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Diaquabis(saccharinato-κN)copper(II)

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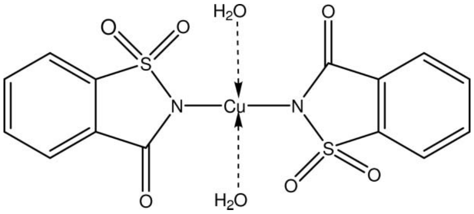
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.027; wR factor = 0.080; data-to-parameter ratio = 25.6.

In the title compound, $[Cu(C_7H_4NO_3S)_2(H_2O)_2]$, the Cu^{II} atom lies on a crystallographic inversion centre and is in a square-planar coordination geometry. The saccharinate ligand is essentially planar and the crystal structure is stabilized by intermolecular O—H···O and C—H···O interactions.

Related literature

For a related crystal structure, see: Yilmaz *et al.* (2001). For general background, see: Allen *et al.* (1987); Baran (2005); Baran & Yilmaz (2006); Groutas *et al.* (1996); Suzuki & Suzuki (1995); Zurlo & Squire (1998).



Experimental

Crystal data

$[Cu(C_7H_4NO_3S)_2(H_2O)_2]$
M_r = 463.92
Triclinic, $P\bar{1}$
a = 4.9171 (1) Å
b = 7.8826 (2) Å
c = 10.5731 (3) Å
α = 96.167 (1)°
β = 102.295 (1)°
γ = 99.211 (1)°
V = 390.97 (2) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 1.72 mm^{-1}
T = 100.0 (1) K
0.74 × 0.13 × 0.09 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.362, T_{max} = 0.861
12980 measured reflections
3411 independent reflections
2975 reflections with $I > 2\sigma(I)$
R_{int} = 0.029

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.080
S = 1.12
3411 reflections
133 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.61 e Å^{-3}
$\Delta\rho_{min}$ = −0.63 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1W1···O3^{i}	0.84 (3)	2.57 (3)	3.0298 (14)	116 (3)
O1W—H1W1···O3^{ii}	0.84 (3)	1.75 (3)	2.5392 (14)	156 (3)
O1W—H2W1···O1	0.78 (3)	2.18 (2)	2.7689 (14)	132 (2)
C4—H4A···O2^{iii}	0.93	2.53	3.4050 (17)	157
C5—H5A···O1^{iv}	0.93	2.48	3.3542 (16)	157

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*, *PARST* (Nardelli, 1995) and *PLATON* (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2507).

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supplementary materials

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Diaquabis(saccharinato-*κN*)copper(II)

F. Adam, I. A. Hassan, M. M. Rosli and H.-K. Fun

Comment

Saccharin (or *O*-sulphobenzoimide) is widely used as an artificial sweetening agent. The chemistry of saccharin has attracted attention because of its suspected carcinogenous nature (Suzuki & Suzuki, 1995; Zurlo & Squire, 1998). Saccharin, its derivatives and some metal saccharinates are found to be enzymatic inhibitors (Groutas *et al.*, 1996). Saccharin itself does not coordinate metal ions, but its deprotonated form (saccharinate) interacts with trace elements in human body and readily forms complexes with a large number of metal ions (Baran, 2005). The saccharinate anion acts as a polyfunctional ligand and may bond to metals by means of its imino nitrogen, carbonyl oxygen, or sulfonyl oxygen atoms, exhibiting different coordination modes such as monodentate (through the N-or the carbonyl O-atom), bidentate (N, O), tridentate (N, O, O) or as bridging ligand (Baran & Yilmaz, 2006). Our current interest in the chemistry of copper complexes with saccharin is because of its potential as a chiral specific catalyst. Our investigation has resulted in the synthesis of a unique square planar copper-saccharin complex in which the N—Cu—N and O—Cu—O angles (from water) are uniquely 180°. We report herein the crystal structure of disaquabis(Saccharinato-κ*N*)Copper(II).

The Cu^{II} atom of the title complex lies on an inversion centre and is coordinated in a square-planar mode by two saccharinate (*sac*) ligands and two water molecules (Fig. 1). All bond lengths and angles in normal ranges (Allen *et al.*, 1987). The *sac* ligand is essentially planar with the maximum deviation is 0.035Å for atom S1.

