

Tris(1*H*-benzimidazole- $\kappa N^3$ )(thiodiacetato- $\kappa^3 O, S, O'$ )cobalt(II) dihydrateLei Cao,<sup>‡</sup> Jia-Geng Liu and  
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## Key indicators

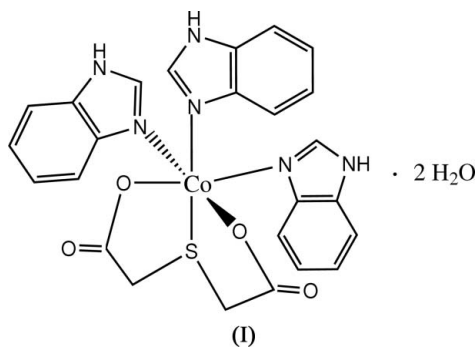
Single-crystal X-ray study  
 $T = 295$  K  
Mean  $\sigma(C-C) = 0.005$  Å  
 $R$  factor = 0.054  
 $wR$  factor = 0.104  
Data-to-parameter ratio = 17.2For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

In the title complex,  $[\text{Co}(\text{C}_4\text{H}_4\text{O}_4\text{S})(\text{C}_7\text{H}_6\text{N}_2)_3] \cdot 2\text{H}_2\text{O}$ , the  $\text{Co}^{\text{II}}$  ion is coordinated by one thiodiacetate dianion and three benzimidazole molecules, with a distorted octahedral geometry. The tridentate thiodiacetate chelates to the Co atom in a facial configuration, with a Co–S bond distance of 2.5597 (8) Å. Intermolecular hydrogen bonding prevents the face-to-face stacking of neighboring benzimidazole ligands.

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## Comment

Several crystal structures of metal complexes incorporating benzimidazole ( $\text{C}_7\text{H}_6\text{N}_2$ ; bzim) as a ligand show  $\pi$ – $\pi$  stacking between neighboring aromatic rings (Chen *et al.*, 2003; Liu & Xu, 2004; Bukowska-Strzyzewska & Tosik, 1983). As part of our ongoing investigations on the nature of  $\pi$ – $\pi$  stacking in metal complexes, (Li *et al.*, 2005), the title bzim complex of  $\text{Co}^{\text{II}}$ , (I) (Fig. 1), is presented here.



The  $\text{Co}^{\text{II}}$  atom is coordinated by three bzim molecules and one tridentate thiodiacetate dianion ( $\text{C}_4\text{H}_4\text{O}_4\text{S}^{2-}$ ; tda) in a distorted octahedral coordination (Table 1). The tda ligand adopts a facial configuration, consistent with that found in triimidazole(thiodiacetato)nickel(II) (Pan & Xu, 2005). The five-membered chelate rings of the tda display envelope conformations, with the Co atom lying at the flap position, displaced from the mean planes formed by the other four atoms by 0.370 (5) and 0.836 (4) Å for the O1 and O3 rings, respectively. The Co–S bond distance in (I) is slightly longer [by 0.0848 (11) Å] than the equivalent Ni–S bond distance found in the above-cited  $\text{Ni}^{\text{II}}$  complex.

Extensive hydrogen bonding (Table 2) occurs in the crystal structure of (I). As shown in the packing diagram (Fig. 2), the uncoordinated tda carboxyl O atoms link with the bzim ligands of neighboring complexes *via* N–H...O hydrogen bonding, preventing any close  $\pi$ – $\pi$  stacking (minimum centroid separation = 4.43 Å) of neighboring bzim ligands in the crystal structure of (I).

Experimental

An aqueous solution (15 ml) solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (1 mmol),  $\text{H}_2\text{tda}$  (1 mmol) and  $\text{Na}_2\text{CO}_3$  (1 mmol) was mixed with an ethanol solution (5 ml) of *bzim* (2 mmol). The solution was refluxed for 6 h and then filtered. Single crystals of (I) were obtained after 6 d.

Crystal data

$[\text{Co}(\text{C}_4\text{H}_4\text{O}_4\text{S})(\text{C}_7\text{H}_6\text{N}_2)_3] \cdot 2\text{H}_2\text{O}$   
 $M_r = 597.51$   
 Orthorhombic, *Pbca*  
 $a = 10.3428$  (4) Å  
 $b = 19.8783$  (4) Å  
 $c = 25.8749$  (8) Å  
 $V = 5319.8$  (3) Å<sup>3</sup>  
 $Z = 8$   
 $D_x = 1.492$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
 Cell parameters from 28828 reflections  
 $\theta = 1.9\text{--}27.4^\circ$   
 $\mu = 0.78$  mm<sup>-1</sup>  
 $T = 295$  (2) K  
 Plate, red  
 $0.24 \times 0.20 \times 0.06$  mm

Data collection

Rigaku R-AXIS RAPID diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan *ABSCOR* (Higashi, 1995)  
 $T_{\min} = 0.888$ ,  $T_{\max} = 0.955$   
 46075 measured reflections

6053 independent reflections  
 3934 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.095$   
 $\theta_{\max} = 27.5^\circ$   
 $h = -13 \rightarrow 13$   
 $k = -25 \rightarrow 24$   
 $l = -33 \rightarrow 33$

Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.054$   
 $wR(F^2) = 0.104$   
 $S = 1.05$   
 6053 reflections  
 352 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0379P)^2 + 3.8108P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.37$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.36$  e Å<sup>-3</sup>

Table 1

Selected bond lengths (Å).

