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Poly[μ_4-succinato-μ_2-succinato-bis[diamminecopper(II)]]

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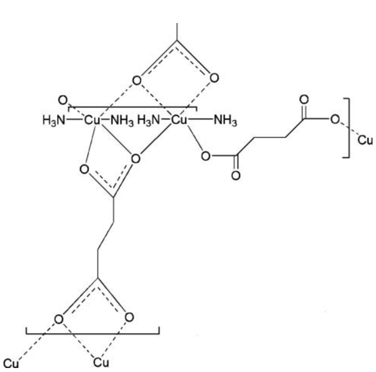
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.006 Å; R factor = 0.026; wR factor = 0.072; data-to-parameter ratio = 10.8.

In the title compound, $[Cu(C_4H_4O_4)(NH_3)_2]_n$, the Cu atom is coordinated by the N atoms of two ammonia molecules and four O atoms from three different succinate ligands in a highly distorted octahedral geometry. The Cu atom and the C and O atoms of the succinate ligands lie on a mirror plane. Two adjacent CuO_4N_2 octahedra share one common O–O edge, forming a $Cu_2O_6N_4$ bioctahedron with a Cu$\cdots$Cu separation of 3.524 (2) Å. Neighboring bioctahedra are connected by bis-unidentate succinate anions in the a-axis direction, while in the c-axis direction bioctahedra are connected by bis-bidentate succinate anions, leading to an infinite two-dimensional network structure. These networks are further connected along the a-axis direction by hydrogen bonds between ammonia ligands and carboxylate O atoms of neighboring network layers, forming a three-dimensional lamellar structure.

Related literature

For related literature, see: Halcrow (2001); Holm *et al.* (1996); Jin & Chen (2007*a*,*b*); Jin *et al.* (2007); Kato & Muto (1988); Lassahn *et al.* (2004); Mehrotra & Bohra (1983); Park *et al.* (2001); Rao *et al.* (2004); Zheng *et al.* (2000, 2001).



Experimental

Crystal data

$[Cu(C_4H_4O_4)(NH_3)_2]$
M_r = 213.68
Monoclinic, $C2/m$
a = 13.761 (6) Å
b = 7.374 (3) Å
c = 8.709 (4) Å
β = 124.515 (4)°
V = 728.2 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.97 mm^{-1}
T = 293 (2) K
0.27 × 0.15 × 0.09 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) T_{min} = 0.501, T_{max} = 0.776
1874 measured reflections
694 independent reflections
641 reflections with $I > 2\sigma(I)$
R_{int} = 0.036

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.072
S = 1.14
694 reflections
64 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.58 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D\cdots A$	D—H$\cdots$$A$
N1—H3$\cdots$O4^{i}	0.86	2.44	3.272 (3)	164
N1—H2$\cdots$O2^{ii}	0.86	2.32	3.133 (3)	159
N1—H1$\cdots$O3^{iii}	0.86	2.48	3.331 (3)	169
N1—H1$\cdots$O4^{iii}	0.86	2.41	3.085 (3)	136

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

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*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2043).

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supplementary materials

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Poly[μ_4-succinato-μ_2-succinato-bis[diamminecopper(II)]]

S. Jin, D. Wang, Y. Yu, G. Luo and Y. Ye

Comment

Carboxylate complexes have been intensively investigated in recent years due to their interesting coordination chemistry allowing for unusual structural features and leading to various physical and chemical properties and practical applications in fields such as dyes, extractants, drugs, pesticides and catalysts (Mehrotra & Bohra, 1983; Rao *et al.*, 2004; Lassahn *et al.*, 2004; Park *et al.*, 2001). Among them copper(II) carboxylates are of special interest as they are easily obtained as polynuclear units having relevance to magnetic materials (Kato & Muto, 1988) and biology (Holm *et al.*, 1996; Halcrow, 2001) As an extension of our research on carboxylate coordination compounds (Jin & Chen, 2007*a*; Jin & Chen, 2007*b*; Jin *et al.*, 2007), we herein report the synthesis and crystal structure of copper succinate diammonia.

