Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Aqua(2,2′-diamino-4,4′-bi-1,3-thiazole-κ^2N,N')(oxydiacetato-κ^3O,O',O'')cobalt(II) trihydrate

Zhi-Yong Wu,* Wei Sun and Yan-Tuan Li

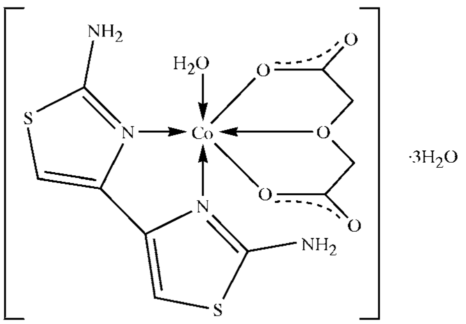
Marine Drug and Food Institute, Ocean University of China, 266003 Qingdao, People's Republic of China
Correspondence e-mail: zd_wzy@hotmail.com

Received 2 March 2007
Accepted 12 March 2007
Online 31 March 2007

The title compound, $[Co(C_4H_4O_5)(C_6H_6N_4S_2)(H_2O)]\cdot3H_2O$, displays a distorted octahedral coordination geometry. The tridentate oxydiacetate dianion chelates the Cu^{II} atom in the meridional mode. In the crystal packing, hydrophilic and hydrophobic layers are arranged in an alternating manner. In addition, a three-dimensional hydrogen-bonding framework and π–π stacking are present.

Comment

The oxydiacetate anion [oda, $O(CH_2COO)_2^{2-}$] has been widely explored as a multidentate bridging and chelating unit toward several metals (Wilkinson *et al.*, 1987). The oda ligand may exist as an anionic noncoordinated species or bind in a mono-, bi-, tri- and multidentate fashion. The more usual chelating mode is tridentate, where oda is planar or puckered (Di Nicola *et al.*, 2005). Aromatic π–π stacking interactions are important for many biological systems (Deisenhofer & Michel, 1989). Metal complexes with 2,2′-diamino-4,4′-bithiazole (dabt) and its derivatives show potential application in inhibitors of DNA (Waring, 1981; Fisher *et al.*, 1985). As part of an ongoing study of transition metal complexes involving oda as a ligand (Wu, Xu *et al.*, 2003), the preparation and crystal structure of the title Co^{II} complex, (I), with dabt and oda is presented here.



(I)

The molecular structure of (I) is illustrated in Fig. 1. The central Co^{II} atom has a distorted $\{CoN_2O_4\}$ octahedral coordination geometry (some parameters are listed in Table 1). The tridentate oda ligand coordinates to the Co^{II} atom in a meridional configuration with two five-membered chelate rings formed by the ether atom O3 and two carboxyethyl groups. The ring containing atoms O1 and O3 is planar, with a maximum displacement from the plane of 0.0184 (12) Å for atom O1. In contrast, the other ring, containing atoms O3 and O4, has an envelope conformation puckered on atom O3; the puckering parameters are $Q = 1.032\ (15)$ Å and $\varphi = 78.6\ (3)^\circ$ (Cremer & Pople, 1975).

Hitherto, 14 six-coordinate transition metal complexes of oda, a coordinated water molecule and an aromatic di-*N*-heterocyclic chelating ligand (L), $[M(oda)L(H_2O)]\cdot nH_2O$, have been structurally investigated by X-ray diffraction (Table 3). It can be inferred that the space groups of these crystalline compounds are correlated with the number of solvent water molecules, which implies that the crystal structures of such complexes are controlled by the solvent water molecules. Actually, the title complex is isostructural with complexes (II) and (III) (Table 3).

