The Crystal Structure of Chlorotris(3-methylpyridine)copper(I), and its Conversion into Hexa-μ-chloro-tetrakis(3-methylpyridine)-μ_4-oxo-tetracopper(II) ‡

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The crystal and molecular structure of [Cu(3Me-py)$_3$Cl] (3Me-py = 3-methylpyridine) has been determined by single-crystal *X*-ray diffraction techniques from diffractometer data. Crystals of the complex are rhombohedral, space group *R*3, with *a* = 14.384(2), *c* = 7.451(2) Å, and *Z* = 3. After full-matrix least-squares refinement the final *R* value was 0.048 for 765 observed reflections. The complex consists of monomeric units with the copper having a tetrahedral co-ordination geometry. The monomers are stacked in such a manner that infinite linear Cu–Cl · · · Cu chains are formed with a separation of 7.451(2) Å between copper atoms. The complexes [CuL$_3$X] [L = py (pyridine), 2Me-py (2-methylpyridine), or 3Me-py, X = Cl; L = 3Me-py, X = Br] are readily oxidised to [Cu$_4$X$_6$OL$_4$] species.

The redox chemistry of copper has long been of interest to transition-metal chemists because of its importance in catalytic systems.[1] Attention has been directed towards two moieties resulting from the binding of oxygen to copper(I) with concomitant oxidation to copper(II). First, the intermediates, produced by oxidation of copper(I) chloride in pyridine or other donor solvents, which have the ability to catalyse cleavage of aromatic ring systems;[2] and secondly, compounds of general formula [Cu$_4$X$_6$OL$_4$] (where X = Cl or Br, L = pyridine or a methylpyridine) which have been used in the oxidation of phenols to polyphenyl ethers and diphenoquinones.[3]

To date the structural characterisation of compounds of the type [CuL$_3$X] (L = pyridine or a methylpyridine, X = Cl or Br) has been limited to information obtainable from i.r. spectral analysis,[4] and interest has focused chiefly on their fluorescence properties.[5] As they are the first intermediates in the preparation of the copper–pyridine catalysts mentioned earlier it seemed pertinent that a single-crystal structure analysis of one of the type be carried out. Therefore, in this paper we report the crystal structure of chlorotris(3-methylpyridine)copper(I), [Cu(3Me-py)$_3$Cl], and the facile oxidation undergone by it and similar compounds to complexes of the type [Cu$_4$X$_6$OL$_4$] (X = Cl or Br, L = pyridine or a methylpyridine). This oxidation reaction provides a general synthetic route to the latter complexes.

Experimental

The physical measurements have been described previously.[6]

Preparations.—[CuL$_3$X] (L = py, 2Me-py, *or* 3Me-py, X = Cl; L = 3Me-py, X = Br). These compounds were prepared by adding CuX to an excess of the appropriate pyridine under dinitrogen following a method similar to that described by de Ahna and Hardt.[5]

[Cu$_4$X$_6$OL$_4$] (L = py, 2Me-py, *or* 3Me-py, X = Cl; L = 3Me-py, X = Br). These were obtained by refluxing the appropriate [CuL$_3$X] complex (1.0 g) in anhydrous ethanol (50 cm^3) for 15 min, followed by immediate filtration of the hot solution. On cooling, crystals of the product appeared which were then collected and washed with anhydrous ethanol. Yield: 0.20 g (35%) [Cu$_4$Cl$_6$O(3Me-py)$_4$] (Found: C, 33.7; H, 3.6; N, 6.2. Calc. for $C_{24}H_{28}Cl_6Cu_4N_4O$: C, 33.7; H, 3.3; N, 6.55%). The other compounds were verified by comparison of their melting points with literature values[7,8] (given in parentheses): [Cu$_4$Cl$_6$O(py)$_4$], m.p. 251—253 (251); [Cu$_4$Cl$_6$O(2Me-py)$_4$], 208 (223); [Cu$_4$Br$_6$O(3Me-py)$_4$], 243—244 (241 °C).

Crystallography.—The crystals of [Cu(3Me-py)$_3$Cl] form yellow-green hollow hexagonal prisms which become amorphous to *X*-rays if left exposed to the air. When the crystals are grown more slowly they form solid, darker yellow-green crystals. Preliminary photography indicated rhombohedral symmetry, and no further systematic absences were observed; subsequent solution and refinement confirmed the space group *R*3. Lattice constants were obtained from the least-squares refinement of the diffractometer settings of seven accurately centred reflections, for which $27 < \theta(\text{Cu-}K_\alpha) < 32°$.