The compound of the formula $(C_4H_{10}CuN_2O_4)_n$ was obtained by reacting copper(II) chloride dihydrate with succinic acid in basic solution in the presence of bis(*N*-benzimidazolyl)methane. However, bis(*N*-benzimidazolyl)methane does not appear in the title compound. Single crystals of the title compound suitable for X-ray diffraction analysis cannot be obtained by evaporating an appropriate solution of the title compound in water or organic solvents. We found that it can be dissolved in a concentrated solution of ammonia obviously substituting bis(*N*-benzimidazolyl)methane ligands bound to Cu(II) cations against ammonia. The title compound is stable in air, insoluble in water and common organic solvents. The basic building blocks in the title compound are the edge-shared $Cu_2O_6N_4$ bioctahedra. The Cu atoms are each coordinated by four oxygen atoms of three different succinato ligands and two ammonia nitrogen atoms to complete CuO_4N_2 octahedral geometry (Fig. 1). Two of the coordinated succinate ions act as bis-tridentate bridging ligands. The other succinate ions function as bis-monodentate bridging ligands. Four succinate ions and four copper atoms form 28-membered rings. One oxygen atom of the succinate ions acts as bidentate ligand bridging two copper atoms. The Cu—O bond distances (varying in the range of 1.978 (3)–2.001 (3) Å), and Cu(1)—N(1) bond distances (1.993 (3) Å), are comparable with some known Cu dicarboxylates (Zheng *et al.*, 2000). The O—Cu—O (O(3)—Cu(1)—O(1),176.92 (9) degree) bond angles exhibit significant close to 180 degree, and O—Cu—N bond angles are close to 90 degree also, which implies the CuO_4N_2 octahedra to be slightly distorted. Two adjacent octahedra are condensed *via* two carboxylate O atoms to form $Cu_2O_6N_4$ bioctahedra. The Cu—Cu separation within the bioctahedra is of 3.035 Å, much shorter than those reported earlier (Zheng *et al.*, 2001). Obviously such large Cu—Cu distance along the acute O—Cu—O (75.7 degree), and obtuse Cu—O—Cu angles (104.3 degree) subtended at the Cu and the bridging O atoms implies that there is no or just a very weak interaction between the paired Cu atoms.

Neighboring bioctahedras are additionally connected by bis-unidentate succinate ions in *a* axis direction, while in *c* axis direction bioctahedra are connected by bis-tridentate succinate ions, leading to a two-dimensional network structure. Within the network, the closest intra-bioctahedra Cu—Cu distance of 3.035 (1) Å is substantially smaller than the nearest inter-bioctahedra Cu—Cu distance of 8.350 (1) Å. The resulting infinite layers are further connected through hydrogen bonds between ammonia molecules and carboxylate O atoms of neighboring network layers to form three-dimensional lamellar structure, as demonstrated in Fig. 2.

Experimental

All reagents and solvents were used as obtained without further purification. The CHN elemental analyses were performed on a Perkin-Elmer model 2400 elemental analyzer.

A mixture of copper chloride dihydrate (34.2 mg, 0.2 mmol), NaOH (16 mg, 0.4 mmol), succinic acid (23.6 mg, 0.2 mmol), and bis(*N*-benzimidazolyl)methane (30 mg, 0.2 mmol), in methanol (10 ml) was refluxed for 1 h. The resulted blue precipitate was collected and dissolved in a minimum amount of concentrated ammonia. Blue single crystals of the title compound were obtained by slow evaporation of the ammonia solution at ambient temperature. Yield: 32 mg, 75%. Anal. Calcd for $C_4H_{10}CuN_2O_4$: C, 22.46; H, 4.68; N 13.10. Found: C, 22.41; H, 4.63; N 13.07.

Refinement

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with N—H = 0.86 Å, C—H = 0.96 Å, and U_{iso}(H) = 1.2Ueq(C). Hydrogen atoms bound to water molecules were located in the Fourier difference map, and their distances were fixed.

Figures

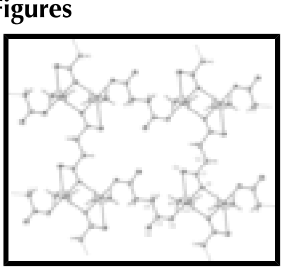

Fig. 1. The molecular structure of one repeating unit the title coordination polymer, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

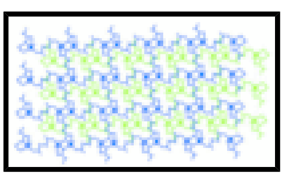

Fig. 2. Three dimensional network structure connected *via* hydrogen bonds.

