Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

(2,2′-Diamino-4,4′-bi-1,3-thiazole-$\kappa^2N^3,N^{3'}$)(oxydiacetato-κ^3O,O',O'')copper(II) monohydrate

Zhi-Yong Wu,[a] Duan-Jun Xu,[a]* Yue Luo,[a] Jing-Yun Wu[b] and Michael Y. Chiang[b]

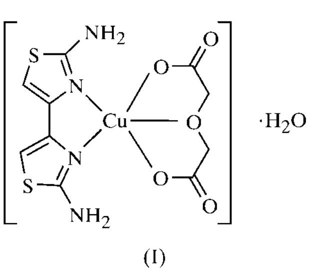
[a]Department of Chemistry, Zhejiang University, Hangzhou, Zhejiang, People's Republic of China, and [b]Department of Chemistry, National Sun Yat-Sen University, Kaohsiung, Taiwan
Correspondence e-mail: xudj@mail.hz.zj.cn

Received 13 May 2003
Accepted 17 June 2003
Online 12 July 2003

The title compound, $[Cu(C_4H_4O_5)(C_6H_6N_4S_2)]\cdot H_2O$, displays a square-pyramidal coordination geometry. The tridentate oxydiacetate dianion chelates the Cu^{II} atom in the facial mode. The large difference [0.487 (4) Å] between the longest Cu—O distance in the basal plane and that in the apical direction correlates with the small displacement of the Cu^{II} atom [0.0576 (13) Å] from the basal plane towards the apex of the square pyramid. The intermolecular hydrogen-bonding network results in a closely overlapped arrangement of the coordination basal plane and the thiazole ring of a neighboring molecule.

Comment

Transition metal complexes with 2,2′-diamino-4,4′-bithiazole (DABT) or its derivatives have shown interesting properties and have potential applications in many fields (Waring, 1981; Fisher *et al.*, 1985). A series of metal complexes with DABT has been prepared in our laboratory (Liu *et al.*, 2001). As part of this investigation, the Cu^{II} complex, (I), with DABT and oxydiacetate (ODA) has recently been prepared and its X-ray structure is presented here.



(I)

The molecular structure of (I) is illustrated in Fig. 1. Two N atoms of the DABT molecule and two O atoms from the carboxyl groups of the ODA ligand form the basal coordination plane, with the maximum deviation being 0.0017 (12) Å for atom N3, while atom O5 of the ODA ligand occupies the apical position, thus completing the square-pyramidal coordination geometry around the Cu^{II} atom. The Cu—O distance of 2.442 (3) Å in the apical direction is longer than those in the basal plane by 0.512 (4) and 0.487 (4) Å (Table 1). These large differences correlate with the small displacement of the Cu^{II} atom [0.0576 (13) Å] from the basal plane towards the apex. This configuration is similar to that found in Cu^{II} complexes with a square-pyramidal geometry. For example, the large difference of 0.478 (6) Å in Cu—O distances correlated with the smaller Cu^{II} displacement of 0.0919 (9) Å in an acetato(aqua)copper(II) complex (Christou *et al.*, 1990), whereas the smaller difference of 0.314 (7) Å correlated with the larger Cu^{II} displacement of 0.1963 (8) Å in an aqua(isonicotinato)copper(II) complex (Xu *et al.*, 1998).

The tridentate ODA ligand chelates to the Cu^{II} atom in the facial coordination mode, with an O atom from each of the carboxyl groups of the ODA ligand coordinating to the Cu^{II} atom in a *cis* configuration. A search of the Cambridge Structural Database (Allen, 2002) indicated that the facial mode is a rare configuration for ODA in transition metal complexes, and only one Cu^{II} complex, namely aqua(2,2′-bipyridyl)(oxydiacetato)copper(II), (II), has previously been found to exhibit the facial mode (Bonomo *et al.*, 1981). The Cu—O5 bond distance of 2.442 (3) Å in (I) is almost identical to the equivalent bond length of 2.458 (4) Å found in (II). The Cu—O5—C12 [102.47 (19)°] and Cu—O5—C14 angles [100.32 (19)°] in (I) are much smaller than those found in transition metal complexes with ODA in a typical meridional mode (120°; Bresciani-Pahor *et al.*, 1983; Hatfield *et al.*, 1987; Powell *et al.*, 1992).

Water atom O6 forms a hydrogen bond with the uncoordinated carboxyl atom O2 but does not coordinate to the Cu^{II} atom as a sixth donor (Fig. 1). In the expected sixth coordination site, there is a thiazole ring from the adjacent complex molecule (see Fig. 2). This thiazole ring is nearly parallel to the coordination basal plane of the Cu atom [dihedral angle = 7.39 (10)°] and the perpendicular out-of-plane distance for the Cu atom is 3.474 (6) Å. A similar observation was made for the tyrosinate–copper(II) complex and was

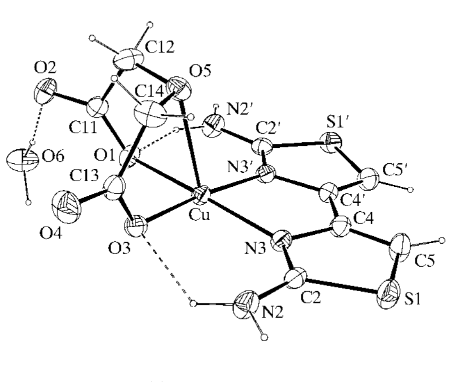


Figure 1
The molecular structure of (I), with displacement ellipsoids shown at the 50% probability level. Dashed lines indicate intramolecular hydrogen bonding.

