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Tetrakis(μ-chloroacetato-κ^2O:O')-bis[(N,N-dimethylformamide-κO)-copper(II)]

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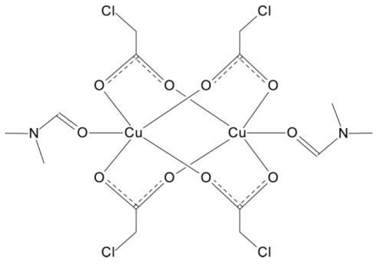
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.003 Å; R factor = 0.023; wR factor = 0.067; data-to-parameter ratio = 17.7.

In the title dimeric complex, $[Cu_2(C_2H_2ClO_2)_4(C_3H_7NO)_2]$, the Cu^{II} atom has a five-coordinate square-pyramidal environment, with the carbonyl O atom of the dimethylformamide ligand at the apical position. The complex molecule is located on a crystallographic inversion centre, with a Cu$\cdots$Cu separation of 2.6614 (4) Å. Intermolecular C—H$\cdots$O hydrogen bonds are present in the crystal structure.

Related literature

For related literature, see: Borthwick (1980); Calderazzo *et al.* (2003); Etter *et al.* (1990); Shi *et al.* (1999, 2001), Sieroń (2007).



Experimental

Crystal data

$[Cu_2(C_2H_2ClO_2)_4(C_3H_7NO)_2]$
M_r = 647.24
Triclinic, $P\overline{1}$
a = 7.9969 (6) Å
b = 8.0326 (5) Å
c = 10.2420 (7) Å
α = 87.824 (5)°
β = 71.974 (6)°
γ = 80.015 (6)°
V = 616.05 (8) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 2.21 mm^{-1}
T = 294 K
0.45 × 0.25 × 0.20 mm

Data collection

Kuma KM-4 CCD diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2006)
T_{min} = 0.511, T_{max} = 0.639
6079 measured reflections
2814 independent reflections
2660 reflections with $I > 2\sigma(I)$
R_{int} = 0.009

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.023
$wR(F^2)$ = 0.067
S = 1.07
2814 reflections
159 parameters
Only H-atom displacement parameters refined
$\Delta\rho_{max}$ = 0.60 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.9856 (14)	O1—C1	1.249 (2)
Cu1—O2	1.9823 (15)	O2—C3	1.262 (2)
Cu1—O3^i	1.9719 (13)	O3—C1	1.259 (2)
Cu1—O4^i	1.9879 (16)	O4—C3	1.247 (2)
Cu1—O5	2.1304 (14)	O5—C5	1.250 (2)
Cu1$\cdots$Cu1^i	2.6614 (4)		
O1—Cu1—O2	88.42 (6)	O2—Cu1—O3^i	90.21 (6)
O1—Cu1—O5	93.93 (6)	O2—Cu1—O4^i	167.87 (6)
O1—Cu1—O3^i	167.75 (6)	O3^i—Cu1—O5	98.32 (5)
O1—Cu1—O4^i	90.31 (6)	O4^i—Cu1—O5	94.78 (6)
O2—Cu1—O5	97.35 (6)	O3^i—Cu1—O4^i	88.48 (6)

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C4—H4$\cdots$O2^{ii}	0.97	2.48	3.394 (3)	158

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *PLATON* (Spek, 2003).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2041).

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supplementary materials

Acta Cryst. (2007). E**63**, m1966 [**doi:10.1107/S1600536807029674**]

Tetrakis(μ-chloroacetato-κ^2*O*:*O'*)bis[(*N*,*N*-dimethylformamide-κ*O*)copper(II)]

L. Sieron

Comment

The structure determination of the title compound, (I), was undertaken as a continuation of earlier studies of copper(II) complexes with monochloroacetic acid (Sieroń, 2007).

The title compound (I) contains a dimeric copper(II) complex, $[Cu_2(CH_2ClCOO)_4(DMF)_2]$, composed of two Cu^{II} centres, four chloroacetate and two DMF ligands (Fig. 1).

The Cu^{II} atom has a regular five-coordinate square-pyramidal environment, with the basal plane defined by the O atoms of four bridging bidentate carboxylate groups of monochloroacetate ligands. The Cu^{II} atom deviates out of the mean plane formed by the four basal O atoms towards the apical O5 atom of the DMF ligand by 0.2104 (7) Å. The O–C distances in the chloroacetate groups are approximately equal and range from 1.247 (2) to 1.262 (2) Å, indicating the distinct delocalization of their π electrons (Borthwick, 1980). The planes of the two independent bridging chloroacetate groups are perpendicular within experimental error. The apical DMF ligand is twisted by a dihedral angle of 33.8 (1)° with respect to the C1/O1/O3^i mean plane. Selected bond distances and bond angles are listed in Table 1. Complex molecules are linked by two Csp^3–H···O hydrogen bonds (Table 2), forming eight-membered rings described by the $R_2^2(8)$ graph-set motif (Etter *et al.*, 1990) as shown in Fig. 2. The Cu···Cu distance of 2.6614 (4) Å is comparable to those found in other dimeric copper(II) monochloroacetates (Shi *et al.*, 1999, 2001; Calderazzo *et al.*, 2003).

