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Aqua(2,2′-diamino-4,4′-bi-1,3-thiazole)(oxydiacetato-κ^3*O*,*O*′,*O*″)cadmium(II) trihydrate

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In the title compound, $[Cd(C_4H_4O_5)(C_6H_6N_4S_2)(H_2O)]\cdot 3H_2O$, the Cd^{II} cation assumes a distorted octahedral CdO_4N_2 coordination formed by a tridentate oxydiacetate (ODA) dianion, a bidentate diaminobithizole (DABT) molecule and a water molecule. ODA chelates to the Cd atom in a meridional configuration, while the two rings of DABT are coplanar. Interplanar distances of 3.438 (4) and 3.382 (10) Å suggest the presence of π–π stacking interactions between adjacent thiazole rings.

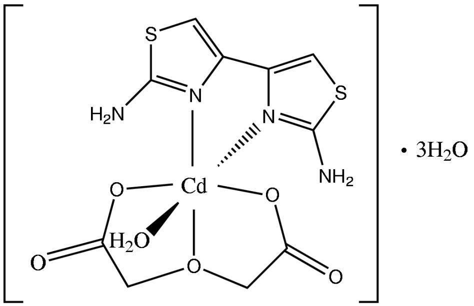
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.005 Å
R factor = 0.031
wR factor = 0.071
Data-to-parameter ratio = 13.4

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

Comment

Transition metal complexes incorporating diaminobithiazole (DABT) molecules have shown potential application in various fields. For example, Co^{II} and Ni^{II} complexes of DABT have been found to be effective inhibitors of DNA synthesis in tumour cells (Waring, 1981; Fisher *et al.*, 1985) and multinuclear Fe^{II} and Cu^{II} complexes with DABT and Schiff bases have proven to be excellent soft magnetic materials (Sun *et al.*, 1997). A series of metal complexes with DABT has been prepared in our laboratory (Liu & Xu, 2004). A striking feature of their X-ray crystal structures is the differing degree of coplanarity for the two aromatic rings in DABT.



(I)

As part of our ongoing investigations into these systems, the title cadmium complex, (I) (Fig. 1), incorporating both DABT and the oxydiacetate (ODA) dianion, has been prepared. The complex has a distorted octahedral coordination geometry about cadmium, formed by the ODA and DABT ligands and water molecules. The O1—Cd—O4 bond angle of 135.57 (8)° is much smaller than the corresponding angles of 149.84 (6) (Cao *et al.*, 2004) and 149.13 (19)° (Li *et al.*, 2003) in ODA complexes of Zn^{II}; this may result from the longer Cd—O(carboxyl) bond distances (Table 1).

The tridentate ODA chelates to the Cd atom in meridional configuration. The chelate ring formed by atoms O3, O4, C13, C14 and Cd is almost planar, with a maximum atomic devia-

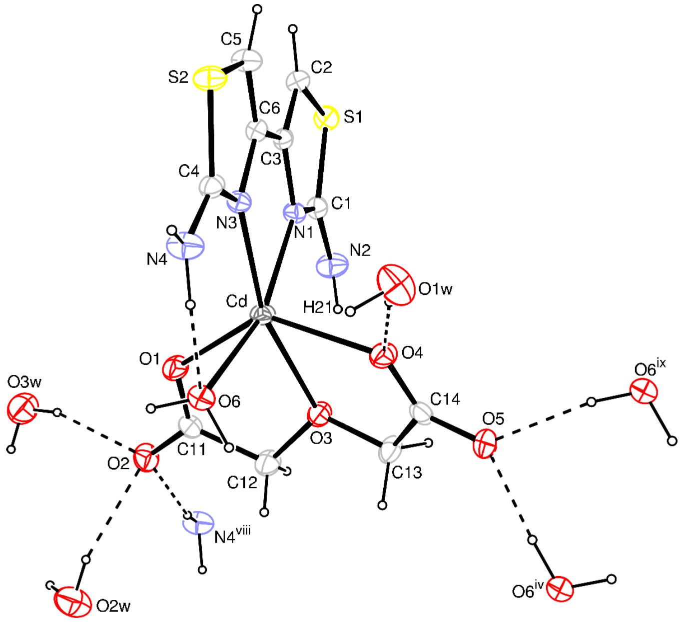


Figure 1
The molecular structure of (I), shown with 30% probability displacement ellipsoids. Dashed lines indicate hydrogen bonds. [Symmetry codes: (iv) $-x, 1-y, 1-z$; (viii) $x, y+1, z$; (ix) $x-1, y, z$.]

