

oxygen O(10). This is due to the fact that O(11) forms only two bonds with the rest of the structure whereas O(10) forms four bonds. The oxygen O(5), which is bonded to two tetrahedrally coordinated boron atoms, has the smallest anisotropy of thermal motion among the oxygen atoms.

Furthermore, the directions of maximum displacement observed for the atoms O(6), O(7), O(9), which form a triangle around B(5), are nearly parallel to the normal of the plane formed by the three atoms. The same is true for the atoms O(1), O(4), O(8) which form the triangle around B(3).

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The Structure of Dichlorobis-(2-methylpyridine)copper(II): A Five-Coordinate Copper Complex

BY V. F. DUCKWORTH* AND N. C. STEPHENSON

School of Chemistry, University of New South Wales, Kensington, Australia

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Dichlorobis-(2-methylpyridine)copper(II) crystallizes in the triclinic system, space group $P\bar{1}$, with lattice constants $a = 8.58 \pm 0.05$, $b = 9.20 \pm 0.05$, $c = 10.99 \pm 0.05$ Å, $\alpha = 86.8 \pm 0.5^\circ$, $\beta = 110.1 \pm 0.05^\circ$ and $\gamma = 123 \pm 1^\circ$. The structure was determined by the heavy-atom method and refined by least-squares analysis to a final R value of 0.11 for 1152 visually estimated intensities. Each copper atom is surrounded by two chlorine and two nitrogen atoms in an approximately square-planar arrangement. The 2-methylpyridine ligands lie approximately in a plane which is perpendicular to the square-coordination plane and the methyl groups are in a *cis* arrangement, effectively hindering any close approach by the chlorine atom of another molecule at one axial coordinating site. There is evidence of some intermolecular association at the other axial site through Cu-Cl bridging, so that the environment of each copper atom may be described as a tetragonal pyramid.

Introduction

Metal halide complexes with pyridine and methylpyridines have been the subject of study for many years. More recently Graddon, Schulz, Watton & Weeden (1963) and Graddon & Watton (1965) have studied some metal halide complexes with 4-methylpyridine and 2-methylpyridine. Whilst they found that the properties of these complexes of cobalt(II) and copper(II) with 4-methylpyridine were substantially the same as those with the analogous pyridine complexes, they observed that the presence of 2-methylpyridine in these types of complexes could provide steric hindrance to

* Present address: Chemistry Department, University of Sheffield, Sheffield, England.

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octahedral coordination. Thus they could not prepare a 2-methylpyridine complex with cobalt(II) which corresponded to the octahedral $\text{CoCl}_2(\text{pyridine})_2$ form (Mellor & Coryell, 1938; Dunitz, 1957). Only a blue tetrahedral form was isolated. The complexes with copper(II) of the form $\text{CuX}_2(2\text{-methylpyridine})_2$ (where X is Cl or Br) were found to have properties which did not correspond to those of the analogous compounds of pyridine and 4-methylpyridine. The colours of the 2-methylpyridine complexes were much deeper and there were differences observed in the solid state visible absorption spectra which indicated a change in the stereochemistry of the copper atom.

On the basis of this evidence, Graddon & Watton (1965) postulated square-planar monomeric structures for these 2-methylpyridine complexes, in which the

Table 1. Observed and calculated structure amplitudes for dichlorobis(2-methylpyridine)copper(II)

Columns from left to right read h, k, l, F_o and F_c . The symbol U denotes an unobserved reflexion which has been assigned an F_o value based upon the minimum observable intensity. An asterisk denotes a reflexion which gave rise to a badly distorted spot on the Weissenberg photographs.

