

Keywords: crystal structure; anhydrous
bis(sarcosinato)copper(II); non-proteinogenic
amino acid

CCDC reference: 961026

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Crystal structure of anhydrous poly[bis(μ_2 -sarcosinato- κ^3 O,N:O')copper(II)]

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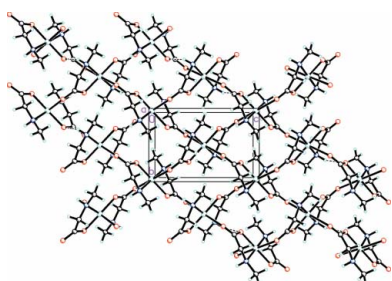
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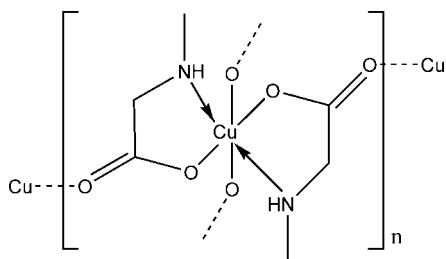
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The title compound, [Cu(C₃H₆NO₂)₂]_n, is a bis-complex of the anion of sarcosine (*N*-methylglycine). The asymmetric unit consists of a copper(II) ion, located on a center of inversion, and one molecule of the uninegative sarcosinate anion. The copper(II) ion exhibits a typical Jahn–Teller distorted [4 + 2] coordination geometry. The four shorter equatorial bonds are to the nitrogen and carboxylate O atoms of two sarcosinate anions, and the longer axial bonds are to carboxylate O atoms of neighboring complexes. The overall structure is made up from two chains formed by these longer axial Cu–O bonds, one extending parallel to [011] and the other parallel to [0 $\bar{1}$ 1]. Each one-dimensional array is connected by the equatorial bridging moieties to the chains on either side, creating an extended two-dimensional framework parallel to (100). There is a single intermolecular hydrogen-bonding interaction within the sheets between the amino NH group and an O atom of an adjacent molecule.

1. Chemical context

The α -amino acids are essential for life as they are the building blocks of all proteins and enzymes and a great deal is known about their structures and complexes. *N*-Methyl amino acids, such as sarcosine, are non-proteinogenic and hence differ from the proteinogenic amino acids used in living systems in that the amino N atom is achiral in the free molecule but chiral, *R* or *S*, when bound to a metal. Examples of complexes of sarcosine that exhibit chirality due to coordination of the amino N atom have been reported (Blount *et al.*, 1967; Larsen *et al.*, 1968; Prout *et al.*, 1972). This is similar to the chirality that is observed on the binding of reduced tripodal Schiff base complexes of metals (Brewer *et al.*, 2014; Al-Obaidi *et al.*, 1996). In these cases, the binding of three achiral (due to rapid inversion) amine N atoms of the free ligand to the same metal resulted in the observation of a single enantiomeric pair (*RRR* and *SSS*) or a single enantiomer (*RRR* or *SSS*) if the molecule crystallized in one of the Sohncke space groups. In these cases, the binding of an organic ligand containing three achiral N atoms to a metal resulted in a preference for chirality correlation of the N atoms, *RRR* or *SSS*, resulting in homochiral complexes. Similarly, the reduced Schiff base complexes of the condensate of amino acids with salicylaldehyde have an energetic preference for the stereoisomer in which the chirality of the α -C atom and the amine N atom are correlated (Koh *et al.*, 1996).





This preference for homochirality is not always observed: the copper complex of a Schiff base condensate of tyrosine is heterochiral as is the bis-adduct of cobalt(III) with histidine (Pradeep *et al.*, 2006; Zie *et al.*, 2007). The present complex was investigated to determine if there was a preference for homo- (*RR* or *SS*) versus heterochirality (*RS*) in a $M(\text{sarcosinato})_2$ complex (M = divalent transition metal). Heterochirality, *RS*, was observed in this complex. Future work will focus on related complexes such as $M'(\text{sarcosinato})_3$ (M' = trivalent transition metal) to determine if the presence of three chiral ligands bound to a single metal favors homochirality, which can serve as a method of enantiomeric separation.

