metal-organic compounds

catena-Poly[[(acetonitrile-*N*)-dichlorocopper(II)]-*μ*-2,5-dimethyl-pyrazine-*κ*²*N*:*N*′]

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In the structure of the title compound, $[CuCl_2(C_2H_3N)(C_6H_8N_2)]$, each Cu^{2+} cation is surrounded by two 2,5-dimethylpyrazine ligands, one acetonitrile ligand and two Cl^- anions within a distorted tetragonal pyramid. The acetonitrile ligand, which forms the apex of the pyramid, the Cu^{2+} cation and the Cl^- anions are all located in general positions, whereas each of the 2,5-dimethylpyrazine ligands is located about a centre of inversion. The 2,5-dimethylpyrazine ligands connect the Cu^{2+} cations *via* *μ*-*N*:*N*′ coordination to form chains.

Comment

This study of the title compound, (I), is part of a project dealing with the synthesis and structural characterization of coordination polymers based on copper halides and multidentate amino ligands (Näther *et al.*, 2001; Näther & Greve, 2001; Näther & Jess, 2001). 2,5-Dimethylpyrazine was selected because it is a suitable compound for the formation of coordination polymers *via* *μ*-*N*:*N*′ coordination of two different


(I)
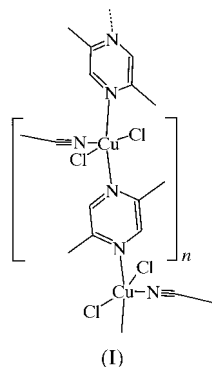
metal cations. There are only a few compounds described in the literature which are based on this ligand, such as *catena*-[(trifluoromethanesulfonato-*O*)(*μ*₂-2,5-dimethylpyrazine-*N*,*N*′)(2,5-dimethylpyrazine-*N*)copper(I)] (Otieno *et al.*, 1990), and *catena*-[tris(*μ*₂-2,5-dimethylpyrazine)dicopper(I) bis(hexafluorophosphate)] and *catena*-[bis(*μ*₂-2,5-dimethylpyra-

zine)copper(I) hexafluorophosphate] (Otieno *et al.*, 1993). In all of these compounds, one- or two-dimensional coordination polymers are formed in which the 2,5-dimethylpyrazine acts as a bridging ligand.

In the crystal structure of (I), the Cu^{2+} cations are fivefold coordinated by two N atoms of two crystallographically independent 2,5-dimethylpyrazine ligands, one N atom of an acetonitrile ligand and two crystallographically independent Cl^- anions (Fig. 1). The 2,5-dimethylpyrazine ligands are located around centres of inversion, whereas the Cu^{2+} cation, the Cl^- anions and the acetonitrile molecule are located in general positions.

The coordination polyhedron around the Cu^{2+} cation can be described as a distorted tetragonal pyramid, with the Cl^- anions and the N atoms of the 2,5-dimethylpyrazine ligands in the basal plane, and the N atom of the acetonitrile ligand at the apex of the pyramid. The deviation of the Cu^{2+} cation from the plane formed by atoms Cu1, Cl1, Cl2, N1 and N2 is 0.1764 (7) Å. The Cu—Cl bond lengths are 2.2577 (9) and 2.2608 (8) Å, and the Cu—N distances to the 2,5-dimethylpyrazine ligands are 2.067 (2) and 2.071 (2) Å. The Cu—N distance of 2.349 (3) Å to the apical N atom is elongated compared with the other Cu—N distances, showing that this is a much weaker interaction. The N—Cu—N, Cl—Cu—Cl and N—Cu—Cl angles are 168.36 (9), 168.22 (3) and 88.32 (6)–90.78 (6)° (Table 1).

