Acta Crystallographica Section E
**Structure Reports**
**Online**
ISSN 1600-5368

# Bis(2,2′-bipyridine-*κN*,*N*′){[5-(carboxymethylsulfanyl)-1,3,4-thiadiazol-2-ylsulfanyl]acetato-*κO*}copper(II) [5-(carboxymethylsulfanyl)-1,3,4-thiadiazol-2-ylsulfanyl]acetate dihydrate

**Shan Gao,[a] Li-Hua Huo,[a] Hui Zhao[a] and Seik Weng Ng[b]***

[a]College of Chemistry and Chemical Technology, Heilongjiang University, Harbin 150080, People's Republic of China, and [b]Department of Chemistry, University of Malaya, Kuala Lumpur 50603, Malaysia

Correspondence e-mail: seikweng@um.edu.my

Received 6 December 2004
Accepted 9 December 2004
Online 18 December 2004

In the title compound, $[Cu(C_6H_5N_2O_4S_3)(C_{10}H_8N_2)_2](C_6H_5N_2O_4S_3)\cdot 2H_2O$, the Cu$^{II}$ atom is coordinated by four N atoms from two bipyridine ligands and one O atom from the [5-(carboxymethylsulfanyl)-1,3,4-thiadiazol-2-ylsulfanyl]acetate unit. The five-coordinate environment is intermediate between a trigonal bipyramid and a square pyramid. The complex cations and anions are connected with the water molecules *via* O—H···O hydrogen bonds to form layers.

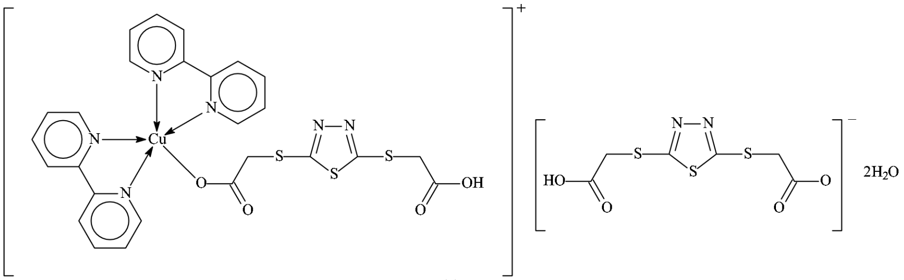
**Key indicators**

Single-crystal X-ray study
*T* = 295 K
Mean σ(C–C) = 0.006 Å
Disorder in main residue
*R* factor = 0.052
*wR* factor = 0.156
Data-to-parameter ratio = 16.1

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

## Comment

We have studied metal complexes of dicarboxylic acids having two –*X*—$CH_2CO_2$ arms on a phenylene unit (Gao *et al.*, 2005; Zhao *et al.*, 2005). The title compound, (I), features a 1,3,4-thiadiazolyl ring, but the presence of basic sites appears to alter the acidity of the dicarboxylic acid reagent, 1,3,4-thiadiazolyl-2,5-dithioacetic acid (tdzdtaH$_2$). In this paper, we report the structure of the title compound, (I), the dicarboxylic acid reagent being only mono-deprotonated.



(I)

In the complex cation, atom Cu1 displays a geometry intermediate between trigonal bipyramidal and square pyramidal (Fig. 1 and Table 1). Atom Cu1 is bonded to carboxylate atom O1 of the tdzdtaH ligand, and its carboxylic acid end is connected to the uncoordinated tdzdtaH$^-$ anion through the water molecules *via* hydrogen bonds (Fig. 2 and Table 2), giving rise to a layer structure.

## Experimental

1,3,4-Thiadiazolyl-2,5-dithioacetic acid (tdzdtaH$_2$) was prepared from 2,5-dimercapto-1,3,4-thiadiazole, using the method for synthesis of benzene-1,4-dioxyacetic acid reported by Liu *et al.* (2004). The copper complex was obtained from the reaction of copper dinitrate hydrate (1.21 g, 5 mmol), 2,2′-bipyridine (1.60 g, 10 mmol) and tdzdtaH$_2$ (2.66 g, 10 mmol) in water; the mixture was heated to dissolve most of the reagents, and the pH was raised to about 6 with 0.2 *M* sodium hydroxide. The hot solution was filtered; the solution yielded crystals of (I) when left aside for several days.

