metal-organic compounds

Bis(4-carboxypyridine-2-carboxylato-$\kappa^2 N,O^2$)copper(II) dimethyl sulfoxide disolvate

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In the title complex, [Cu(C$_7$H$_4$NO$_4$)$_2$]·2C$_2$H$_6$OS, the Cu^{II} atom is situated on an inversion centre and is N,O-chelated by two monoanionic 4-carboxypyridine-2-carboxylate ligands in a slightly distorted square-planar coordination geometry. The dimethyl sulfoxide solvent molecules and Cu^{II} complex molecules are linked by O—H···O hydrogen bonding. In addition, C—H···O contacts and π–π interactions [centroid–centroid distance = 3.590 (1) Å] occur.

Related literature

For the design and synthesis of coordination compounds and complexes derived from pyridine-2,4-dicarboxylic acid, see: Aghabozorg et al. (2008); Noro et al. (2005).
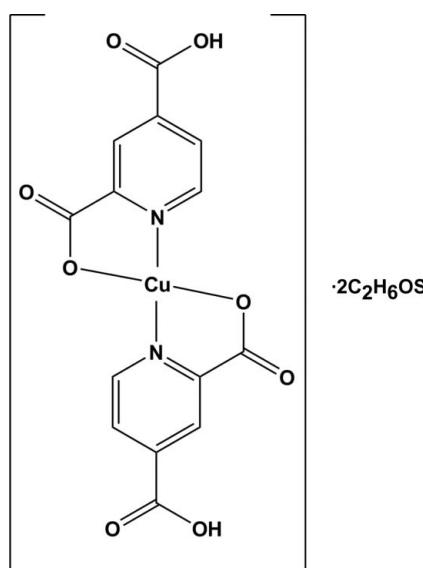
Experimental

Crystal data

[Cu(C$_7$H$_4$NO$_4$)$_2$]·2C$_2$H$_6$OS
M_r = 552.05
Triclinic, $P\bar{1}$
a = 6.8831 (14) Å
b = 7.5218 (15) Å
c = 11.719 (2) Å
α = 102.95 (3)°
β = 91.86 (3)°
γ = 111.12 (3)°
V = 547.3 (2) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 1.25 mm^{-1}
T = 298 K
$0.2 \times 0.10 \times 0.05$ mm

Data collection

Stoe IPDS II diffractometer
6125 measured reflections
2928 independent reflections
2428 reflections with $I > 2\sigma(I)$
R_{int} = 0.034

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.092
S = 1.08
2928 reflections
157 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O5^i	0.84 (4)	1.68 (4)	2.518 (3)	173 (4)
C4—H4···O3^{ii}	0.93	2.55	3.427 (3)	158
C5—H5···O5^{iii}	0.93	2.55	3.370 (3)	147
C8—H8B···O2^{iv}	0.96	2.38	3.223 (3)	147
C9—H9C···O4	0.96	2.51	3.448 (4)	164

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

Data collection: *X-AREA* (Stoe & Cie, 2005); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

References

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Noro, S.-L., Miyasaka, H., Kitagawa, S., Wada, T., Okubo, T., Yamashita, M. & Mitani, T. (2005). *Inorg. Chem.* **44**, 133–146.
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supporting information

Bis(4-carboxypyridine-2-carboxylato-κ^2N,O^2)copper(II) dimethyl sulfoxide disolvate

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S1. Comment

Great interest has been focused on the rapidly expanding field of supramolecular chemistry and crystal engineering of the coordination compounds in recent years because of their intriguing network topologies as well as their potential application as functional materials in many areas (Aghabozorg *et al.*, 2008). Pyridine-2,4-dicarboxylic acid (2,4-pydcH$_2$) is a good building block for constructing complexes. However, plenty of researches have focused on the supramolecular chemistry and coordination polymers which only include single carboxylic acid ligands, (Noro *et al.*, 2005). In this paper, we report the crystal structure of the title compound prepared from Cu(NO$_3$)$_2$.3H$_2$O, 2,4-pydcH$_2$ and acridine.