The H atoms of the water molecules participate in both intra and intermolecular hydrogen bonding with the carbonyl and sulfonyl O atoms of the *sac* ligand (Table 1, Fig. 2). Intermolecular O1W-H1W1···$O3^{ii}$ interactions link molecules into one-dimensional chains along the *b* axis and these chains are stacked along the *a* axis by C4—H4A···$O2^{iii}$, C5- H5A···$O1^{iv}$ interactions [symmetry codes as in Table 1] and Cu···O short contacts [Cu1···O1(1 + *x*, *y*, *z*) = 2.488 Å] (Fig. 3).

Experimental

To a solution of saccharin (0.732 g, 4 mmol) in 95% ethanol (20 ml), copper(II) nitrate (0.4832 g, 2 mmol) in ethanol (10 ml) was added, followed by triethylamine (0.5 ml, 3.6 mmol). The mixture was refluxed with stirring for 3 h. The resulting blue solution was filtered and left to evaporate slowly at room temperature. Blue needle-shaped single crystals suitable for X-ray diffraction were obtained after one week. Analysis found: C 36.21, H 2.28, N 6.67%; calculated: C 36.25, H 2.61, N 6.04%.

Refinement

All C-bound H atoms were placed in calculated positions with C—H = 0.93Å and refined as riding, with $U_{iso}(H) = 1.2U_{eq}(C)$. The H atoms for water molecules were located in a difference map and freely refined.

Figures

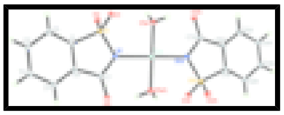

Fig. 1. The molecular structure showing 50% probability displacement ellipsoids and the atomic numbering [symmetry code: A, $-x-1$, $-y$, $-z$]

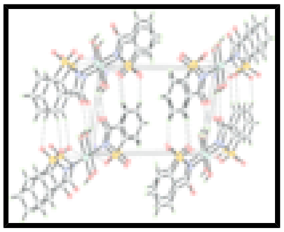

Fig. 2. The crystal packing viewed along the *a* axis. Hydrogen bonds are shown as dashed lines.

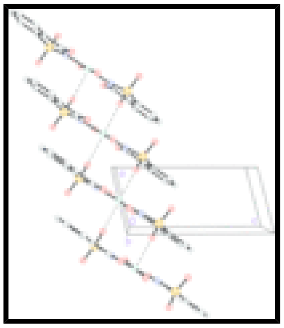

Fig. 3. Packing viewed along the *b* axis, showing an extended chain along the *a* axis. Dashed lines denote Cu···O short contacts.

Diaquabis(saccharinato-κ*N*)copper(II)

Crystal data

$[Cu(C_7H_4NO_3S)_2(H_2O)_2]$
$M_r = 463.92$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 4.9171\ (1)$ Å
$b = 7.8826\ (2)$ Å
$c = 10.5731\ (3)$ Å
$\alpha = 96.167\ (1)^\circ$
$\beta = 102.295\ (1)^\circ$
$\gamma = 99.211\ (1)^\circ$
$V = 390.968\ (17)$ Å^3

$Z = 1$
$F_{000} = 235$
$D_x = 1.970$ Mg m^{-3}
Mo *K*α radiation
λ = 0.71073 Å
Cell parameters from 14734 reflections
θ = 2.7–37.5°
$\mu = 1.72$ mm^{-1}
$T = 100.0\ (1)$ K
Block, blue
0.74 × 0.13 × 0.09 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Monochromator: graphite
Detector resolution: 8.33 pixels mm^{-1}
$T = 100.0(1)$ K

3411 independent reflections
2975 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$
$\theta_{max} = 35.0^\circ$
$\theta_{min} = 2.7^\circ$

ω scans	$h = -7 \rightarrow 7$
Absorption correction: multi-scan (SADABS; Bruker, 2005)	$k = -12 \rightarrow 12$
$T_{\min} = 0.362$, $T_{\max} = 0.861$	$l = -17 \rightarrow 16$
12980 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.027$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.080$	$w = 1/[\sigma^2(F_o^2) + (0.0421P)^2 + 0.1186P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.12$	$(\Delta/\sigma)_{\max} < 0.001$
3411 reflections	$\Delta\rho_{\max} = 0.61$ e Å^{-3}
133 parameters	$\Delta\rho_{\min} = -0.63$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Experimental. The data was collected with the Oxford Cyrosystem Cobra low-temperature attachment.