There are several structures reported in the literature in which Cu^{2+} cations are five-coordinate to two Cl^- ligands and three N atoms of organic ligands. A detailed analysis of their coordination polyhedra shows that most of them have a distorted tetragonal pyramidal coordination. In these cases,
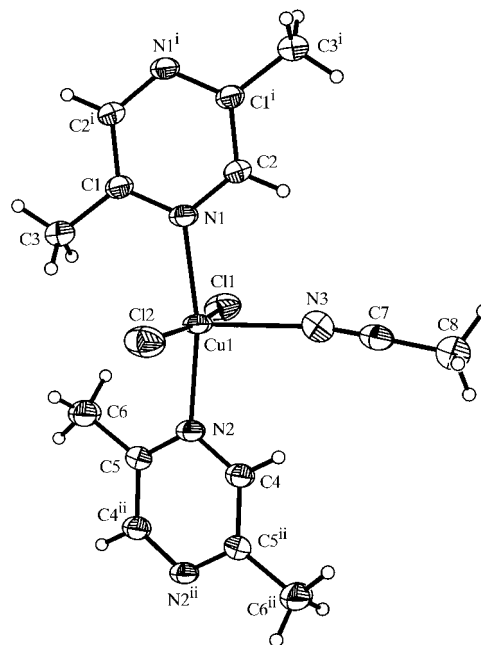
Figure 1
The molecular structure of (I), showing the copper coordination and the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii [symmetry codes: (i) $1 - x$, $2 - y$, $1 - z$; (ii) $2 - x$, $1 - y$, $1 - z$].

either the Cl⁻ or the N ligand can occupy the apical position. However, the Cu−X distance to the apical ligand (X is Cl or N) is always much longer than those within the basal plane. The geometrical parameters in (I) are comparable with those found in some of the structures mentioned above if they contain one N atom in the apical position, *e.g.* dichloro-[6-ethoxy-6-hydroxy-1,3,5-tri(2,6)pyridacyclohexaphane-2,4-dione]copper(II) ethanol solvate (Newkome *et al.*, 1990) or dichloro-[1-(pent-3-ynyl)-1,4,7-triazacyclononane]copper(II) (Ellis *et al.*, 1999). However, the exact geometry depends strongly on the nature of the organic ligands, *e.g.* whether mono- or multidentate ligands are present.

The 2,5-dimethylpyrazine ligands in (I) connect the Cu²⁺ cations into chains *via* μ-N:N' coordination (Fig. 2). The C−N−Cu angles deviate only slightly from 120° and the Cu²⁺
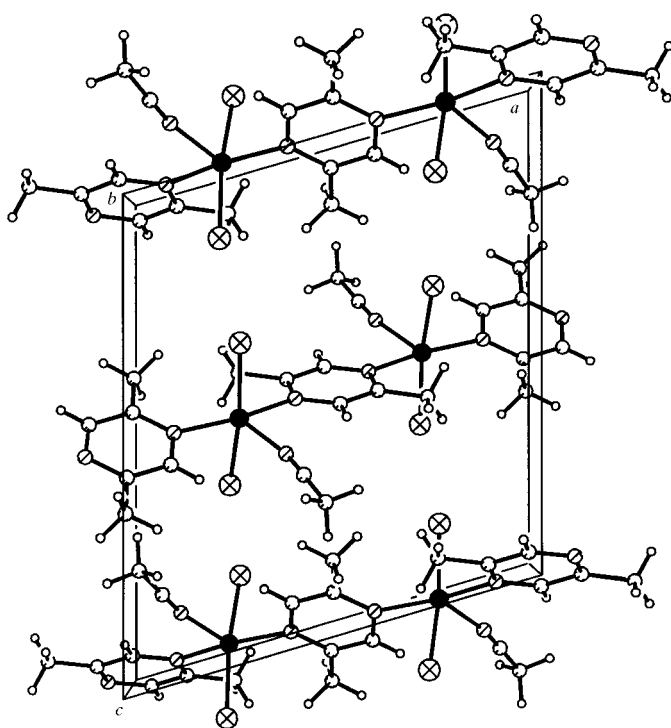

Figure 2
A view of the crystal structure of (I) along (010) showing the infinite chains.

cation is located in the plane of the six-membered ring, which shows that the cation is oriented in the direction of the lone pair on the N atom. For the longer Cu−N distance to the apical N atom, the lone-pair directionality is much less distinctive. The methyl groups of the 2,5-dimethylpyrazine ligands are located below the basal plane of the pyramid. Therefore, a possible coordination of the cations with the formation of an octahedral geometry, which is frequently observed for Cu²⁺ cations, is prevented.