DOI: 10.1107/S0108270103013581

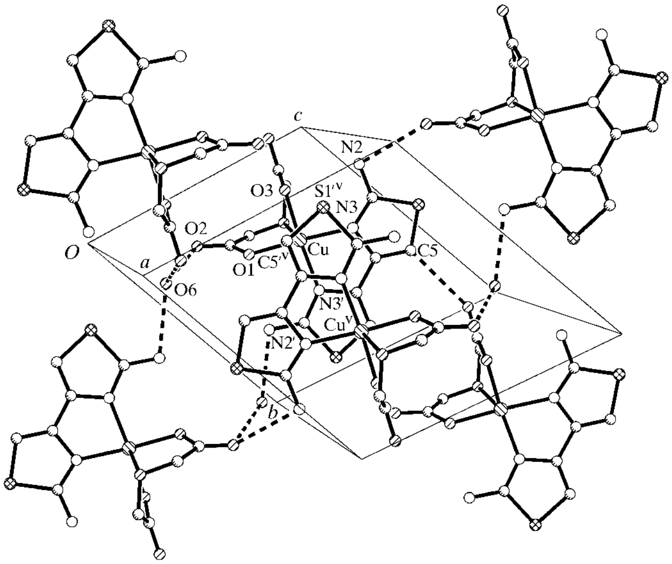


Figure 2
A view of the hydrogen-bonding network, showing the thiazole ring located beneath the basal plane of the Cu atom. [Symmetry code: (v) $1 - x, 1 - y, 1 - z$.]

interpreted as a weak interaction between the π-electron system of the aromatic ring and the neighboring Cu^{II} atom (Van der Helm & Tatsch, 1972). However, in (I), the shortest separation [3.383 (4) Å for Cu$\cdots$C5'^{v}; symmetry code: (v) $1 - x, 1 - y, 1 - z$] between the Cu atom and the thiazole ring is slightly larger than the sum of the van der Waals radii of the Cu and C atoms (Rodgers, 1994). Therefore, it can be assumed that a normal van der Waals contact occurs between the Cu atom and the neighboring thiazole ring.

The DABT molecule chelates the Cu^{II} atom in a *cis* configuration. The angle between the planes of the thiazole rings is 6.52 (9)°, while an angle of 8.44 (8)° is found in a DABT complex of Cd^{II} (Liu *et al.*, 2003) and an angle of 7.91 (9)° is found in a DABT complex of Ni^{II} (Baker & Goodwin, 1985).

An intermolecular hydrogen-bonding network occurs in the crystal structure (Fig. 2 and Table 2). Lattice water molecules bridge complex molecules *via* hydrogen bonds, and the complex molecules are also linked directly to one another *via* hydrogen bonds between the carboxyl and amine groups of adjacent molecules. Weak C—H$\cdots$O hydrogen bonding occurs between a carboxyl group and the thiazole ring. This extensive hydrogen bonding results in a closely overlapped arrangement of the coordination basal plane and the thiazole ring of a neighboring molecule.

Experimental

An aqueous solution (20 ml) containing $CuCl_2 \cdot 2H_2O$ (0.086 g, 0.5 mmol), oxydiacetic acid hydrate (0.076 g, 0.5 mmol) and NaOH (0.04 g, 1 mmol) was refluxed for 5 h. Heating of the reaction mixture was stopped and DABT (0.10 g, 0.5 mmol) was added to the solution. The DABT dissolved quickly in the hot solution and the product precipitated shortly afterwards. The hot solution was filtered immediately and the filtrate was cooled to room temperature and filtered again. The final filtrate was kept at room temperature and green crystals of suitable size were obtained after 5 d.