   The structure of title complex is shown in Fig. 1. In the complex, 2,4-pydcH ligands are bound to one Cu^{II} ion through pyridine N and deprotonated carboxylate O atoms at 2-positions, leading to a distorted square planar geometry around the metal ion. The carboxylic groups at the 4-position of 2,4-pydcH ligands are not coordinating. [Cu(C$_{14}$H$_8$N$_2$O$_8$)] complex is connected into two-dimensional layers through H-bonding interactions (Table 1). The crystal packing is additionally stabilized by π-π stacking interactions (Fig. 2).

S2. Experimental

A mixture of 2,4-pydcH$_2$ (83 mg, 0.50 mmol), Cu(NO$_3$)$_2$.3H$_2$O (120 mg, 0.50 mmol), acridine (179 mg, 1.0 mmol) in 18 ml me thanol/DMSO were heated and stirred for 2 hrs, and then cooled to room temperature. The reaction yielded purple plate crystals of the title compound after 2 months.

S3. Refinement

The hydrogen atoms of the carboxylic acid group was found in a difference Fourier map and refined isotropically without restraint. The C—H protons were positioned geometrically and refined as riding atoms with C—H = 0.93 Å and Uiso(H) = 1.2 Ueq(C) for aromatic C—H groups and C—H = 0.96 Å and Uiso(H) = 1.5 Ueq(C) for the methyl groups.
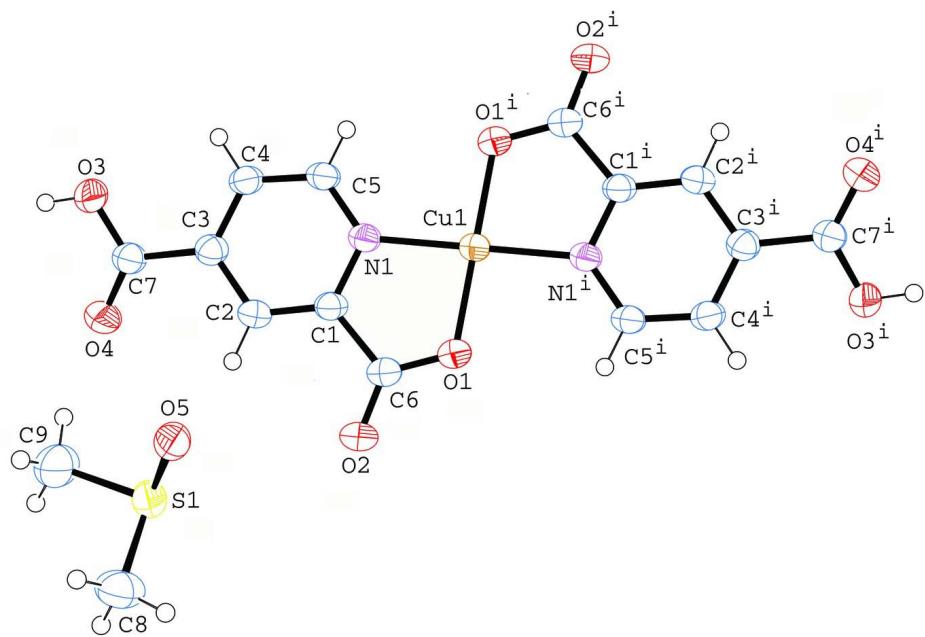
Figure 1