### Crystal data

$[Cu(C_6H_5N_2O_4S_3)(C_{10}H_8N_2)_2]$-$(C_6H_5N_2O_4S_3)\cdot 2H_2O$
$M_r = 942.54$
Triclinic, $P\bar{1}$
$a = 10.900$ (2) Å
$b = 12.197$ (2) Å
$c = 14.772$ (3) Å
$\alpha = 91.86$ (1)°
$\beta = 91.53$ (2)°
$\gamma = 92.28$ (1)°
$V = 1960.6$ (7) Å$^3$

$Z = 2$
$D_x = 1.597$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 16 305 reflections
$\theta = 3.2$–27.5°
$\mu = 0.94$ mm$^{-1}$
$T = 295$ (2) K
Block, blue
0.37 × 0.26 × 0.17 mm

### Data collection

Rigaku R-AXIS RAPID diffractometer
$\omega$ scan
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{\min} = 0.605$, $T_{\max} = 0.856$
18 913 measured reflections

8693 independent reflections
6237 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.032$
$\theta_{\max} = 27.5°$
$h = -12 \rightarrow 14$
$k = -15 \rightarrow 15$
$l = -19 \rightarrow 19$

### Refinement

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.156$
$S = 1.03$
8693 reflections
541 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.091P)^2 + 0.5195P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.69$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.44$ e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Cu1—O1 | 2.001 (2) | Cu1—N3 | 2.157 (3) |
| Cu1—N1 | 1.972 (3) | Cu1—N4 | 1.994 (3) |
| Cu1—N2 | 2.045 (3) | | |
| O1—Cu1—N1 | 94.0 (1) | N1—Cu1—N3 | 94.9 (1) |
| O1—Cu1—N2 | 143.8 (1) | N1—Cu1—N4 | 173.3 (1) |
| O1—Cu1—N3 | 113.7 (1) | N2—Cu1—N3 | 102.4 (1) |
| O1—Cu1—N4 | 90.9 (1) | N2—Cu1—N4 | 97.9 (1) |
| N1—Cu1—N2 | 80.7 (1) | N3—Cu1—N4 | 79.0 (1) |

**Table 2**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1$w$—H1$w$2···O2 | 0.85 (1) | 2.24 (4) | 2.926 (5) | 137 (5) |
| O1$w$—H1$w$1···O8$^{\rm i}$ | 0.85 (1) | 1.97 (2) | 2.793 (5) | 163 (6) |
| O2$w$—H2$w$1···O8$^{\rm ii}$ | 0.86 (1) | 1.91 (2) | 2.733 (6) | 161 (5) |
| O2$w$—H2$w$2···O1$w$ | 0.86 (1) | 1.84 (2) | 2.673 (5) | 163 (5) |
| O3—H3O···O2$w^{\rm iii}$ | 0.85 | 1.80 | 2.643 (5) | 174 |
| O7—H7O···O5$'^{\rm i}$ | 0.85 | 1.72 | 2.47 (1) | 146 |
| O7—H7O···O6$^{\rm i}$ | 0.85 | 1.92 | 2.680 (6) | 149 |

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

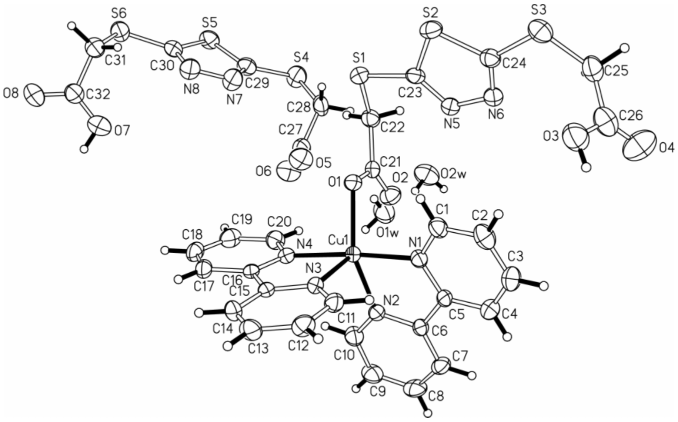


**Figure 1**
The molecular structure of (I), showing displacement ellipsoids at the 30% probability level. The major site occupation factor of atoms O5, O6, C27 and C28 is 0.735 (6). The minor disorder component has been omitted.