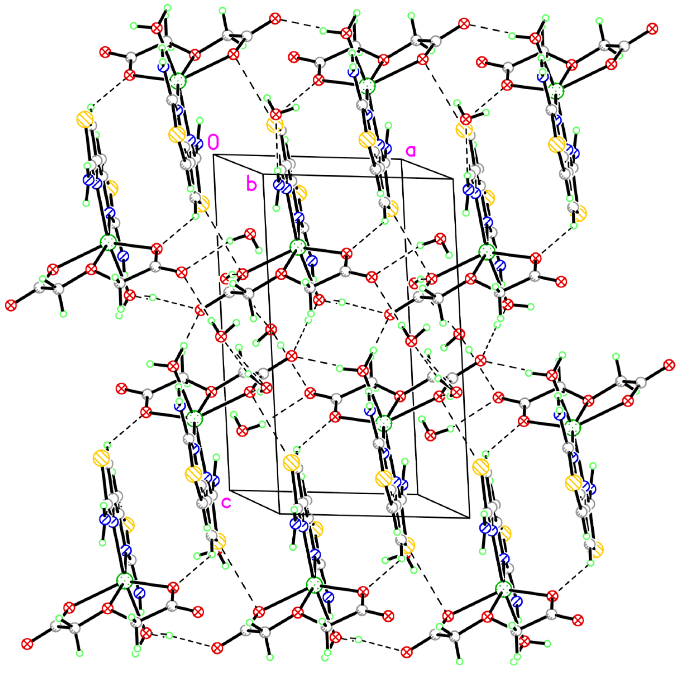


Figure 2
Packing diagram for (I), with the intermolecular hydrogen bonding shown as dashed lines.

tion of 0.0373 (17) Å for O4, whereas the other chelate ring (atoms O3, O1, C11, C12 and Cd) displays an envelope conformation with atom O3 in the flap position, 0.302 (5) Å out of the mean plane formed by the other four atoms. The carboxyl groups of ODA coordinate to the Cd atom in a monodentate mode. The uncoordinated carboxyl O atoms (O2 and O5) act as acceptors for hydrogen bonds from uncoordinated water molecules or the amine groups of neighbouring molecules (Fig. 1), resulting in the extended hydrogen-bonded structure shown in Fig. 2.

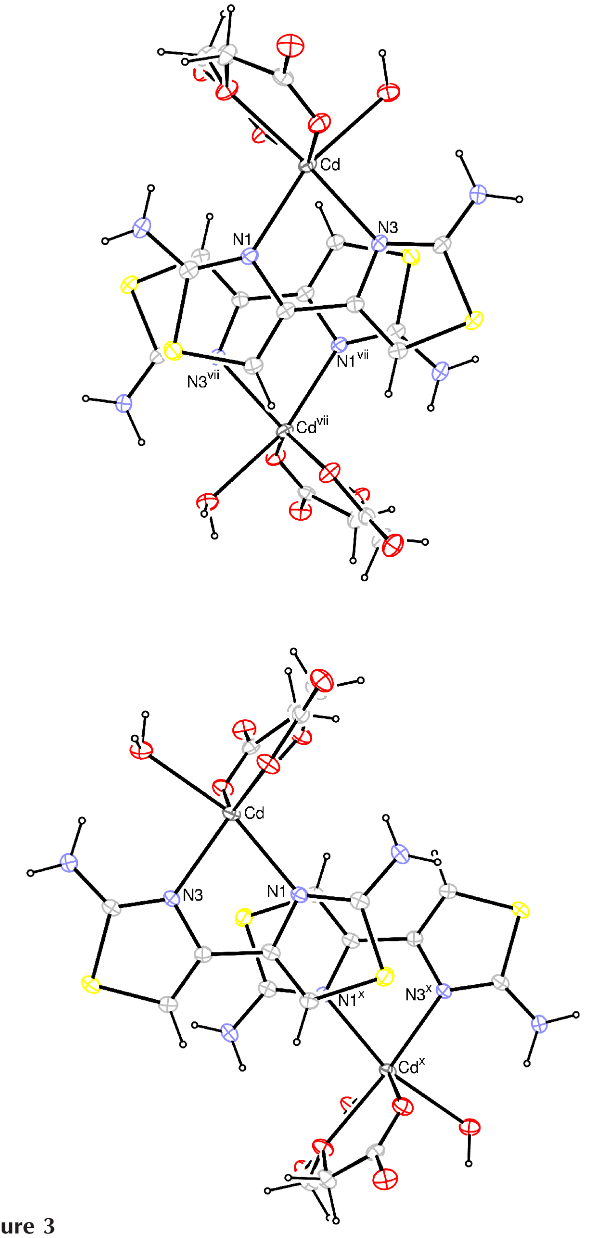


Figure 3
Two views of the overlapped disposition of parallel DABT rings. [Symmetry codes: (vii) $1-x, 1-y, -z$; (x) $-x, 1-y, -z$.]