0	0	0	378.4	480.3	U	-5	0	2.2	-11.4	4	1	-1	35.3	-25.3	2	-7	2	7.4	7.3	8	-7	2	2.3	-5.2	5	-7	2	4.2	-8.4	6	-7	2	4.2	-8.4	7	-7	2	4.2	-8.4	8	-7	2	4.2	-8.4	9	-7	2	4.2	-8.4	10	-7	2	4.2	-8.4	11	-7	2	4.2	-8.4	12	-7	2	4.2	-8.4	13	-7	2	4.2	-8.4	14	-7	2	4.2	-8.4	15	-7	2	4.2	-8.4	16	-7	2	4.2	-8.4	17	-7	2	4.2	-8.4	18	-7	2	4.2	-8.4	19	-7	2	4.2	-8.4	20	-7	2	4.2	-8.4	21	-7	2	4.2	-8.4	22	-7	2	4.2	-8.4	23	-7	2	4.2	-8.4	24	-7	2	4.2	-8.4	25	-7	2	4.2	-8.4	26	-7	2	4.2	-8.4	27	-7	2	4.2	-8.4	28	-7	2	4.2	-8.4	29	-7	2	4.2	-8.4	30	-7	2	4.2	-8.4	31	-7	2	4.2	-8.4	32	-7	2	4.2	-8.4	33	-7	2	4.2	-8.4	34	-7	2	4.2	-8.4	35	-7	2	4.2	-8.4	36	-7	2	4.2	-8.4	37	-7	2	4.2	-8.4	38	-7	2	4.2	-8.4	39	-7	2	4.2	-8.4	40	-7	2	4.2	-8.4	41	-7	2	4.2	-8.4	42	-7	2	4.2	-8.4	43	-7	2	4.2	-8.4	44	-7	2	4.2	-8.4	45	-7	2	4.2	-8.4	46	-7	2	4.2	-8.4	47	-7	2	4.2	-8.4	48	-7	2	4.2	-8.4	49	-7	2	4.2	-8.4	50	-7	2	4.2	-8.4	51	-7	2	4.2	-8.4	52	-7	2	4.2	-8.4	53	-7	2	4.2	-8.4	54	-7	2	4.2	-8.4	55	-7	2	4.2	-8.4	56	-7	2	4.2	-8.4	57	-7	2	4.2	-8.4	58	-7	2	4.2	-8.4	59	-7	2	4.2	-8.4	60	-7	2	4.2	-8.4	61	-7	2	4.2	-8.4	62	-7	2	4.2	-8.4	63	-7	2	4.2	-8.4	64	-7	2	4.2	-8.4	65	-7	2	4.2	-8.4	66	-7	2	4.2	-8.4	67	-7	2	4.2	-8.4	68	-7	2	4.2	-8.4	69	-7	2	4.2	-8.4	70	-7	2	4.2	-8.4	71	-7	2	4.2	-8.4	72	-7	2	4.2	-8.4	73	-7	2	4.2	-8.4	74	-7	2	4.2	-8.4	75	-7	2	4.2	-8.4	76	-7	2	4.2	-8.4	77	-7	2	4.2	-8.4	78	-7	2	4.2	-8.4	79	-7	2	4.2	-8.4	80	-7	2	4.2	-8.4	81	-7	2	4.2	-8.4	82	-7	2	4.2	-8.4	83	-7	2	4.2	-8.4	84	-7	2	4.2	-8.4	85	-7	2	4.2	-8.4	86	-7	2	4.2	-8.4	87	-7	2	4.2	-8.4	88	-7	2	4.2	-8.4	89	-7	2	4.2	-8.4	90	-7	2	4.2	-8.4	91	-7	2	4.2	-8.4	92	-7	2	4.2	-8.4	93	-7	2	4.2	-8.4	94	-7	2	4.2	-8.4	95	-7	2	4.2	-8.4	96	-7	2	4.2	-8.4	97	-7	2	4.2	-8.4	98	-7	2	4.2	-8.4	99	-7	2	4.2	-8.4	100	-7	2	4.2	-8.4	101	-7	2	4.2	-8.4	102	-7	2	4.2	-8.4	103	-7	2	4.2	-8.4	104	-7	2	4.2	-8.4	105	-7	2	4.2	-8.4	106	-7	2	4.2	-8.4	107	-7	2	4.2	-8.4	108	-7	2	4.2	-8.4	109	-7	2	4.2	-8.4	110	-7	2	4.2	-8.4	111	-7	2	4.2	-8.4	112	-7	2	4.2	-8.4	113	-7	2	4.2	-8.4	114	-7	2	4.2	-8.4	115	-7	2	4.2	-8.4	116	-7	2	4.2	-8.4	117	-7	2	4.2	-8.4	118	-7	2	4.2	-8.4	119	-7	2	4.2	-8.4	120	-7	2	4.2	-8.4	121	-7	2	4.2	-8.4	122	-7	2	4.2	-8.4	123	-7	2	4.2	-8.4	124	-7	2	4.2	-8.4	125	-7	2	4.2	-8.4	126	-7	2	4.2	-8.4	127	-7	2	4.2	-8.4	128	-7	2	4.2	-8.4	129	-7	2	4.2	-8.4	130	-7	2	4.2	-8.4	131	-7	2	4.2	-8.4	132	-7	2	4.2	-8.4	133	-7	2	4.2	-8.4	134	-7	2	4.2	-8.4	135	-7	2	4.2	-8.4	136	-7	2	4.2	-8.4	137	-7	2	4.2	-8.4	138	-7	2	4.2	-8.4	139	-7	2	4.2	-8.4	140	-7	2	4.2	-8.4	141	-7	2	4.2	-8.4	142	-7	2	4.2	-8.4	143	-7	2	4.2	-8.4	144	-7	2	4.2	-8.4	145	-7	2	4.2	-8.4	146	-7	2	4.2	-8.4	147	-7	2	4.2	-8.4	148	-7	2	4.2	-8.4	149	-7	2	4.2	-8.4	150	-7	2	4.2	-8.4	151	-7	2	4.2	-8.4	152	-7	2	4.2	-8.4	153	-7	2	4.2	-8.4	154	-7	2	4.2	-8.4	155	-7	2	4.2	-8.4	156	-7	2	4.2	-8.4	157	-7	2	4.2	-8.4	158	-7	2	4.2	-8.4	159	-7	2	4.2	-8.4	160	-7	2	4.2	-8.4	161	-7	2	4.2	-8.4	162	-7	2	4.2	-8.4	163	-7	2	4.2	-8.4	164	-7	2	4.2	-8.4	165	-7	2	4.2	-8.4	166	-7	2	4.2	-8.4	167	-7	2	4.2	-8.4	168	-7	2	4.2	-8.4	169	-7	2	4.2	-8.4	170	-7	2	4.2	-8.4	171	-7	2	4.2	-8.4	172	-7	2	4.2	-8.4	173	-7	2	4.2	-8.4	