Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

catena-Poly[[tetra-μ-formato-κ^8O:O'-dicopper(II)]-μ-hexamethylenetetramine-κ^2N^1:N^5]

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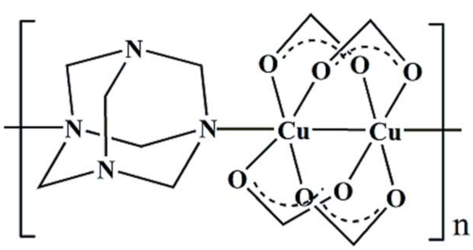
Received 12 October 2013; accepted 22 November 2013

Key indicators: single-crystal X-ray study; T = 103 K; mean σ(N–C) = 0.006 Å; R factor = 0.028; wR factor = 0.077; data-to-parameter ratio = 11.7.

In the title polymeric compound, $[Cu_2(HCO_2)_4(C_6H_{12}N_4)]_n$, the Cu^{II} atom is five-coordinated in a square-pyramidal geometry that is defined by four O atoms from four formate ligands and one N atom from a hexamethylenetetramine ligand. The two Cu^{II} atoms are separated by 2.6850 (7) Å, and together with the four formate ligands they form a paddle-wheel unit. The hexamine ligand uses only two of its four N atoms to link Cu_2 cluster units, affording a zigzag chain running along the b-axis direction. The hexamine ligand lies on a mirror plane.

Related literature

For background to hexamine chemistry, see: Dreyfors *et al.* (1989); Kirillov (2011). For hexamine as a bridging ligand, see: Pickardt (1981); Konar *et al.* (2003); Wang *et al.* (2002). For paddle-wheel Cu_2-cluster units, see: Konar *et al.* (2003); Chiari *et al.* (1988); Wu & Wang (2004); Sun *et al.* (2009).



Experimental

Crystal data

$[Cu_2(CHO_2)_4(C_6H_{12}N_4)]$	V = 1469.3 (4) Å^3
M_r = 447.36	Z = 4
Orthorhombic, *Pnma*	Mo $K\alpha$ radiation
a = 13.1252 (19) Å	μ = 2.95 mm^{-1}
b = 17.281 (3) Å	T = 103 K
c = 6.4777 (9) Å	0.26 × 0.24 × 0.18 mm

Data collection

Bruker SMART APEX area-detector diffractometer	5203 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	1550 independent reflections
T_{min} = 0.469, T_{max} = 0.588	1345 reflections with $I > 2\sigma(I)$
	R_{int} = 0.021

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.028	115 parameters
$wR(F^2)$ = 0.077	H-atom parameters constrained
S = 1.04	$\Delta\rho_{max}$ = 0.69 e Å^{-3}
1550 reflections	$\Delta\rho_{min}$ = −0.71 e Å^{-3}

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

This work was partially supported by the Mid-aged and Young Foundation of Qinghai University (2012-QGT-2).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG5345).

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supporting information

Acta Cryst. (2013). E**69**, m690 [doi:10.1107/S160053681303184X]

catena-Poly[[tetra-μ-formato-κ^8O:O'-dicopper(II)]-μ-hexamethylenetetramine-κ^2N^1:N^5]

Jianfang Cao, Ziping Huang, Changnian Cao, Chunchun Cheng and Chunyan Sun

S1. Comment

The design and synthesis of metal-organic complexes or coordination polymers is a rapidly developing field in coordination and supramolecular chemistry during the past decades. Hexamethylenetetramine (hmt), also known as hexamine or urotropine, can be considered as one such simple heterocyclic compound with a cagelike structure which,owing to its high solubility in water and polar organic solvents, has found a broad variety of applications (Dreyfors *et al.*, 1989). With regard to coordination chemistry, hmt is a versatile ligand capable of adopting different coordination modes that span from the terminal monodentate to bridging bi-, tri- and tetradentate modes. The well known [Cu_2(carboxylate)$_4$] units with four bridging carboxylate ligands in the familiar η_1:η_1:μ coordination mode have accessible apical coordination sites and are ideally suited to serve as a metal-based linear spacer (Konar *et al.* 2003; Chiari *et al.*, 1988; Wu *et al.*, 2004; Sun *et al.*, 2009). To date, the title copper(II) carboxylate complex, represents an exception, as only few formate copper(II) complexes have been studied.

