

In search of conformationally chiral square-planar complexes: dichlorido-bis(2-methoxypyridine- κN)copper(II)

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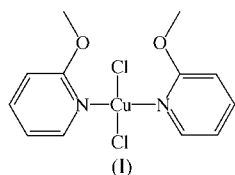
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The title compound, $[\text{CuCl}_2(\text{C}_6\text{H}_7\text{NO})_2]$, was synthesized during a study of conformationally chiral square-planar coordination compounds. The coordination geometry deviates from the square-planar geometry generally adopted by copper(II) chloride complexes with pyridine ligands towards a tetrahedral arrangement of ligands. The complex is conformationally chiral but crystallizes in a centrosymmetric space group with both enantiomers present in the unit cell.

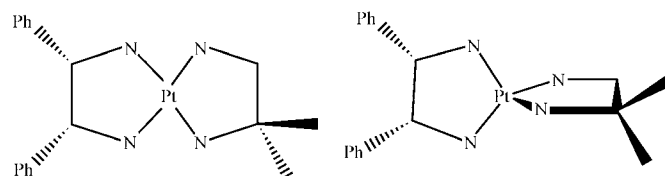
Comment

Mononuclear square-planar complexes may be chiral under certain circumstances, but this phenomenon has gained little attention. It was first pointed out by Werner (1893) that four-coordinate complexes of platinum were most likely to be square planar rather than tetrahedral. An elegant evidence for this hypothesis appeared in 1935 (Mills & Quibell, 1935), the first optical resolution of a square-planar complex (with no chiral ligands). The complex was designed to display a mirror plane in the case of tetrahedral coordination geometry and to be chiral in the case of square-planar geometry (Fig. 1). In 1999, the chirality of square-planar complexes was discussed and exemplified by four complexes of PdCl_2 and PtCl_2 with substituted pyridine ligands (Fig. 2), although none of the complexes were resolved (Biagini *et al.*, 1999). Inspired by this work, we prepared a series of CuCl_2 complexes with different pyridine ligands in order to find a square-planar chiral compound that crystallizes in a Sohncke space group (Flack, 2003), which would make crystallization-induced asymmetric transformation (Jacques *et al.*, 1984) possible.

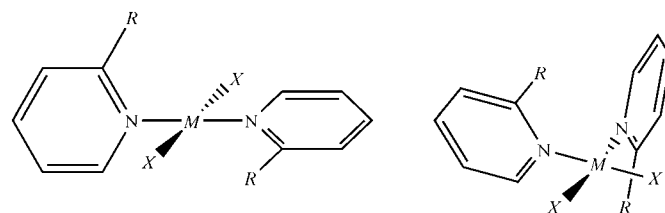


Using 2-methoxypyridine as the ligand, we obtained blue crystals of dichlorido-bis(2-methoxypyridine)copper(II), (I).

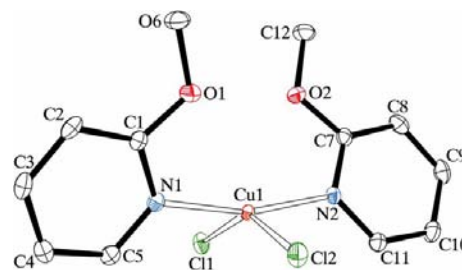
Compared with the structures of CuCl_2 -pyridine complexes found in the Cambridge Structural Database (CSD; Version 5.28 of November 2006; Allen 2002), the coordination geometry in (I) deviates considerably from ideal square-planar geometry (Fig. 3). The N—Cu—Cl angles are all between $91.09(4)$ and $94.08(4)^\circ$, but the N1—Cu1—N2 and Cl1—Cu1—Cl2 angles are $164.05(5)$ and $142.640(19)^\circ$, respectively (Table 1). The coordination geometry around the Cu atom may be explained by the donor atom being in the *ortho* position. Weak $\text{Cu1}\cdots\text{O1}$ and $\text{Cu1}\cdots\text{O2}$ interactions might decrease the N1—Cu1—N2 angle and the two Cl atoms are forced out of the plane (Fig. 4). There are no other copper complexes of 2-methoxypyridine in the CSD for comparison, but there is one comparable example of a copper(II)-chloride-pyridine complex with an O-donor atom in the *ortho* position, *viz.* *catena*-poly[[[dichloridocopper(II)]- μ -1,3,5-tris(2-pyridyloxymethyl)benzene] methanol solvate] (Bray *et al.*, 2004). In this case, a similar effect was observed; the compound has a Cl—Cu—Cl angle of $131.983(17)^\circ$ and an N—Cu—N angle of $147.39(5)^\circ$. The distances from the central Cu atom to the *ortho* O atoms are 2.6445(11) and 2.8146(11) Å. In *trans*-dichlorido-bis[4-(*N*-*tert*-butyl-*N*-oxy-