174	-7	2	4.2	-8.4	175	-7	2	4.2	-8.4	176	-7	2	4.2	-8.4	177	-7	2	4.2	-8.4	178	-7	2	4.2	-8.4	179	-7	2	4.2	-8.4	180	-7	2	4.2	-8.4	181	-7	2	4.2	-8.4	182	-7	2	4.2	-8.4	183	-7	2	4.2	-8.4	184	-7	2	4.2	-8.4	185	-7	2	4.2	-8.4	186	-7	2	4.2	-8.4	187	-7	2	4.2	-8.4	188	-7	2	4.2	-8.4	189	-7	2	4.2	-8.4	190	-7	2	4.2	-8.4	191	-7	2	4.2	-8.4	192	-7	2	4.2	-8.4	193	-7	2	4.2	-8.4	194	-7	2	4.2	-8.4	195	-7	2	4.2	-8.4	196	-7	2	4.2	-8.4	197	-7	2	4.2	-8.4	198	-7	2	4.2	-8.4	199	-7	2	4.2	-8.4	200	-7	2	4.2	-8.4	201	-7	2	4.2	-8.4	202	-7	2	4.2	-8.4	203	-7	2	4.2	-8.4	204	-7	2	4.2	-8.4	205	-7	2	4.2	-8.4	206	-7	2	4.2	-8.4	207	-7	2	4.2	-8.4	208	-7	2	4.2	-8.4	209	-7	2	4.2	-8.4	210	-7	2	4.2	-8.4	211	-7	2	4.2	-8.4	212	-7	2	4.2	-8.4	213	-7	2	4.2	-8.4	214	-7	2	4.2	-8.4	215	-7	2	4.2	-8.4	216	-7	2	4.2	-8.4	217	-7	2	4.2	-8.4	218	-7	2	4.2	-8.4	219	-7	2	4.2	-8.4	220	-7	2	4.2	-8.4	221	-7	2	4.2	-8.4	222	-7	2	4.2	-8.4	223	-7	2	4.2	-8.4	224	-7	2	4.2	-8.4	225	-7	2	4.2	-8.4	226	-7	2	4.2	-8.4	227	-7	2	4.2	-8.4	228	-7	2	4.2	-8.4	229	-7	2	4.2	-8.4	230	-7	2	4.2	-8.4	231	-7	2	4.2	-8.4	232	-7	2	4.2	-8.4	233	-7	2	4.2	-8.4	234	-7	2	4.2	-8.4	235	-7	2	4.2	-8.4	236	-7	2	4.2	-8.4	237	-7	2	4.2	-8.4	238	-7	2	4.2	-8.4	239	-7	2	4.2	-8.4	240	-7	2	4.2	-8.4	241	-7	2	4.2	-8.4	242	-7	2	4.2	-8.4	243	-7	2	4.2	-8.4	244	-7	2	4.2	-8.4	245	-7	2	4.2	-8.4	246	-7	2	4.2	-8.4	247	-7	2	4.2	-8.4	248	-7	2	4.2	-8.4	249	-7	2	4.2	-8.4	250	-7	2	4.2	-8.4	251	-7	2	4.2	-8.4	252	-7	2	4.2	-8.4	253	-7	2	4.2	-8.4	254	-7	2	4.2	-8.4	255	-7	2	4.2	-8.4	256	-7	2	4.2	-8.4	257	-7	2	4.2	-8.4	258	-7	2	4.2	-8.4	259	-7	2	4.2	-8.4	260	-7	2	4.2	-8.4	261	-7	2	4.2	-8.4	262	-7	2	4.2	-8.4	263	-7	2	4.2	-8.4	264	-7	2	4.2	-8.4	265	-7	2	4.2	-8.4	266	-7	2	4.2	-8.4	267	-7	2	4.2	-8.4	268	-7	2	4.2	-8.4	269	-7	2	4.2	-8.4	270	-7	2	4.2	-8.4	271	-7	2	4.2	-8.4	272	-7	2	4.2	-8.4	273	-7	2	4.2	-8.4	274	-7	2	4.2	-8.4	275	-7	2	4.2	-8.4	276	-7	2	4.2	-8.4	277	-7	2	4.2	-8.4	278	-7	2	4.2	-8.4	279	-7	2	4.2	-8.4	280	-7	2	4.2	-8.4	281	-7	2	4.2	-8.4	282	-7	2	4.2	-8.4	283	-7	2	4.2	-8.4	284	-7	2	4.2	-8.4	285	-7	2	4.2	-8.4	286	-7	2	4.2	-8.4	287	-7	2	4.2	-8.4	288	-7	2	4.2	-8.4	289	-7	2	4.2	-8.4	290	-7	2	4.2	-8.4	291	-7	2	4.2	-8.4	292	-7	2	4.2	-8.4	293	-7	2	4.2	-8.4	294	-7	2	4.2	-8.4	295	-7	2	4.2	-8.4	296	-7	2	4.2	-8.4	297	-7	2	4.2	-8.4	298	-7	2	4.2	-8.4	299	-7	2	4.2	-8.4	300	-7	2	4.2	-8.4	301	-7	2	4.2	-8.4	302	-7	2	4.2	-8.4	303	-7	2	4.2	-8.4	304	-7	2	4.2	-8.4	305	-7	2	4.2	-8.4	306	-7	2	4.2	-8.4	307	-7	2	4.2	-8.4	308	-7	2	4.2	-8.4	309	-7	2	4.2	-8.4	310	-7	2	4.2	-8.4	311	-7	2	4.2	-8.4	312	-7	2	4.2	-8.4	313	-7	2	4.2	-8.4	314	-7	2	4.2	-8.4	315	-7	2	4.2	-8.4	316	-7	2	4.2	-8.4	317	-7	2	4.2	-8.4	318	-7	2	4.2	-8.4	319	-7	2	4.2	-8.4	320	-7	2	4.2	-8.4	321	-7	2	4.2	-8.4	322	-7	2	4.2	-8.4	323	-7	2	4.2	-8.4	324	-7	2	4.2	-8.4	325	-7	2	4.2	-8.4	326	-7	2	4.2	-8.4	327	-7	2	4.2	-8.4	328	-7	2	4.2	-8.4	329	-7	2	4.2	-8.4	330	-7	2	4.2	-8.4	331	-7	2	4.2	-8.4	332	-7	2	4.2	-8.4	333	-7	2	4.2	-8.4	334	-7	2	4.2	-8.4	335	-7	2	4.2	-8.4	336	-7	2	4.2	-8.4	337	-7	2	4.2	-8.4
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Table 1 (cont.)