The molecular structure of the title compound with displacement ellipsoids drawn at 50% probability level (symmetry code: i: 1 - *x*,-*y*,1 - *z*).
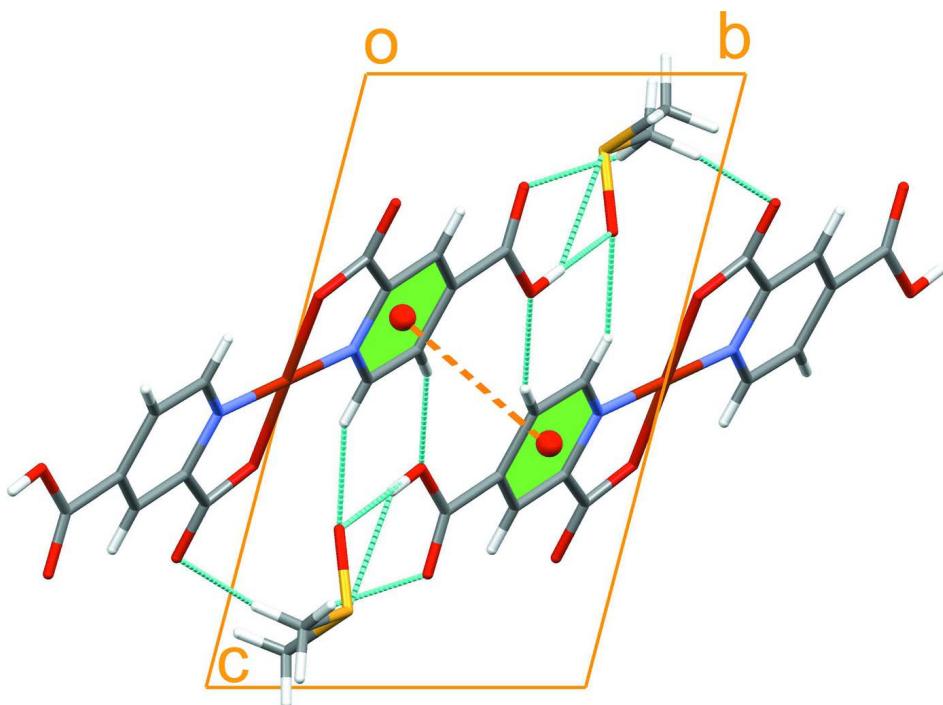
Figure 2

Packing diagram of the title compound. The intermolecular O—H⋯O, and C—H⋯O hydrogen bonds and π⋯π contacts are shown as blue and orange dashed lines, respectively.

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Crystal data

[Cu(C₇H₄NO₄)₂]·2C₂H₆OS	$Z = 1$
$M_r = 552.05$	$F(000) = 283$
Triclinic, $P\overline{1}$	$D_x = 1.675$ Mg m⁻³
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 6.8831$ (14) Å	Cell parameters from 2928 reflections
$b = 7.5218$ (15) Å	$\theta = 3.0–29.1°$
$c = 11.719$ (2) Å	$\mu = 1.25$ mm⁻¹
$\alpha = 102.95$ (3)°	$T = 298$ K
$\beta = 91.86$ (3)°	Plate, purple
$\gamma = 111.12$ (3)°	$0.2 \times 0.1 \times 0.05$ mm
$V = 547.3$ (2) Å³	

Data collection

Stoe IPDS II diffractometer	2928 independent reflections
Radiation source: fine-focus sealed tube	2428 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.034$
Detector resolution: 0.15 mm pixels mm⁻¹	$\theta_{max} = 29.1°$, $\theta_{min} = 3.0°$
rotation method scans	$h = -9\rightarrow9$
6125 measured reflections	$k = -10\rightarrow10$
	$l = -16\rightarrow15$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.040$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.092$	
$S = 1.08$	H atoms treated by a mixture of independent and constrained refinement
2928 reflections	
157 parameters	$w = 1/[\sigma^2(F_o^2) + (0.0365P)^2 + 0.2725P]$
0 restraints	where $P = (F_o^2 + 2F_c^2)/3$
Primary atom site location: structure-invariant direct methods	$(\Delta/\sigma)_{max} = 0.002$
	$\Delta\rho_{max} = 0.38$ e Å⁻³
	$\Delta\rho_{min} = -0.30$ 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 (Å²)

	x	y	z	U_{iso}*/U_{eq}
O5	0.7477 (3)	0.7579 (3)	0.25725 (15)	0.0572 (5)
S1	0.74093 (10)	0.67910 (10)	0.12483 (5)	0.04660 (16)
Cu1	0.5000	0.0000	0.5000	0.03607 (12)
O1	0.3689 (2)	0.0279 (3)	0.36230 (14)	0.0448 (4)