Experimental

A mixture of chloroacetic acid (1 mmol) and $CuCO_3\cdot Cu(OH)_2\cdot H_2O$ (0.5 mmol) in a mixture of water (50 ml) and DMF (25 ml) was heated to boiling. The solution was filtered and allowed to cool to room temperature. Turquoise prismatic crystals of (I) were obtained after a few days.

Refinement

All H atoms were initially located in a difference Fourier synthesis, but were positioned with idealized geometry, with C–H = 0.93, 0.96 and 0.97 Å, and refined using a riding model. The methyl H atoms were allowed to rotate to best fit the experimental electron density (AFIX 137). The isotropic displacement parameters of all H atoms were refined freely.

Figures

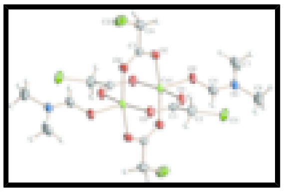

Fig. 1. A view of (I), showing the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 40% probability level. Unlabelled atoms are related to labelled atoms by the symmetry code ($-x$, $-y + 1$, $-z$).

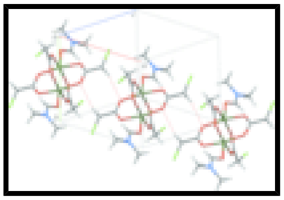

Fig. 2. The packing of (I), showing a hydrogen-bonded chain (dashed lines) running along the *a* axis.

Tetrakis(μ-chloroacetato-κ^2*O*:*O*')bis[(*N*,*N*-\ dimethylformamide-κ*O*)copper(II)]

Crystal data

$[Cu_2(C_2H_2ClO_2)_4(C_3H_7NO)_2]$

M_r = 647.24

Triclinic, $P\overline{1}$

Hall symbol: -P 1

a = 7.9969 (6) Å

b = 8.0326 (5) Å

c = 10.2420 (7) Å

α = 87.824 (5)°

β = 71.974 (6)°

γ = 80.015 (6)°

V = 616.05 (8) Å^3

Z = 1

F_{000} = 326

D_x = 1.745 Mg m^{-3}

Mo *K*α radiation
λ = 0.71073 Å

Cell parameters from 3751 reflections

θ = 2.6–31.2°

μ = 2.21 mm^{-1}

T = 294 K

Prism, blue-green

0.45 × 0.25 × 0.20 mm

Data collection

Kuma KM-4 CCD diffractometer

Monochromator: graphite

Detector resolution: 8.2356 pixels mm^{-1}

T = 294 K

ω scans

Absorption correction: multi-scan
(CrysAlis RED; Oxford Diffraction, 2006)

T_{min} = 0.511, T_{max} = 0.639

6079 measured reflections

2814 independent reflections

2660 reflections with $I > 2\sigma(I)$

R_{int} = 0.009

θ_{max} = 27.5°

θ_{min} = 2.6°

$h = -10\rightarrow10$

$k = -10\rightarrow8$

$l = -11\rightarrow13$

Refinement

Refinement on F^2

Least-squares matrix: full

Hydrogen site location: difference Fourier map

Only H-atom displacement parameters refined

$R[F^2 > 2\sigma(F^2)] = 0.023$	$w = 1/[\sigma^2(F_o^2) + (0.0379P)^2 + 0.2335P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.067$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.07$	$\Delta\rho_{max} = 0.60$ e Å^{-3}
2814 reflections	$\Delta\rho_{min} = -0.35$ e Å^{-3}
159 parameters	Extinction correction: SHELXL97, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0116 (18)

