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

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Key indicators

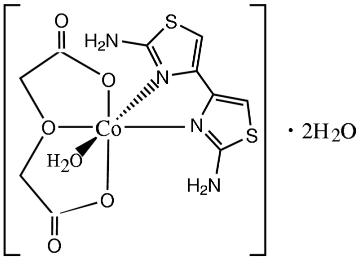
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.006 Å
H-atom completeness 88%
Disorder in solvent or counterion
R factor = 0.050
wR factor = 0.123
Data-to-parameter ratio = 16.6

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

The title compound, $[Co(C_4H_4O_5)(C_6H_6N_4S_2)(H_2O)]\cdot 2H_2O$, contains one Co^{II} complex and two water molecules in the asymmetric unit. The tridentate oxydiacetate dianion meridionally chelates a Co atom, and both five-membered chelate rings assume an envelope conformation. Diaminobithiazole chelates the Co atom, in a planar configuration. Parallel thiazole rings of neighboring complex molecules are separated by 3.504 (5) Å, suggesting the existence of π–π stacking interactions.

Comment

A series of transition metal complexes with 2,2′-diamino-4,4′-bi-1,3-thiazole (DABT), which promise potential application in the field of soft magnetic materials, has been prepared in our laboratory (Wu *et al.*, 2003; Liu & Xu, 2004). Among these is aqua(DABT)(oxydiacetato)cobalt(II) monohydrate (Luo *et al.*, 2004), in the crystal structure of which, with D_x equal to 1.79 Mg m^{-3}, the Co atom is situated on a crystallographic twofold axis, resulting in a disordered distribution of chelating ligands. Recently, we repeated the synthesis of that Co^{II} complex and obtained new crystals with the lower value of D_m = 1.65 Mg m^{-3}. We report here the structure of this new form, (I), which correspond to the title compound, an ordered Co^{II} complex as its dihydrate.



(I)

The molecular structure of (I) is presented in Fig. 1. The Co^{II} complex displays the same molecular structure as that found in the monohydrate. The Co atom has a distorted octahedral coordination geometry, formed by an oxydiacetate dianion (ODA), a DABT ligand and a coordinated water molecule. The coordinate bond distances and angles are similar to those found in the monohydrate, except for significantly different Co—N3 and Co—N3′ bond distances [2.068 (3) and 2.126 (3) Å]. Tridentate ODA chelates to the Co atom in a meridional configuration, and both five-membered chelate rings assume an envelope conformation, with ether atom O3 in the flap position, lying out of the mean plane formed by the other four atoms by 0.500 (4) and

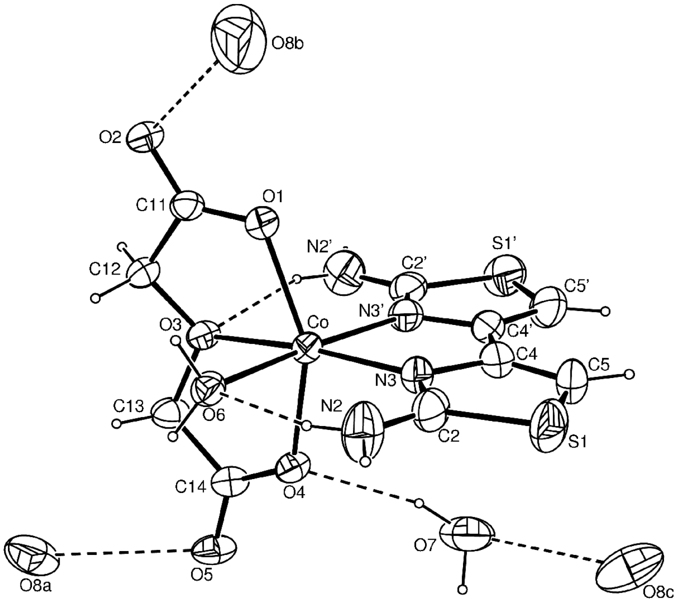


Figure 1
The structure of the asymmetric unit of (I), with 30% probability displacement ellipsoids. Dashed lines indicate the hydrogen bonding.

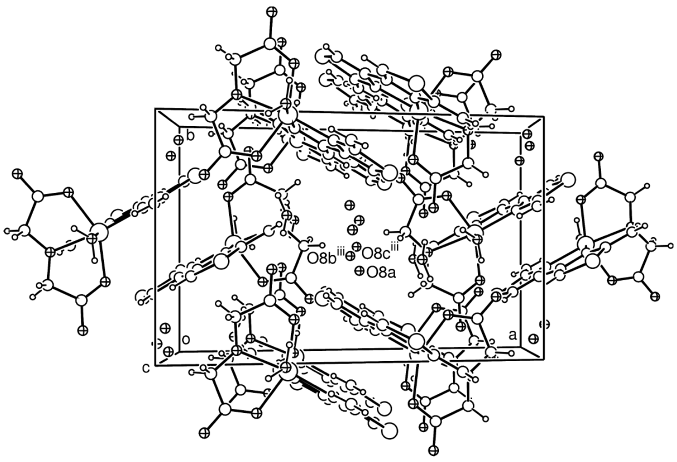


Figure 2
The molecular packing, showing the ample space for the disordered uncoordinated water molecules [symmetry code: (iii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$].

0.314 (5) Å. The DABT ligand chelates the Co atom, showing a planar configuration; the maximum atomic deviation is 0.032 (2) Å for atom S1. Intramolecular hydrogen bonds between the amine groups of DABT and coordinated O atoms stabilize the molecular structure (Fig. 1).