C6	0.4947 (3)	0.1284 (4)	0.30111 (19)	0.0383 (5)
C2	0.8846 (3)	0.3107 (3)	0.29424 (18)	0.0362 (4)
H2	0.8551	0.3418	0.2249	0.043*
C1	0.7250 (3)	0.2025 (3)	0.34780 (18)	0.0339 (4)
O2	0.4440 (3)	0.1668 (3)	0.21140 (16)	0.0540 (5)
N1	0.7628 (3)	0.1553 (3)	0.44860 (15)	0.0331 (4)
C7	1.2654 (4)	0.4892 (4)	0.28672 (19)	0.0387 (5)
C5	0.9603 (3)	0.2151 (3)	0.49832 (18)	0.0358 (4)
H5	0.9857	0.1825	0.5678	0.043*
C4	1.1283 (3)	0.3242 (3)	0.44914 (19)	0.0368 (4)
H4	1.2648	0.3647	0.4853	0.044*
C3	1.0910 (3)	0.3727 (3)	0.34541 (19)	0.0355 (4)
O3	1.4430 (3)	0.5841 (3)	0.35694 (15)	0.0481 (4)
O4	1.2395 (3)	0.4936 (3)	0.18477 (15)	0.0526 (5)
C8	0.6304 (5)	0.8138 (5)	0.0578 (2)	0.0612 (7)
H8A	0.4882	0.7847	0.0744	0.092*
H8B	0.6323	0.7782	−0.0260	0.092*
H8C	0.7104	0.9522	0.0883	0.092*
C9	1.0046 (5)	0.7850 (6)	0.0982 (3)	0.0713 (9)
H9A	1.0577	0.9246	0.1323	0.107*
H9B	1.0111	0.7597	0.0147	0.107*
H9C	1.0879	0.7280	0.1332	0.107*
H3	1.538 (6)	0.645 (5)	0.320 (3)	0.076 (11)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O5	0.0428 (9)	0.0775 (13)	0.0357 (9)	0.0011 (9)	0.0015 (7)	0.0208 (9)
S1	0.0437 (3)	0.0481 (4)	0.0400 (3)	0.0059 (3)	0.0025 (2)	0.0150 (3)
Cu1	0.03021 (19)	0.0481 (2)	0.03117 (19)	0.01310 (16)	0.00208 (14)	0.01565 (16)
O1	0.0315 (8)	0.0623 (11)	0.0408 (8)	0.0127 (7)	−0.0007 (6)	0.0226 (8)
C6	0.0351 (11)	0.0454 (12)	0.0332 (10)	0.0140 (9)	−0.0016 (8)	0.0110 (9)
C2	0.0378 (11)	0.0411 (11)	0.0286 (9)	0.0131 (9)	−0.0010 (8)	0.0105 (8)
C1	0.0341 (10)	0.0378 (11)	0.0288 (9)	0.0133 (8)	−0.0010 (8)	0.0077 (8)
O2	0.0437 (9)	0.0719 (12)	0.0461 (10)	0.0140 (9)	−0.0067 (7)	0.0293 (9)
N1	0.0336 (8)	0.0394 (9)	0.0272 (8)	0.0142 (7)	0.0019 (6)	0.0096 (7)
C7	0.0362 (11)	0.0479 (13)	0.0343 (10)	0.0167 (10)	0.0045 (8)	0.0134 (9)
C5	0.0359 (10)	0.0437 (12)	0.0296 (9)	0.0161 (9)	−0.0002 (8)	0.0117 (8)
C4	0.0321 (10)	0.0452 (12)	0.0324 (10)	0.0149 (9)	−0.0008 (8)	0.0089 (9)
C3	0.0354 (10)	0.0402 (11)	0.0302 (9)	0.0146 (9)	0.0032 (8)	0.0072 (8)
O3	0.0342 (8)	0.0658 (12)	0.0363 (8)	0.0073 (8)	0.0045 (7)	0.0169 (8)
O4	0.0450 (10)	0.0746 (13)	0.0379 (9)	0.0159 (9)	0.0047 (7)	0.0249 (9)
C8	0.0671 (18)	0.079 (2)	0.0426 (14)	0.0313 (16)	0.0007 (13)	0.0185 (14)
C9	0.0473 (16)	0.109 (3)	0.0604 (18)	0.0251 (17)	0.0136 (14)	0.0325 (18)

Geometric parameters (Å, º)