Figure 1

Mills & Quibell's (1935) chiral square-planar complex (left). Tetrahedral coordination geometry around the central atom would give an achiral complex (right).


Figure 2

Two different possibilities of obtaining chiral square-planar complexes using two substituted pyridine ligands coordinated by a divalent central atom.


Figure 3

The molecular structure of (I), showing the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. All H atoms have been omitted.

amino)-2-(methoxymethyl)pyridine- κ^2N,O]copper(II), there is a one-C-atom bridge between the O atom and the pyridine ring, and 2-(methoxymethyl)pyridine acts as a bidentate ligand with Cu—O distances of 2.477 (3) and 2.549 (3) Å for the two independent molecules in the asymmetric unit (Zhu *et al.*, 2005). Two metal complexes of 2-methoxypyridine are found in the CSD, *viz.* dichloridobis(2-methoxypyridine- κN)-cobalt(II) (Allan *et al.*, 1981) and *cis*-dichlorido(dimethyl sulfoxide- κS)(2-methoxypyridine- κN)platinum(II) (Arvanitis *et al.*, 2000). In both cases, 2-methoxypyridine is best described as a monodentate ligand with only weak metal–oxygen interactions. Since the two aromatic rings in (I) are not in the same plane, molecules of (I) are conformationally chiral, the C1—N1—N2—C7 torsion angle being -33.4 (2)° (*cf.* Fig. 2). Only one of the complexes of CuCl₂ with pyridine ligands found in the CSD is chiral in the sense shown in Fig. 2, namely *cis*-dichloridobis(1,8-naphthyridine)copper(II) (Enwall & Emerson, 1979). However, since (I) crystallizes in a centrosymmetric space group, both enantiomers are present in the unit cell and no spontaneous resolution occurs in (I).

Atoms Cl1 and Cl2 both form two short contacts within van der Waals radii (geometric parameters and symmetry codes are given in Table 2). The H atoms are attached directly to the aromatic rings in all four cases. The short contacts involving atom Cl2 give rise to infinite racemic chains extending along

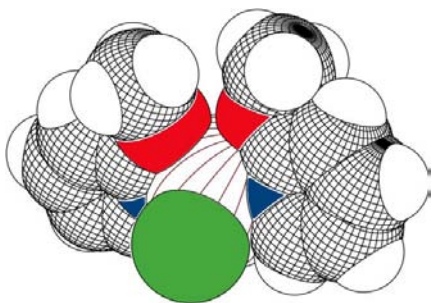


Figure 4

A space-filling plot of (I), showing the Cu...O interactions. The interactions decrease the N1—Cu1—N2 angle and the two Cl atoms are forced out of the plane.

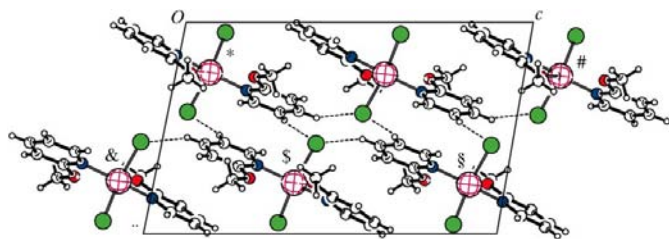


Figure 5

The packing of (I), viewed along the *b* axis. Four different Cl...H contacts result in a three-dimensional network structure. Molecules marked with an asterisk (*), hash (#), ampersand (&), dollar sign (\$) or section sign (§) are at the symmetry positions $(x, -y + \frac{1}{2}, z - \frac{1}{2})$, $(x, -y + \frac{1}{2}, z + \frac{1}{2})$, $(-x + 1, y + \frac{1}{2}, -z + \frac{1}{2})$, $(-x + 1, -y + 1, -z + 1)$ and $(-x + 1, y + \frac{1}{2}, -z + \frac{3}{2})$, respectively.

