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Hexakis-μ-chlorido-dichloridobis[(3,5-dimethylpyrazol-1-yl)acetic acid-κ^2N,N']tetracopper(II): an unexpected neutral bis-pyrazolyl ligand in a tetracopper(II) complex

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A new centrosymmetric tetranuclear complex, $[Cu_4(\mu\text{-}Cl)_6Cl_2(C_{12}H_{16}N_4O_2)_2]$, was obtained in varied yields by reaction of bis(3,5-dimethylpyrazol-1-yl)acetic acid (Hbdmpza) with $CuCl_2{\cdot}2H_2O$ in a highly concentrated acetonitrile solution. Two different types of coordination environment for the Cu atoms characterize the title compound, namely square-pyramidal $CuCl_2N_2Cl$ and distorted square-planar $CuCl_4$ donor sets. The tetranuclear molecule is located on a centre of inversion in the crystal structure and the molecules are connected *via* very strong bis-carboxylate hydrogen bonds, resulting in a polymeric chain.

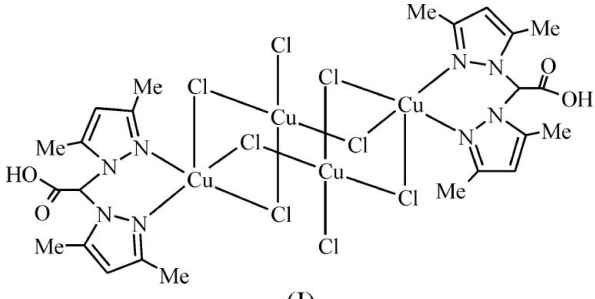
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.031
wR factor = 0.071
Data-to-parameter ratio = 18.4

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

Comment

Chloride bridges are very common in copper chemistry, although mostly in dinuclear molecules. Additionally, there are some infinite ladder structures (Julve *et al.*, 1988; Neels *et al.*, 1997; Massaux & Le Bihan, 1976; Näther & Jess, 2002, 2004), often with Cu^I species. Discrete units with several Cu atoms are found as one-, two- or three-dimensional networks, *e.g.* as cages (Baker *et al.*, 1971; Murray & Willett, 1993; Colombo *et al.*, 1985; Bond *et al.*, 1995; Haije *et al.*, 1986; Cole *et al.*, 2003; Churchill *et al.*, 1975; Håkansson & Jagner, 1990).



(I)

Here, we present the structure of the centrosymmetric title compound, (I), where two different copper(II) coordination geometries are present in a discrete tetranuclear molecule. The central Cu_4Cl_8 unit is limited by a neutral bidentate Hbdmpza ligand (Fig. 1 and Table 1). The Cu atoms coordinated by the Hbdmpza are in a square-pyramidal $CuCl_2N_2Cl$ coordination environment formed by two N atoms of the ligand and three bridging chlorides. A similar coordination mode was found in a dinuclear pyrazolato complex (Mezei & Raptis, 2004). The inner Cu atom (Cu2) is within a $CuCl_4$ distorted square-planar environment. Tetranuclear cores related to that of the title structure have been observed for complexes with Cu_4Cl_4 units limited by 2,2-bipyridine or sparteine, both with copper(I) (Cui *et al.*, 2001; Johansson *et al.*, 2004). Two strong hydrogen bonds connect the molecules,

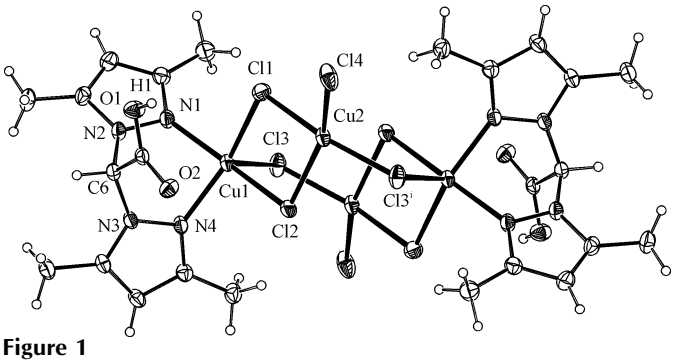


Figure 1
The molecular structure of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) $1-x, 1-y, 1-z$.]

producing an infinite chain (Fig. 2 and Table 2). This type of hydrogen bonding is usually found for free carboxylic acids. There is also a short contact distance between the bridging atom C6 and the terminal atom Cl4 [3.364 (4) Å], which is slightly displaced from the Cu2 square-planar coordination plane. The distance between Cl4 and the least-squares plane through atoms Cl1, Cl2, Cl3 and Cu2 is 1.333 (2) Å (Fig. 2). We assume that this distortion arises from a weak intermolecular C6—H6···Cl4($-x+1, -y, -z+1$) interaction (Desiraju & Steiner, 2001).