Poly[μ4-succinato-μ2-succinato-bis[diamminecopper(II)]]

Crystal data

$[Cu(C_4H_4O_4)(NH_3)_2]$	F_{000} = 436
M_r = 213.68	D_x = 1.949 Mg m^{-3}
Monoclinic, *C*2/*m*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -C 2y	Cell parameters from 1618 reflections
a = 13.761 (6) Å	θ = 2.8–28.2°
b = 7.374 (3) Å	μ = 2.97 mm^{-1}
c = 8.709 (4) Å	*T* = 293 (2) K
β = 124.515 (4)°	Block, blue

V = 728.2 (5) Å^3	0.27 × 0.15 × 0.09 mm
Z = 4	

Data collection

Bruker SMART APEX CCD diffractometer	694 independent reflections
Radiation source: fine-focus sealed tube	641 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.036
T = 293(2) K	θ_{max} = 25.0°
φ and ω scans	θ_{min} = 2.8°
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -15 \rightarrow 16$
T_{min} = 0.501, T_{max} = 0.776	$k = -8 \rightarrow 8$
1874 measured reflections	$l = -9 \rightarrow 10$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.026	H-atom parameters constrained
$wR(F^2)$ = 0.072	$w = 1/[\sigma^2(F_o^2) + (0.0361P)^2 + 0.9127P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.14	$(\Delta/\sigma)_{max}$ = 0.001
694 reflections	$\Delta\rho_{max}$ = 0.37 e Å^{-3}
64 parameters	$\Delta\rho_{min}$ = −0.58 e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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}
Cu1	0.84469 (3)	0.5000	0.85475 (5)	0.0211 (2)
O1	0.9788 (2)	0.5000	0.8255 (3)	0.0239 (6)
O2	0.8291 (2)	0.5000	0.5275 (4)	0.0387 (8)

O3	0.7184 (2)	0.5000	0.8984 (4)	0.0280 (6)
O4	0.5330 (2)	0.5000	0.8099 (4)	0.0381 (7)
N1	0.83799 (18)	0.7693 (4)	0.8316 (3)	0.0280 (5)
H1	0.8335	0.8263	0.9134	0.042*
H2	0.7797	0.8073	0.7251	0.042*
H3	0.8990	0.8131	0.8407	0.042*
C1	0.9363 (3)	0.5000	0.6510 (5)	0.0223 (8)
C2	1.0265 (3)	0.5000	0.6041 (5)	0.0275 (9)
H2A	1.0763	0.3939	0.6599	0.033*
C3	0.6069 (3)	0.5000	0.7718 (5)	0.0241 (8)
C4	0.5663 (3)	0.5000	0.5694 (5)	0.0261 (8)
H4	0.5987	0.3939	0.5480	0.031*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0203 (3)	0.0245 (3)	0.0180 (3)	0.000	0.0106 (2)	0.000
O1	0.0217 (13)	0.0359 (16)	0.0144 (12)	0.000	0.0104 (11)	0.000
O2	0.0267 (15)	0.068 (2)	0.0187 (13)	0.000	0.0111 (12)	0.000
O3	0.0188 (13)	0.0446 (17)	0.0191 (12)	0.000	0.0097 (11)	0.000
O4	0.0252 (15)	0.066 (2)	0.0255 (14)	0.000	0.0159 (12)	0.000
N1	0.0283 (12)	0.0266 (14)	0.0233 (11)	0.0018 (10)	0.0111 (10)	−0.0004 (10)
C1	0.0249 (18)	0.024 (2)	0.0183 (16)	0.000	0.0127 (15)	0.000
C2	0.0256 (19)	0.039 (2)	0.0200 (19)	0.000	0.0139 (16)	0.000
C3	0.0256 (19)	0.0239 (19)	0.0215 (17)	0.000	0.0126 (16)	0.000
C4	0.028 (2)	0.031 (2)	0.0179 (17)	0.000	0.0118 (17)	0.000

Geometric parameters (Å, °)

Cu1—O3	1.978 (3)	N1—H2	0.8599
Cu1—N1^{i}	1.993 (3)	N1—H3	0.8599
Cu1—N1	1.993 (3)	C1—C2	1.510 (5)
Cu1—O1	2.001 (3)	C2—C2^{ii}	1.524 (7)
O1—C1	1.282 (4)	C2—H2A	0.9698
O2—C1	1.240 (5)	C3—C4	1.517 (5)
O3—C3	1.286 (5)	C4—C4^{iii}	1.514 (7)
O4—C3	1.236 (5)	C4—H4	0.9696
N1—H1	0.8599		
O3—Cu1—N1^{i}	91.38 (6)	H2—N1—H3	104.0
O3—Cu1—N1	91.38 (6)	O2—C1—O1	123.2 (3)
N1^{i}—Cu1—N1	170.34 (12)	O2—C1—C2	121.5 (3)
O3—Cu1—O1	176.92 (9)	O1—C1—C2	115.3 (3)
N1^{i}—Cu1—O1	88.87 (6)	C1—C2—C2^{ii}	114.1 (4)
N1—Cu1—O1	88.87 (6)	C1—C2—H2A	108.7
C1—O1—Cu1	108.5 (2)	C2^{ii}—C2—H2A	108.8
C3—O3—Cu1	125.9 (2)	O4—C3—O3	122.2 (3)
Cu1—N1—H1	115.1	O4—C3—C4	119.7 (3)