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	−0.5000	0.0000	0.0000	0.00928 (6)
S1	−0.16480 (6)	0.00582 (4)	−0.23237 (3)	0.00896 (6)
O1	0.03679 (19)	−0.08789 (12)	−0.16235 (10)	0.01210 (16)
O2	−0.3837 (2)	−0.09943 (12)	−0.33636 (10)	0.01312 (17)
O3	−0.3156 (2)	0.40733 (12)	−0.07145 (10)	0.01392 (17)
O1W	−0.4091 (2)	−0.22110 (13)	−0.05806 (11)	0.01448 (18)
N1	−0.2966 (2)	0.11832 (13)	−0.12802 (11)	0.01013 (17)
C1	0.0086 (2)	0.18416 (15)	−0.28886 (12)	0.01025 (19)
C2	0.1765 (3)	0.18638 (16)	−0.37910 (12)	0.0119 (2)
H2A	0.2172	0.0850	−0.4181	0.014*
C3	0.2806 (3)	0.34929 (17)	−0.40792 (13)	0.0139 (2)

H3A	0.3928	0.3571	−0.4684	0.017*
C4	0.2201 (3)	0.50066 (17)	−0.34815 (13)	0.0143 (2)
H4A	0.2941	0.6075	−0.3688	0.017*
C5	0.0504 (3)	0.49440 (16)	−0.25788 (13)	0.0132 (2)
H5A	0.0091	0.5953	−0.2183	0.016*
C6	−0.0548 (2)	0.33242 (15)	−0.22911 (12)	0.01049 (19)
C7	−0.2353 (2)	0.29281 (16)	−0.13564 (12)	0.01059 (19)
H1W1	−0.467 (7)	−0.301 (4)	−0.018 (3)	0.051 (8)*
H2W1	−0.259 (5)	−0.232 (3)	−0.067 (2)	0.030 (6)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01117 (10)	0.00630 (9)	0.01183 (10)	0.00185 (6)	0.00573 (7)	0.00140 (7)
S1	0.01026 (12)	0.00659 (12)	0.01066 (13)	0.00134 (8)	0.00412 (9)	0.00103 (9)
O1	0.0129 (4)	0.0100 (4)	0.0151 (4)	0.0039 (3)	0.0049 (3)	0.0036 (3)
O2	0.0142 (4)	0.0107 (4)	0.0128 (4)	−0.0002 (3)	0.0029 (3)	−0.0009 (3)
O3	0.0180 (4)	0.0090 (4)	0.0169 (4)	0.0031 (3)	0.0087 (3)	0.0010 (3)
O1W	0.0173 (4)	0.0094 (4)	0.0205 (5)	0.0036 (3)	0.0114 (3)	0.0031 (3)
N1	0.0124 (4)	0.0076 (4)	0.0118 (4)	0.0023 (3)	0.0059 (3)	0.0007 (3)
C1	0.0114 (4)	0.0083 (5)	0.0112 (5)	0.0011 (3)	0.0034 (4)	0.0016 (4)
C2	0.0129 (5)	0.0108 (5)	0.0125 (5)	0.0019 (4)	0.0045 (4)	0.0017 (4)
C3	0.0150 (5)	0.0137 (5)	0.0137 (5)	0.0006 (4)	0.0058 (4)	0.0032 (4)
C4	0.0176 (5)	0.0111 (5)	0.0151 (5)	0.0004 (4)	0.0065 (4)	0.0034 (4)
C5	0.0153 (5)	0.0088 (5)	0.0158 (5)	0.0011 (4)	0.0054 (4)	0.0019 (4)
C6	0.0114 (5)	0.0085 (5)	0.0121 (5)	0.0017 (3)	0.0040 (4)	0.0015 (4)
C7	0.0115 (5)	0.0092 (5)	0.0116 (5)	0.0019 (3)	0.0036 (4)	0.0021 (4)

Geometric parameters (Å, °)

