

PREPARATION AND MOLECULAR STRUCTURE OF $[\text{CuCl}(\text{L})]_6$; $\text{L} = 2\text{-(METHYLAMINO)PYRIDINE}$

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ABSTRACT : The 2- (methylamino) pyridine, L, reacts with CuCl in THF to give hexameric copper (I) complex, $[\text{CuCl}(\text{L})]_6$. The molecular structure has been determined by using single-crystal X-ray diffraction method. The complex crystallizes in the monoclinic space group $P2_1/n$ with four molecules per unit cell. The unit cell dimensions are $a = 8.3495(15)$, $b = 15.622(6)$, and $c = 17.030(4)\text{\AA}$ with $\beta = 98.55(2)^\circ$. The final R value is 0.062 for 4261 reflections measured. Coordination number around Cu(1) and Cu(3) is four (nearly tetrahedral), but around Cu(2) is three (nearly trigonal). The Cu(2) - Cu(3) bond distance is $2.682(2)\text{\AA}$.

KEY WORDS : Preparation, Molecular Structure, $[\text{CuCl}(\text{L})]_6$, L = 2-(Methylamino) pyridine.

INTRODUCTION :

Copper(I) complexes show a variety of coordination environments ranging in coordination number from two to five in monomeric species [1-11]. The number of ligands bound to the univalent metal seems to be influ-

enced greatly by both the chemical nature of the ligands and the geometry they impose. The three center anionic chelating ligands have a remarkable ability for enforcing dimeric, trimeric, and tetrameric aggregation, and short metal-metal

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contacts in some cases [12-20]. Penta-, octa-, and dodecanuclear copper(I) complexes are unusual [21-23]. Several infinite- sheet, chain, and layer copper(I) complex polymers have been investigated by the X- ray and neutron diffraction methods [24-27]. Copper(I), but not copper(II), forms a variety of compounds with Cu-Cu bonds [6, 7, 14, 17, 19, 20]. A few hexameric copper(I) complexes have also been reported [28-30]. In this research project, complex of 2- (methylamino) pyridine with CuCl has been prepared and investigated by a single- crystal X- ray diffraction.

EXPERIMENTAL :

All the operations were performed under dry nitrogen with use of standard *Schlenk* techniques or in a nitrogen-filled dry-box. THF and 2-(methylamino)pyridine were dried and distilled by standard method before using. Infrared spectrum was recorded on a *Perkin- Elmer 393* instrument from Nujol mull prepared in a dry-box.

Preparation of complex

To a stirred 100mL THF solution of dry 2-(methylamino)pyridine (4.00g, 36.98mmol) was added one equivalent of CuCl (3.66g, 36.98 mmol). The resulting slurry was boiled and filtered and allowed to cool at ambient temperature. Large white crystals separated upon standing at room temperature after two days. The large single white crystals were filtered and dried and stored under nitrogen in sealed ampoules (yield $\approx 60\%$). IR (Nujol mull, KBr, cm^{-1}): [Nujol: 3000-2865(vs), 1455(s), 1375(s), 1345(w, sh), 3320(m, NH stretching vibration), 1610(s), 1570(s), 1520(s), 1280(m), 1255(m), 1165(s), 1155(m), 1080(w), 1005(vw), 962(vw), 845(vw), 810 (vw), 770(s), 735(w), 720(vw), 595(vw), 445(w).

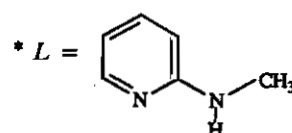
Data collection and reduction

A white crystal of $\text{C}_{18}\text{H}_{24}\text{Cu}_3\text{Cl}_3\text{N}_6$ having approximate dimensions of $0.20 \times 0.20 \times 0.20\text{mm}$ was mounted on a glass fiber. All measurements were made on a Rigaku AFC6S diffractometer

with graphite monochromated Mo- $K\alpha$ radiation and 12kW rotating anode generator, using the $\theta/2\theta$ scan mode. Cell dimensions were obtained from 24 reflections with 2θ angle in the range of 40.00-50.00 degrees. The crystals are monoclinic space group $P2_1/n$. The unit cell and crystal data are reported in Table 1.