2. Structural commentary

The title compound, $[\text{Cu}(\text{C}_3\text{H}_6\text{NO}_2)_2]_n$, is a bis-complex of the sarcosinate anion with copper(II). The central metal cation is located on a center of inversion. It is six-coordinate and has a distorted octahedral [4 + 2] coordination sphere characteristic for Jahn–Teller systems. The four shorter equatorial bonds are to the amino N atom and carboxylate O atom of two sarcosinate anions (Fig. 1). The N and O atoms are *trans* to one another. The related $[\text{Cu}(\text{sarcosinato})_2] \cdot 2\text{H}_2\text{O}$ structure (Krishnakumar *et al.*, 1994) is much simpler in that the two longer axial bonds are to water molecules so that there is no extended bonding to neighboring complexes. In both structures, the equatorial Cu–O and Cu–N bond lengths are very similar [Cu–O = 1.9758 (8) Å and Cu–N = 2.0046 (9) Å in the title compound, and 1.970 and 2.007 Å in the dihydrate], but the axial Cu–O distances are significantly different at 2.5451 (10) and 2.461 Å.

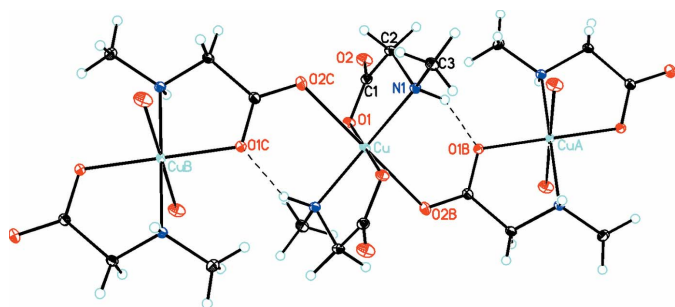


Figure 1

Part of a chain in the title compound, with the atom-numbering scheme and atomic displacement parameters drawn at the 30% probability level. Hydrogen bonding is shown by dashed lines. [Symmetry codes: (A) $1 - x, 1 - y, 1 - z$; (B) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (C) $x, \frac{3}{2} - y, \frac{1}{2} + z$.]

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{N1}-\text{H1A} \cdots \text{O1}^i$	0.93	2.13	2.9729 (13)	150

Symmetry code: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$.

3. Supramolecular features

In the title compound, the individual coordination polyhedra are linked by longer axial Cu–O bonds into two chains, one extending parallel to [011] and the other parallel to $[0\bar{1}1]$. The one-dimensional array is linked by equatorial bridging bonds to the chains on either side, creating an extended two-dimensional framework (Fig. 2) parallel to (100). There is a single intermolecular hydrogen-bonding interaction within the sheets between the amino NH and an carboxylate O atom of an adjacent molecule (Table 1).

4. Database survey

The structure of the zwitterionic form of sarcosine has been reported by Rodrigues *et al.* (2005). The structure of the copper(II) and nickel(II) complexes of this same ligand have been reported as their dihydrates by Krishnakumar *et al.* (1994) and Guha (1973), respectively.

5. Synthesis and crystallization

Sarcosine (*N*-methylglycine) was purchased from Aldrich Chemical. Sarcosine (1.87 mmol, 0.166 g) was dissolved in 0.10 *M* aqueous potassium hydroxide (18.7 ml, 1.87 mmol). Copper chloride dihydrate (0.468 mmol, 0.078 g) was added to the above solution and crystals of the title compound were grown by slow evaporation.

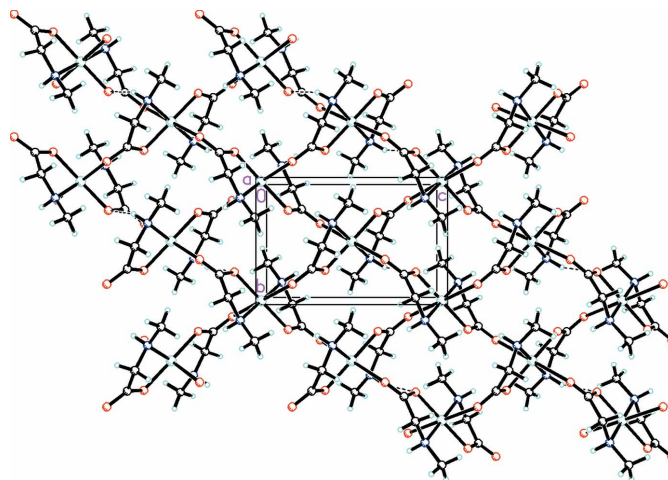


Figure 2

Packing diagram of the title compound viewed along the *a* axis. Hydrogen bonding is shown by dashed lines.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were positioned geometrically and refined using a riding model, with C—H distances of 0.93–0.99 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{C})$ for methyl H atoms. The H attached to N was located in a difference Fourier map and refined using a riding model, with an N—H distance of 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$.

Acknowledgements

RJB wishes to acknowledge the NSF–MRI program (grant No. CHE-0619278) for funds to purchase the diffractometer. GB wishes to acknowledge support of this work from NASA (NNX10AK71A)

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Table 2

Experimental details.