As shown in Fig. 2, two complex molecules are linked to each other by $O6-H6D\cdots O2^{i}$ hydrogen bonds to form a centrosymmetric dimer [Table 2; symmetry code: (i) $-x, -y, -z$]. The dimers interact *via* $O6-H6C\cdots O2^{ii}$ and $N4-H4B\cdots O5^{iii}$ hydrogen bonds and extend to form a layer of dimers parallel to the (001) plane [symmetry codes: (ii) $x+1, y, z$; (iii) $x, y-1, z$]. Both surfaces of these layers are covered by the hydrophobic dabt ligands, while the hydrophilic ligands, the coordinated water molecule and oda, and the solvent water molecules lie internally. These two-dimensional sheets stack to form a three-dimensional hydrophilic and hydrophobic layered structure, which is also observed in the

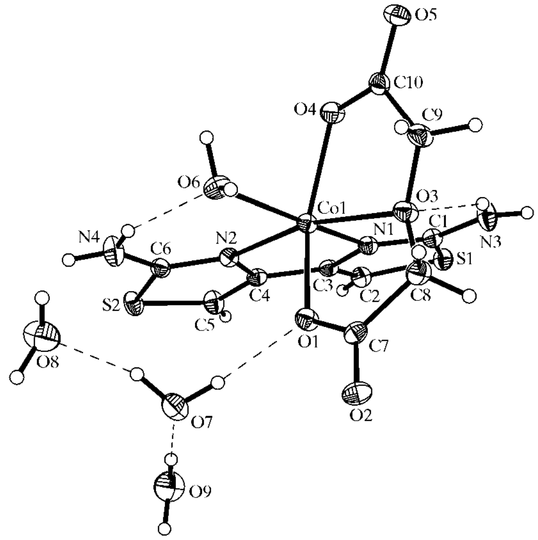


Figure 1
A view of (I). Displacement ellipsoids are drawn at the 30% probability level. Dashed lines indicate hydrogen bonding.

DOI: 10.1107/S0108270107011468

complexes in Table 3, except for (VII)–(IX). In the interface of two layers, nonclassical C—H···O hydrogen bonding and π–π stacking interactions are involved (Fig. 3). The thiazole rings are approximately parallel and partially overlap. The separation between the plane of the S1-thiazole ring and atom N1 in the S1-thiazole ring at ($-x$, $-y$, $1 - z$) is 3.384 (3) Å, while atom N2 in the S2-thiazole ring at ($1 - x$, $-y$, $1 - z$) on the opposite side of the S1-thiazole ring plane is 3.312 (3) Å away. Consequently, a three-dimensional supramolecular structure is completed.