Two uncoordinated water molecules are present in the asymmetric unit. The ordered uncoordinated water molecule (O7) links with the coordinated O atom (O4) of ODA *via* a hydrogen bond (Fig. 1), whereas in the Co^{II} complex hydrate, the uncoordinated water molecules hydrogen bond with the uncoordinated O atom of ODA. The disordered water atom O8 appears in three different positions, each with different site occupancy factors. Although the H atoms attached to O8 were not located, distances of 2.97 (2) (O8*a*···O5), 3.154 (14) (O8*b*···O2) and 3.09 (2) Å (O8*c*···O7) suggest hydrogen bonding involving them (Fig. 1). The molecular packing is illustrated in Fig. 2, which shows the ample space available for the disordered uncoordinated water molecules.

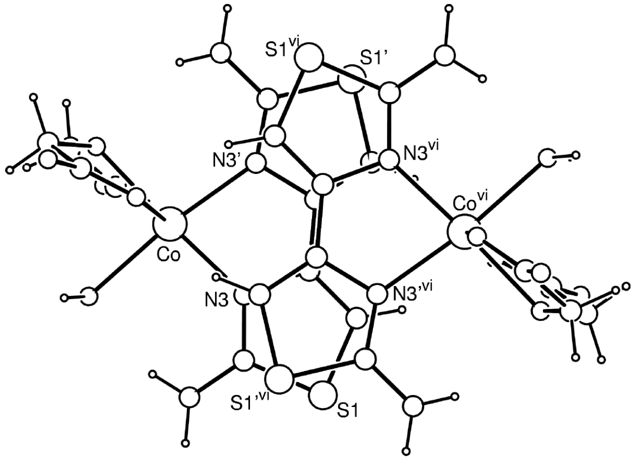


Figure 3
π-π stacking between the thiazole rings [symmetry code: (vi) $-x, 1 - y, 1 - z$].

Parallel thiazole rings, related by an inversion center at $(0, \frac{1}{2}, \frac{1}{2})$, overlap each other, as shown in Fig. 3. The distance [3.504 (5) Å] between the mean planes suggests the existence of π–π stacking interactions between the neighboring thiazole rings.

Experimental

An aqueous solution (10 ml) of DABT (0.20 g, 1 mmol) and $CoCl_2\cdot6H_2O$ (0.24 g, 1 mmol) was mixed with an aqueous solution (5 ml) of ODA (0.14 g, 1 mmol) and Na_2CO_3 (0.11 g 1 mmol). The mixture was refluxed for 2 h, and then the solution was cooled to room temperature and filtered. Single crystals of the title compound were obtained from the filtrate after 2 d.

Crystal data

$[Co(C_4H_4O_5)(C_6H_6N_4S_2)(H_2O)]\cdot2H_2O$
$M_r = 443.32$
Monoclinic, $P2_1/n$
$a = 16.6389$ (11) Å
$b = 10.1097$ (8) Å
$c = 11.205$ (3) Å
$\beta = 109.247$ (10)°
$V = 1779.5$ (5) Å^3
$Z = 4$
$D_x = 1.655$ Mg m^{-3}
$D_m = 1.65$ Mg m^{-3}
D_m measured by flotation in CCl_4 and $C_2H_4Br_2$
Mo $K\alpha$ radiation
Cell parameters from 13 082 reflections
$\theta = 2.5$–26.0°
$\mu = 1.25$ mm^{-1}
$T = 295$ (2) K
Prism, pink
0.42 × 0.32 × 0.30 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.59$, $T_{max} = 0.69$
15 733 measured reflections
4045 independent reflections
3200 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$
$\theta_{max} = 27.4°$
$h = -19 \rightarrow 21$
$k = -13 \rightarrow 13$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.123$
$S = 1.03$
4045 reflections
244 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0467P)^2 + 2.3289P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.91$ e Å^{-3}
$\Delta\rho_{min} = -0.77$ e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N2-H2A\cdots O6$	0.88	2.03	2.875 (4)	161
$N2-H2B\cdots O5^{i}$	0.93	1.96	2.817 (4)	152
$N2'-H2C\cdots O7^{ii}$	0.90	2.07	2.928 (5)	158
$N2'-H2D\cdots O3$	0.85	2.41	3.158 (4)	148
$O6-H6A\cdots O5^{iii}$	0.92	1.77	2.676 (3)	168
$O6-H6B\cdots O2^{iv}$	0.90	1.81	2.711 (4)	176
$O7-H7A\cdots O4$	0.92	2.16	3.048 (4)	161
$O7-H7B\cdots O2^{v}$	0.90	1.90	2.799 (4)	175

Symmetry codes: (i) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iv) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (v) $x, y-1, z$.

Site occupancy factors of disordered water molecule O8 were refined independently and converged to 0.30, 0.52 and 0.27, respectively, and then were fixed at 0.25, 0.50 and 0.25 for atoms O8*a*, O8*b* and O8*c*. H atoms of the disordered water molecule were not located. H atoms of the coordinated water molecule and H atoms on N atoms were located in a difference Fourier map and included in the refinement with fixed positional parameters and an isotropic displacement parameter of 0.08 Å^2. H atoms on C atoms were placed in calculated positions, with C—H = 0.97 (methylene) or 0.93 Å (aromatic), and included in the final cycles of refinement in the riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}$(carrier atom).

Data collection: *PROCESS-AUTO* (Rigaku Corporation, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC & Rigaku Corporation, 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); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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