Crystal data. $C_{18}H_{21}ClCuN_3$, *M* = 378.39, rhombohedral, *a* = 14.384(2), *c* = 7.451(2) Å, *Z* = 3, D_c = 1.41 g cm^{-3}, *F*(000) = 588, Cu-K_α radiation, λ = 1.5418 Å, $\mu(\text{Cu-}K_\alpha)$ = 70.72 cm^{-1}, space group *R*3.

Data collection and structure solution. A crystal was coated with epoxy-resin to prevent the loss of 3-methylpyridine. Data were collected using a Hilger and Watts autodiffractometer with Cu-K_α radiation and a θ—2θ scan consisting of 60 steps of 0.01° with 1 s per step. The local background was measured at either side of the scan for 10 s using a stationary counter/stationary crystal. 1 323 Reflections for which $\theta(\text{Cu-}K_\alpha) <$ 53° were measured, which yielded 765 reflections (including Friedel equivalents) for which $I > 3\sigma(I)$. The intensities of

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‡ *Supplementary data available* (No. SUP 23865, 8 pp.): thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.
Non-S.I. unit employed: G = 10^{-4} T.

Table 1. Final atomic co-ordinates ($\times 10^4$) for [Cu(3Me-py)$_3$Cl] with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Cu	0	0	0
Cl	0	0	−3 298(3)
N(1)	759(4)	−806(3)	719(6)
C(2)	1 055(5)	−868(5)	2 397(8)
C(3)	1 557(5)	−1 419(6)	2 904(9)
C(4)	1 772(7)	−1 969(6)	1 587(11)
C(5)	1 484(9)	−1 929(8)	−117(12)
C(6)	965(7)	−1 351(7)	−505(8)
C(7)	1 887(9)	−1 407(10)	4 827(11)

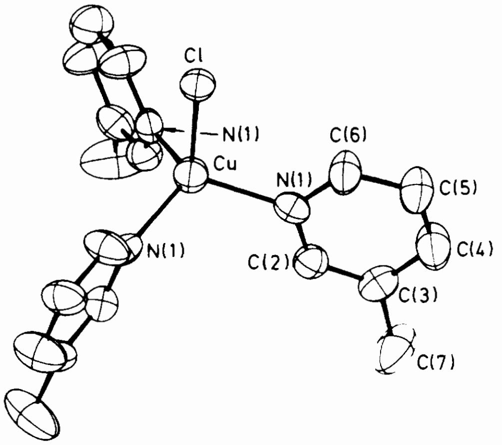

Figure 1. The molecular structure of [Cu(3Me-py)$_3$Cl] showing the atom labelling

Table 2. Bond lengths (Å) and angles (°) for [Cu(3Me-py)$_3$Cl] with estimated standard deviations in parentheses

Cu–Cl	2.458(2)	C(3)–C(4)	1.389(13)
Cu–N(1)	2.021(5)	C(3)–C(7)	1.507(11)
N(1)–C(2)	1.338(8)	C(4)–C(5)	1.345(13)
N(1)–C(6)	1.329(9)	C(5)–C(6)	1.398(11)
C(2)–C(3)	1.366(10)		

Cl–Cu–N(1)	105.4(1)	C(2)–C(3)–C(4)	117.9(7)
N(1)–Cu–N(1)	113.2(3)	C(2)–C(3)–C(7)	120.7(7)
Cu–N(1)–C(2)	124.6(4)	C(4)–C(3)–C(7)	121.4(8)
Cu–N(1)–C(6)	120.0(4)	C(3)–C(4)–C(5)	118.8(7)
C(2)–N(1)–C(6)	115.4(6)	C(4)–C(5)–C(6)	119.2(7)
N(1)–C(2)–C(3)	125.2(6)	C(5)–C(6)–N(1)	123.6(6)

three reflections, measured periodically throughout the data collection, showed only random fluctuations of ±3%. Absorption corrections were not applied due to the difficulty of describing the crystal and allowing for the effect of the encasing resin.

