

Tetraaquabis(1,3-benzimidazol-3-ium-1,3-di-  
acetato)cobalt(II) hemihydrate

Ling Huang\* and Ding-Ben Chen

Department of Chemistry, Taizhou University,  
Taizhou 317000, People's Republic of China

Correspondence e-mail: huangltzu@yahoo.com

In the centrosymmetric title compound,  $[\text{Co}(\text{C}_{11}\text{H}_9\text{N}_2\text{O}_4)_2(\text{H}_2\text{O})_4] \cdot 0.5\text{H}_2\text{O}$ , the  $\text{Co}^{\text{II}}$  complex has a distorted octahedral coordination geometry with two monodentate ligands and four water molecules. The crystal packing is stabilized by intermolecular  $\text{O}-\text{H} \cdots \text{O}$  and  $\text{C}-\text{H} \cdots \text{O}$  hydrogen bonds and a  $\pi-\pi$  stacking interaction.

Received 6 October 2006

Accepted 21 November 2006

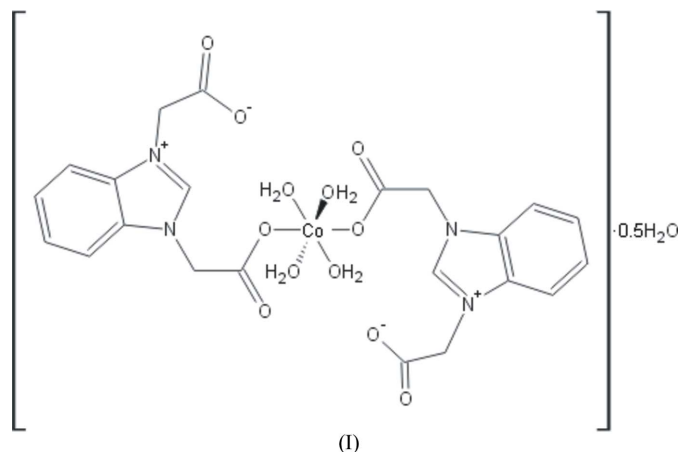
## Key indicators

Single-crystal X-ray study  
 $T = 273 \text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$   
Disorder in solvent or counterion  
 $R$  factor = 0.045  
 $wR$  factor = 0.103  
Data-to-parameter ratio = 11.9

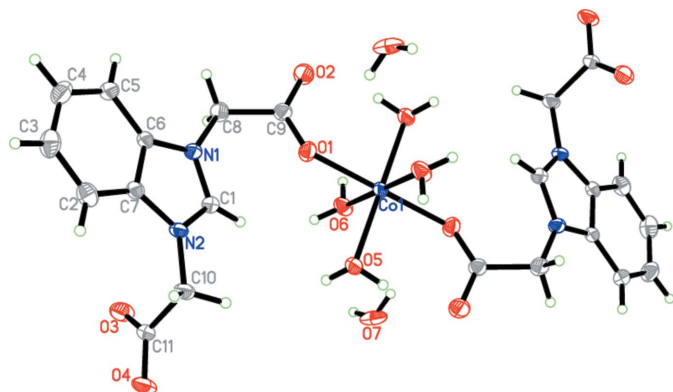
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

## Comment

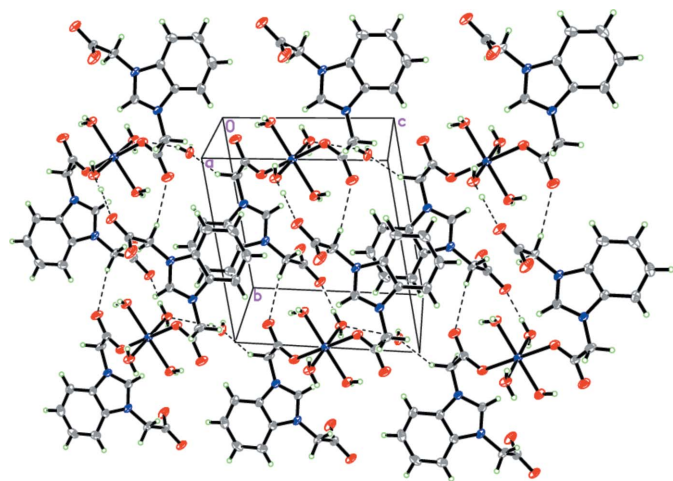
Imidazole and benzimidazole carboxylic acids and their derivatives are of practical importance in the design of therapeutic agents, such as antifilarial and antineoplastic (Ram *et al.*, 1992), anthelmintic (Dubey *et al.*, 1985) and antiviral compounds (Garuti *et al.*, 2000) and 5-HT<sub>4</sub> receptor antagonists (Maria *et al.*, 1999). In addition, these compounds are of fundamental value as ligands in the coordination chemistry of supramolecular metal complexes, as an N atom in the imidazole or benzimidazole ring and O atoms in the carboxylate groups can act as donor sites (Liu *et al.*, 2005). Metal complexes with such ligands, *e.g.* the 1,3-bis(carboxymethyl)imidazolium Zn complex (Fei, Geldbach *et al.*, 2005) and Sr complex (Fei, Zhao *et al.*, 2005), have been reported. To extend this research, we report here the synthesis and crystal structure of the title Co complex, (I).



