

trans-Dichloridotetrakis(3,5-dimethylpyridine)copper(II)

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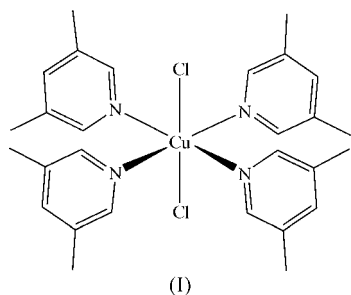
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The title compound, $[\text{CuCl}_2(\text{C}_7\text{H}_9\text{N})_4]$, lies on a site of crystallographic 42 (D_4) symmetry in the space group $P4/nnc$, and is isomorphous with the Ni and Co analogues. The Cu and Cl atoms thus lie on a fourfold axis, and the 3,5-lutidine ligands lie on twofold axes. The Cu—Cl distance is 2.7649 (7) Å and the Cu—N distance is 2.0510 (12) Å. The space group of the Co analogue is revised from $Pnmm$ to $P4/nnc$.

Comment

The title compound, (I), was prepared during an investigation of the reactions of a cofacial binuclear bis(ketoenamine) complex, $\text{Cu}_2(\text{BBI})_2$, where BBI is 5-*tert*-butyl-*m*-xylylenebis(acetylacetonate iminate) (Bradbury *et al.*, 1989), with 3,5-lutidine and related Lewis bases. Electronic spectroscopic changes during these reactions suggested that simple adducts, such as $\text{Cu}_2(\text{BBI})_2L_2$, were forming. However, these products could not be isolated. Instead, the complex apparently decomposed, and the title compound fortuitously crystallized after many years. No chloride was added to the $\text{Cu}_2(\text{BBI})_2$ –3,5-lutidine solution, nor were any other copper sources present. However, dichloromethane is known to be attacked by amines, with displacement of a Cl^- anion (Fronczek *et al.*, 1990; Maverick *et al.*, 1990). Thus, formation of the title compound may have occurred by slow hydrolysis of $\text{Cu}_2(\text{BBI})_2$ to release Cu^{2+} , and subsequent combination with displaced Cl^- anion and excess lutidine.



The molecule of (I) lies on a site of 42 symmetry and $Z' = \frac{1}{8}$. Space group $P4/nnc$ is uncommon, with only three occurrences

reported by Brock & Dunitz (1994) in their compilation of well determined structures from the Cambridge Structural Database (CSD; Allen, 2002). All three have $Z' = \frac{1}{8}$. A search of the complete database (Version 5.28 of November 2006) yielded 101 hits, of which 65 have $Z' = \frac{1}{8}$, 34 have $Z' = \frac{1}{4}$, one has $Z' = \frac{9}{8}$ and one has $Z' = 2$.

The crystallographic symmetry requires strict square-planar geometry of the CuN_4 unit, and the axial octahedral elongation is likewise undistorted. The Cu—N distance is comparable with those in *trans*-dichlorotetrakis(pyridine)copper(II) pyridine disolvate [2.028 (3)–2.064 (4) Å; CSD refcode OMIROR; Bond *et al.*, 2003], but that compound has a somewhat longer Cu—Cl distance [2.957 (2) Å] than in (I). Likewise, in *trans*-dichlorotetrakis(3-pyridylmethanol- κ N)-copper(II) (CSD refcode PACYUO; Moncol *et al.*, 2004), the Cu—N distances are comparable [2.0322 (15)–2.0747 (17) Å], and the Cu—Cl distance is even longer [3.0752 (8) Å].

There are differences among these three structures with respect to the twisting of the pyridine ring out of the coordination plane, as measured by the Cl—Cu—N—C torsion angles. Compound (I) has a torsion angle of 42.35 (6)°, OMIROR has torsion angles of 25.4 and 32.0°, while PACYUO has torsion angles within the range 10.1–32.8°.