Crystal data

$[Cu(C_4H_4O_5)(C_6H_6N_4S_2)] \cdot H_2O$
$M_r = 411.93$
Triclinic, $P\overline{1}$
$a = 9.688$ (4) Å
$b = 9.720$ (4) Å
$c = 9.831$ (4) Å
$\alpha = 68.64$ (3)°
$\beta = 62.33$ (3)°
$\gamma = 71.74$ (3)°
$V = 751.8$ (6) Å^3

$Z = 2$
$D_x = 1.820$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 5.1$–12.8°
$\mu = 1.77$ mm^{-1}
$T = 298$ (2) K
Prism, green
0.20 × 0.18 × 0.16 mm

Data collection

Rigaku AFC-7*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.702$, $T_{max} = 0.761$
3116 measured reflections
2932 independent reflections
2166 reflections with $I > 2\sigma(I)$

$R_{int} = 0.014$
$\theta_{max} = 26.0°$
$h = -11 \rightarrow 11$
$k = -11 \rightarrow 0$
$l = -12 \rightarrow 11$
3 standard reflections every 150 reflections intensity decay: 0.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.093$
$S = 1.03$
2932 reflections
208 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0397P)^2 + 0.1631P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.55$ e Å^{-3}
$\Delta\rho_{min} = -0.43$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu—O3	1.930 (2)	Cu—N3′	1.990 (3)
Cu—O1	1.955 (2)	Cu—N3	2.005 (3)
Cu—O5	2.442 (3)		
O3—Cu—O1	89.27 (10)	O5—Cu—O3	77.19 (9)
O3—Cu—N3′	174.53 (10)	O5—Cu—N3	106.27 (10)
O1—Cu—N3′	94.86 (11)	O5—Cu—N3′	107.18 (10)
O3—Cu—N3	93.14 (11)	Cu—O5—C12	102.47 (19)
O1—Cu—N3	175.90 (10)	Cu—O5—C14	100.32 (19)
N3′—Cu—N3	82.53 (11)	C12—O5—C14	113.6 (3)
O5—Cu—O1	77.50 (9)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2$A\cdots$O3	0.98	2.16	2.894 (4)	130
N2—H2$B\cdots$O2^{i}	0.92	2.09	2.935 (4)	153
N2′—H2$C\cdots$O1	0.94	2.06	2.891 (4)	147
N2′—H2$D\cdots$O6^{ii}	0.99	1.83	2.781 (4)	159
O6—H6$A\cdots$O4^{iii}	0.97	1.87	2.796 (5)	159
O6—H6$B\cdots$O2	0.97	1.86	2.824 (4)	170
C5—H5$\cdots$O4^{iv}	0.93	2.16	3.088 (5)	179

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

H atoms attached to C atoms were placed in calculated positions, with C—H distances of 0.93 or 0.97 Å, and were included in the final cycles of refinement as riding, with U_{iso}(H) values equal to $1.2U_{eq}$ of the carrier atoms. Other H atoms were located in a difference Fourier map and were included in the structure-factor calculations with fixed positional and isotropic displacement parameters [$U_{\rm iso}$(H) = 0.06 Å^2].

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1992); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997) and *XP* (Siemens, 1994); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

This project was supported by the National Natural Science Foundation of China (grant Nos. 29973036 and 20240430654).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1428). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.

Baker, A. T. & Goodwin, H. A. (1985). *Aust. J. Chem.* **38**, 851–856.

Bonomo, R. P., Rizzarelli, E., Bresciani-Pahor, N. & Nardin, G. (1981). *Inorg. Chim. Acta*, **54**, L17–19.

Bresciani-Pahor, N., Nardin, G., Bonomo, R. P. & Rizzarelli, E. (1983). *J. Chem. Soc. Dalton Trans.* pp. 1797–1799.

Christou, G., Perlepes, S. P., Libby, E., Folting, K., Huffman, J. C., Webb, R. J. & Hendrickson, D. N. (1990). *Inorg. Chem.* **29**, 3657–3666.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Fisher, L. M., Kurod, R. & Sakai, T. (1985). *Biochemistry*, **24**, 3199–3207.

Hatfield, W. E., Helms, J. H., Rohrs, B. R., Singh, P., Wasson, J. R. & Weller, R. R. (1987). *Proc. Indian Acad. Sci. Chem. Sci.* **98**, 23–31.

Liu, J.-G., Nie, J.-J., Xu, D.-J., Xu, Y.-Z., Wu, J.-Y. & Chiang, M. Y. (2001). *Acta Cryst.* C**57**, 354–355.

Liu, J.-G., Xu, D.-J., Sun, W.-L., Wu, Z.-Y., Xu, Y.-Z., Wu, J.-Y. & Chiang, M. Y. (2003). *J. Coord. Chem.* **56**, 71–76.

Molecular Structure Corporation (1992). *MSC/AFC Diffractometer Control Software* and *TEXSAN* (Version 1.6). MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Powell, A. K., Charnock, J. M., Flood, A. C., Garner, C. D., Ware, M. J. & Clegg, W. J. (1992). *J. Chem. Soc. Dalton Trans.* pp. 203–207.

Rodgers, G. E. (1994). In *Introduction to Coordination, Solid State, and Descriptive Inorganic Chemistry*. Singapore: McGraw–Hill.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Siemens (1994). *XP*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Van der Helm, D. & Tatsch, C. E. (1972). *Acta Cryst.* B**28**, 2307–2312.

Waring, M. J. (1981). *Ann. Rev. Biochem.* **50**, 159–192.

Xu, D.-J., Xie, A.-L., Xu, Y.-Z., Nishikawa, K. & Yasuoka, N. (1998). *J. Coord. Chem.* **43**, 237–242.