Cu1—O1W^{i}	1.9366 (10)	C1—C6	1.3800 (17)
Cu1—O1W	1.9366 (10)	C1—C2	1.3878 (17)
Cu1—N1^{i}	2.0618 (10)	C2—C3	1.3943 (17)
Cu1—N1	2.0619 (10)	C2—H2A	0.9300
S1—O2	1.4387 (10)	C3—C4	1.394 (2)
S1—O1	1.4546 (10)	C3—H3A	0.9300
S1—N1	1.6438 (11)	C4—C5	1.3949 (18)
S1—C1	1.7532 (12)	C4—H4A	0.9300
O3—C7	1.2363 (16)	C5—C6	1.3891 (17)
O1W—H1W1	0.84 (3)	C5—H5A	0.9300
O1W—H2W1	0.78 (3)	C6—C7	1.4875 (17)
N1—C7	1.3750 (16)		
O1W^{i}—Cu1—O1W	180.0	C2—C1—S1	129.07 (10)
O1W^{i}—Cu1—N1^{i}	90.97 (4)	C1—C2—C3	116.20 (12)
O1W—Cu1—N1^{i}	89.03 (4)	C1—C2—H2A	121.9
O1W^{i}—Cu1—N1	89.03 (4)	C3—C2—H2A	121.9
O1W—Cu1—N1	90.97 (4)	C4—C3—C2	121.47 (12)

N1^{i}—Cu1—N1	179.999 (1)	C4—C3—H3A	119.3
O2—S1—O1	114.97 (6)	C2—C3—H3A	119.3
O2—S1—N1	111.85 (6)	C3—C4—C5	121.06 (11)
O1—S1—N1	109.84 (6)	C3—C4—H4A	119.5
O2—S1—C1	110.82 (6)	C5—C4—H4A	119.5
O1—S1—C1	111.27 (6)	C6—C5—C4	117.75 (12)
N1—S1—C1	96.63 (6)	C6—C5—H5A	121.1
Cu1—O1W—H1W1	113 (2)	C4—C5—H5A	121.1
Cu1—O1W—H2W1	123.5 (19)	C1—C6—C5	120.30 (11)
H1W1—O1W—H2W1	108 (3)	C1—C6—C7	112.00 (10)
C7—N1—S1	110.67 (8)	C5—C6—C7	127.70 (11)
C7—N1—Cu1	127.87 (8)	O3—C7—N1	124.73 (11)
S1—N1—Cu1	121.35 (6)	O3—C7—C6	122.43 (11)
C6—C1—C2	123.22 (11)	N1—C7—C6	112.83 (10)
C6—C1—S1	107.69 (9)		

O2—S1—N1—C7	−111.62 (9)	C1—C2—C3—C4	0.51 (19)
O1—S1—N1—C7	119.47 (9)	C2—C3—C4—C5	−0.6 (2)
C1—S1—N1—C7	3.99 (9)	C3—C4—C5—C6	0.4 (2)
O2—S1—N1—Cu1	71.93 (8)	C2—C1—C6—C5	−0.06 (19)
O1—S1—N1—Cu1	−56.99 (8)	S1—C1—C6—C5	−178.70 (10)
C1—S1—N1—Cu1	−172.47 (7)	C2—C1—C6—C7	−179.28 (11)
O1W^{i}—Cu1—N1—C7	8.84 (10)	S1—C1—C6—C7	2.09 (13)
O1W—Cu1—N1—C7	−171.16 (10)	C4—C5—C6—C1	−0.02 (19)
O1W^{i}—Cu1—N1—S1	−175.36 (7)	C4—C5—C6—C7	179.06 (12)
O1W—Cu1—N1—S1	4.64 (7)	S1—N1—C7—O3	177.59 (10)
O2—S1—C1—C6	112.89 (9)	Cu1—N1—C7—O3	−6.24 (18)
O1—S1—C1—C6	−117.86 (9)	S1—N1—C7—C6	−3.34 (13)
N1—S1—C1—C6	−3.53 (10)	Cu1—N1—C7—C6	172.83 (8)
O2—S1—C1—C2	−65.64 (13)	C1—C6—C7—O3	179.78 (12)
O1—S1—C1—C2	63.60 (13)	C5—C6—C7—O3	0.6 (2)
N1—S1—C1—C2	177.93 (12)	C1—C6—C7—N1	0.69 (15)
C6—C1—C2—C3	−0.18 (18)	C5—C6—C7—N1	−178.46 (12)
S1—C1—C2—C3	178.15 (10)		