the *b* axis, since atom H8 forms a short contact with atom Cl2ⁱⁱⁱ, and atom H10 forms a short contact with atom Cl2^{iv}. The Cl1...H3ⁱ contacts give rise to infinite chains extending along the *c* axis, and the Cl1...H4ⁱⁱ contacts give rise to chains extending along the *b* axis. The C—H...Cl angles deviate considerably from 180°. Altogether, this results in a network structure (Fig. 5).

Experimental

Copper(II) chloride dihydrate (*ca* 10 mg) was dissolved in hot 2-methoxypyridine (*ca* 1 ml) and a clear dark-green solution was obtained. Small blue crystals were formed on slow cooling to ambient temperature.

Crystal data

[CuCl ₂ (C ₆ H ₇ NO) ₂]	<i>V</i> = 1433.2 (4) Å ³
<i>M_r</i> = 352.69	<i>Z</i> = 4
Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Mo <i>K</i> α radiation
<i>a</i> = 10.5303 (19) Å	μ = 1.89 mm ⁻¹
<i>b</i> = 8.0531 (13) Å	<i>T</i> = 100 (2) K
<i>c</i> = 16.977 (3) Å	0.35 × 0.2 × 0.1 mm
β = 95.435 (7)°	

Data collection

Rigaku R-Axis-IIC image-plate system diffractometer	9641 measured reflections
Absorption correction: multi-scan (<i>CrystalClear</i> ; Rigaku, 2000)	2762 independent reflections
<i>T_{min}</i> = 0.511, <i>T_{max}</i> = 0.827	2534 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R_{int}</i> = 0.036

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$	172 parameters
$wR(F^2) = 0.060$	H-atom parameters constrained
<i>S</i> = 1.06	$\Delta\rho_{\max} = 0.30$ e Å ⁻³
2762 reflections	$\Delta\rho_{\min} = -0.31$ e Å ⁻³

Table 1

Selected geometric parameters (Å, °).

N1—Cu1	1.9929 (14)	Cl2—Cu1	2.2599 (5)
N2—Cu1	1.9941 (13)	Cu1—O1	2.835 (1)
Cl1—Cu1	2.2527 (5)	Cu1—O2	2.877 (1)
N1—Cu1—N2	164.05 (5)	O2—Cu1—Cl2	119.03 (3)
N1—Cu1—Cl1	91.43 (4)	O2—Cu1—N1	113.79 (3)
N2—Cu1—Cl1	93.57 (4)	O2—Cu1—O1	68.13 (3)
N1—Cu1—Cl2	91.09 (4)	O1—Cu1—N2	113.24 (5)
N2—Cu1—Cl2	94.08 (4)	O1—Cu1—N1	51.28 (5)
Cl1—Cu1—Cl2	142.640 (19)	O1—Cu1—Cl2	93.55 (3)
O2—Cu1—N2	50.79 (5)	O1—Cu1—Cl1	116.58 (3)
O2—Cu1—Cl1	93.70 (3)		

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C3 ⁱ —H3 ⁱ ...Cl1	0.93	2.85	3.501 (2)	128
C4 ⁱⁱ —H4 ⁱⁱ ...Cl1	0.93	2.82	3.705 (2)	160
C8 ⁱⁱⁱ —H8 ⁱⁱⁱ ...Cl2	0.93	2.90	3.503 (2)	123
Cl10 ^{iv} —H10 ^{iv} ...Cl2	0.93	2.85	3.519 (2)	130

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

All H atoms were included in calculated positions (C—H = 0.96 Å for methyl and 0.93 Å for others) and refined using a riding model, with *U_{iso}*(H) values of 1.5*U_{eq}*(C) for methyl or 1.2*U_{eq}*(C) for others.

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: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); 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: GD3150). Services for accessing these data are described at the back of the journal.

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