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catena-Poly[[(3-acetylpyridine)copper(I)]-μ_3-chloro]

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Key indicators

Single-crystal X-ray study
T = 291 K
Mean σ(C–C) = 0.006 Å
R factor = 0.053
wR factor = 0.142
Data-to-parameter ratio = 15.4

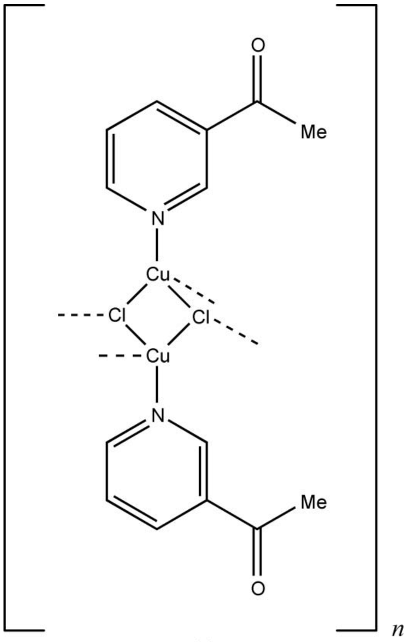
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the search for ketone complexes suitable for absolute asymmetric synthesis, that is, complexes crystallizing in Sohncke space groups, we have studied complexes between copper(I) halides and acetylpyridines. The structure of polymeric [CuCl(3-acpy)]$_n$ (3-acpy is 3-acetylpyridine, C_7H_7NO), a compound which was found to form achiral chains crystallizing in a centrosymmetric space group, is reported here. The complex forms ladder-type chains, in which the Cu^I atom is coordinated by one N atom and three Cl atoms in a tetrahedral geometry. In the crystal structure, the chains are interconnected through C—H$\cdots$Cl and C—H$\cdots$O intermolecular contacts.

Comment

Nucleophilic additions to pro-chiral ketones or aldehydes give rise to chiral alcohols, and hence coordination compounds displaying pro-chiral ketones or aldehydes as ligands are interesting starting materials for the absolute asymmetric synthesis of stereochemically inert organic compounds (Johansson *et al.*, 2005). Absolute asymmetric synthesis will be possible if the aldehyde/ketone complex crystallizes in one of the Sohncke space groups (Flack, 2003) and undergoes crystallization-induced asymmetric transformation (Eliel & Wilen, 1994). In order to obtain complexes with ketone or aldehyde ligands, one can either rely on the electron-donating effect of the carbonyl group, or one can use ketones containing another, more potent, electron-donating centre. Many metals readily form complexes with pyridine derivatives, and thus we focused our study on acetyl pyridines. We were intrigued to find that [Cu^I(4-acpy)]$_n$, where 4-acpy is 4-acetylpyridine, was reported to crystallize in space group $P2_12_12_1$ (Cariati *et al.*, 2002), but when we prepared this compound we found that it displayed extensive inversion twinning. It was possible, however, to detect weak solid-state circular dichroism from bulk samples, but on solid-state reduction with sodium borohydride, the alcohol which was obtained showed no sign of enantiomeric enrichment when analysed by enantioselective high-performance liquid chromatography. Consequently, we prepared a number of related compounds, and in this paper we report the structure of the polymeric title compound [CuCl(3-acpy)]$_n$, (I) (Fig. 1).

The crystal structure of (I) is built up by ladder-type chains (Fig. 2) extending along the a axis, where the coordination geometry around the Cu^I centre is best described as tetrahedral, showing only a small degree of distortion (Table 1). The Cl atoms, taking intermolecular contacts into account, are five-coordinate, with coordination geometries best described as intermediate between highly distorted trigonal–bipyramidal and square-pyramidal. The structure is comparable to those of similar complexes, with Cu—N and Cu—halogen bond lengths well within the range of values published previously (Healy *et al.*, 1989; Goher *et al.*, 1985; Rath *et al.*, 1986).



(I)

The polymeric chains are further stabilized by π–π stacking interactions, which may increase the rigidity of the structure. The distances N1—N1^{i}, C1—C1^{i}, C2—C2^{i}, C3—C3^{i}, C4—C4^{i} and C5—C5^{i} [symmetry code: (i) $-1 + x, y, z$] correspond to a translation along the *a* axis, and hence are 3.8230 (14) Å, which is within the range normally established for π–π stacking interactions (Jones, 2001). With respect to this, the structure of (I) resembles that of [Cu^{I}(4-acpy)]$_n$ but, in contrast with that structure, the polymeric chains of (I) are achiral and the complex crystallizes in the centrosymmetric space group $P2_1/c$.

The polymeric chains of (I) are connected to each other through intermolecular contacts of two distinct types (Fig. 3). The first type acts between the Cl atom and two H atoms from two different 3-acetylpyridine ligands in an adjacent chain. The second type connects the O atom with H atoms in two different adjacent chains (Table 2). In this way, every chain is surrounded by, and bonded to, six other chains.

The polymeric nature of (I), taking the extensive intermolecular interactions into account, explains the low solubility observed in most common solvents. A more striking property of the compound, namely its relatively high inertness with respect to oxidation in air, may perhaps also be rationalized by the well packed structure, with many bonds that would have to be broken upon oxidation.

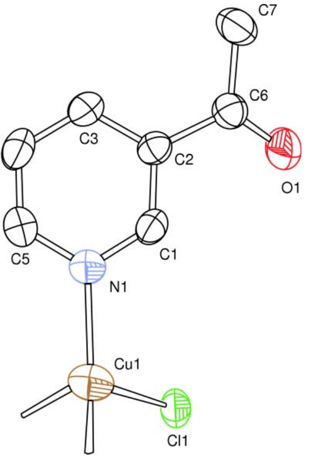


Figure 1
The asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. All H atoms have been omitted.