Compound (I) is isomorphous with the analogous Ni^{II} compound (Xu *et al.*, 2005). The Co^{II} analogue (refcode YIZSIJ; Kansikas *et al.*, 1994) has been reported in the space group $Pnmm$, with $a = b$, the molecule lying on a site of 222 (D_2) symmetry and having one full 3,5-lutidine ligand in the asymmetric unit. However, the coordinates of the lutidine conform to twofold symmetry, with a maximum deviation of 0.013 Å. Thus, it appears that the structure should be properly

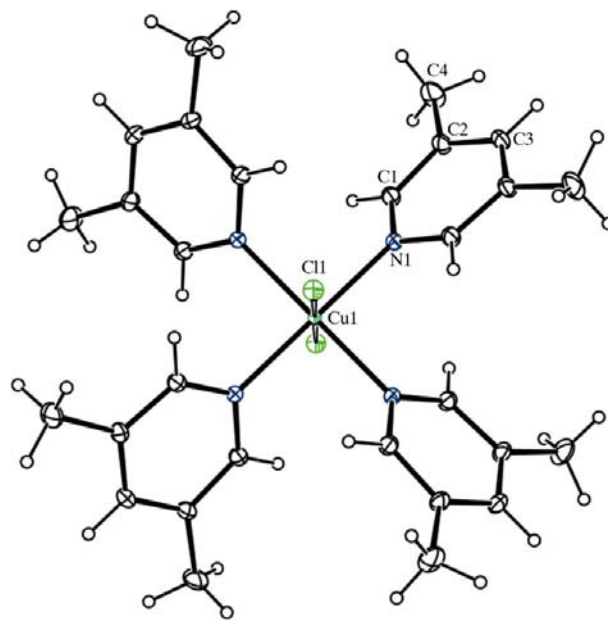


Figure 1

The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Only the asymmetric unit is labelled.

described in the space group $P4/nnc$, isomorphous with the Ni and Cu compounds. Symmetrized coordinates for YIZSIJ in the tetragonal space group are provided as supplementary material.

Experimental

The title compound was prepared from a solution of $\text{Cu}_2(\text{BBI})_2 \cdot \text{DMF}$ in CH_2Cl_2 , where BBI is 5-*tert*-butyl-*m*-xylylenebis(acetylacetonate imine), by addition of an excess of 3,5-lutidine (Bradbury *et al.*, 1989). Over a period of 1–2 weeks, the CH_2Cl_2 evaporated, and blue crystals formed in the residual liquid. However, those crystals were not of sufficient quality for crystal structure determination, and the sample was retained in a sealed vial. After approximately 18 years, high-quality blue prisms of (I) were discovered in the sample.

Crystal data

$[\text{CuCl}_2(\text{C}_7\text{H}_9\text{N})_4]$	$Z = 2$
$M_r = 563.05$	Mo $K\alpha$ radiation
Tetragonal, $P4/nnc$	$\mu = 1.00 \text{ mm}^{-1}$
$a = 11.3324 (15) \text{ \AA}$	$T = 110 \text{ K}$
$c = 10.894 (2) \text{ \AA}$	$0.20 \times 0.20 \times 0.17 \text{ mm}$
$V = 1399.0 (4) \text{ \AA}^3$	

Data collection

Nonius KappaCCD diffractometer with an Oxford Cryosystems Cryostream cooler	13834 measured reflections
Absorption correction: multi-scan (SCALEPACK; Otwinowski & Minor, 1997)	1547 independent reflections
$T_{\min} = 0.826$, $T_{\max} = 0.849$	1195 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.035$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$	45 parameters
$wR(F^2) = 0.081$	H-atom parameters constrained
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.40 \text{ e \AA}^{-3}$
1547 reflections	$\Delta\rho_{\text{min}} = -0.65 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Cu1—Cl1	2.7649 (7)	C1—C2	1.3912 (14)
Cu1—N1	2.0510 (12)	C2—C3	1.3924 (13)
N1—C1	1.3422 (12)	C2—C4	1.5034 (16)

Cl1—Cu1—N1—Cl1¹ 42.35 (6)

Symmetry code: (i) $y, x, -z + \frac{1}{2}$.

For Csp^2 atoms, a C—H distance of 0.95 \AA was used, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. For the methyl group, C—H = 0.98 \AA and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$, and a torsional parameter was refined.

Data collection: COLLECT (Nonius, 2000); cell refinement: SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO (Otwinowski & Minor, 1997) and SCALEPACK; program(s) used to solve structure: SIR97 (Altomare *et al.*, 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GZ3084). Services for accessing these data are described at the back of the journal.

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