Crystal data	
Chemical formula	[Cu(C ₃ H ₆ NO ₂) ₂]
M_r	239.72
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	123
a, b, c (Å)	7.9031 (3), 5.9461 (2), 8.9907 (3)
β (°)	90.039 (3)
V (Å ³)	422.50 (3)
Z	2
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	2.57
Crystal size (mm)	0.51 × 0.45 × 0.12
Data collection	
Diffractometer	Agilent Xcalibur Ruby Gemini
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Agilent, 2012)
$T_{\text{min}}, T_{\text{max}}$	0.478, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5479, 1768, 1542
R_{int}	0.025
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.808
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.023, 0.061, 1.08
No. of reflections	1768
No. of parameters	63
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.64, -0.36

Computer programs: *CrysAlis PRO* (Agilent, 2012), *SIR97* (Altomare *et al.*, 1999), *SHELXL97* and *SHELXTL* (Sheldrick, 2008).

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supporting information

Acta Cryst. (2014). E70, 207-209 [doi:10.1107/S1600536814020418]

Crystal structure of anhydrous poly[bis(μ_2 -sarcosinato- $\kappa^3 O,N:O'$)copper(II)]

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Computing details

Data collection: *CrysAlis PRO* (Agilent, 2012); cell refinement: *CrysAlis PRO* (Agilent, 2012); data reduction: *CrysAlis PRO* (Agilent, 2012); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

Poly[bis(μ_2 -sarcosinato- $\kappa^3 O,N:O'$)copper(II)]

Crystal data

[Cu(C₃H₆NO₂)₂]

$M_r = 239.72$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 7.9031$ (3) Å

$b = 5.9461$ (2) Å

$c = 8.9907$ (3) Å

$\beta = 90.039$ (3)°

$V = 422.50$ (3) Å³

$Z = 2$

$F(000) = 246$

$D_x = 1.884$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2393 reflections

$\theta = 3.4$ – 35.0°

$\mu = 2.57$ mm⁻¹

$T = 123$ K

Plate, dark blue

$0.51 \times 0.45 \times 0.12$ mm

Data collection

Agilent Xcalibur Ruby Gemini
diffractometer

Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator

Detector resolution: 10.5081 pixels mm⁻¹

ω scans

Absorption correction: multi-scan
(*CrysAlis PRO*; Agilent, 2012)

$T_{\min} = 0.478$, $T_{\max} = 1.000$

5479 measured reflections

1768 independent reflections

1542 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.025$

$\theta_{\max} = 35.0^\circ$, $\theta_{\min} = 4.1^\circ$

$h = -12 \rightarrow 11$

$k = -9 \rightarrow 8$

$l = -14 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.023$

$wR(F^2) = 0.061$

$S = 1.08$

1768 reflections

63 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0285P)^2 + 0.0835P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.64$ e Å⁻³

$\Delta\rho_{\min} = -0.36$ e Å⁻³

Extinction correction: *SHELXTL* (Sheldrick, 2008), $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.014 (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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu	0.5000	0.5000	0.5000	0.01076 (7)
O1	0.53710 (10)	0.74236 (14)	0.35326 (9)	0.01390 (16)
O2	0.72233 (12)	0.85036 (16)	0.17943 (10)	0.0221 (2)
N1	0.69539 (12)	0.35314 (16)	0.39628 (10)	0.01218 (17)
H1A	0.6524	0.2775	0.3140	0.015*
C1	0.67866 (14)	0.72698 (19)	0.28370 (12)	0.01373 (19)
C2	0.79685 (14)	0.5444 (2)	0.34046 (13)	0.0135 (2)
H2A	0.8718	0.4933	0.2590	0.016*
H2B	0.8685	0.6048	0.4215	0.016*
C3	0.79798 (15)	0.1919 (2)	0.48149 (14)	0.0171 (2)
H3A	0.8941	0.1425	0.4209	0.026*
H3B	0.7284	0.0615	0.5080	0.026*
H3C	0.8398	0.2642	0.5723	0.026*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu	0.00955 (10)	0.01254 (10)	0.01019 (10)	0.00153 (6)	0.00211 (6)	0.00253 (6)
O1	0.0127 (3)	0.0158 (4)	0.0132 (3)	0.0014 (3)	0.0018 (3)	0.0034 (3)
O2	0.0215 (4)	0.0249 (5)	0.0199 (4)	0.0014 (4)	0.0060 (3)	0.0105 (4)
N1	0.0111 (4)	0.0142 (4)	0.0112 (4)	−0.0001 (3)	0.0001 (3)	0.0001 (3)
C1	0.0132 (4)	0.0152 (5)	0.0128 (4)	−0.0016 (4)	0.0005 (4)	0.0008 (4)
C2	0.0107 (4)	0.0165 (5)	0.0132 (5)	−0.0008 (4)	0.0011 (4)	0.0012 (4)
C3	0.0161 (5)	0.0168 (5)	0.0183 (5)	0.0040 (4)	0.0003 (4)	0.0020 (4)