Co—S	2.5597 (8)	Co—N13	2.154 (3)
Co—O1	2.056 (2)	Co—N23	2.109 (2)
Co—O3	2.156 (2)	Co—N33	2.136 (2)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O5—H5A...O6 <sup>i</sup>	0.95	2.04	2.870 (4)	145
O5—H5B...O4	0.96	1.85	2.805 (4)	177
O6—H6A...O2	0.94	1.93	2.769 (4)	148
O6—H6B...O5 <sup>ii</sup>	0.96	1.88	2.816 (4)	162
N11—H11...O4 <sup>iii</sup>	0.86	1.93	2.766 (4)	163
N21—H21...O3 <sup>iv</sup>	0.86	2.39	3.217 (3)	161
N21—H21...O4 <sup>iv</sup>	0.86	2.42	3.072 (3)	133
N31—H31...O2 <sup>v</sup>	0.86	1.93	2.780 (4)	168

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

Water H atoms were located in a difference Fourier map and refined as riding in their as-found relative positions with fixed  $U_{\text{iso}}(\text{H}) = 0.05$  Å<sup>2</sup>. Other H atoms were placed in idealized positions ( $\text{C—H} = 0.93\text{--}0.97$ ;  $\text{N—H} = 0.86$  Å) and refined as riding, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$ .

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

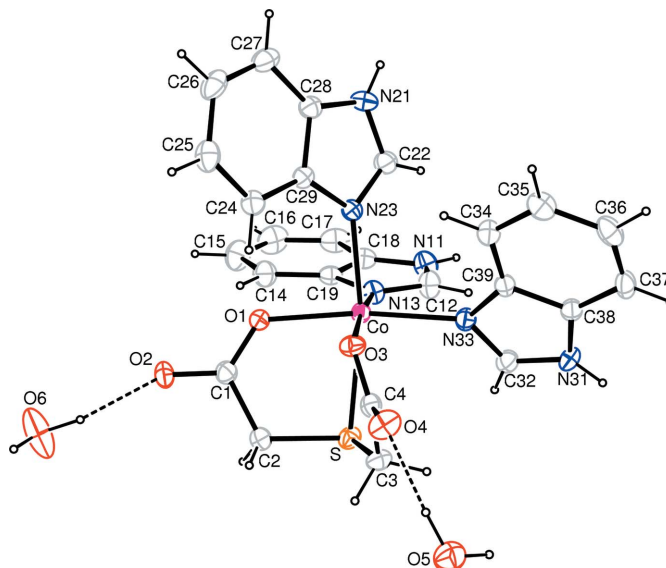


Figure 1 The molecular structure of (I) with 30% probability displacement ellipsoids (arbitrary spheres for H atoms). Dashed lines indicate hydrogen bonds.

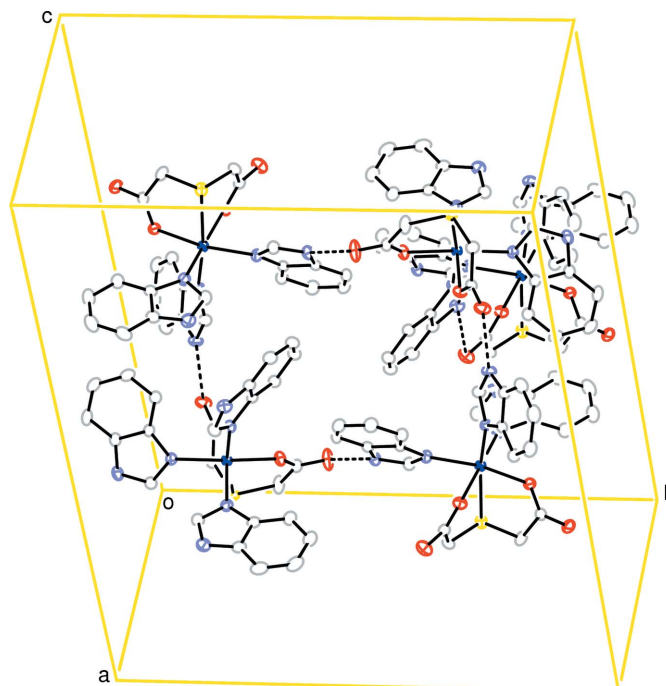


Figure 2 The packing of (I), showing N—H...O hydrogen bonds as dashed lines. Non-coordinated water molecules and H atoms have been omitted for clarity.

MSC and Rigaku, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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**References**

- Altomare, A., Cascarano, G., Giacobozzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
- Bukowska-Strzyzewska, M. & Tosik, A. (1983). *Acta Cryst.* **C39**, 203–205.
- Chen, Z., Xu, D.-J., Li, Z.-Y., Wu, J.-Y. & Chiang, M. Y. (2003). *J. Coord. Chem.* **56**, 253–259.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
- Li, H., Yin, K.-L. & Xu, D.-J. (2005). *Acta Cryst.* **C61**, m19–m21.
- Liu, Y. & Xu, D.-J. (2004). *Acta Cryst.* **E60**, m1002–m1004.
- Pan, T.-T. & Xu, D.-J. (2005). *Acta Cryst.* **E61**, m1735–1737.
- Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
- Rigaku/MSO and Rigaku (2002). *CrystalStructure*. Version 3.00. Rigaku/MSO, 900 New Trails Drive, The Woodlands, TX 77381-5209, USA.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.