Table with multiple columns of numerical data, organized in a grid-like structure. The data appears to be a continuation of a table from a previous page, showing various values across different rows and columns.

presence of the methyl groups in the *ortho* position of the pyridine rings sterically hinders coordination in octahedral sites.

The determination of the crystal structure of dichlorobis-(2-methylpyridine)copper(II) has been undertaken to establish whether axial bonding to the copper has been prevented by the presence of *ortho* methyl groups, thereby reducing the environment of the copper to a square-planar one. A modified tetrahedral arrangement of ligands could be another possibility although this stereochemistry is comparatively rare amongst cupric compounds. However, if it were found for this complex, it would closely parallel the behaviour of the related cobalt compounds in which a breakdown from the violet polymeric to a tetrahedral monomeric form is observed when a methyl group is introduced into the *ortho* position.

Experimental

Crystals of the compound were obtained by dissolving copper chloride dihydrate in absolute alcohol, warming the solution and then adding excess 2-methylpyridine. A green precipitate of unknown composition was first obtained and then filtered off. The product which slowly separated out from the filtrate as dark blue plates analysed as $\text{CuC}_{12}\text{H}_{14}\text{N}_2\text{Cl}_2$.

Zero level Weissenberg and precession photographs with Cu $K\alpha$ and Mo $K\alpha$ radiation, respectively, enabled the unit-cell dimensions to be determined and established the crystal system as triclinic. The space group $P\bar{1}$ was confirmed by the structure analysis.

Dichlorobis-(2-methylpyridine)copper(II)

$\text{CuC}_{12}\text{H}_{14}\text{N}_2\text{Cl}_2$, F.W. 320.7.

Triclinic, $a=8.58 \pm 0.05$, $b=9.20 \pm 0.05$, $c=10.99 \pm$

0.05 \AA , $\alpha=86.8 \pm 0.5^\circ$, $\beta=110.1 \pm 0.5^\circ$, $\gamma=123 \pm 1^\circ$.
 $U=670.6 \text{ \AA}^3$, $D_m=1.58 \text{ g.cm}^{-3}$, $D_c=1.59 \text{ g.cm}^{-3}$, $Z=2$, $F(000)=326$, Space group $P\bar{1}$.

The crystals decomposed in the X-ray beam with the loss of pyridine base, so that it was necessary to mount the single crystal in a lithium borate capillary tube together with a small amount of mother liquor from the preparation. In this way the crystal was maintained in an atmosphere of free base and decomposition was delayed for several days.

The intensity data were estimated visually from multifilm equi-inclination Weissenberg photographs collected about [001], ($l=0, \dots, 9$) and internally correlated with data collected about [010]. Three crystals were used owing to decomposition. Lorentz and polarization corrections were applied on UTECOM using the programs of Rollett (1961). Neither extinction nor absorption corrections were applied to these data and the observed structure amplitudes F_o are listed for comparison with F_c in Table 1. The reliability index R for these observed data is 0.11.

Structure determination and refinement

The positions of the copper and chlorine atoms were determined from the three-dimensional Patterson function. Gradual refinement of these parameters together with the location of the remaining atoms was obtained with successive cycles of structure factors and electron-density difference syntheses.

Refinement of positional parameters and isotropic temperature factors was initially carried out with Rollett's structure factor least-squares program. Weighting scheme 1 (Rollett, 1961) was used and the calculations were performed on UTECOM, an English Electric DEUCE computer. Some time later, access was ob-

Table 2. Fractional atomic coordinates and temperature factors for dichlorobis-(2-methylpyridine)copper(II)

Standard deviations are given in brackets and refer to the last two preceding decimal places.

	x/a	y/b	z/c	r.m.s.* standard deviations (\AA)	Temperature factor, B (\AA^2)
Cu(1)	0.1483 (02)	0.0368 (02)	0.2151 (02)	0.002	2.31 (06)
Cl(2)	0.2126 (04)	-0.1399 (04)	0.3322 (04)	0.004	3.48 (07)
Cl(3)	0.0721 (04)	0.2061 (04)	0.0850 (03)	0.004	3.14 (07)
N(4)	0.4215 (13)	0.1771 (11)	0.2092 (10)	0.011	2.27 (17)
C(5)	0.4535 (17)	0.1336 (16)	0.1126 (15)	0.016	3.24 (23)
C(6)	0.6466 (20)	0.2401 (17)	0.0941 (16)	0.016	3.94 (27)
C(7)	0.7993 (17)	0.3752 (15)	0.1950 (14)	0.015	3.12 (23)
C(8)	0.7700 (20)	0.4071 (18)	0.3010 (16)	0.018	4.20 (28)
C(9)	0.5885 (15)	0.3137 (14)	0.3094 (13)	0.014	2.50 (20)
C(10)	0.5595 (22)	0.3536 (18)	0.4317 (15)	0.017	4.59 (30)
N(11)	-0.1186 (12)	-0.0860 (11)	0.2373 (10)	0.010	2.28 (17)
C(12)	-0.2590 (19)	-0.2594 (17)	0.1653 (15)	0.017	3.93 (27)
C(13)	-0.4503 (17)	-0.3537 (16)	0.1812 (14)	0.015	3.03 (22)
C(14)	-0.4994 (18)	-0.2718 (16)	0.2480 (14)	0.015	3.70 (26)
C(15)	-0.3514 (18)	-0.0970 (15)	0.3199 (14)	0.015	3.30 (23)
C(16)	-0.1579 (14)	-0.0168 (14)	0.3100 (14)	0.014	2.24 (21)
C(17)	0.0073 (20)	0.1710 (17)	0.3951 (14)	0.016	3.95 (26)

* Root mean square standard deviations in atomic positions.

tained to an IBM 7040 computer and the Busing, Martin & Levy (1962, 1964) programs were used to obtain the coordinates and standard errors listed in Table 2. These coordinates were used to derive the interatomic distances listed in Table 3 and the bond angles listed in Table 4. The standard errors in these values were computed from the variance-covariance matrix obtained in the final least-squares refinement and the unit-cell errors with the *ORFFE* program of Busing, Martin & Levy (1964). The standard deviation in the value of each observed structure amplitude F_o was assumed to be $F_o/10$.