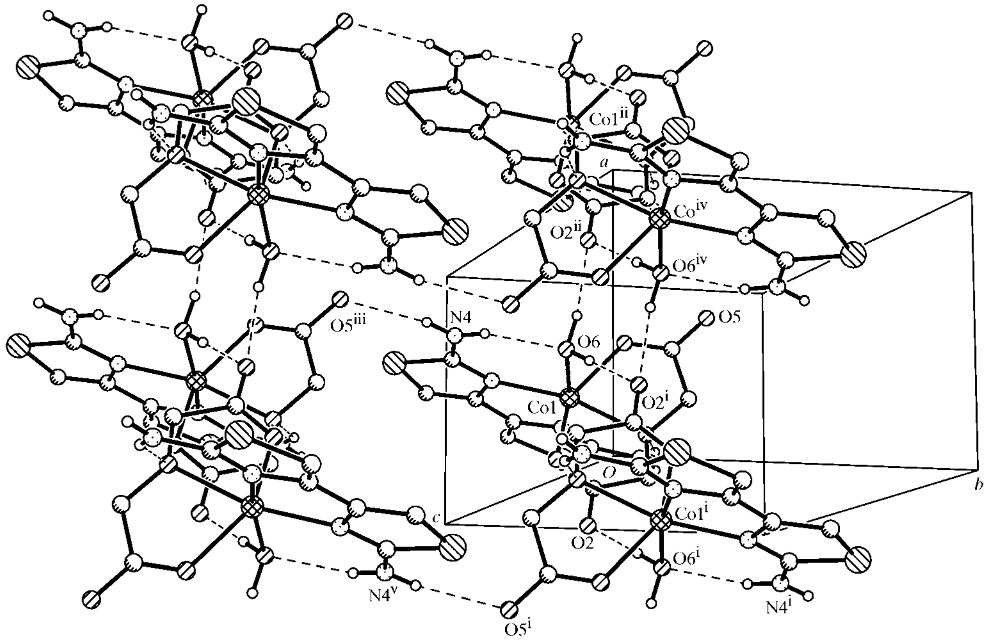


Figure 2

A hydrogen-bonded sheet formed by complex molecules. H atoms on C atoms have been omitted for clarity. [Symmetry codes: (i) $-x$, $-y$, $-z$; (ii) $x + 1$, y, z; (iii) x, $y - 1$, z; (iv) $-x + 1$, $-y$, $-z$; (v) $-x$, $-y - 1$, $-z$.]

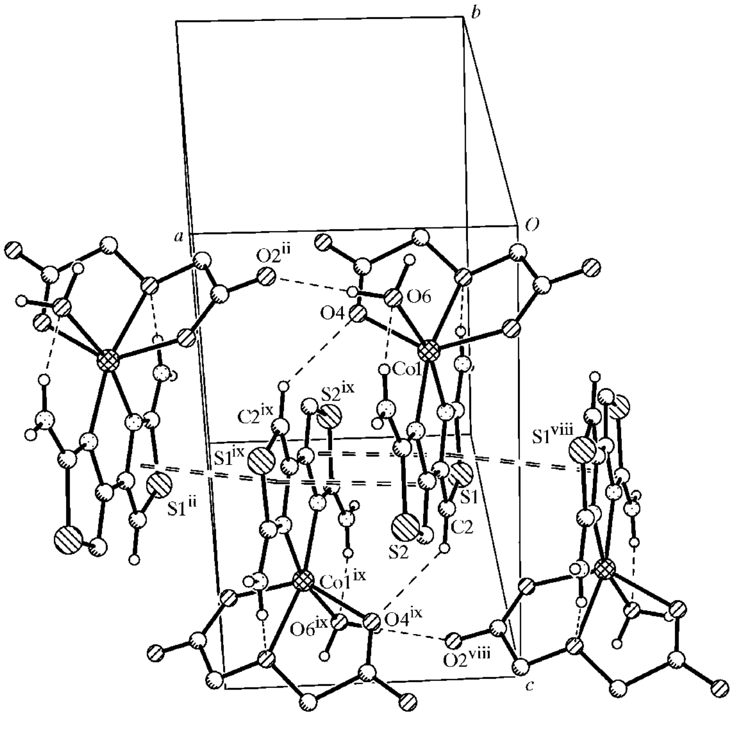


Figure 3

The molecular packing, showing the hydrophilic and hydrophobic layered structure. Solvent water molecules have been omitted for clarity. Double dashed lines indicate π–π stacking. [Symmetry codes: (ii) $x + 1$, y, z; (viii) $-x$, $-y$, $-z + 1$; (ix) $-x + 1$, $-y$, $-z + 1$.]

m178 Wu *et al.* • $[Co(C_4H_4O_5)(C_6H_6N_4S_2)(H_2O)]\cdot 3H_2O$ *Acta Cryst.* (2007). **C63**, m177–m180