Table 1 : Crystal Data for $[\text{CuCl}(\text{L})]_6^*$

Empirical Formula	$\text{C}_{18}\text{H}_{24}\text{Cu}_3\text{Cl}_3\text{N}_6$
Formula Weight	621.4
Crystal Dimensions(mm)	$0.20 \times 0.20 \times 0.20$
Crystal System	Monoclinic
Lattice Parameters	$a = 8.3495(15)\text{\AA}$ $b = 15.622(6)\text{\AA}$ $c = 17.030(4)\text{\AA}$ $\beta = 98.548(18)^\circ$ $V = 2196.5(11)\text{\AA}^3$
Space Group	$P2_1/n$
Z	4
$D_{\text{calc}}(\text{g}/\text{cm}^3)$	1.879
R	0.062



Structure determination and refinement

Data were collected at -160°C . The structure was solved by direct method. The non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated but not refined. The final cycles of full- matrix least-squares refinement was based on the number of observed reflections with $I > 2.5 \sigma(I)$ and corresponding parameters. The final R value ($R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$) was 0.062 for 4261 reflections measured. Absorption correction was made. The minimum and maximum transmission factors are 0.4501 and 0.5972. The last least squares cycle was calculated with 54 atoms, 340 parameters and 3030 out of 3859 reflections. Weights based on counting- statistics

were used. The maximum and minimum peaks on the final difference Fourier map corresponded to $-1.370/\text{\AA}^3$ and $1.620/\text{\AA}^3$. Fractional atomic coordinates are given in Table 2. Anisotropic thermal parameters for non-hydrogen atoms, the hydrogen atom parameters and distances are available.

RESULTS AND DISCUSSION :

The crystal consists of $[\text{CuCl}(\text{L})]_6$ complex, illustrated in Fig. 1. Stereoview of this complex and also stereoview of the packing of $[\text{CuCl}(\text{L})]_6$ in the unit cell are given in Figs. 2 and 3 respectively. Coordination number around Cu(1) and Cu(3) are four (nearly tetrahedral), but around Cu(2) is three (nearly trigonal). Selected bond distances and angles are given in Table 3. Crystals are monoclinic space group $P2_1/n$ with four molecules per unit cell. The short Cu...Cu

distances in the various Cu aggregates, ranging from 2.38\AA which is nearly 0.2\AA shorter than the Cu-Cu distance in metallic copper (2.56\AA) to about 2.8\AA , raise the question of whether significant direct Cu-Cu bonding occurs. In this complex, the Cu(2)...Cu(3) distance is $2.682(2)\text{\AA}$ and indicates weak to moderate Cu...Cu interactions. Copper(I) compounds are diamagnetic and colorless, except when the anion present is colored or when charge-transfer absorptions take place in the visible region of the spectrum. The $[\text{CuCl}(\text{L})]_6$ complex is diamagnetic, air and moisture sensitive, and white color which is not surprising for Cu(I) complexes.