Table 3. *Interatomic distances in the molecule of dichlorobis-(2-methylpyridine)copper(II)*

Bond	Length	Estimated standard deviation
Cu(1)—Cl(2)	2.21 Å	0.005 Å
—Cl(3)	2.26	0.005
—N(4)	1.98	0.012
—N(11)	2.02	0.011
N(4)—C(5)	1.32	0.019
C(5)—C(6)	1.47	0.025
C(6)—C(7)	1.36	0.025
C(7)—C(8)	1.35	0.024
C(8)—C(9)	1.34	0.025
C(9)—N(4)	1.39	0.018
C(9)—C(10)	1.54	0.023
N(11)—C(12)	1.41	0.018
C(12)—C(13)	1.45	0.028
C(13)—C(14)	1.38	0.022
C(14)—C(15)	1.43	0.022
C(15)—C(16)	1.44	0.022
C(16)—N(11)	1.28	0.017
C(16)—C(17)	1.57	0.023

Table 4. *Bond angles in the molecule of dichlorobis-(4-methylpyridine)copper(II)*

Angle	Value	e.s.d.
Cl(2)—Cu(1)—N(4)	91.5°	0.9°
Cl(3)—Cu(1)—N(4)	89.3	0.9
Cl(2)—Cu(1)—N(11)	89.4	0.9
Cl(3)—Cu(1)—N(11)	90.2	0.9
Cu(1)—N(4)—C(9)	123	1.3
Cu(1)—N(4)—C(5)	120	1.2
C(9)—N(4)—C(5)	117	1.3
N(4)—C(5)—C(6)	123	1.5
C(5)—C(6)—C(7)	115	1.8
C(6)—C(7)—C(8)	121	1.5
C(7)—C(8)—C(9)	122	1.6
C(8)—C(9)—N(4)	121	1.7
C(8)—C(9)—C(10)	121	1.5
N(4)—C(9)—C(10)	118	1.3
Cu(1)—N(11)—C(16)	124	1.2
Cu(1)—N(11)—C(12)	113	1.4
C(16)—N(11)—C(12)	123	1.3
N(11)—C(12)—C(13)	115	1.8
C(12)—C(13)—C(14)	122	1.6
C(13)—C(14)—C(15)	121	1.5
C(14)—C(15)—C(16)	114	1.8
C(15)—C(16)—N(11)	125	1.5
C(15)—C(16)—C(17)	114	1.8
N(11)—C(16)—C(17)	121	1.3
Cl(3)—Cu(1)—Cl*(3)	78.6	0.7
Cl(2)—Cu(1)—Cl*(3)	98.2	0.7

Table 4 (cont.)

Angle	Value	e.s.d.
N(4)—Cu(1)—Cl*(3)	94	1.2
N(11)—Cu(1)—Cl*(3)	92	1.2

* Denotes atom at $\bar{x} \bar{y} \bar{z}$ (*i.e.* in the other molecule of the dimer).

The atomic form factors of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) and Thomas & Umeda (1957) were used in structure factor calculations. The copper and chlorine curves were corrected for the real component of the anomalous dispersion of Cu $K\alpha$ radiation with the $\Delta f'$ values given by Dauben & Templeton (1955).

Description of the structure

The atomic arrangement within each molecule of dichlorobis-(2-methylpyridine)copper(II) is shown in Fig. 1, which is a projection of the unit-cell contents on the (010) plane. The stereochemistry of the copper atom is shown more clearly in Fig. 2, where it can be seen that each copper atom is surrounded by two chlorine and two nitrogen atoms in an approximately square-planar arrangement. The orientations of the heterocyclic rings about this square-plane are not related and the molecule does not possess any symmetry. The 2-methylpyridine ligands lie approximately in a plane which is perpendicular to the plane of the coordinating atoms and the methyl groups are in a *cis* arrangement, effectively hindering any close approach by the chlorine of another molecule at one axial coordinating site. There is evidence of some intermolecular association at the other site through Cu(1)...Cl(3) bridging, so that the environment of each copper atom may be described in terms of a distorted tetragonal pyramidal arrangement. The approach distances below 4 Å between the associated molecules are listed in Table 5.

Table 5. *Intermolecular approach distances of less than 4 Å between the associated molecules of dichlorobis-(2-methylpyridine)copper(II)*

Atom in molecule (1)	Atom in molecule (2)	Distance	e.s.d.
Cu(1)	Cl(3)	3.37 Å	0.005 Å
Cl(3)	Cl(3)	3.67	0.007
Cl(3)	C(5)	3.66	0.017
Cl(3)	N(11)	3.98	0.011
Cl(3)	C(12)	3.52	0.018
C(5)	N(11)	3.80	0.019
C(5)	C(12)	3.42	0.023
C(5)	C(13)	3.71	0.022
C(6)	C(12)	3.65	0.023
C(6)	C(13)	3.34	0.022
C(6)	C(14)	3.58	0.022

The environment of the copper atom

The environment of atoms involved in square-planar coordination to the copper atom is shown in Fig. 3. The two Cu—N bonds are equivalent in length but the

Table 6. *Least-squares planes*

Equations in the form $Ax + By + Cz + D = 0$, referred to the crystallographic axes, calculated after Schomaker, Waser, Marsh & Bergman (1959) with all weights equal to 1. All values have been multiplied by 10^3 .

