacent reflections alternated from the smooth trace of the festoons. The alternation was such that those reflections with both h and k odd could be separated into two groups; those for which h + k = 4n lay on one side of the festoon while those with h + k = (4n − 2) lay on the other side. All other reflections (*i.e.* those with both h and k even) were split, although this was clearly seen only at higher θ. By observing that the split reflections could also be separated, the diffraction record was resolved into a monoclinic pattern, and (after reassigning axes) the space group $P2_1/c$ was obtained with cell constants: *a* = 9.57 Å, *b* = 3.932 Å, *c* = 19.14 Å, and β = 111.8(2)°. A twinning model which assumed the folding of two crystal domains about the (102) monoclinic plane, which becomes one of the pseudo-orthorhombic (010) planes, was developed. The relationship between these two cells is demonstrated in Fig. 1. This description seems reasonable in that the resulting monoclinic *a* axis is half the length of the *c* axis for the primitive unit, and the twinning is viewed as stacking faults along the unique axis. An alternative model can be related to the pseudo-orthorhombic (100) planes, but we chose the first model because the reflections along the monoclinic (102) are unsplit in omega while the $(10\bar{2})$ planes appear split in the photographs by about 2°. This could be explained by the necessity that *a* is not exactly equal to *c*/2 and, therefore, that twinned *a* does not exactly lie along *c*. The reflections were indexed according to the monoclinic model with split reflections resolved into their overlapping contributors and each given half the intensity estimated for the pair. The usual Lorentz and polarization corrections were applied to the 290 observed reflections.

The structure was solved by assuming that the copper atom lay at the origin as in $Cu(4\text{-}Etpy)_2Cl_2$,

TABLE II. Bond Distances (A) and Interbond Angles (°) in $Cu(4\text{-}Mepy)_2Cl_2$.

	Distances		
Cu···Cu′	3.932(4)	C2–C3	1.44(6)
Cu–Cl	2.35(1)	C3–C4	1.42(6)
Cu···Cl′	3.19(1)	C4–C7	1.59(6)
Cu–N	2.07(3)	C4–C5	1.43(6)
N–C2	1.47(5)	C5–C6	1.38(5)
N–C6	1.41(4)		
	Angles		
Cl–Cu–N	91.0(11)	C2–C3–C4	120.7(49)
Cl′···Cu–N	90.2(12)	C3–C4–C7	117.5(47)
Cu–Cl···Cu′	89.0(4)	C3–C4–C5	118.5(45)
Cu–N–C2	117.1(28)	C5–C4–C7	123.9(46)
Cu–N–C6	120.2(27)	C4–C5–C6	123.7(44)
N–C2–C3	116.8(44)	C5–C6–N	117.4(40)
C2–N–C6	122.6(34)		

which crystallizes in a similar cell. The chlorine atom was located in a difference Fourier map and, after two least-squares cycles of refinement on the Cu and Cl atoms and their isotropic amplitudes of libration (B), the soundness of the model was graphically demonstrated when a second map showed all of the resolved atoms of the substituted pyridine ring. Consequently, the nitrogen and six carbon atoms were added to the model from map positions in two passes. The whole model was refined using anisotropic B's for Cu and Cl and isotropic B's for N and C, and after four cycles of full-matrix least-squares refinement the conventional R-factor, defined as $\Sigma||F_{obs}|-|F_{calc}||/\Sigma|F_{obs}|$, converged to 0.163. The correct cell constants for *a* and *c* were then remeasured from films, since the model was tenable. The splitting of the reflections along the pseudo-orthorhombic (110) and ($1\bar{1}0$) planes was recognized as the near superpositions of the *a* and *c* axes respectively in the twinned model. The relationship $a = c/2$ was revised to $a = 9.745(7)$ Å, and $c = 19.035(9)$ Å. After recomputing the Lp correction and performing several final least-squares cycles on the above model, the refinement converged to R = 0.157. Unit weights were used throughout. Form factors and dispersion factors (for Cu and Cl) were taken from International Tables for X-ray Crystallography [14]. Final atom positions and B values are given in Table I, and bond distances and angles are reported in Table II. A list of observed and calculated structure amplitudes is available [15].

Discussion

Necessarily, given the quality of the crystalline sample used in this study, the metrical parameters derived from this structure analysis are of limited precision. Nonetheless, the overall features of the structure are remarkably clear and can be compared with those reported for other complexes.

The ordered theme in $Cu(4\text{-}Mepy)_2Cl_2$ is a linear chain of copper atoms along the *b* axis linked by two closely bonded (2.35(1) Å) and two loosely bonded