The coordination of neutral Hbdmpza ligands in the title compound represents, to the best of our knowledge (CSD, Version 5.27 of August 2006; Allen, 2002), a new bidentate binding mode of this usually tridentate scorpionate-type ligand. Other metal complexes with Hbdmpza and related bis(pyrazol-1-yl)acetic acids reveal only the dehydronated forms (Hegelmann *et al.*, 2003; Otero *et al.*, 2004; Kozlevčar *et al.*, 2003).

Experimental

The ligand Hbdmpza was prepared as described by Beck *et al.* (2001). For the preparation of compound (I), $CuCl_2{\cdot}2H_2O$ (80 mg, 0.47 mmol) and Hbdmpza (50 mg, 0.20 mmol) were stirred in acetonitrile (50 ml). Dark-green crystals, suitable for X-ray diffraction, were obtained in the solution at room temperature after a week.

Crystal data

$[Cu_4Cl_8(C_{12}H_{16}N_4O_2)_2]$
$M_r = 1034.34$
Triclinic, $P\overline{1}$
$a = 9.3869$ (2) Å
$b = 10.6666$ (2) Å
$c = 10.7902$ (3) Å
$\alpha = 117.6094$ (10)°
$\beta = 98.6850$ (10)°
$\gamma = 98.2172$ (16)°
$V = 918.00$ (4) Å^3
$Z = 1$
$D_x = 1.871$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 2.91$ mm^{-1}
$T = 293$ (2) K
Prism, green
0.15 × 0.13 × 0.10 mm

Data collection

Nonius KappaCCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997)
$T_{min} = 0.669$, $T_{max} = 0.760$
5946 measured reflections
4088 independent reflections
3395 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 27.4°$

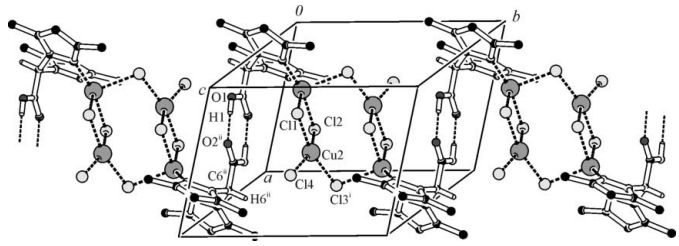


Figure 2
The packing in (I) showing O1—H1···O2 hydrogen bonding and the resulting polymeric chain in the structure. The methyl H atoms have been omitted for clarity. [Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $1-x, -y, 1-z$.]

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.071$
$S = 1.04$
4088 reflections
222 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0056P)^2 + 0.8188P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.38$ e Å^{-3}
$\Delta\rho_{min} = -0.39$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N4	2.009 (2)	Cu2—Cl2	2.3087 (7)
Cu1—N1	2.012 (2)	Cl3—Cu2^{i}	2.2485 (7)
Cu1—Cl1	2.3205 (8)	O1—C7	1.271 (3)
Cu1—Cl2	2.3354 (7)	O2—C7	1.239 (3)
Cu1—Cl3	2.5042 (8)	N1—N2	1.370 (3)
Cu2—Cl4	2.2050 (8)	N2—C6	1.445 (3)
Cu2—Cl3^{i}	2.2485 (7)	N3—N4	1.375 (3)
Cu2—Cl1	2.2823 (7)	N3—C6	1.434 (3)
N4—Cu1—N1	88.39 (8)	Cl1—Cu1—Cl3	102.94 (3)
N4—Cu1—Cl1	152.83 (7)	Cl2—Cu1—Cl3	94.65 (2)
N1—Cu1—Cl1	89.33 (7)	Cl4—Cu2—Cl3^{i}	95.05 (3)
N4—Cu1—Cl2	91.75 (6)	Cl4—Cu2—Cl2	155.10 (3)
N1—Cu1—Cl2	165.17 (7)	N3—C6—N2	110.5 (2)

Symmetry code: (i) $-x+1, -y+1, -z+1$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2^{ii}	0.82	1.83	2.638 (3)	170

Symmetry code: (ii) $-x+1, -y, -z+1$.

All H atoms were positioned geometrically and constrained to ride on their parent atoms, with C—H bond lengths of 0.93–0.98 Å, an O—H distance of 0.82 Å, and U_{iso}(H) values of $1.5U_{eq}$(O,C) for OH and methyl H atoms or $1.2U_{eq}$(C) otherwise.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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