The crystal structure of the title complex, which is isostructural with its copper analog (Wang *et al.*, 2002), is built of hexamethylenetetramine molecules and paddle-wheel dicopper units, both of which occupy special positions. The structure of the centrosymmetric [$Cu_2(HCO_2)_4$] moiety is shown in Fig. 1. The coordination geometry of the Cu atom may be described as a square pyramid, formed by four formatee O atoms and the N atom of the hexamine . The four basal Cu—O distances fall in the range from 1.963 (2) to 1.978 (2) Å. The central hmt has mirror symmetry, and therefore there is only one independent Cu^{II} atom in the asymmetric unit. The Cu—Cu distance within the [$Cu_2(HCO_2)_4$] unit is 2.6850 (7) Å indicating a strong interaction. The axial Cu(1)—N(1) distance is 2.212 (2) Å. The hexamine ligand uses only two of its four N atoms to link adjacent paddle-wheel Cu_2-cluster units, to afford a zigzag chain running along the *b* axis of the unit cell (Fig. 2).

S2. Experimental

The title compound was synthesized by the following method. Copper(II) formate tetrahydrate (0.015 g, 0.1 mmol) was dissolved in 20 ml me thanol to obtain solution A. Hexamine (0.007 g, 0.05 mmol) was dissolved in 10 ml methanol to obtain solution B. Solution B was layered carefully on solution A, and the tube was sealed and stored in room temperature. Green block crystals were obtained after two weeks. Analysis calculated for $C_5H_8CuN_2O_4$: C 26.85, H 3.60, N 12.52%; found: C 26.66, H 3.82, N 12.65%.

S3. Refinement

All non-hydrogen atoms were refined anisotropically. The H atoms of formate were positioned geometrically and allowed to ride on their parent atoms, with C–H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C). The H atoms of hexamethylenetetramine the were placed in geometrically idealized positions and refined as riding atoms, with C–H(CH_2) = 0.99 Å and U_{iso}(H) =

$1.2U_{eq}$(C).

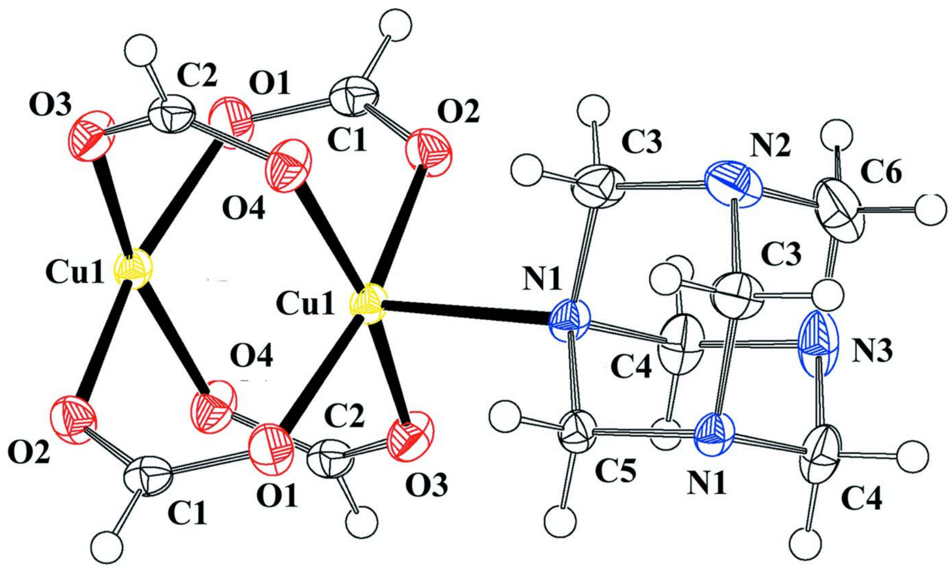

Figure 1

The molecular structure of $[Cu_2(HCO_2)_4(C_6H_{12}N_4)]_n$ showing the atomic dlabelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

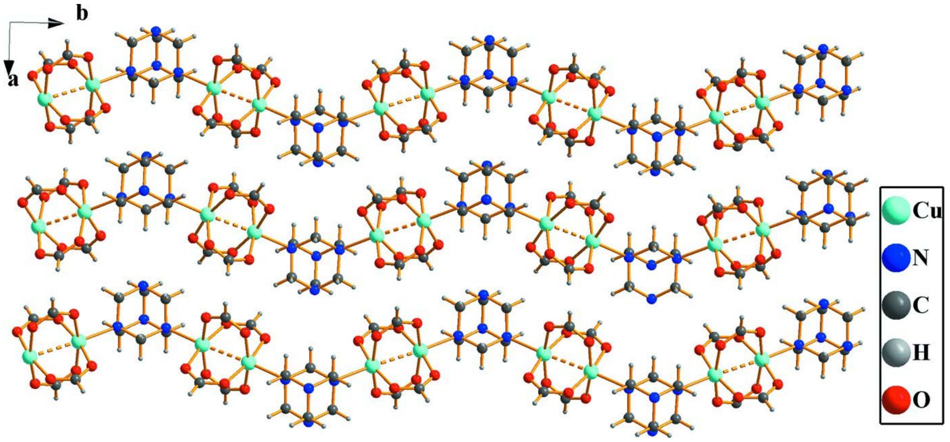

Figure 2

The zigzag chain in the crystal packing structure of $[Cu_2(HCO_2)_4(C_6H_{12}N_4)]_n$ along *b* the axis.