The DABT chelates to the Cd^{II} atom, with the two rings coplanar and with a maximum atomic deviation from the mean plane of 0.063 (2) Å for C4. This differs from the twisted configuration of DABT found in dichlorobis(DABT)-cadmium(II) methanol solvate (Liu *et al.*, 2003), but is similar to the coplanar structure of DABT found in aqua(DABT)(ODA)zinc(II) dihydrate (Li *et al.*, 2003).

The N2—C1 and N4—C4 bond distances (Table 1) are appreciably shorter than typical N—C single bonds and suggest electron delocalization between amine groups and thiazole rings. Intramolecular hydrogen bonding occurs between the N4-amino group and the coordinated water

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molecule (Fig. 1). Compared to the Cd—N3 distance and N3—Cd—O6 angle, the Cd—N1 bond is longer and the N1—Cd—O3 angle larger. This results in a longer H21···O3 separation (2.61 Å) and suggests that no hydrogen bonding occurs between the N2-amine group and the ether atom O3. An overlapped arrangement of parallel thiazole rings from neighbouring complex molecules is observed in the crystal structure (Fig. 3). Interplanar distances of 3.438 (4) [symmetry code: 1 $-x$, 1 $-$ y, 1 $-$ z; see Fig. 3 (top)] and 3.382 (10) Å [symmetry code: $-x, 1 - y, 1 - z$; see Fig. 3 (bottom)] strongly suggest the existence of π–π stacking interactions in the crystal structure of (I).

Experimental

Microcrystals of DABT were obtained in the manner reported by Erlenmeyer (1948). An aqueous solution (20 ml) containing DABT (0.20 g, 1 mmol) and $CdCl_2·2H_2O$ (0.22 g, 1 mmol) was mixed with another aqueous solution (10 ml) of oxydiacetic acid (0.14 g, 1 mmol) and NaOH (0.08 g, 2 mmol). The mixture was refluxed for 5 h. The solution was filtered after cooling to room temperature. Yellow single crystals were obtained from the filtrate after 10 d.

Crystal data

$[Cd(C_4H_4O_5)(C_6H_6N_4S_2)(H_2O)]·3H_2O$
$M_r = 514.80$
Triclinic, $P\overline{1}$
$a = 7.1804$ (9) Å
$b = 9.8372$ (12) Å
$c = 12.6069$ (15) Å
$\alpha = 81.478$ (2)°
$\beta = 86.528$ (2)°
$\gamma = 89.760$ (2)°
$V = 879.03$ (19) Å^3
$Z = 2$
$D_x = 1.945$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5208 reflections
$\theta = 2.5$–24.0°
$\mu = 1.53$ mm^{-1}
$T = 295$ (2) K
Prism, yellow
0.30 × 0.25 × 0.10 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.632$, $T_{max} = 0.855$
6520 measured reflections
3159 independent reflections
2923 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 25.2°$
$h = -8 \rightarrow 8$
$k = -11 \rightarrow 11$
$l = -14 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.071$
$S = 1.04$
3159 reflections
235 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0323P)^2 + 0.7156P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.51$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cd—N1	2.298 (3)	Cd—O4	2.302 (2)
Cd—N3	2.258 (3)	Cd—O6	2.377 (2)
Cd—O1	2.260 (2)	N2—C1	1.349 (4)
Cd—O3	2.353 (2)	N4—C4	1.334 (4)
N1—Cd—O3	98.62 (9)	N3—Cd—O6	89.80 (9)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1A···O2W^{i}	0.89	1.99	2.842 (4)	159
O1W—H1B···O4	0.90	2.02	2.912 (4)	170
O2W—H2A···O2	0.88	2.12	2.900 (4)	148
O2W—H2B···O1W^{ii}	0.88	1.91	2.781 (4)	169
O3W—H3A···O2	0.83	2.18	2.975 (4)	163
O3W—H3B···O1W^{ii}	0.82	2.20	3.016 (4)	171
O6—H6A···O5^{iii}	0.87	1.88	2.742 (3)	170
O6—H6B···O5^{iv}	0.93	1.81	2.722 (3)	166
N2—H22···O3W^{v}	0.83	2.42	3.205 (4)	158
N4—H41···O6	0.96	2.01	2.910 (4)	156
N4—H42···O2^{vi}	0.87	2.07	2.891 (4)	158
C2—H2···O1^{vii}	0.93	2.44	3.218 (4)	142

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

H atoms attached to C atoms were placed in calculated positions, with C—H distances of 0.97 (methylene) or 0.93 Å (aromatic), and were included in the final cycles of refinement in riding mode, with $U_{iso}(H) = 1.2U_{eq}$ of the carrier atoms. The other H atoms were located in a difference Fourier map and refined by riding in their as-found positions relative to O or N atoms with fixed isotropic displacement parameters of 0.06 Å^2.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); 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).

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