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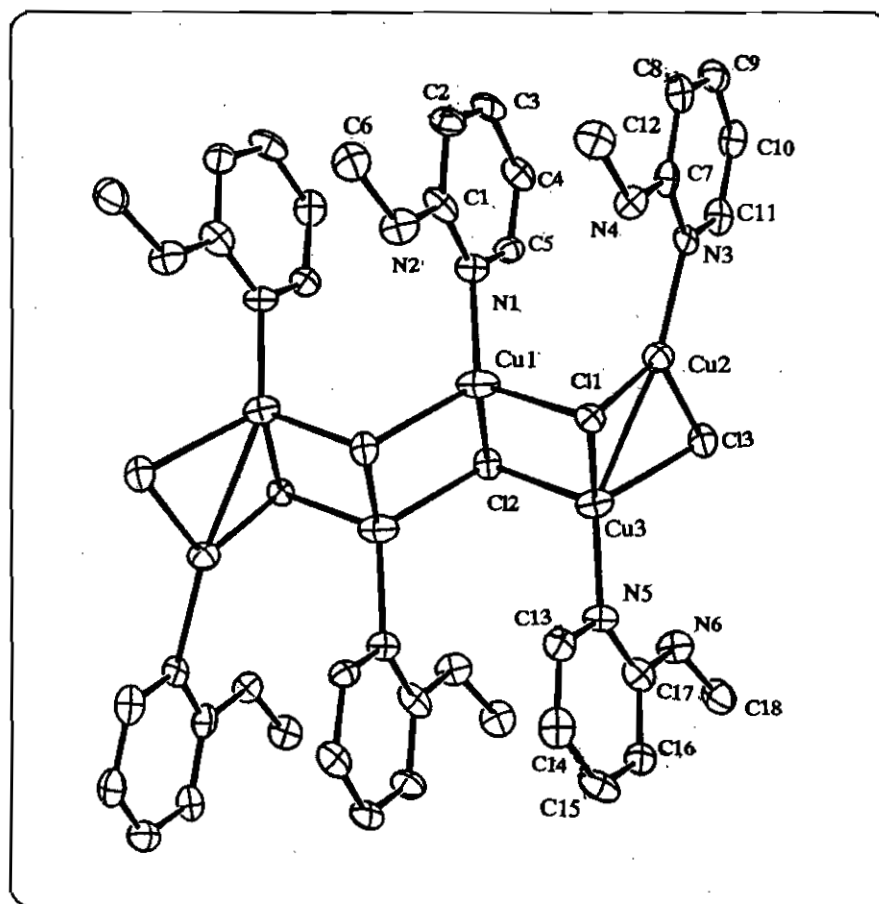
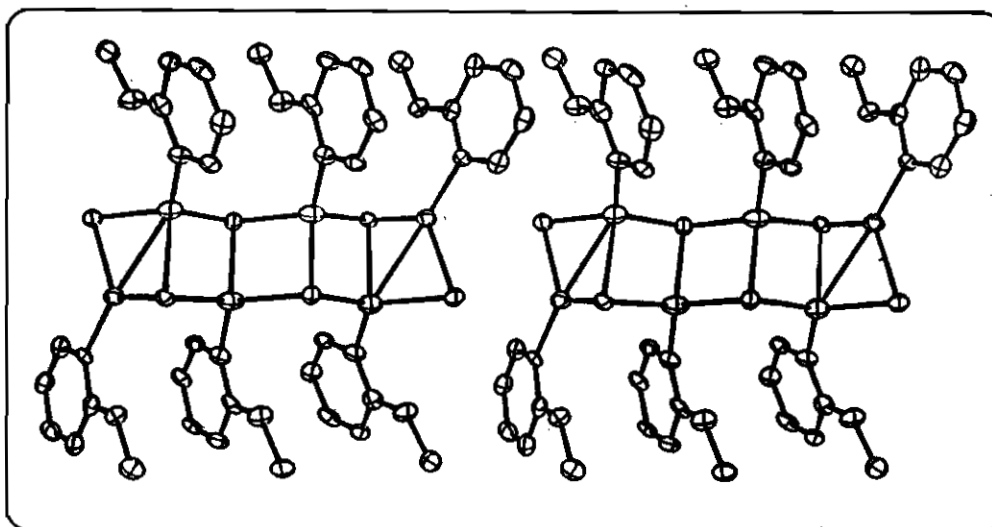
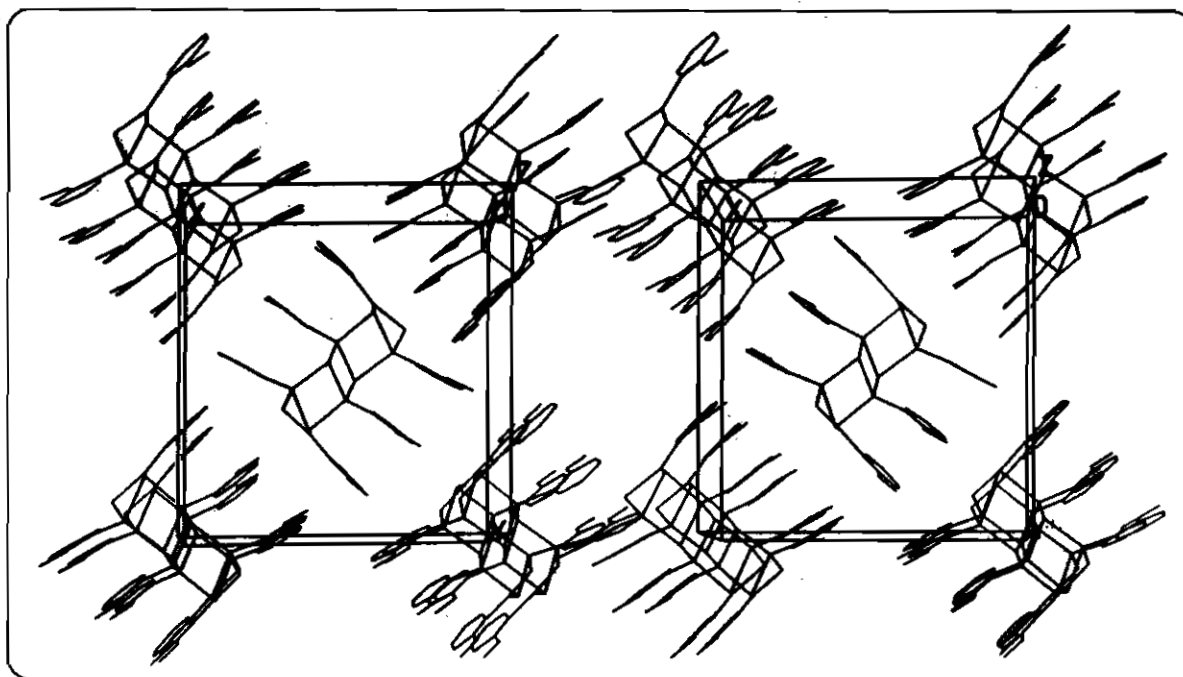


Fig. 1 : ORTEP drawing of $[\text{CuCl}(\text{L})]_6$; L = 2-(methylamino) pyridine, with selected bond distances.