Symmetry codes: (i) −*x*−1, −*y*, −*z*.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1W—H1W1···O3^{ii}	0.84 (3)	2.57 (3)	3.0298 (14)	116 (3)
O1W—H1W1···O3^{i}	0.84 (3)	1.75 (3)	2.5392 (14)	156 (3)
O1W—H2W1···O1	0.78 (3)	2.18 (2)	2.7689 (14)	132 (2)
C4—H4A···O2^{iii}	0.93	2.53	3.4050 (17)	157
C5—H5A···O1^{iv}	0.93	2.48	3.3542 (16)	157

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

Fig. 1

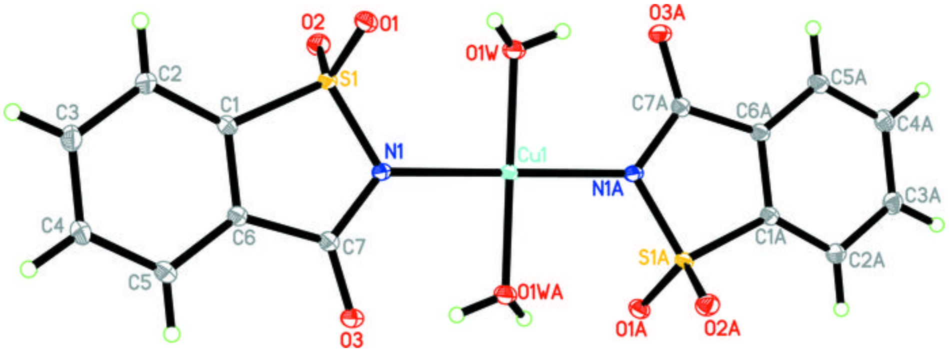
O2
O1
S1
C2
C3
C1
N1
Cu1
O1W
O3A
C7A
C6A
C5A
C4A
N1A
C3A
C4
C6
C7
C5
O3
O1WA
S1A
C1A
C2A
O1A
O2A

Fig. 2

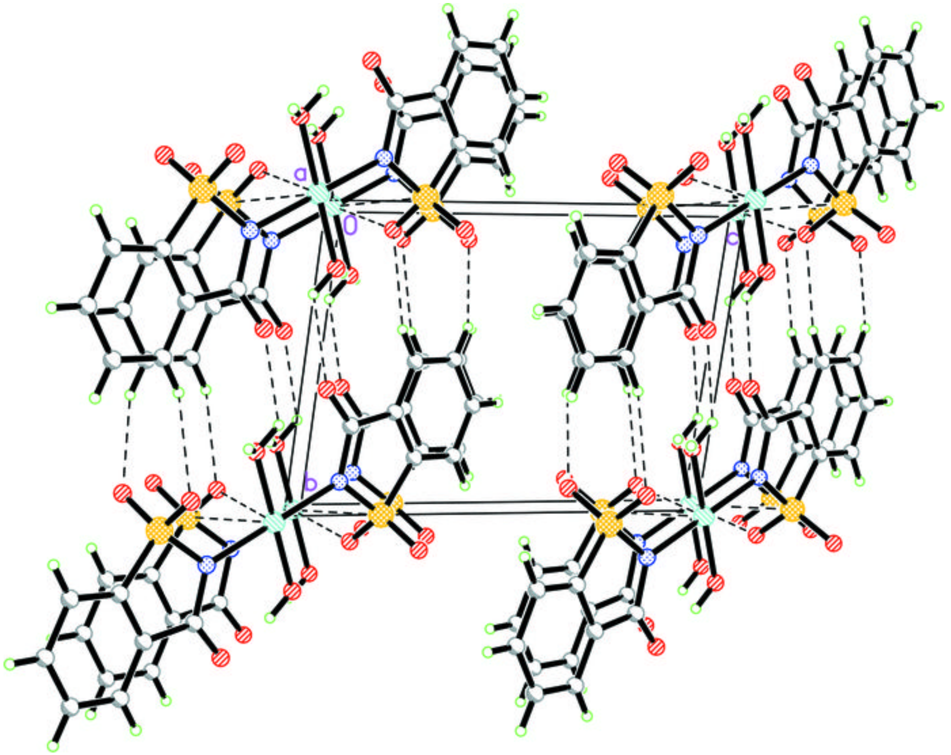

Fig. 3