O5—S1	1.5247 (19)	C7—O4	1.212 (3)
S1—C8	1.760 (3)	C7—O3	1.313 (3)
S1—C9	1.770 (3)	C7—C3	1.499 (3)
Cu1—O1	1.9123 (16)	C5—C4	1.384 (3)
Cu1—O1^i	1.9123 (16)	C5—H5	0.9300
Cu1—N1	1.9657 (19)	C4—C3	1.387 (3)
Cu1—N1^i	1.9657 (19)	C4—H4	0.9300
O1—C6	1.284 (3)	O3—H3	0.84 (4)
C6—O2	1.223 (3)	C8—H8A	0.9600
C6—C1	1.514 (3)	C8—H8B	0.9600
C2—C1	1.376 (3)	C8—H8C	0.9600
C2—C3	1.392 (3)	C9—H9A	0.9600
C2—H2	0.9300	C9—H9B	0.9600
C1—N1	1.351 (3)	C9—H9C	0.9600
N1—C5	1.334 (3)		
O5—S1—C8	105.52 (14)	O3—C7—C3	113.21 (19)
O5—S1—C9	104.03 (14)	N1—C5—C4	121.70 (19)
C8—S1—C9	99.68 (17)	N1—C5—H5	119.2
O1—Cu1—O1^i	180.00 (5)	C4—C5—H5	119.2
O1—Cu1—N1	84.57 (7)	C5—C4—C3	119.3 (2)
O1^i—Cu1—N1	95.43 (7)	C5—C4—H4	120.4
O1—Cu1—N1^i	95.43 (7)	C3—C4—H4	120.4
O1^i—Cu1—N1^i	84.57 (7)	C4—C3—C2	118.7 (2)
N1—Cu1—N1^i	180.0	C4—C3—C7	122.2 (2)
C6—O1—Cu1	115.22 (14)	C2—C3—C7	119.08 (19)
O2—C6—O1	125.9 (2)	C7—O3—H3	111 (2)
O2—C6—C1	119.3 (2)	S1—C8—H8A	109.5
O1—C6—C1	114.78 (18)	S1—C8—H8B	109.5
C1—C2—C3	118.97 (19)	H8A—C8—H8B	109.5
C1—C2—H2	120.5	S1—C8—H8C	109.5
C3—C2—H2	120.5	H8A—C8—H8C	109.5
N1—C1—C2	121.90 (19)	H8B—C8—H8C	109.5
N1—C1—C6	114.33 (19)	S1—C9—H9A	109.5
C2—C1—C6	123.77 (18)	S1—C9—H9B	109.5
C5—N1—C1	119.41 (19)	H9A—C9—H9B	109.5
C5—N1—Cu1	129.51 (15)	S1—C9—H9C	109.5
C1—N1—Cu1	111.07 (14)	H9A—C9—H9C	109.5
O4—C7—O3	124.8 (2)	H9B—C9—H9C	109.5
O4—C7—C3	122.0 (2)		
N1—Cu1—O1—C6	−0.79 (18)	O1^i—Cu1—N1—C5	0.0 (2)
N1^i—Cu1—O1—C6	179.21 (18)	O1—Cu1—N1—C1	−0.07 (15)
Cu1—O1—C6—O2	−178.7 (2)	O1^i—Cu1—N1—C1	179.93 (15)
Cu1—O1—C6—C1	1.4 (3)	C1—N1—C5—C4	−0.1 (3)
C3—C2—C1—N1	0.1 (3)	Cu1—N1—C5—C4	179.81 (16)

C3—C2—C1—C6	179.5 (2)	N1—C5—C4—C3	−0.1 (3)
O2—C6—C1—N1	178.6 (2)	C5—C4—C3—C2	0.4 (3)
O1—C6—C1—N1	−1.5 (3)	C5—C4—C3—C7	−179.5 (2)
O2—C6—C1—C2	−0.8 (4)	C1—C2—C3—C4	−0.4 (3)
O1—C6—C1—C2	179.2 (2)	C1—C2—C3—C7	179.5 (2)
C2—C1—N1—C5	0.1 (3)	O4—C7—C3—C4	162.8 (2)
C6—C1—N1—C5	−179.27 (19)	O3—C7—C3—C4	−17.7 (3)
C2—C1—N1—Cu1	−179.83 (17)	O4—C7—C3—C2	−17.1 (4)
C6—C1—N1—Cu1	0.8 (2)	O3—C7—C3—C2	162.4 (2)
O1—Cu1—N1—C5	180.0 (2)		

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O5ii	0.84 (4)	1.68 (4)	2.518 (3)	173 (4)
C4—H4···O3iii	0.93	2.55	3.427 (3)	158
C5—H5···O5iv	0.93	2.55	3.370 (3)	147
C8—H8*B*···O2v	0.96	2.38	3.223 (3)	147
C9—H9*C*···O4	0.96	2.51	3.448 (4)	164

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