Fig. 2 : Stereoview of $[\text{CuCl}(\text{L})]_6$ complex.Fig. 3 : Stereoview of the packing of $[\text{CuCl}(\text{L})]_6$ complex in the unit cell.Table 2 : Atomic parameters x , y , z and Biso. E.S.D.s. refer to the last digit printed

	x	y	z	Biso
Cu1	-0.94844(20)	0.01565(11)	-0.08135(10)	2.60(6)
Cu2	-0.74411(18)	-0.09120(10)	-0.17315(8)	1.92(6)
Cu3	-0.84061(20)	-0.15381(11)	-0.04122(10)	2.55(6)
Cl1	-1.0183(3)	-0.10058(18)	-0.17620(15)	1.55(10)
Cl2	-0.7924(3)	-0.03653(19)	0.04209(16)	1.76(10)

Table 2 Continued :

	x	y	z	Biso
Cl3	-0.5927(4)	-0.18106(20)	-0.08717(16)	2.09(10)
N1	-0.8240(12)	0.1127(6)	-0.1184(5)	1.8(4)
N2	-1.0610(12)	0.1720(7)	-0.1847(6)	2.3(4)
N3	-0.6273(12)	-0.0219(6)	-0.2429(5)	1.6(4)
N4	-0.8674(11)	0.0270(6)	-0.3127(6)	1.8(4)
N5	-0.9804(12)	-0.2484(7)	-0.0122(6)	1.9(4)
N6	-0.7493(12)	-0.3206(7)	0.0427(6)	2.3(4)
C1	-0.8932(14)	0.1730(9)	-0.1691(6)	2.0(5)
C2	-0.8021(15)	0.2336(8)	-0.2031(7)	2.2(5)
C3	-0.6347(15)	0.2311(8)	-0.1853(6)	2.0(5)
C4	-0.5622(15)	0.1695(9)	-0.1315(6)	2.1(5)
C5	-0.6624(14)	0.1124(7)	-0.1007(6)	1.8(5)
C6	-1.1503(15)	0.2406(9)	-0.2289(7)	2.4(5)
C7	-0.7024(14)	0.0295(7)	-0.2993(7)	1.8(4)
C8	-0.6155(15)	0.0843(8)	-0.3416(7)	2.2(5)
C9	-0.4480(16)	0.0833(8)	-0.3260(7)	2.3(5)
C10	-0.3699(14)	0.0303(8)	-0.2688(7)	2.2(5)
C11	-0.4634(14)	-0.0208(8)	-0.2298(7)	2.0(4)
C12	-0.9646(15)	0.0854(9)	-0.3646(7)	2.4(5)
C13	-1.1427(15)	-0.2427(8)	-0.0271(6)	2.0(5)
C14	-1.2453(15)	-0.3031(9)	-0.0041(7)	2.3(5)
C15	-1.1763(15)	-0.3741(9)	0.0372(7)	2.4(5)
C16	-1.0111(15)	-0.3816(8)	0.0531(7)	2.0(5)
C17	-0.9139(14)	-0.3167(8)	0.0285(7)	2.1(5)
C18	-0.6610(16)	-0.3926(9)	0.0817(8)	2.7(5)

Table 3 : Selected bond distances(Å) and angles(deg) for $[CuCl(L)]_6$; L=2- (methyl- amino) pyridine. Estimated standard deviations are given in parentheses.

$Cu(2) - Cu(3) = 2.682(2)$	
$Cu(1) - Cl(1) = 2.443(3)$	$Cu(3) - Cl(2) = 2.316(3)$
$Cu(1) - Cl(2) = 2.443(3)$	$Cu(3) - Cl(3) = 2.358(3)$
$Cu(2) - Cl(1) = 2.287(3)$	$Cu(1) - N(1) = 1.992(10)$
$Cu(2) - Cl(3) = 2.272(3)$	$Cu(2) - N(3) = 1.970(10)$
$Cu(3) - Cl(1) = 2.676(3)$	$Cu(3) - N(5) = 1.990(10)$
$Cl(1) - Cu(1) - Cl(2) = 111.4(1)$	$Cl(1) - Cu(3) - Cl(3) = 100.0(1)$
$Cl(1) - Cu(2) - Cl(3) = 115.7(1)$	$Cl(1) - Cu(3) - N(5) = 100.0(3)$
$Cl(1) - Cu(2) - N(3) = 127.3(3)$	$Cl(2) - Cu(3) - Cl(3) = 105.4(1)$
$Cl(3) - Cu(2) - N(3) = 116.7(3)$	$Cl(2) - Cu(3) - N(5) = 119.4(3)$
$Cl(1) - Cu(3) - Cl(2) = 107.7(1)$	$Cl(3) - Cu(3) - N(5) = 121.6(3)$

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