Plane	A	B	C	D	Atoms defining the plane
I	-246	570	776	-1732	Cu(1), Cl(2), Cl(3), N(4), N(11)
II	-494	828	-340	1270	N(4), C(5), C(6), C(7), C(8), C(9), C(10)
III	326	-591	659	-1900	N(11), C(12), C(13), C(14), C(15), C(16), C(17)

Deviations from planes (10^{-3} Å)

Plane	Cu(1)	Cl(2)	Cl(3)	N(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)
I	-18	-82	-80	90	—	—	—	—	—	—
II	—	—	—	53	-53	8	14	-15	12	-19
III	—	—	—	—	—	—	—	—	—	—

	N(11)	C(12)	C(13)	C(14)	C(15)	C(16)	C(17)
I	90	—	—	—	—	—	—
II	—	—	—	—	—	—	—
III	-46	-16	77	-22	-39	-6	51

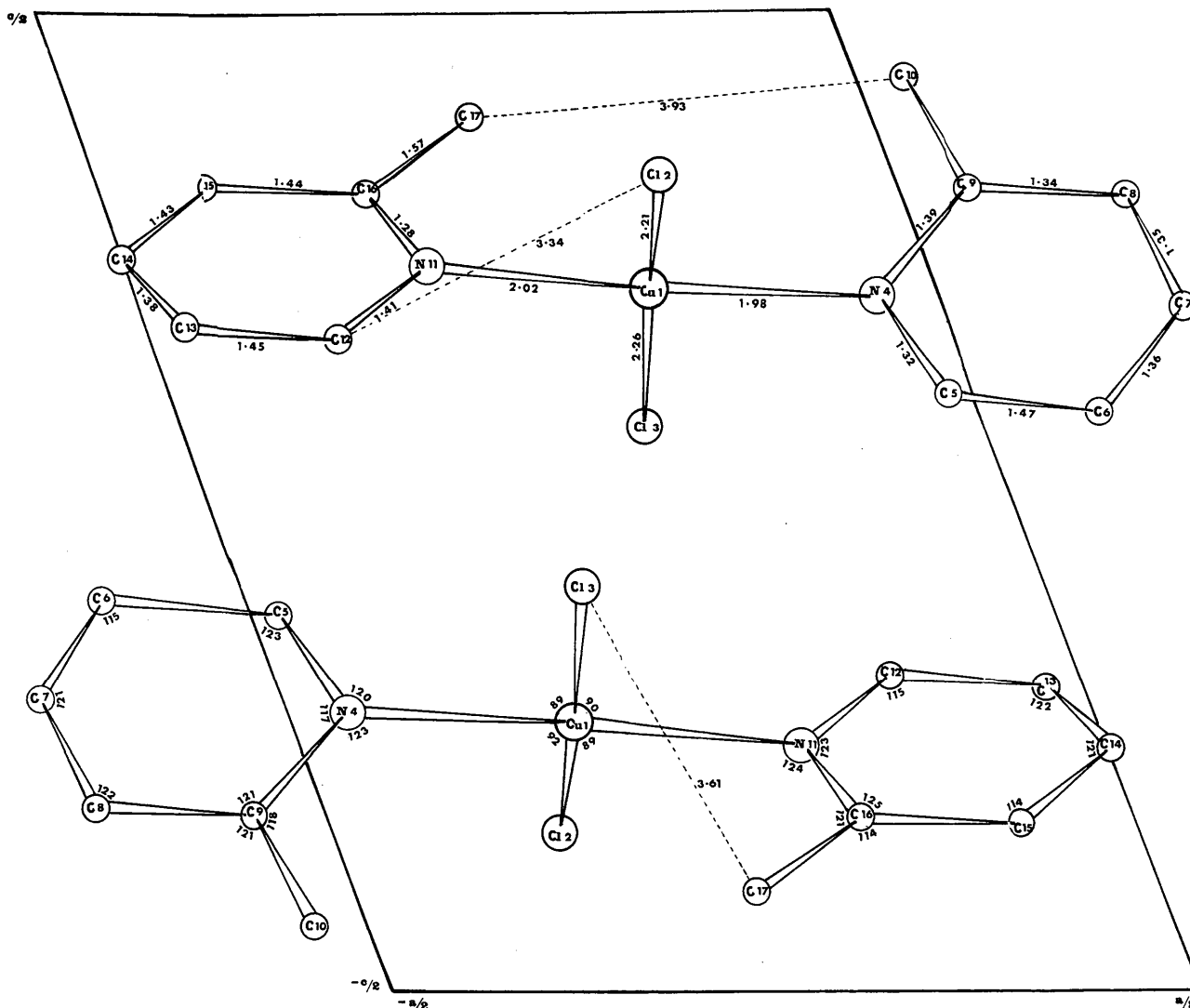


Fig. 1. An (010) projection of the unit cell of dichlorobis-(2-methylpyridine)copper(II). Broken lines indicate non-bonding distances.

difference of 0.05 Å between the two Cu–Cl bond lengths is real ($\Delta/\sigma = 7$). The longer Cu–Cl(3) distance is in keeping with the fact that Cl(3) is the bridging chlorine atom. The four interatomic angles in the plane which have copper at the vertex do not differ significantly from 90°.

The equation of the plane of best fit through these five atoms is given in Table 6 and there are significant deviations of all these atoms from planarity. The copper and chlorine atoms lie out of the plane towards the associated molecule whilst the nitrogen atoms deviate in the opposite direction.