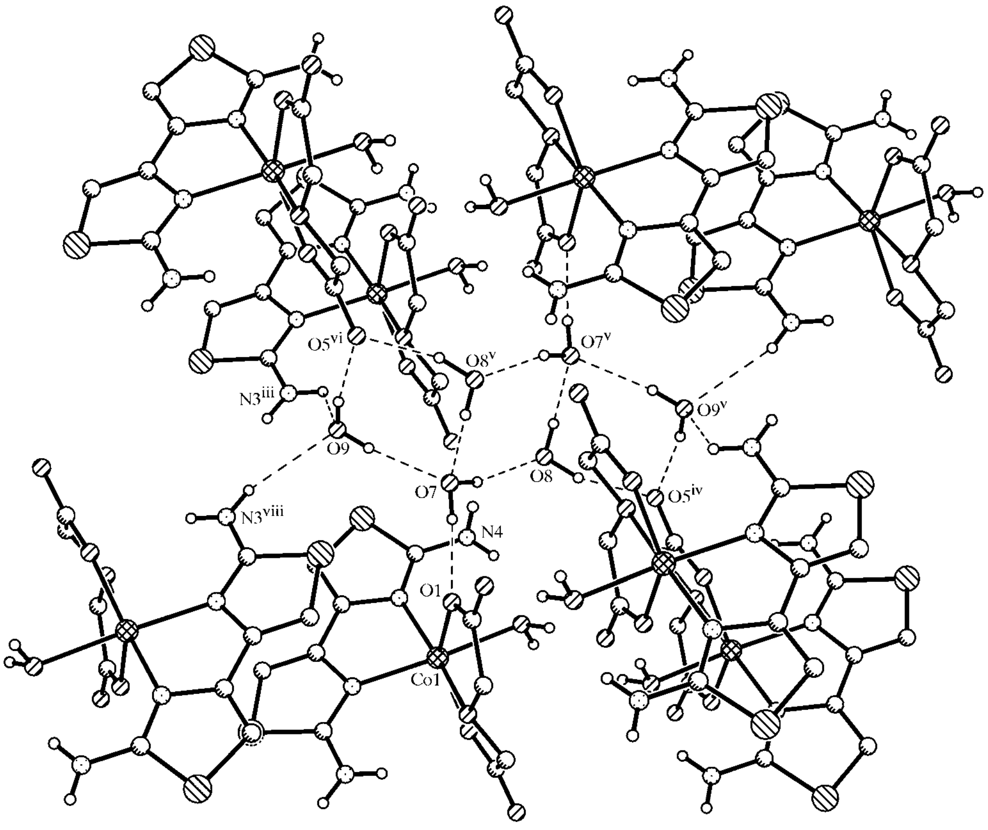


Figure 4
The hydrogen-bonding interactions involving solvent water molecules. [Symmetry codes: (iii) $x, y - 1, z$; (iv) $-x + 1, -y, -z$; (v) $-x, -y - 1, -z$; (vi) $x - 1, y - 1, z$; (viii) $-x, -y, -z + 1$.]

In the structure, the solvent water molecules fill the hydrophilic layers. Six solvent water molecules hydrogen bond with one another to form a hexamer, and then hydrogen bond to eight neighboring complex molecules (Table 2 and Fig. 4). These interactions not only assist in the hydrogen-bonding structure of the hydrophilic layers, but also strengthen the stack of the two-dimensional sheets *via* the $N3^{viii}-H3B^{viii}\cdots O9$ interaction [symmetry code: (viii) $-x, -y, -z + 1$].

Experimental

To an aqueous solution (10 ml) of H_2oda (30 mg, 0.2 mmol) and ethylenediamine (27 µl, 0.4 mmol) were added $CoCl_2\cdot 6H_2O$ (48 mg, 0.2 mmol) and dabt (40 mg, 0.2 mmol) in turn. After refluxing for 2 h, the red solution was cooled to room temperature and filtered. The filtrate was kept at room temperature and red crystals of suitable size were obtained after 5 d.

