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Diamminediaquabis(4-pyridylthioacetato)-copper(II)

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.003 Å
R factor = 0.034
wR factor = 0.090
Data-to-parameter ratio = 14.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The Cu atom in the title compound, [Cu($C_7H_6NO_2S$)$_2$-(H_2O)$_2$(NH_3)$_2$], lies on a special position at a crystallographic inversion centre and has a tetragonally distorted octahedral coordination involving the N atoms of two ammine ligands [Cu—N = 2.010 (2) Å], the N atoms of two pyridylthioacetate ligands [Cu—N = 2.033 (2) Å] and the O atoms of two water molecules [Cu—O = 2.472 (2) Å].

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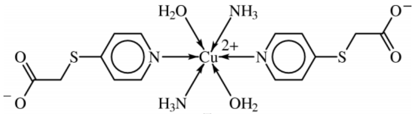
Comment

The reaction of 4-pyridylthioacetic acid with zinc nitrate in the presence of an amine affords 4-pyridylthioacetatozinc hydroxide (Kondo *et al.*, 2002). The hydroxy group bridges two Zn atoms to form a helical [Zn—O]$_n$ chain, and the Zn atom in the chain is linked to the carboxyl O atom of one anion as well as to the pyridyl N atom of an adjacent anion. The report by Kondo *et al.* (2002) did not furnish details of the synthesis; the hydroxide ion that was present in the reaction product was apparently generated from an excess of the amine reagent.

A similar reaction with copper nitrate in place of zinc nitrate did not yield the analogous hydroxide; the product is diamminediaquabis(4-pyridylthioacetato)copper, (I), in which the anionic ligand is bonded to the metal atom only through the pyridyl N atom (Fig. 1).



(I)

The Cu atom in (I) lies on a special position at an inversion centre, and its coordination geometry is that of a tetragonally distorted octahedron [Cu1—N1 = 2.033 (2) Å, Cu1—N2 = 2.010 (2) Å and Cu1—O1w = 2.472 (2) Å; Table 1]. The carboxylate —CO_2^- group shows complete delocalization, with almost identical C7—O1 and C7—O2 bonds [1.242 (3) and 1.245 (3) Å, respectively], which attests to the zwitterionic nature of the complex. The preference of the anions of pyridylcarboxylic acid to bind through the pyridyl N atom rather than through the carboxyl O atom has been noted in a number of transition metal complexes, *e.g.* tetraaquabis(isonicotinato)copper(II) (Ng, 2003).

The coordinated ammine and water molecules engage in extensive hydrogen bonding (Table 2), leading to a two-dimensional motif parallel to the *ab* plane.

Experimental

Copper nitrate (0.09 g, 0.5 mmol) and 4-pyridylthioacetic acid (0.17 g, 1 mmol), a commercially available reagent, were placed in water (10 ml), and ammonium hydroxide was added until the acid dissolved completely (pH ~11). The solution was left to stand, and after one day, pale-blue crystals of the title compound separated out (yield 80%). Analysis found: C 35.35, H 4.65, N 11.57%; calculated for $C_{14}H_{22}N_4O_6S_2Cu$: C 35.77, H 4.72, N 11.92%. IR (KBr, cm^{-1}): 3323, 3250, 3177, 2950, 1635, 1596, 1488, 1428, 1365, 1271,1227, 1206, 1116, 1063, 1022, 910, 809, 799, 727, 661, 581, 526.

Crystal data

$[Cu(C_7H_6NO_2S)_2(H_2O)_2(NH_3)_2]$
$M_r = 470.02$
Monoclinic, $C2/c$
$a = 23.263$ (1) Å
$b = 7.0762$ (3) Å
$c = 11.5216$ (5) Å
$\beta = 100.989$ (1)°
$V = 1861.8$ (1) Å^3
$Z = 4$
$D_x = 1.677$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6563 reflections
$\theta = 3.0$–28.3°
$\mu = 1.44$ mm^{-1}
$T = 298$ (2) K
Plate, blue
0.40 × 0.30 × 0.12 mm

Data collection

Bruker APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.434$, $T_{\max} = 0.841$
10 239 measured reflections
2139 independent reflections
1744 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.041$
$\theta_{\max} = 27.5°$
$h = -30 \rightarrow 30$
$k = -9 \rightarrow 9$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.090$
$S = 0.95$
2139 reflections
144 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0477P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.40$ e Å^{-3}
$\Delta\rho_{\min} = -0.48$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	2.033 (2)	Cu1—O1*w*	2.472 (2)
Cu1—N2	2.010 (2)		
N1—Cu1—N1^{i}	180	N2—Cu1—N2^{i}	180
N1—Cu1—N2	88.9 (1)	N2—Cu1—O1*w*	83.7 (1)
N1—Cu1—N2^{i}	91.1 (1)	N2—Cu1—O1*w*^{i}	96.3 (1)
N1—Cu1—O1*w*	92.7 (1)	O1*w*—Cu1—O1*w*^{i}	180
N1—Cu1—O1*w*^{i}	87.3 (1)		

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2n2···O1^{ii}	0.88 (1)	2.40 (1)	3.267 (2)	167 (2)
N2—H2n1···O2^{iii}	0.89 (1)	2.20 (1)	3.092 (2)	178 (2)
N2—H2n3···O1^{iv}	0.89 (1)	2.16 (1)	3.045 (2)	177 (2)
O1*w*—H1*w*1···O1^{iii}	0.83 (1)	1.98 (1)	2.790 (2)	164 (2)
O1*w*—H1*w*2···O2^{ii}	0.82 (1)	2.01 (1)	2.828 (2)	176 (2)

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

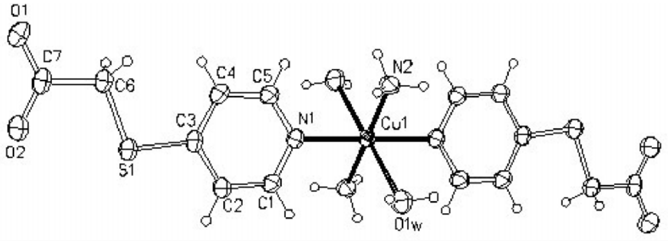


Figure 1
*ORTEP*II (Johnson, 1976) plot of $(C_7H_6NO_2S)_2(NH_3)_2(H_2O)_2Cu$, with displacement ellipsoids shown at the 50% probability level. H atoms are drawn as spheres of arbitrary radii.

The ammine and water H atoms were located in a difference map and were included in the refinement with distance restraints [O—H = 0.85 (1) Å and N—H = 0.89 (1) Å]. The aromatic (C—H = 0.93 Å) and aliphatic (C—H = 0.97 Å) H atoms were placed in calculated positions and refined in the riding-model approximation, with displacement parameters set to $1.2U_{\rm eq}$ of the parent C atoms.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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