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted *R*-factors *wR* and all goodnesses of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The observed criterion of $F^2 > \sigma(F^2)$ is used only for calculating -*R*-factor-obs *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.10233 (3)	0.56685 (2)	−0.11043 (2)	0.0311 (1)
Cl1	0.09850 (10)	0.09076 (8)	−0.39180 (6)	0.0685 (2)
Cl2	0.41733 (10)	0.10139 (9)	0.20517 (8)	0.0734 (3)
O1	0.0899 (2)	0.35412 (17)	−0.19692 (14)	0.0464 (4)
O2	0.30126 (17)	0.44111 (18)	−0.05042 (14)	0.0444 (4)
O3	−0.08262 (19)	0.24157 (16)	−0.01133 (13)	0.0440 (4)
O4	0.12946 (18)	0.32648 (19)	0.13481 (15)	0.0469 (4)
O5	0.26071 (19)	0.66002 (18)	−0.29703 (13)	0.0454 (4)
N1	0.3366 (2)	0.6631 (2)	−0.52957 (16)	0.0482 (5)
C1	0.0121 (2)	0.2386 (2)	−0.13520 (17)	0.0348 (5)
C2	0.0355 (3)	0.0721 (3)	−0.2111 (2)	0.0499 (6)
C3	0.2762 (2)	0.3470 (2)	0.05293 (18)	0.0348 (5)
C4	0.4480 (3)	0.2523 (3)	0.0732 (2)	0.0496 (6)
C5	0.2393 (3)	0.6247 (3)	−0.4080 (2)	0.0485 (6)
C6	0.3121 (5)	0.6134 (6)	−0.6568 (3)	0.0921 (13)
C7	0.4803 (4)	0.7616 (3)	−0.5441 (3)	0.0669 (8)
H1	0.12560	−0.00930	−0.18720	0.100 (11)*
H2	−0.07580	0.02850	−0.18020	0.080 (9)*
H3	0.52120	0.19530	−0.01230	0.068 (8)*
H4	0.51300	0.33380	0.09390	0.084 (9)*
H5	0.14680	0.56640	−0.40360	0.069 (8)*
H61	0.22190	0.54310	−0.63630	0.18 (2)*

H62	0.42240	0.55170	−0.71460	0.138 (16)*
H63	0.27580	0.71250	−0.70330	0.16 (2)*
H71	0.58380	0.71390	−0.61730	0.099 (11)*
H72	0.50970	0.75850	−0.45990	0.114 (13)*
H73	0.44110	0.87660	−0.56460	0.160 (19)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0345 (1)	0.0302 (1)	0.0256 (1)	−0.0117 (1)	−0.0016 (1)	0.0007 (1)
Cl1	0.0935 (5)	0.0635 (4)	0.0471 (3)	−0.0030 (3)	−0.0226 (3)	−0.0226 (3)
Cl2	0.0839 (4)	0.0667 (4)	0.0857 (5)	−0.0212 (3)	−0.0482 (4)	0.0314 (3)
O1	0.0620 (8)	0.0387 (7)	0.0344 (7)	−0.0211 (6)	−0.0014 (6)	−0.0072 (5)
O2	0.0375 (6)	0.0468 (7)	0.0452 (7)	−0.0104 (5)	−0.0067 (5)	0.0106 (6)
O3	0.0575 (8)	0.0348 (6)	0.0368 (7)	−0.0173 (6)	−0.0046 (6)	−0.0034 (5)
O4	0.0394 (7)	0.0560 (8)	0.0429 (7)	−0.0116 (6)	−0.0090 (6)	0.0136 (6)
O5	0.0524 (8)	0.0470 (7)	0.0303 (6)	−0.0182 (6)	0.0015 (5)	0.0043 (5)
N1	0.0490 (9)	0.0533 (10)	0.0316 (8)	0.0045 (7)	−0.0043 (7)	0.0022 (7)
C1	0.0404 (8)	0.0298 (8)	0.0351 (9)	−0.0075 (6)	−0.0114 (7)	−0.0042 (6)
C2	0.0699 (13)	0.0351 (9)	0.0458 (11)	−0.0136 (9)	−0.0158 (10)	−0.0088 (8)
C3	0.0381 (8)	0.0302 (8)	0.0370 (9)	−0.0099 (6)	−0.0101 (7)	−0.0026 (6)
C4	0.0436 (10)	0.0430 (10)	0.0626 (13)	−0.0090 (8)	−0.0171 (9)	0.0097 (9)
C5	0.0437 (10)	0.0527 (11)	0.0426 (10)	−0.0095 (8)	−0.0036 (8)	0.0021 (9)
C6	0.080 (2)	0.143 (3)	0.0394 (13)	0.012 (2)	−0.0140 (13)	−0.0079 (16)
C7	0.0647 (14)	0.0596 (14)	0.0565 (14)	−0.0130 (11)	0.0101 (12)	0.0130 (11)

Geometric parameters (Å, °)