Crystal data

$[Co(C_4H_4O_5)(C_6H_6N_4S_2)(H_2O)]\cdot 3H_2O$
$M_r = 461.33$
Triclinic, $P\overline{1}$
$a = 7.2265$ (14) Å
$b = 9.6980$ (19) Å
$c = 12.319$ (3) Å
$\alpha = 96.69$ (3)°
$\beta = 93.34$ (3)°
$\gamma = 90.29$ (3)°
$V = 855.9$ (3) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 1.30$ mm^{-1}
$T = 298$ (2) K
0.22 × 0.19 × 0.18 mm

Data collection

Bruker APEX area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.763$, $T_{max} = 0.800$
4583 measured reflections
3047 independent reflections
2570 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.078$
$S = 1.01$
3047 reflections
235 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.51$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—N1	2.111 (2)	Co1—O6	2.2304 (18)
Co1—N2	2.0998 (19)	C7—O1	1.264 (3)
Co1—O1	2.0934 (18)	C7—O2	1.247 (3)
Co1—O3	2.2149 (17)	C10—O4	1.261 (3)
Co1—O4	2.0820 (18)	C10—O5	1.249 (3)
N1—Co1—N2	80.19 (7)	O1—Co1—O3	73.82 (7)
N1—Co1—O1	107.35 (7)	O1—Co1—O4	141.33 (7)
N2—Co1—O3	166.67 (7)	O3—Co1—O4	73.75 (6)
O1—C7—C8—O3	0.4 (3)	O3—C9—C10—O4	14.4 (3)

The H atoms of the water molecules were located in a difference Fourier map, while the other H atoms were placed in calculated

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O6—H6*D*···O2^{i}	0.91	1.83	2.741 (3)	178
O6—H6*C*···O2^{ii}	0.91	1.93	2.822 (2)	165
N3—H3*A*···O3	0.86	2.37	3.124 (3)	146
N4—H4*B*···O5^{iii}	0.86	2.25	3.053 (3)	155
N4—H4*A*···O6	0.86	2.10	2.872 (3)	149
O7—H7*C*···O1	0.91	1.95	2.848 (3)	171
O7—H7*D*···O8	0.92	1.97	2.846 (3)	158
O8—H8*C*···O5^{iv}	0.95	1.96	2.867 (3)	160
O8—H8*D*···O7^{v}	0.88	1.90	2.772 (3)	171
O9—H9*C*···O5^{vi}	0.85	2.13	2.968 (3)	170
O9—H9*D*···O7	0.85	2.10	2.939 (3)	169
N3—H3*A*···O9^{vii}	0.86	2.50	2.918 (3)	111
N3—H3*B*···O9^{viii}	0.86	2.51	3.292 (3)	152
C2—H2···O4^{ix}	0.93	2.43	3.194 (3)	139

Symmetry codes: (i) $-x, -y, -z$; (ii) $x+1, y, z$; (iii) $x, y-1, z$; (iv) $-x+1, -y, -z$; (v) $-x, -y-1, -z$; (vi) $x-1, y-1, z$; (vii) $x, y+1, z$; (viii) $-x, -y, -z+1$; (ix) $-x+1, -y, -z+1$.

Table 3
Reported six-coordinated [M(oda)L(H$_2$O)]·nH$_2$O complexes (M is a transition metal and L is an aromatic di-*N*-heterocyclic chelating ligand).

Complex	Metal ions	CSD refcode (Allen, 2002)	*L*	*n*	Space group
(I)^{a}	Co	–	dabt	3	$P\overline{1}$
(II)^{b}	Mn	ACAGUH	dabt	3	$P\overline{1}$
(III)^{c}	Cd	MAHPAN	dabt	3	$P\overline{1}$
(IV)^{d}	Ni	MUHLEG	bipy	2.5	*Fdd*2
(V)^{d}	Co	MUHLIK	bipy	2.5	*Fdd*2
(VI)^{e}	Zn	TISBOM	bipy	2.5	*Fdd*2
(VII)^{f}	Ni	SALJOF	dabt	2	$P2_1/n$
(VIII)^{g}	Co	IWOYAU	dabt	2	$P2_1/n$
(IX)^{h}	Zn	OJETEC	dabt	2	$P2_1/n$
(X)^{i}	Mn	ESUNAH	bipy	2	$P2_1/n$
(XI)^{j}	Co	EKETAP	phen	1.5	$P2_1/c$
(XII)^{e}	Zn	TISBUS	phen	1.5	$P2_1/c$
(XIII)^{k}	Ni	QAVBUK	phen	1.5	$P2_1/c$
(XIV)^{l}	Co	ETEQUP	dabt	1	$C2/c$

