Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Diaquabis(3-hydroxybenzoato-κO)bis(5-nitro-1*H*-benzimidazole-κN^3)cobalt(II) bis(5-nitro-1*H*-benzimidazole) dihydrate

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Received 18 May 2006
Accepted 18 May 2006

Key indicators

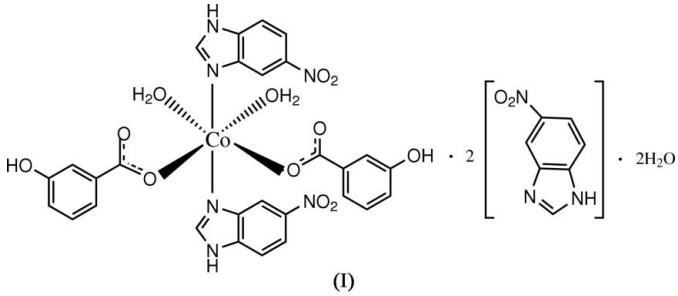
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.003 Å
R factor = 0.037
wR factor = 0.099
Data-to-parameter ratio = 15.2

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

The title compound, $[Co(C_7H_5O_3)_2(C_7H_5N_3O_2)_2(H_2O)_2]\cdot 2C_7H_5N_3O_2\cdot 2H_2O$, is composed of neutral Co^{II}-containing complexes, accompanied by uncoordinated nitrobenzimidazole (Nbzim) molecules and water molecules. The Co^{II} atom is located on a twofold axis and coordinated by two Nbzim molecules, two 3-hydroxybenzoate anions and two water molecules in a slightly distorted octahedral geometry. The crystal packing is stabilized by extensive hydrogen bonding and π–π stacking between coordinated and uncoordinated Nbzim molecules.

Comment

As part of our ongoing investigations of the nature of π–π stacking in metal complexes (Li *et al.*, 2005; Zhang *et al.*, 2005), the title Co^{II} compound, (I), incorporating 5-nitrobenzimidazole (Nbzim) ligands, has been prepared and its crystal structure is presented here.



(I)

Compound (I) is composed of Co^{II} complexes, accompanied by non-coordinated Nbzim molecules and water molecules (Fig. 1). The Co^{II} atom is located on a twofold axis and is coordinated by two 3-hydroxybenzoate (HBA) anions, two Nbzim molecules and two water molecules in a slightly distorted octahedral geometry (Table 1). The *cis* bond angles about Co range from 85.88 (8) to 93.88 (6)° and the *trans* angles lie between 175.22 (7) and 175.97 (5)°. The monodentate HBA anions coordinate to the Co atom in a *cis* configuration, while the Nbzim molecules coordinate to the Co atom in a *trans* configuration. Within both the coordinated and uncoordinated Nbzim species, the nitro groups are almost coplanar with the benzimidazole skeleton, the dihedral angles being 2.9 (2) (N12-nitro) and 1.89 (19)° (N22-nitro). The coordinated N11-Nbzim molecule is approximately parallel to the uncoordinated Nbzim molecule, the dihedral angle being 10.87 (10)°.

A partially overlapped arrangement of the coordinated Nbzim and uncoordinated Nbzim molecules is observed (Fig. 2). The distances of atoms of N11-Nbzim to the N21-

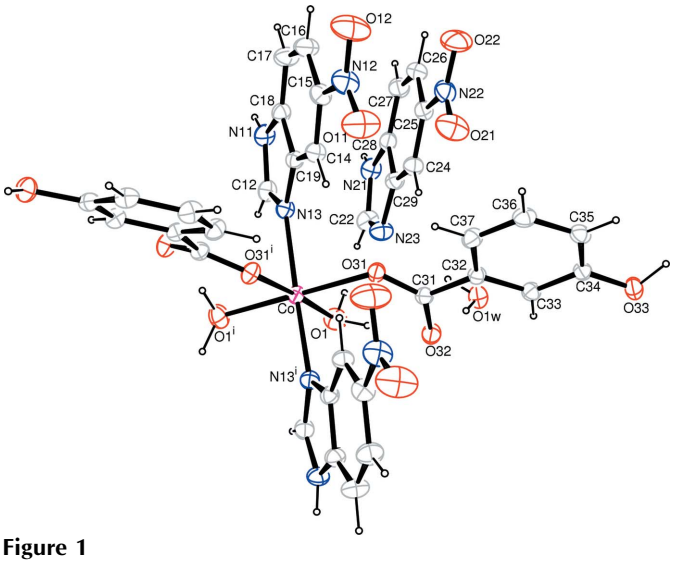


Figure 1
The molecular structure of (I), shown with 30% probability displacement ellipsoids (arbitrary spheres for H atoms) [symmetry code: (i) $1-x, y, \frac{1}{2}-z$].