The copper and chlorine atom positions were found from a Patterson map and the remaining atoms were found by the normal succession of structure factor and Fourier difference calculations. Hydrogen atoms were placed in their calculated positions, those of the methyl group being at idealised positions calculated from the orientation of one peak in the Fourier difference map. The non-hydrogen atoms were refined with anisotropic thermal parameters; the hydrogen-atom thermal parameters were set to $U_H = 0.07$ Å^2 for the aromatic and $U_H = 0.08$ Å^2 for the methyl hydrogens. At convergence $R_1 = \Sigma\Delta/\Sigma|F_o| = 0.048$, $R_2 = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}} = 0.049$: $\Delta = |F_o| - |F_c|$. The function minimised was $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/[\sigma(F)]^2$. A final Fourier difference map showed no peaks of chemical significance. When the structure with the opposite polarity was refined to convergence, $R_1 = 0.056$ and $R_2 = 0.059$. The only other space group which might be considered is *R*3*m*. This would require the molecule to have perfect 3*m* symmetry. Although there is approximate 3*m* symmetry, the deviation is such that the space group was left as *R*3. Final atomic co-ordinates are listed in Table 1.

Results and Discussion

The Structure of Chlorotris(3-*methylpyridine*)*copper*(I), [Cu(3Me-py)$_3$Cl].—The stereochemistry of the complex is shown in Figure 1 and the bond lengths and angles are given in Table 2. The CuN$_3$Cl unit, which has C_{3v} symmetry, is only slightly distorted from tetrahedral. While the Cu–N(1) bond distance of 2.021(5) Å is within the range of 2.00—2.05 Å found for copper(I) complexes with pyridine and substituted-pyridine ligands,[6] the Cu–Cl bond at 2.458(2) Å is slightly longer than expected[9] (2.24—2.40 Å) for a terminal Cu^I–Cl bond. The predicted Cu^I–Cl bond length is 2.34 Å (taking the covalent radii of Cu^I and Cl to be 1.35 and 0.99 Å respectively[10]).

For the phosphine ligand complexes [Cu(PPh$_3$)$_3$Cl] and [Cu(PMePh$_2$)$_3$Cl], which both have a similar tetrahedral geometry,[11] the Cu–Cl distances are 2.335(15) and 2.366(4) Å. The significantly longer Cu–Cl distance found for [Cu(3Me-py)$_3$Cl] can in part be related to the 3Me-py ligand being a weaker π acceptor than the phosphine ligands, and hence having a greater effective contribution to the charge density on the copper. However, steric factors should also be considered. Since the *ortho*-hydrogen atoms, H(6), of the 3Me-py ligands make intramolecular contacts with the Cl atom of 2.82 Å, which are slightly less than the van der Waals Cl · · · H distance of 2.95 Å, the Cu · · · H(2) distance is 3.07 Å, somewhat greater than the van der Waals distance (2.60 Å).

Figure 2 shows that the monomeric [Cu(3Me-py)$_3$Cl] units are stacked in such a manner that infinite linear Cu–Cl · · · Cu chains are formed, the intermolecular Cu · · · Cl distance 4.994(2) Å giving a separation of 7.451(2) Å between copper atoms. The *ortho*-hydrogen atoms, H(2), make intermolecular contacts with the Cl atom in the same chain and the *para*-hydrogen atoms, H(4), make interchain contacts (see Figure 2). Overall then, each Cl atom is surrounded by nine hydrogen atoms, which suggests these interactions may be important in stabilising the complex in the solid state.

Reactivity of [Cu(3Me-py)$_3$Cl].—The electronic spectrum (Nujol mull) displays an absorption at 360 nm, assigned as a $3d^{10}\rightarrow 3d^9\ \pi^*$ metal-to-ligand charge-transfer transition.[12] In addition, even freshly prepared samples show two weak bands at 700 and 875 nm, in the region normally associated with *d-d* transitions for copper(II) complexes. Magnetic and e.s.r. studies confirm the presence of trace amounts of copper(II). The compound possesses a low magnetic moment (after diamagnetic correction) of *ca.* 0.6 μ_B at 295 K, and shows a rhombic type e.s.r. spectrum at both room temperature and 110 K (Table 3). The visible electronic and e.s.r. spectral features are identical to those of [Cu$_4$Cl$_6$O(3Me-py)$_4$] thus indicating its presence in the copper(I) complex.