Cu1—O1	1.9856 (14)	N1—C7	1.473 (4)
Cu1—O2	1.9823 (15)	C1—C2	1.527 (3)
Cu1—O3^{i}	1.9719 (13)	C3—C4	1.520 (3)
Cu1—O4^{i}	1.9879 (16)	C2—H1	0.97
Cu1—O5	2.1304 (14)	C2—H2	0.97
Cl1—C2	1.769 (2)	C4—H3	0.97
Cl2—C4	1.769 (2)	C4—H4	0.97
O1—C1	1.249 (2)	C5—H5	0.93
O2—C3	1.262 (2)	C6—H61	0.96
O3—C1	1.259 (2)	C6—H62	0.96
O4—C3	1.247 (2)	C6—H63	0.96
O5—C5	1.250 (2)	C7—H71	0.96
N1—C5	1.306 (3)	C7—H72	0.96
N1—C6	1.456 (4)	C7—H73	0.96
Cu1···Cu1^{i}	2.6614 (4)		
O1—Cu1—O2	88.42 (6)	O5—C5—N1	125.1 (2)
O1—Cu1—O5	93.93 (6)	Cl1—C2—H1	109
O1—Cu1—O3^{i}	167.75 (6)	Cl1—C2—H2	109
O1—Cu1—O4^{i}	90.31 (6)	C1—C2—H1	109

O2—Cu1—O5	97.35 (6)	C1—C2—H2	109
O2—Cu1—O3^{i}	90.21 (6)	H1—C2—H2	108
O2—Cu1—O4^{i}	167.87 (6)	Cl2—C4—H3	109
O3^{i}—Cu1—O5	98.32 (5)	Cl2—C4—H4	109
O4^{i}—Cu1—O5	94.78 (6)	C3—C4—H3	109
O3^{i}—Cu1—O4^{i}	88.48 (6)	C3—C4—H4	109
Cu1—O1—C1	125.19 (12)	H3—C4—H4	108
Cu1—O2—C3	122.57 (12)	O5—C5—H5	117
Cu1^{i}—O3—C1	120.41 (12)	N1—C5—H5	117
Cu1^{i}—O4—C3	122.77 (13)	N1—C6—H61	109
Cu1—O5—C5	119.27 (15)	N1—C6—H62	109
C5—N1—C6	123.4 (2)	N1—C6—H63	109
C5—N1—C7	120.42 (19)	H61—C6—H62	109
C6—N1—C7	116.1 (2)	H61—C6—H63	109
O1—C1—O3	126.43 (16)	H62—C6—H63	110
O1—C1—C2	119.16 (16)	N1—C7—H71	109
O3—C1—C2	114.37 (15)	N1—C7—H72	109
Cl1—C2—C1	113.61 (15)	N1—C7—H73	109
O2—C3—O4	126.68 (17)	H71—C7—H72	109
O2—C3—C4	113.55 (16)	H71—C7—H73	109
O4—C3—C4	119.78 (16)	H72—C7—H73	109
Cl2—C4—C3	114.60 (15)		

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···O2^{ii}	0.97	2.48	3.394 (3)	158

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

Fig. 1

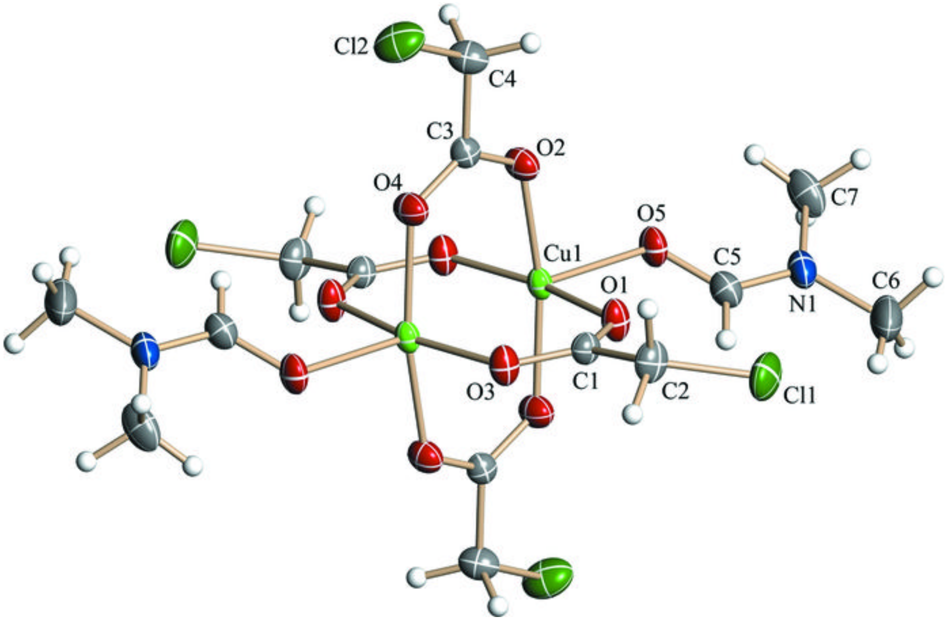

Fig. 2