There are some short intermolecular Cl···H distances between the Cl⁻ anions and the methyl H atoms of neighbouring parallel chains, which may be interpreted as hydrogen bonds (Table 2).

Experimental

Compound (I) was prepared by the reaction of CuCl (155.25 mg, 1.60 mmol), freshly prepared according to the method given in Gmelin (1958), and 2,5-dimethylpyrazine (81 mg, 0.75 mmol) in acetonitrile (6 ml) at room temperature in a glass container. After stirring for 2 d, the mixture was allowed to stand at room temperature until most of the solvent had evaporated. The resulting precipitate was filtered off. The product consisted of a phase mixture of equivalent amounts of blue crystals of (I) and red crystals of a new compound, CuCl–2,5-dimethylpyrazine, which could be separated by hand.

Crystal data

[CuCl₂(C₂H₃N)(C₆H₈N₂)]	D_x = 1.703 Mg m⁻³
M_r = 283.64	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 46
a = 11.653 (2) Å	reflections
b = 7.3533 (12) Å	θ = 12.5–17.5°
c = 13.443 (2) Å	μ = 2.42 mm⁻¹
β = 106.190 (12)°	T = 293 (2) K
V = 1106.2 (3) Å³	Block, blue
Z = 4	0.11 × 0.09 × 0.08 mm

Data collection

Stoe AED-II diffractometer	R_{int} = 0.027
ω/θ scans	θ_{max} = 27°
Absorption correction: numerical	h = 0 → 14
(X-$SHAPE$; Stoe & Cie, 1998)	k = −9 → 1
T_{min} = 0.770, T_{max} = 0.824	l = −17 → 16
3045 measured reflections	4 standard reflections
2415 independent reflections	frequency: 120 min
1678 reflections with $I > 2\sigma(I)$	intensity decay: none

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.029	$w = 1/[\sigma^2(F_o^2) + (0.0369P)^2]$
$wR(F^2)$ = 0.073	where $P = (F_o^2 + 2F_c^2)/3$
S = 1.00	$(\Delta/\sigma)_{max}$ = 0.001
2415 reflections	$\Delta\rho_{max}$ = 0.34 e Å⁻³
130 parameters	$\Delta\rho_{min}$ = −0.28 e Å⁻³

Table 1
Selected geometric parameters (Å, °).

Cu1−N1	2.067 (2)	Cu1−Cl2	2.2608 (8)
Cu1−N2	2.071 (2)	Cu1−N3	2.349 (3)
Cu1−Cl1	2.2577 (9)		
N1−Cu1−N2	168.36 (9)	N2−Cu1−N3	95.12 (9)
N1−Cu1−Cl1	88.75 (6)	Cl1−Cu1−N3	95.67 (7)
N2−Cu1−Cl1	90.78 (6)	Cl2−Cu1−N3	96.11 (7)
N1−Cu1−Cl2	89.77 (6)	C2−N1−Cu1	121.62 (18)
N2−Cu1−Cl2	88.32 (6)	C1−N1−Cu1	120.46 (18)
Cl1−Cu1−Cl2	168.22 (3)	C4−N2−Cu1	119.84 (18)
N1−Cu1−N3	96.50 (9)	C5−N2−Cu1	122.82 (18)

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

D−H···A	D−H	H···A	D···A	D−H···A
C3−H3B···Cl1ⁱ	0.96	2.72	3.673 (3)	171
C8−H8A···Cl2ⁱⁱ	0.96	2.80	3.724 (3)	163

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

Aromatic H atoms were positioned with idealized geometry and refined isotropically using a riding model, with C−H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C). Methyl H atoms were identified from difference

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syntheses and their positions idealized, and were then refined as rigid groups allowed to rotate but not tip, with C—H = 0.96 Å and $U_{iso}(H) = 1.5U_{eq}(C)$.

Data collection: *DIF*4 (Stoe & Cie, 1992); cell refinement: *DIF*4; data reduction: *REDU*4 (Stoe & Cie, 1992); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXL*97.

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