catena-Poly[[tetra-*μ*-formato-κ^8O:O'-dicopper(II)]-*μ*-hexamethylenetetramine-κ^2N^1:N^5]

Crystal data

$[Cu_2(CHO_2)_4(C_6H_{12}N_4)]$
M_r = 447.36
Orthorhombic, *Pnma*
Hall symbol: -P 2ac 2n
a = 13.1252 (19) Å
b = 17.281 (3) Å
c = 6.4777 (9) Å
V = 1469.3 (4) Å^3
Z = 4
F(000) = 904
D_x = 2.022 Mg m^{-3}
D_m = 2.022 Mg m^{-3}
D_m measured by not measured
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 1680 reflections
θ = 2.4–26.4°
μ = 2.95 mm^{-1}
T = 103 K
Block, green
0.26 × 0.24 × 0.18 mm

Data collection

Bruker SMART APEX area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 16.0143 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.469, T_{max} = 0.588

5203 measured reflections
1550 independent reflections
1345 reflections with $I > 2\sigma(I)$
R_{int} = 0.021
θ_{max} = 26.4°, θ_{min} = 2.4°
$h = -7\rightarrow16$
$k = -16\rightarrow21$
$l = -8\rightarrow8$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.077
S = 1.04
1550 reflections
115 parameters

0 restraints
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0488P)^2 + 0.5436P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.69 e Å^{-3}
$\Delta\rho_{min}$ = −0.71 e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness 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 threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *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}	Occ. (<1)
Cu1	0.03147 (2)	0.569254 (15)	0.06885 (4)	0.01482 (13)	
N1	0.09051 (15)	0.67876 (11)	0.1987 (3)	0.0167 (4)	
C6	0.2292 (3)	0.7500	0.4773 (7)	0.0376 (11)	
H6A	0.2607	0.7963	0.5407	0.045*	0.50
H6B	0.2607	0.7037	0.5407	0.045*	0.50
O1	−0.06061 (14)	0.61313 (10)	−0.1393 (3)	0.0243 (4)	
O2	−0.11320 (13)	0.49698 (10)	−0.2546 (3)	0.0222 (4)	
O3	−0.08446 (14)	0.55920 (9)	0.2587 (3)	0.0229 (4)	
O4	−0.13726 (14)	0.44265 (9)	0.1462 (3)	0.0228 (4)	
C1	−0.11161 (19)	0.56950 (13)	−0.2535 (4)	0.0189 (5)	
H1	−0.1544	0.5944	−0.3515	0.023*	
C2	−0.14152 (18)	0.50082 (13)	0.2619 (4)	0.0186 (5)	
H2	−0.1938	0.5007	0.3634	0.022*	
C3	0.20300 (19)	0.68165 (14)	0.1630 (4)	0.0256 (6)	
H3A	0.2347	0.6346	0.2222	0.031*	
H3B	0.2164	0.6817	0.0126	0.031*	
C4	0.0729 (2)	0.68132 (15)	0.4251 (4)	0.0256 (6)	
H4A	−0.0014	0.6813	0.4520	0.031*	
H4B	0.1020	0.6342	0.4889	0.031*	

C5	0.0455 (3)	0.7500	0.1069 (5)	0.0164 (7)
H5A	−0.0290	0.7500	0.1301	0.020*
H5B	0.0576	0.7500	−0.0440	0.020*
N2	0.2502 (3)	0.7500	0.2553 (6)	0.0306 (8)
N3	0.1187 (3)	0.7500	0.5219 (5)	0.0299 (8)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01667 (19)	0.01185 (19)	0.01595 (19)	−0.00041 (10)	−0.00034 (10)	−0.00042 (10)
N1	0.0205 (10)	0.0106 (9)	0.0191 (10)	0.0003 (8)	−0.0004 (8)	0.0002 (8)
C6	0.047 (3)	0.0180 (19)	0.048 (3)	0.000	−0.028 (2)	0.000
O1	0.0307 (10)	0.0168 (9)	0.0253 (9)	0.0018 (7)	−0.0092 (8)	0.0001 (7)
O2	0.0245 (9)	0.0181 (9)	0.0240 (9)	0.0009 (7)	−0.0066 (7)	0.0015 (7)
O3	0.0232 (10)	0.0207 (9)	0.0248 (10)	−0.0027 (7)	0.0062 (7)	−0.0043 (7)
O4	0.0253 (9)	0.0197 (9)	0.0234 (9)	−0.0044 (7)	0.0056 (8)	−0.0033 (7)
C1	0.0182 (12)	0.0205 (12)	0.0181 (13)	0.0038 (9)	0.0019 (9)	0.0032 (9)
C2	0.0171 (12)	0.0195 (12)	0.0192 (12)	0.0037 (10)	−0.0002 (9)	0.0018 (9)
C3	0.0215 (13)	0.0151 (12)	0.0401 (16)	0.0018 (10)	−0.0030 (11)	−0.0002 (11)
C4	0.0407 (16)	0.0161 (13)	0.0199 (13)	−0.0014 (12)	−0.0026 (11)	0.0029 (9)
C5	0.0196 (17)	0.0127 (16)	0.0169 (16)	0.000	−0.0021 (13)	0.000
N2	0.0226 (16)	0.0167 (15)	0.052 (2)	0.000	−0.0107 (14)	0.000
N3	0.053 (2)	0.0145 (15)	0.0219 (16)	0.000	−0.0136 (15)	0.000