Oxidation of [Cu(3Me-py)$_3$Cl] in solution is rapid, the crystals dissolving in a variety of solvents (*e.g.* acetonitrile nitromethane, acetone, dichloromethane, and ethanol) to give orange-yellow solutions. Again the electronic [430 (sh), 785, and 875 nm] and e.s.r. (Table 3) spectra point to the

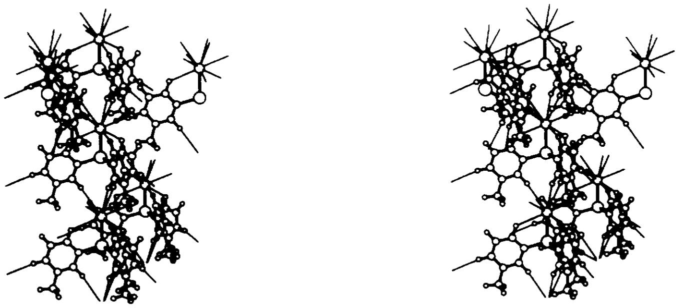

Figure 2. A stereoscopic view of [Cu(3Me-py)$_3$Cl] chains showing Cl ··· H distances less than 3 Å. The distances are: intrachain Cl ··· H(2) 2.97, interchain Cl ··· H(4) 2.82, and intramolecular Cl ··· H(6) 2.82 Å

Table 3. E.s.r. data for the [Cu$_4$X$_6$OL$_4$] complexes

Complex	State [a]	$g_\parallel$	$10^4 A_\parallel$/cm^{-1}	$g_\perp$
[Cu$_4$Cl$_6$O(py)$_4$]	Nitromethane soln.	2.272	180	2.062
[Cu$_4$Cl$_6$O(2Me-py)$_4$]	Nitromethane soln.	2.258	162	2.055
[Cu$_4$Cl$_6$O(3Me-py)$_4$]	Nitromethane soln.[b]	2.266	182	2.059
	Powder	2.240(g_3)		2.070(g_2) 2.042(g_1)
[Cu$_4$Br$_6$O(3Me-py)$_4$]	Nitromethane soln.	2.265	180	2.058

[a] At 110 K. [b] Identical parameters observed for copper(II) species in [Cu(3Me-py)$_3$Cl].

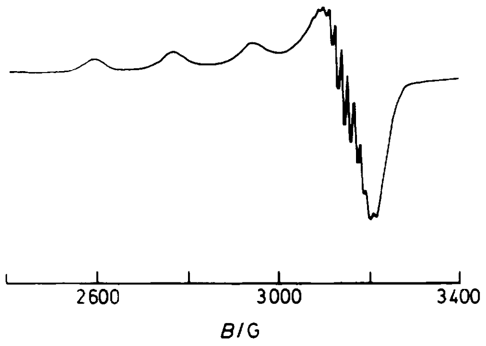

Figure 3. E.s.r. spectrum (110 K) of [Cu$_4$Br$_6$O(3Me-py)$_4$] in nitromethane

formation of [Cu$_4$Cl$_6$O(3Me-py)$_4$]. Indeed, refluxing [Cu(3Me-py)$_3$Cl] in ethanol produces orange-brown crystals of the compound [Cu$_4$Cl$_6$O(3Me-py)$_4$]. Similarly [Cu(3Me-py)$_3$Br], [Cu(py)$_3$Cl], and [Cu(2Me-py)$_3$Cl] gave complexes identified as [Cu$_4$Br$_6$O(3Me-py)$_4$], [Cu$_4$Cl$_6$O(py)$_4$], and [Cu$_4$Cl$_6$O(2Me-py)$_4$] respectively. The last two have been previously structurally characterised by *X*-ray crystallography.[13,14] In each case the copper atoms are not entirely equivalent, but all are found in essentially a trigonal-bipyramidal stereochemistry with varying degrees of distortion. Three halogen atoms are present in the trigonal plane and oxygen and pyridine or methylpyridine occupy the axial positions. The e.s.r. solution spectral profiles of these complexes are all very similar (*e.g.* Figure 3) showing nine hyperfine lines in the perpendicular region, and are typical of compounds possessing structures intermediate between trigonal bipyramidal and square pyramidal.[15] This is not the first occasion that a copper(I) starting material has been used to produce these compounds. Indeed an early report by Blanchard and Finkbeiner[3] described refluxing CuCl and pyridine in methanol to produce [Cu$_4$Cl$_6$O(py)$_4$], although the authors formulated it as $\{[(py)_2CuCl_2]_2CuCl_2{\cdot}CuO\}_n$. A reaction in many respects analogous to ours was reported by Churchill *et al.*[16] who prepared [Cu$_4$Cl$_6$O(PEt$_3$O)$_4$] by air oxidation of [{Cu(PEt$_3$)Cl}$_4$] in CH$_2$Cl$_2$–CCl$_4$. Carr and Harrod[8] also postulate a copper(I) intermediate in their synthesis of [Cu$_4$Cl$_6$O(py)$_4$] from the thermal decomposition of bis(pyridine)bis(2,4,6-trichlorophenolato)copper(II).

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