Notes: (*a*) this work; (*b*) Luo, Xu, Wu & Chiang (2004); (*c*) Liu *et al.* (2004); (*d*) Grirrane *et al.* (2002) (bipy is 2,2′-bipyridine); (*e*) Baggio *et al.* (1996); (*f*) Luo, Xu & Yin (2004); (*g*) Shen *et al.* (2004); (*h*) Li *et al.* (2003); (*i*) Grirrane *et al.* (2004); (*j*) Wu, Xue & Xu (2003) (phen is phenanthroline); (*k*) Baggio *et al.* (2000); (*l*) Luo, Xu, Wu, Wu & Chiang (2004).

positions [N—H = 0.86 Å and C—H = 0.97 (methylene) or 0.93 Å (aromatic)]. All H atoms were included in the final cycles of refinement as riding, with U_{iso}(H) values of 1.2U_{eq}(C,N) or with a fixed isotropic displacement parameter of 0.08 Å^2 for the water molecules.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *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 (No. 30672515).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3044). Services for accessing these data are described at the back of the journal.

References

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

Baggio, R., Garland, M. T. & Perec, M. (1996). *J. Chem. Soc. Dalton Trans.* pp. 2747–2753.

Baggio, R., Garland, M. T. & Perec, M. (2000). *Inorg. Chim. Acta*, **310**, 103–109.

Bruker (2002). *SAINT* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Deisenhofer, J. & Michel, H. (1989). *EMBO J.* **8**, 2149–2170.

Di Nicola, C., Galindo, A., Hanna, J. V., Marchetti, F., Pettinari, C., Pettinari, R., Rivarola, E., Skelton, B. W. & White, A. H. (2005). *Inorg. Chem.* **44**, 3094–3102.

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

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

Grirrane, A., Pastor, A., Alvarez, E., Mealli, C., Lenco, A., Rosa, P., Montilla, F. & Galindo, A. (2004). *Eur. J. Inorg. Chem.* pp. 707–717.

Grirrane, A., Pastor, A., Lenco, A., Mealli, C. & Galindo, A. (2002). *J. Chem. Soc. Dalton Trans.* pp. 3771–3777.

Li, H., Luo, Y., Xu, D.-J., Wu, J.-Y. & Chiang, M. Y. (2003). *Acta Cryst.* E**59**, m622–m624.

Liu, B.-X., Tian, Y.-G. & Xu, D.-J. (2004). *Acta Cryst.* E**60**, m1453–m1455.

Luo, Y., Xu, D.-J., Wu, J.-Y. & Chiang, M. Y. (2004). *J. Coord. Chem.* **57**, 1125–1130.

Luo, Y., Xu, D.-J., Wu, Z.-Y., Wu, J.-Y. & Chiang, M. Y. (2004). *Acta Cryst.* E**60**, m270–m272.

Luo, Y., Xu, D.-J. & Yin, K.-L. (2004). *Chin. J. Struct. Chem.* **23**, 1095–1098.

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

Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.

Shen, Y.-H., Liu, J.-G. & Xu, D.-J. (2004). *Acta Cryst.* E**60**, m842–m844.

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

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

Wilkinson, G., Gillard, R. D. & McCleverty, J. A. (1987). *Comprehensive Coordination Chemistry*, Vol. 2, pp. 435–442. London: Pergamon.

Wu, Z.-Y., Xu, D.-J., Luo, Y., Wu, J.-Y. & Chiang, M. Y. (2003). *Acta Cryst.* C**59**, m307–m309.

Wu, Z.-Y., Xue, Y.-H. & Xu, D.-J. (2003). *Acta Cryst.* E**59**, m809–m811.