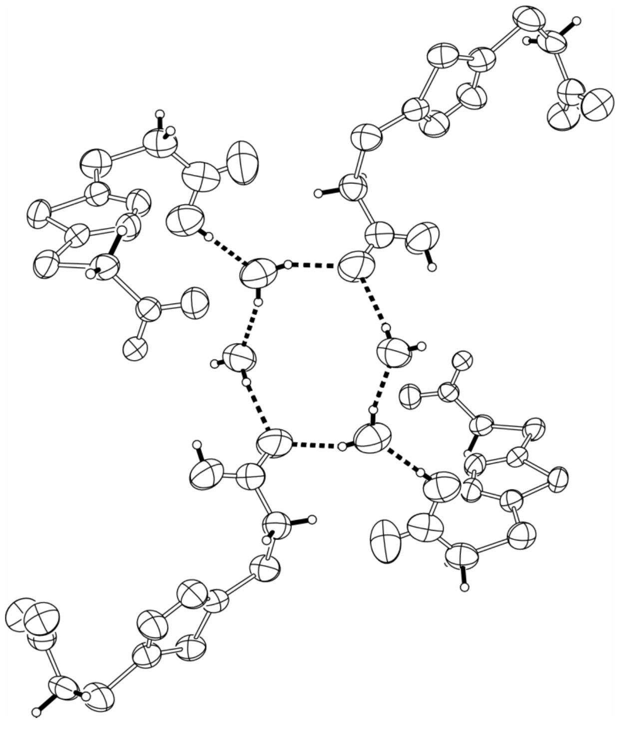


**Figure 2**
Hydrogen-bonding interactions (dashed lines) involving the coordinated and uncoordinated tdzdtaH$^-$ anions with the water molecules.

The structure is disordered in the acetato $-CH_2CO_2$ arm of the uncoordinated tdzdtaH$^-$ anion. This arm has two possible positions, O5/O6/C27/C28 and O5$'$/O6$'$/C27$'$/C28$'$, the site occupation factors being 0.735 (6) and 0.265 (6), respectively. Restraints were applied for the C—C, C—S and C—O distances, and the atomic displacement parameters of the minor component were set equal to those of the corresponding atom of the major component. The carbon-bound H atoms were placed at calculated positions [C—H = 0.93–0.97 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C)] and were included in the refinement in the riding-model approximation. The water H atoms were located and were refined with distance restraints of O—H = 0.85 (1) Å and H···H = 1.39 (1) Å. The carboxylic acid O—H groups were rotated to fit the electron density [O—H = 0.85 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(O)].

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

We thank the National Natural Science Foundation of China (No. 20101003), the Scientific Fund for Remarkable

*Acta Cryst.* (2005). E**61**, m126–m128 Gao *et al.* • $[Cu(C_6H_5N_2O_4S_3)(C_{10}H_8N_2)_2](C_6H_5N_2O_4S_3)\cdot 2H_2O$ **m127**

Teachers of Heilongjiang Province (No. 1054 G036) and the University of Malaya for supporting this study.

## References

Gao, S., Su, H., Huo, L.-H. & Ng, S. W. (2004). *Acta Cryst.* E. Submitted.

Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, USA.

Liu, J.-W., Huo, L.-H., Gao, S., Zhao, H., Zhu, Z.-B. & Zhao, J.-G. (2004). *Chin. J. Inorg. Chem.* **20**, 707–710.

Rigaku (1998). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.

Rigaku/MSC (2002). *CrystalStructure*. Rigaku/MSC Inc., The Woodlands, Texas, USA.

Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.

Zhao, J.-G., Gao, S., Huo, L.-H. & Ng, S. W. (2005). *Acta Cryst.* E**61**, m115–m116.

**m128** Gao *et al.* • $[Cu(C_6H_5N_2O_4S_3)(C_{10}H_8N_2)_2](C_6H_5N_2O_4S_3)\cdot 2H_2O$ *Acta Cryst.* (2005). E**61**, m126–m128