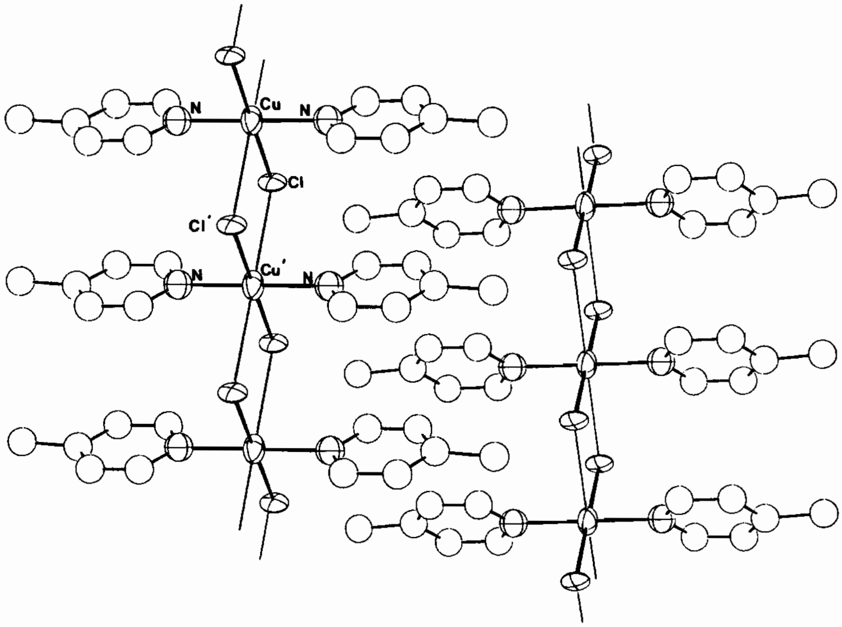

Fig. 2. View of the chain structure in $Cu(4\text{-}Mepy)_2Cl_2$. The view direction is parallel to the crystallographic *a* axis.

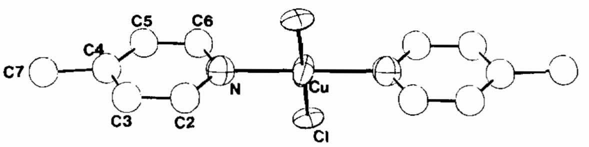

Fig. 3. View of a single formula unit of $Cu(4\text{-}Mepy)_2Cl_2$. The view direction is parallel to the crystallographic *b* axis.

(3.19(1) Å) chlorine atoms; the Cu–Cu separation in the chain is simply the *b*-axis length [3.932(4) Å], the bridging Cu–Cl–Cu angle being 89.0(4)°. Hence the coordination geometry at each copper(II) center is the commonly-observed tetragonally-elongated (4 + 2) coordination; the geometry of the chain is illustrated in Fig. 2. The base plane, which can be seen in Fig. 3, consists of *trans*- nitrogen and *trans*-chlorine atoms with Cu–N and Cu–Cl distances of 2.07(3) Å and 2.35(1) Å, respectively. The *cis* N–Cu–Cl angles are 89.0(11) and 91.0(11)°, while *trans* angles are constrained to be 180° by the inversion symmetry at copper. These bond lengths and angles are very similar to those in $Cu(py)_2Cl_2$ [1], $Cu(4\text{-}Etpy)_2Cl_2$, [4], $Cu(4\text{-}vinylpy)_2Cl_2$ [5], $Cu(thz)_2Cl_2$ [16], and other related chain structures. Hence, the geometry of any given chain in Fig. 2 is substantially similar to that in $Cu(py)_2Cl_2$, but different from that observed in the hydrazine complex [17] $Cu(hydrH)Cl_3$ and in related systems [18]. As in the $Cu(py)_2Cl_2$ system, the pyridine rings are tilted away from the base plane (see Fig. 3), the angle between the normals to the base plane and the least-squares plane through the pyridine ring being 59.7° in the present case and 58.2° in the pyridine complex [1c].

It is, however, noteworthy that the arrangement of the chains in the crystal of $Cu(4\text{-}Mepy)_2Cl_2$ is quite different from that in $Cu(py)_2Cl_2$. In the latter complex, since the chain direction is parallel to the monoclinic *c*-axis, the base planes in each chain are parallel [1]; in $Cu(4\text{-}Mepy)_2Cl_2$, however, where the chain direction is parallel to the monoclinic *b*-axis, the angle between the normals to the base planes in adjacent chains is 71.0; this feature of the structure is readily observed in Fig. 2, where the base planes in each chain are represented by bolder bonds. Hence, in this respect the structure of the present complex is more similar to those of the thiazole [16], 4-ethylpyridine [4], and 4-vinylpyridine [5] complexes than to that of the pyridine complex. Indeed, the angle of 71.5° here can be compared with the value of 77.9° reported for the thiazole complex [16].

The twinning in crystals of $Cu(4\text{-}Mepy)_2Cl_2$ is associated with the similarity of the packing motif, particularly of the pyridine rings, between adjacent layers in *b* that have *a* laid on −*c* or *c* laid on −*a*. A perfect fit requires $a = c/2$, and since this relation is not exactly fulfilled, the multiple twins give ris rise to large mosaicity. The nature of the twinning is such that Cu positions in chains along the *b* axis appear folded about the monoclinic (102) and overlay the ordered theme. A pseudomirror plane is apparent along this plane, and the twinning is not consistent with domains that are intergrown.

The present analysis, therefore, confirms that the ordered theme in $Cu(4\text{-}Mepy)_2Cl_2$ at room temperature does indeed consist of a linear chain, but that these chains are of finite (and presumably small) length because of the presence of the dislocations described above; regrettably, the average chain length cannot be deduced from the crystallographic data, so the potential impact of these dislocations on the magnetic interactions cannot be calculated. Moreover, our recent examination of the temperature dependence of the capacitance of this complex [19] demonstrates the presence of a phase transformation at approximately 53 K. Thus, while the present structural study provides some insight into the magnetic properties of the complex, further low-temperature analyses will be required before a complete understanding is available.

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