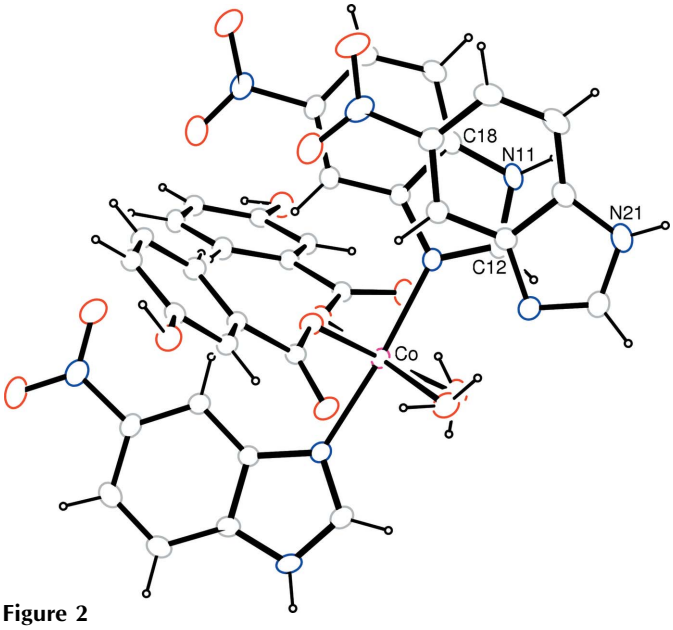


Figure 2
A diagram showing the π–π stacking in (I).

Nbzim mean plane are 3.505 (2) (N11), 3.277 (3) (C12) and 3.493 (2) Å (C18). These findings suggest the existence of π–π stacking between coordinated Nbzim and uncoordinated Nbzim.

An extensive network of O—H···O, O—H···N and N—H···O hydrogen bonds helps to stabilize the crystal structure of (I) (Table 2).

Experimental

$CoCl_2\cdot6H_2O$ (0.24 g, 1 mmol), Na_2CO_3 (0.053 g, 0.5 mmol) and sodium 3-hydroxybenzoate (0.16 g, 1 mmol) were dissolved in a water–ethanol solution (15 ml, 1:2). 6-Nitrobenzimidazole (6-Nbzim) (0.33 g, 1 mmol) was then added to the above solution. The mixture was refluxed for 2.5 h, and then filtered after cooling to room temperature. Single crystals of (I) were obtained from the filtrate after one week. It should be noted that 6-Nbzim is used as a starting material in the preparation of (I), but 5-Nbzim is found in the crystal structure of (I). This means that the 1-H atom of 6-Nbzim is transferred to the 3-position during the reaction (Solomons & Fryhle, 2000).

Crystal data

$[Co(C_7H_5O_3)_2(C_7H_5N_3O_2)_2(H_2O)_2]\cdot2C_7H_5N_3O_2\cdot2H_2O$
$M_r = 1057.77$
Monoclinic, $C2/c$
$a = 26.536$ (8) Å
$b = 9.547$ (3) Å
$c = 18.026$ (4) Å
$\beta = 106.79$ (1)°
$V = 4372$ (2) Å^3
$Z = 4$
$D_x = 1.607$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.49$ mm^{-1}
$T = 295$ (2) K
Prism, pink
0.31 × 0.18 × 0.11 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.857$, $T_{max} = 0.945$
20853 measured reflections
5000 independent reflections
3990 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$
$\theta_{max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.099$
$S = 1.05$
5000 reflections
330 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0541P)^2 + 1.4439P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Co—O1	2.1375 (14)	C12—N13	1.313 (2)
Co—O31	2.0821 (12)	C12—N11	1.348 (2)
Co—N13	2.1400 (15)	C22—N23	1.311 (3)
C31—O31	1.262 (2)	C22—N21	1.349 (3)
C31—O32	1.265 (2)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···N23	0.93	2.13	3.041 (3)	166
O1—H1B···O32	0.95	1.78	2.736 (2)	175
O33—H3···O1W^{i}	0.95	1.76	2.704 (2)	172
O1W—H1···N23	0.93	2.08	2.994 (2)	168
O1W—H2···O32	0.89	2.00	2.884 (2)	173
N11—H11···O32^{ii}	0.86	2.17	2.934 (2)	147
N21—H21···O33^{ii}	0.86	2.10	2.887 (2)	153

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

Water H atoms and the hydroxy H atom were located in a difference Fourier map and refined as riding in their as-found relative positions (O—H = 0.89–0.95 Å), with $U_{iso}(H) = 1.5U_{eq}(O)$. Other H atoms were placed in calculated positions, C—H = 0.93 Å and N—H = 0.86 Å, and refined as riding, with $U_{iso}(H) = 1.2U_{eq}(C,N)$.

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

The project was supported by the National Natural Science Foundation of China (20443003).

References

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
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.* C**61**, m19–m21.
Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
Rigaku/MSC (2002). *CrystalStructure*. Version 3.00. Rigaku/MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Solomons, T. W. G. & Fryhle, C. B. (2000). *Organic Chem*istry, 7th ed. Jefferson, Missouri: von Hoffmann.
Zhang, B.-Y., Liu, J.-G. & Xu, D.-J. (2005). *Acta Cryst.* E**61**, m1128–m1130.