Geometric parameters (\AA , $^\circ$)

Cu—O1 ⁱ	1.9758 (8)	N1—C2	1.4796 (15)
Cu—O1	1.9758 (8)	N1—H1A	0.9300
Cu—N1 ⁱ	2.0046 (9)	C1—C2	1.5200 (17)
Cu—N1	2.0046 (9)	C2—H2A	0.9900
Cu—O2 ⁱⁱ	2.5451 (10)	C2—H2B	0.9900
Cu—O2 ⁱⁱⁱ	2.5451 (10)	C3—H3A	0.9800

O1—C1	1.2853 (13)	C3—H3B	0.9800
O2—C1	1.2396 (14)	C3—H3C	0.9800
N1—C3	1.4705 (15)		
O1 ⁱ —Cu—O1	180.0	C3—N1—H1A	107.4
O1 ⁱ —Cu—N1 ⁱ	83.82 (3)	C2—N1—H1A	107.4
O1—Cu—N1 ⁱ	96.18 (3)	Cu—N1—H1A	107.4
O1 ⁱ —Cu—N1	96.18 (3)	O2—C1—O1	124.66 (11)
O1—Cu—N1	83.82 (3)	O2—C1—C2	120.34 (10)
N1 ⁱ —Cu—N1	180.0	O1—C1—C2	114.98 (10)
O1 ⁱ —Cu—O2 ⁱⁱ	86.24 (3)	N1—C2—C1	109.26 (9)
O1—Cu—O2 ⁱⁱ	93.76 (3)	N1—C2—H2A	109.8
N1 ⁱ —Cu—O2 ⁱⁱ	94.85 (3)	C1—C2—H2A	109.8
N1—Cu—O2 ⁱⁱ	85.15 (3)	N1—C2—H2B	109.8
O1 ⁱ —Cu—O2 ⁱⁱⁱ	93.76 (3)	C1—C2—H2B	109.8
O1—Cu—O2 ⁱⁱⁱ	86.24 (3)	H2A—C2—H2B	108.3
N1 ⁱ —Cu—O2 ⁱⁱⁱ	85.15 (3)	N1—C3—H3A	109.5
N1—Cu—O2 ⁱⁱⁱ	94.85 (3)	N1—C3—H3B	109.5
O2 ⁱⁱ —Cu—O2 ⁱⁱⁱ	180.0	H3A—C3—H3B	109.5
C1—O1—Cu	113.74 (7)	N1—C3—H3C	109.5
C3—N1—C2	112.28 (9)	H3A—C3—H3C	109.5
C3—N1—Cu	117.79 (7)	H3B—C3—H3C	109.5
C2—N1—Cu	103.93 (7)		
O1 ⁱ —Cu—O1—C1	-64 (100)	O1—Cu—N1—C2	29.24 (7)
N1 ⁱ —Cu—O1—C1	166.53 (8)	N1 ⁱ —Cu—N1—C2	80 (100)
N1—Cu—O1—C1	-13.47 (8)	O2 ⁱⁱ —Cu—N1—C2	-65.08 (7)
O2 ⁱⁱ —Cu—O1—C1	71.23 (8)	O2 ⁱⁱⁱ —Cu—N1—C2	114.92 (7)
O2 ⁱⁱⁱ —Cu—O1—C1	-108.77 (8)	Cu—O1—C1—O2	174.29 (10)
O1 ⁱ —Cu—N1—C3	-25.85 (8)	Cu—O1—C1—C2	-6.96 (12)
O1—Cu—N1—C3	154.15 (8)	C3—N1—C2—C1	-167.81 (9)
N1 ⁱ —Cu—N1—C3	-155 (100)	Cu—N1—C2—C1	-39.44 (10)
O2 ⁱⁱ —Cu—N1—C3	59.83 (8)	O2—C1—C2—N1	-148.69 (11)
O2 ⁱⁱⁱ —Cu—N1—C3	-120.17 (8)	O1—C1—C2—N1	32.50 (13)
O1 ⁱ —Cu—N1—C2	-150.76 (7)		

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1A \cdots O1 ⁱⁱⁱ	0.93	2.13	2.9729 (13)	150

Symmetry code: (iii) $-x+1, y-1/2, -z+1/2$.