The molecules in the dimeric unit are held together by two weaker Cu(1)...Cl(3) bonds which form the axes of the pyramidal arrangements about the copper atoms and which are 3.37 Å in length. Details of the bridging are presented in Fig. 3 where a comparison is made with the analogous pyridine complex. In this complex the heterocyclic rings in each square-planar unit are centrosymmetrically related through the copper atoms and the units pack in such a way that the pyridine rings in adjacent units are parallel. The spacing between adjacent units is 3.87 Å and the Cu...Cl bridging distance is 3.05 Å. The introduction of a me-

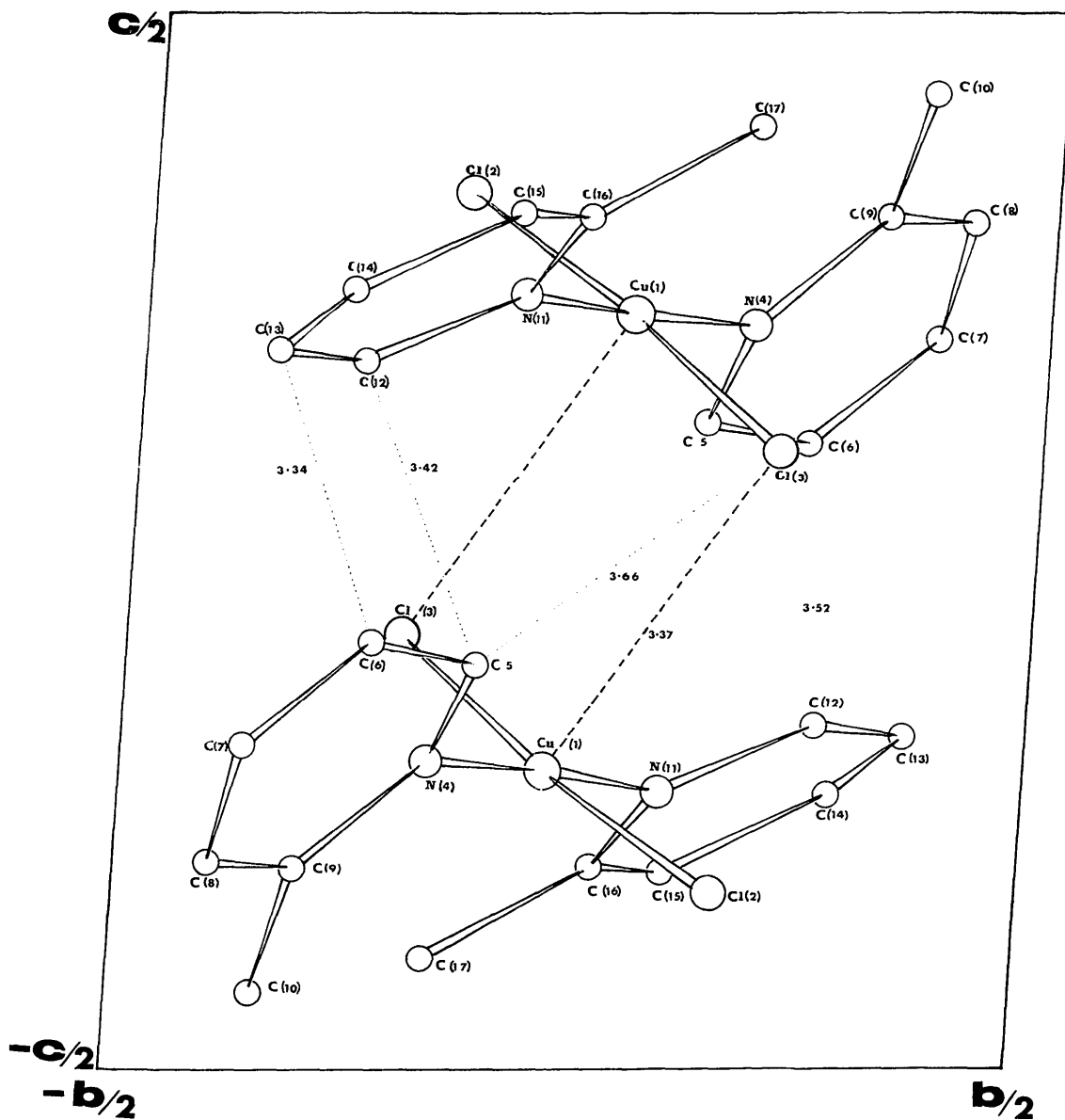


Fig. 2. A (100) projection of the unit cell of dichlorobis-(2-methylpyridine)copper(II). Broken lines indicate copper–chlorine bridges whereas dotted lines indicate some close non-bonding approaches.

thyl group into the *ortho* position of each pyridine ring results in a reduction in the symmetry of the square planar unit. The symmetry is sacrificed to enable an increase in the coordination number of copper, for if the methyl groups had assumed symmetrical *trans* positions, the coordination in both axial sites would have been completely hindered. The resulting non-parallel arrangement of rings in the dimeric unit prevents the bridging chlorine atom from reaching a position as close to the copper atom as is obtained in the pyridine complex. The displacements of Cu(1) and Cl(3) atoms from the square-plane towards the associated molecule represent an effort to shorten the bridging bond distances.

The 2-methylpyridine ligands

Within the rather large standard deviations obtained for the C–C and C–N bond distances, none of the dimensions associated with the ligand are anomalous (for comparison see Bak, Hansen & Rastrup-Andersen, 1954; Kiedel & Bauer, 1956).

The mean value of the interatomic angles in the two rings is 120°, but two of these angles [C(14)–C(15)–C(16) and C(15)–C(16)–N(11)] are more than three standard deviations removed from this value.

The mean plane through each ligand is listed in Table 6. Atoms N(4) and C(5) are significantly displaced from plane II, whilst N(11), C(13) and C(17) are significantly displaced from plane III. The dihedral angle between the ligand planes is 24°, whilst ligand planes II and III are inclined at 84° and 72° to the square-plane through the copper and coordinated atoms. Both 2-methylpyridine ligands are inclined more sharply to the square-plane than are the pyridine rings in CuCl₂(pyridine)₂, where this angle is 59° (Kabalkina, 1956).

The distortions which are evident in the geometry of the 2-methylpyridine ligands can be shown to arise, in the main, from the efforts of the copper atom to overcome the steric hindrance provided by the methyl groups and increase its coordination number to greater than four. To a lesser extent the packing of the dimers affects the regular geometry of each molecule.