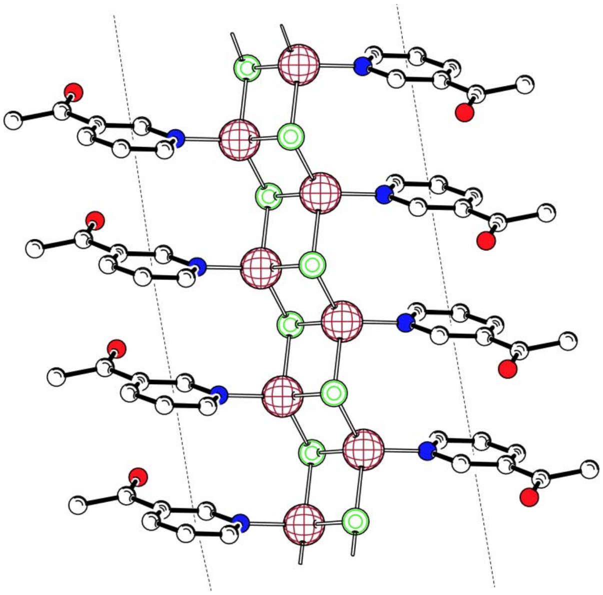


Figure 2
A plot showing the polymeric structure of (I), viewed along [013], with π–π stacking interactions indicated by dashed lines.

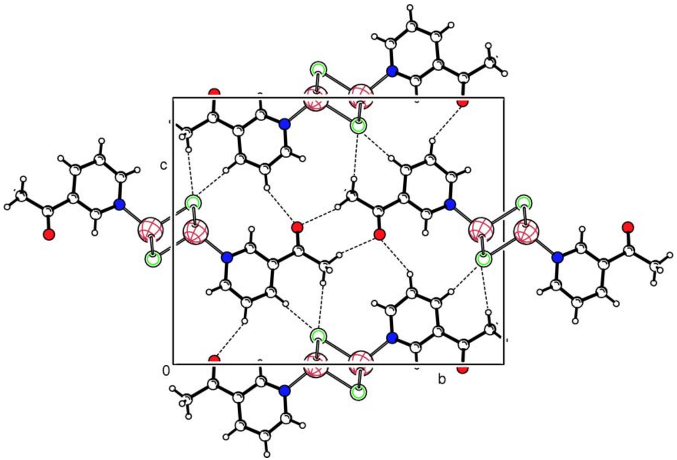


Figure 3
A plot showing the intermolecular contacts (dashed lines) between polymeric chains of (I).

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Experimental

A Schlenk tube was charged with a solution of 3-acetylpyridine (0.32 ml, 2.4 mmol) in dichloromethane (3 ml). A 2:1 mixture of toluene–dichloromethane (10 ml) was carefully layered on the 3-acetylpyridine solution. Finally, a solution of copper(I) chloride (0.30 g, 30 mmol) in acetonitrile (3 ml) was carefully added as a third layer. After a few days, pale-yellow needles of (I) formed as the top and bottom layers slowly mixed by diffusion (yield 0.30 g, 53%).

Crystal data

$[CuCl(C_7H_7NO)]$
$M_r = 220.13$
Monoclinic, $P2_1/c$
$a = 3.8230$ (14) Å
$b = 15.990$ (5) Å
$c = 13.100$ (4) Å
$\beta = 99.768$ (9)°
$V = 789.2$ (5) Å^3
$Z = 4$
$D_x = 1.853$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5457 reflections
$\theta = 3.0$–26.0°
$\mu = 3.04$ mm^{-1}
$T = 291$ (2) K
Needle, yellow
0.5 × 0.2 × 0.2 mm

Data collection

Rigaku R-AXIS IIc image-plate diffractometer
φ scans
Absorption correction: multi-scan (Crystal Clear; Rigaku, 2000)
$T_{min} = 0.211$, $T_{max} = 0.542$
5457 measured reflections
1540 independent reflections
1081 reflections with $I > 2\sigma(I)$
$R_{int} = 0.079$
$\theta_{max} = 26.0°$
$h = -4 \rightarrow 4$
$k = -19 \rightarrow 19$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.142$
$S = 0.91$
1540 reflections
100 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0821P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.58$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—Cu1	1.992 (3)	Cl1—Cu1^{ii}	2.4366 (14)
Cl1—Cu1^{i}	2.3013 (12)	Cl1—Cu1	2.4378 (13)
N1—Cu1—Cl1^{i}	124.56 (10)	Cl1^{i}—Cu1—Cl1^{ii}	107.55 (5)
N1—Cu1—Cl1^{ii}	103.95 (10)	N1—Cu1—Cl1	108.27 (10)

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $-x+1, -y+1, -z+1$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C3—H3$\cdots$Cl1^{iii}	0.93	2.86	3.542 (4)	131
C7—H7$C\cdots$Cl1^{iv}	0.96	2.77	3.713 (5)	168
C4—H4$\cdots$O1^{v}	0.93	2.56	3.390 (5)	148
C7—H7$A\cdots$O1^{vi}	0.96	2.71	3.641 (6)	165

Symmetry codes: (iii) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$; (iv) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (v) $x-1, -y+\frac{3}{2}, z-\frac{1}{2}$; (vi) $-x+2, -y+2, -z+1$.

All H atoms were placed in calculated positions and refined using a riding model, with C—H distances of 0.93 Å for aromatic CH and 0.96 Å for methyl CH$_3$, and with $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic H atoms and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms.

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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