Cu1—N1—H2	113.3	O3—C3—C4	118.1 (3)
H1—N1—H2	105.8	C4^{iii}—C4—C3	114.3 (4)
Cu1—N1—H3	112.2	C4^{iii}—C4—H4	108.9
H1—N1—H3	105.4	C3—C4—H4	108.5
O3—Cu1—O1—C1	180.000 (10)	Cu1—O1—C1—C2	180.000 (1)
N1^{i}—Cu1—O1—C1	85.31 (6)	O2—C1—C2—C2^{ii}	0.000 (1)
N1—Cu1—O1—C1	−85.31 (6)	O1—C1—C2—C2^{ii}	180.000 (2)
N1^{i}—Cu1—O3—C3	−85.37 (6)	Cu1—O3—C3—O4	180.000 (1)
N1—Cu1—O3—C3	85.37 (6)	Cu1—O3—C3—C4	0.000 (2)
O1—Cu1—O3—C3	180.000 (12)	O4—C3—C4—C4^{iii}	0.0
Cu1—O1—C1—O2	0.0	O3—C3—C4—C4^{iii}	180.000 (2)

Symmetry codes: (i) *x*, −*y*+1, *z*; (ii) −*x*+2, −*y*+1, −*z*+1; (iii) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H3···O4^{iv}	0.86	2.44	3.272 (3)	164
N1—H2···O2^{v}	0.86	2.32	3.133 (3)	159
N1—H1···O3^{vi}	0.86	2.48	3.331 (3)	169
N1—H1···O4^{vi}	0.86	2.41	3.085 (3)	136

Symmetry codes: (iv) *x*+1/2, *y*+1/2, *z*; (v) −*x*+3/2, −*y*+3/2, −*z*+1; (vi) −*x*+3/2, −*y*+3/2, −*z*+2.

Fig. 1

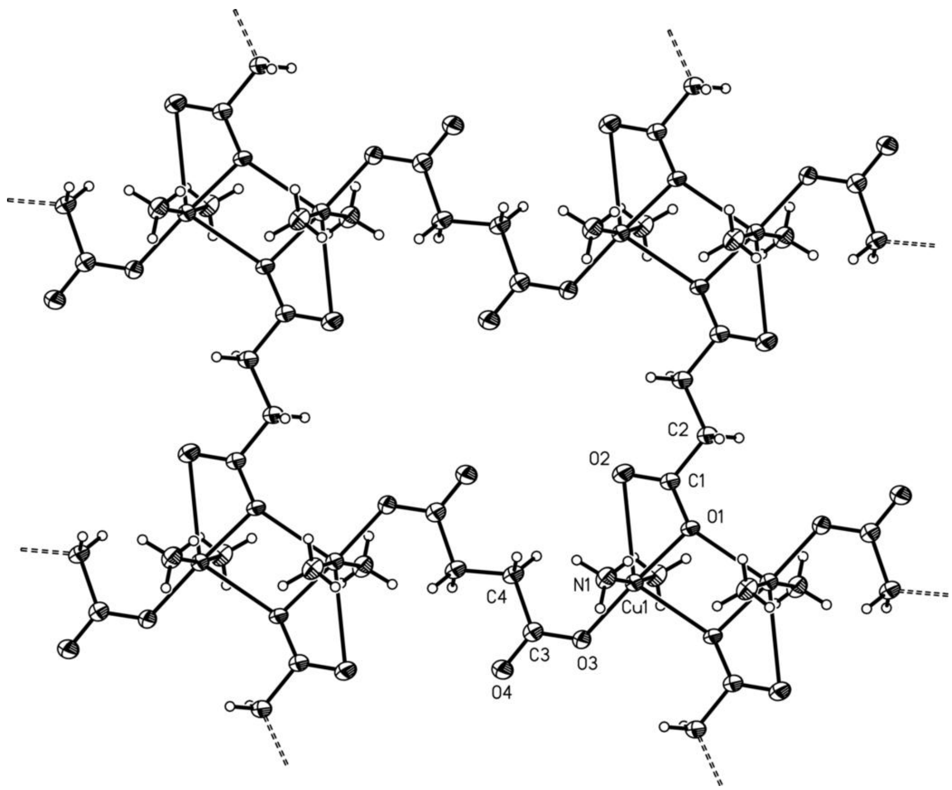

Fig. 2