One 2-methylpyridine ligand (plane III, Table 6) has rotated as far as possible about the Cu–N axis so that the methyl group C(17) and *ortho* carbon C(12) have been forced into close contact with atoms Cl(3) and Cl(2), respectively (approach distances 3.61 and 3.34 Å). The remaining 2-methylpyridine ligand has rotated about the Cu–N axis until methyl groups C(10) and C(17) are in close contact (*i.e.* 3.93 Å apart). In this way the copper atom has been partially exposed in one axial site, enabling further coordination to occur, but at the same time the ligands have suffered geometric distortions due to close approaches from neighbouring atoms. Relevant non-bonding distances are listed in Table 7 where they are contrasted with the sum of the van der Waals radii appropriate to each contact (Pauling, 1960).

Table 7. Some close non-bonding approach distances between atoms in the crystal of dichlorobis(2-methylpyridine)copper(II)

The atomic numbering used is the same as in Table 2; the number in the second bracket denotes the following symmetry transformation:

No bracket	x	y	z	
i	\bar{x}	\bar{y}	\bar{z}	
ii	$x-1$	$y-1$	z	
iii	\bar{x}	\bar{y}	$1-z$	
iv	$x-1$	y	z	
v	$1-x$	\bar{y}	$1-z$	

Atom 1	Atom 2	Distance	e.s.d.	Sum of van der Waals radii
C(5)–Cl(3)		3.60 Å	0.017 Å	3.5 Å
–Cl(2)		3.67	0.017	3.5
–Cl(3) (i)		3.66	0.017	3.5–3.8
–C(12) (i)		3.42	0.023	3.4
C(12)–Cl(2)		3.34	0.017	3.5
–Cl(3) (i)		3.52	0.017	3.5
–C(8) (ii)		3.43	0.026	3.4
C(13)–C(6) (i)		3.34	0.022	3.4
–C(9) (ii)		3.43	0.020	3.4
C(16)–C(17) (iii)		3.58	0.020	3.7
C(17)–C(10)		3.93	0.024	4.0
–Cl(3)		3.61	0.017	3.8
–C(7) (iv)		3.47	0.021	3.7
–C(8) (iv)		3.62	0.025	3.7
Cl(2)–C(10) (v)		3.82	0.018	3.8

* Van der Waals radii taken from Pauling (1960).

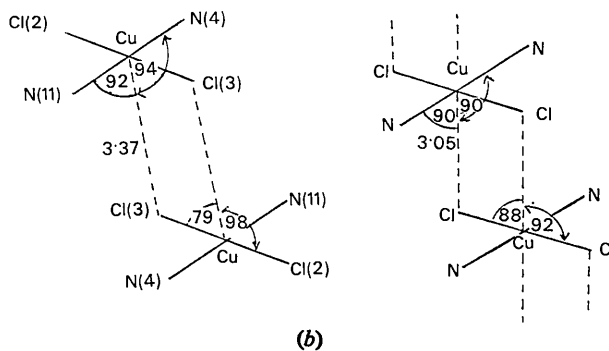
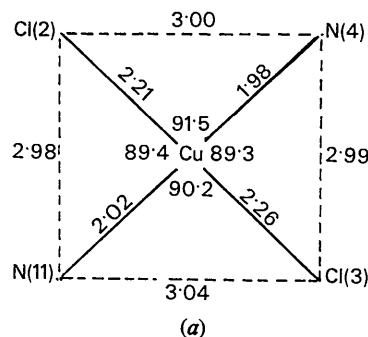


Fig. 3. (a) A diagram of the square-planar environment of the copper atom in dichlorobis(2-methylpyridine)copper(II). (b) Copper-chlorine bridging in dichlorobis(2-methylpyridine)copper(II) and dichlorobispyridinecopper(II) (Dunitz, 1957).

Discussion

Although a structure involving five-coordinate copper (II) was not originally envisaged for dichlorobis-(2-methylpyridine)copper(II), the result is not an unlikely one, since the bridged dimeric five-coordinate arrangement is frequently found amongst cupric compounds. This result demonstrates the disinclination of copper (II) to obtain a tetrahedral environment such as that found in the analogous cobalt complex.

An interesting comparison can be made between the structure of dichlorobis-(2-methylpyridine)copper(II) and that of $\text{SeOCl}_2(\text{pyridine})_2$. This structure also consists of dimeric units in which the centrosymmetrically related molecules are held together by weak Se...Cl bridges (Lindquist & Nahringerbauer, 1959). The selenium atom in this structure has a tetragonal pyramidal environment with the oxygen at the apex of the pyramid and a *trans* arrangement of nitrogen and chlorine atoms in the basal plane. The weak interaction of the selenium with the chlorine from the other molecule in the triclinic cell completes the distorted octahedron. The two Se-Cl distances in the square-plane are different and the longer one involves the bridging chlorine atom. The two pyridine rings are inclined at different angles to the square-plane about the selenium. There are thus several points of similarity between this structure and that of dichlorobis-(2-methylpyridine)copper(II). However, in the selenium compound there is no evidence of distortion in the geometry of the pyridine rings or in the angles of the polyhedron about the selenium. All non-bonding distances are reported as normal. The Se-Cl bridging distance (3.65 Å) is obtained without any strains being produced in the dimer. (The closest intermolecular C-C approaches in the dimer are 3.51 and 3.79 Å, as compared with 3.34 and 3.42 Å in the cupric complex.)

The improved packing in this structure, as compared with that of dichlorobis-(2-methylpyridine)copper(II) may be attributed to the absence of methyl groups in the pyridine rings and the smaller tendency of the selenium atom to complete the octahedral coordination. The bridging distance, 3.65 Å, presumably is a

true measure of this tendency, whilst in the cupric complex there is evidence to suggest that steric effects prevent the formation of a stronger Cu-Cl bond which, at a bond distance of 3.37 Å, is longer than other reported Cu-Cl bridging distances (Wells, 1947; Dunitz, 1957; Willett, 1966).

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