The central  $\text{Co}^{\text{II}}$  atom, lying on a centre of symmetry, is coordinated by four water molecules and two monodentate 1-(carboxymethyl)-1,3-benzimidazol-3-ium-3-acetate ligands (Fig. 1). This  $\text{CoO}_6$  octahedron is slightly distorted, as the  $\text{Co}-\text{O}_{\text{aqua}}$  bond lengths are shorter than the other  $\text{Co}-\text{O}$  bonds (Table 1). The  $\text{Co}-\text{O}$  coordination distances are similar to those found in octahedral  $\text{Co}^{\text{II}}$  complexes containing monodentate carboxylate and water as ligands, such as tetraaqua-bis(*p*-nitrobenzoato)cobalt(II) dihydrate (Nadzhafov *et al.*, 1981) and tetraaqua-bis(3,5-dinitrobenzoato)cobalt(II) tetrahydrate (Tahir *et al.*, 1996). The bond lengths and angles



**Figure 1**  
The molecular structure of (I), showing 30% probability displacement ellipsoids and atom-numbering scheme. Unlabelled atoms are related to labelled atoms by  $2 - x, -y, 1 - z$ .



**Figure 2**  
Partial packing diagram of (I). Dashed lines indicate hydrogen bonds.

of the 1-(carboxymethyl)-1,3-benzimidazol-3-ium-3-acetate ligand in (I) are in good agreement with those in the free ligand (Chen & Huang, 2006).

In the crystal structure, the uncoordinated water molecule is involved in hydrogen bonds ( $O7-H7A \cdots O6$ ). The coordinated water molecules are hydrogen-bonded to the carboxylate O atoms (Table 2). These intermolecular hydrogen bonds as well as non-classical C-H $\cdots$ O hydrogen bonds (Fig. 2) link adjacent molecules to generate a three-dimensional network. In addition, there is a  $\pi$ - $\pi$  stacking interaction between benzimidazolium units, the centroid-centroid( $2 - x, 1 - y, -z$ ) distance and the interplanar distance being 3.63 (2) and 3.49 (3) Å, respectively.

## Experimental

An ethanol (50%) solution of 1-(carboxymethyl)-1*H*-benzimidazol-3-ium-3-acetate (0.0937 g, 0.4 mmol) was dissolved in ethanol (50%, 20 ml) containing NaOH (0.0161 g, 0.4 mmol). The resulting solution was added dropwise to a hot solution of  $CoCl_2 \cdot 6H_2O$  (0.0952 g, 0.4 mmol) dissolved in the same solvent (20 ml) with continuous stirring for 1 h. After one month, red crystals suitable for X-ray diffraction were obtained (yield 42% based on Co). Thermogravi-

metric analysis (TGA) performed on a single crystalline sample under a nitrogen atmosphere over the range 303–1173 K gave the weight loss of one half of an uncoordinated water molecule and four coordinated water molecules between 303 and 405 K (calculated 13.37; found 13.40%).

## Crystal data

$[Co(C_{11}H_9N_2O_4)_2(H_2O)_4] \cdot 0.5H_2O$   
 $M_r = 606.41$   
 Triclinic,  $P\bar{1}$   
 $a = 7.4237$  (9) Å  
 $b = 9.4197$  (11) Å  
 $c = 9.6478$  (11) Å  
 $\alpha = 81.432$  (2)°  
 $\beta = 75.952$  (2)°  
 $\gamma = 77.838$  (2)°

$V = 636.38$  (13) Å<sup>3</sup>  
 $Z = 1$   
 $D_x = 1.582$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 $\mu = 0.75$  mm<sup>-1</sup>  
 $T = 273$  (2) K  
 Block, red  
 $0.22 \times 0.14 \times 0.10$  mm