Geometric parameters (Å, º)

Cu1—O1	1.9632 (17)	O2—Cu1^{i}	1.9769 (16)
Cu1—O3	1.9640 (18)	O3—C2	1.257 (3)
Cu1—O2^{i}	1.9769 (17)	O4—C2	1.255 (3)
Cu1—O4^{i}	1.9777 (18)	C2—H2	0.950
Cu1—N1	2.2112 (19)	O4—Cu1^{i}	1.9777 (18)
Cu1—Cu1^{i}	2.6848 (6)	C3—N2	1.461 (3)
N1—C4	1.485 (3)	C3—H3A	0.990
N1—C5	1.489 (3)	C3—H3B	0.990
N1—C3	1.495 (3)	C4—N3	1.471 (3)
C6—N2	1.464 (6)	C4—H4A	0.991
C6—N3	1.479 (6)	C4—H4B	0.990
C6—H6A	0.990	C5—N1^{ii}	1.489 (3)
C6—H6B	0.990	C5—H5A	0.989
O1—C1	1.251 (3)	C5—H5B	0.990
O2—C1	1.253 (3)	N2—C3^{ii}	1.461 (3)
C1—H1	0.951	N3—C4^{ii}	1.471 (3)
O1—Cu1—O3	89.26 (8)	H5B—C5—N1	109.30
O1—Cu1—O2^{i}	167.34 (7)	C4—N1—Cu1	110.27 (15)
H1—C1—O1	116.00	H4A—C4—N3	109.13
H1—C1—O2	116.04	H4B—C4—N3	109.16
O3—Cu1—O2^{i}	89.33 (7)	C5—N1—Cu1	114.62 (15)

O1—Cu1—O4^{i}	89.34 (8)	C3—N1—Cu1	108.41 (14)
O3—Cu1—O4^{i}	167.36 (7)	N2—C6—N3	112.1 (3)
O2^{i}—Cu1—O4^{i}	89.28 (8)	C1—O1—Cu1	120.20 (15)
H2—C2—O3	116.33	C1—O2—Cu1^{i}	124.51 (16)
H2—C2—O4	116.33	C2—O3—Cu1	122.90 (15)
O1—Cu1—N1	98.43 (7)	C2—O4—Cu1^{i}	122.36 (16)
O3—Cu1—N1	96.26 (7)	H3A—C3—H3B	107.88
O2^{i}—Cu1—N1	94.24 (7)	H4A—C4—H4B	107.83
O4^{i}—Cu1—N1	96.37 (7)	H5B—C5—H5A	107.97
O1—Cu1—Cu1^{i}	85.79 (5)	O1—C1—O2	127.9 (2)
O3—Cu1—Cu1^{i}	83.73 (5)	O4—C2—O3	127.3 (2)
O2^{i}—Cu1—Cu1^{i}	81.54 (5)	N2—C3—N1	112.5 (2)
O4^{i}—Cu1—Cu1^{i}	83.64 (5)	N3—C4—N1	112.4 (2)
N1—Cu1—Cu1^{i}	175.78 (5)	N1—C5—N1^{ii}	111.5 (3)
H3A—C3—N1	109.11	C3—N2—C3^{ii}	107.9 (3)
H3B—C3—N1	109.13	C3—N2—C6	108.8 (2)
H3A—C3—N2	109.08	H6A—C6—N2	109.20
H4B—C4—N3	109.06	H6B—C6—N2	109.20
C4—N1—C5	107.9 (2)	H6A—C6—N3	109.18
C4—N1—C3	107.8 (2)	H6B—C6—N3	109.18
H4A—C4—N1	109.08	C3^{ii}—N2—C6	108.8 (2)
H4B—C4—N1	109.13	C4^{ii}—N3—C4	107.6 (3)
C5—N1—C3	107.6 (2)	C4^{ii}—N3—C6	108.5 (2)
H5A—C5—N1	109.35	C4—N3—C6	108.5 (2)

Symmetry codes: (i) $-x$, $-y+1$, $-z$; (ii) x, $-y+3/2$, z.