## Data collection

Siemens SMART CCD area-detector diffractometer  
 $\omega$  and  $\varphi$  scans  
 Absorption correction: multi-scan (SADABS; Bruker, 2002)  
 $T_{min} = 0.853, T_{max} = 0.929$

3375 measured reflections  
 2224 independent reflections  
 2019 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.016$   
 $\theta_{max} = 25.1^\circ$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.045$   
 $wR(F^2) = 0.103$   
 $S = 1.06$   
 2224 reflections  
 187 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0489P)^2 + 0.3708P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.37$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.29$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Co1—O1	2.0677 (19)	O4—C11	1.254 (3)
Co1—O5	2.0995 (19)	N1—C1	1.330 (4)
Co1—O6	2.114 (2)	N1—C6	1.397 (4)
O1—C9	1.253 (3)	N2—C1	1.325 (4)
O2—C9	1.238 (3)	N2—C7	1.392 (4)
O3—C11	1.236 (4)		
O1 <sup>i</sup> —Co1—O5	89.76 (8)	O1—Co1—O6 <sup>i</sup>	91.42 (8)
O5—Co1—O6	92.73 (8)	O3—C11—O4	126.2 (3)

Symmetry code: (i)  $-x + 2, -y, -z + 1$ .

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O5—H5A $\cdots$ O2 <sup>i</sup>	0.85	1.92	2.744 (3)	163
O5—H5B $\cdots$ O3 <sup>ii</sup>	0.85	1.82	2.666 (3)	176
O6—H6A $\cdots$ O4 <sup>iii</sup>	0.85	1.94	2.738 (3)	157
O6—H6B $\cdots$ O4 <sup>ii</sup>	0.85	1.91	2.750 (3)	169
O7—H7A $\cdots$ O6	0.85	2.52	2.993 (9)	116
C1—H1 $\cdots$ O1	0.93	2.32	2.681 (3)	102
C1—H1 $\cdots$ O3 <sup>ii</sup>	0.93	2.59	3.367 (4)	141
C1—H1 $\cdots$ O4 <sup>ii</sup>	0.93	2.54	3.208 (4)	129
C10—H10A $\cdots$ O2 <sup>iv</sup>	0.97	2.46	3.375 (4)	157

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

The uncoordinated water molecule is statistically disordered. Refinement converged with the site-occupation factor of 0.50 consistent with the TGA result. H atoms were placed in calculated positions (C—H = 0.93–0.97 Å and O—H = 0.85 Å) and refined as riding, with  $U_{iso}(H) = 1.2U_{eq}(C)$  and  $1.5U_{eq}(O)$ .

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINTE* (Bruker, 2002); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2002); software used to prepare material for publication: *SHELXL97*.

The authors thank Taizhou University for research grant No. 06ND29.

## References

- Bruker (2002). *SADABS* (Version 2.03), *SAINTE* (Version 6.02), *SMART* (Version 5.62) and *SHELXTL* (Version 6.10). Bruker AXS Inc., Madison, Wisconsin, USA.
- Chen, D.-B. & Huang, L. (2006). *Acta Cryst.* **E62**, o4686–o4688.
- Dubey, R., Abuzar, S., Sharma, S., Chatterjee, R. K. & Katiyar, J. C. (1985). *J. Med. Chem.* **28**, 1748–1750.
- Fei, Z., Geldbach, T. J., Zhao, D., Scopelliti, R. & Dyson, P. J. (2005). *Inorg. Chem.* **44**, 5200–5202.
- Fei, Z., Zhao, D., Geldbach, T. J., Scopelliti, R., Dyson, P. J. & Antonijevic, S. (2005). *Angew. Chem. Int. Ed.* **44**, 5720–5725.
- Garuti, L., Roberti, M. & Gentilomi, G. (2000). *Farmaco*, **55**, 35–39.
- Liu, Z., Chen, Y., Liu, P., Wang, J. & Huang, M. (2005). *J. Solid State Chem.* **178**, 2306–2312.
- Maria, L., Lopez, R. & Bellinda, B. (1999). *Bioorg. Med. Chem.* **7**, 2271–2281.
- Nadzhafov, G. N., Shnulin, A. N. & Marnedov, Kh. S. (1981). *Zh. Strukt. Khim.* **22**, 124–126.
- Ram, S., Wise, D. S., Wotring, L. L., McCall, J. W. & Townsend, L. B. (1992). *J. Med. Chem.* **35**, 539–547.
- Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
- Tahir, M. N., Ülkü, D. & Mövsümov, E. M. (1996). *Acta Cryst.* **C52**, 1392–1394.