

Tetrakis(benzimidazole- κN)(malonato- $\kappa^2 O, O'$)cobalt(II)

Dong-Dong Lin, Yu Liu and Duan-Jun Xu*

Department of Chemistry, Zhejiang University, People's Republic of China

Correspondence e-mail: xudj@mail.hz.zj.cn

Key indicators

Single-crystal X-ray study

 $T = 295$ KMean $\sigma(C-C) = 0.005$ Å R factor = 0.045 wR factor = 0.092

Data-to-parameter ratio = 13.5

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

The title cobalt(II) compound, $[\text{Co}(\text{C}_3\text{H}_2\text{O}_4)(\text{C}_7\text{H}_6\text{N}_2)_4]$, displays an octahedral coordination geometry formed by four benzimidazole ligands and one malonate dianion. The malonate chelates to the Co^{II} atom with both terminal carboxyl groups in a boat configuration. The uncoordinated carboxyl O atoms of the malonate are hydrogen bonded to the neighboring benzimidazole ligands.

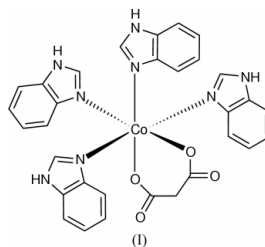
Received 29 July 2003

Accepted 13 August 2003

Online 23 August 2003

Comment

Aromatic π - π -stacking interactions have been observed in a number of metal complexes with aromatic heteropolycyclic ligands, such as phenanthroline, bithiazole and benzimidazole (Chen *et al.*, 2003). As part of our investigation into the π - π -stacking interactions in metal complexes, a new Co^{II} complex with benzimidazole has recently been prepared. However, its X-ray structure, presented here, shows no π - π stacking occurring in the complex.



The molecular structure of (I) is presented in Fig. 1. Four benzimidazole molecules and one malonate dianion form an octahedral coordination geometry around a Co^{II} atom. The $\text{Co}-\text{N}13-\text{C}19$ angle of 133.02 (17) $^\circ$ is much larger than the $\text{Co}-\text{N}13-\text{C}12$ angle of 122.45 (19) $^\circ$. Likewise the $\text{Co}-\text{N}33-\text{C}39$ angle of 134.97 (17) $^\circ$ is much larger than the $\text{Co}-\text{N}33-\text{C}32$ angle of 120.99 (19) $^\circ$. However, the $\text{Co}-\text{N}$ bonds involving atoms $\text{N}13$ and $\text{N}33$ are not significantly longer than the other two $\text{Co}-\text{N}$ bonds (Table 1).

The malonate dianion chelates to the Co^{II} atom with both terminal carboxyl groups in a boat configuration. The uncoordinated carboxyl O atoms of the malonate are hydrogen bonded to the neighboring benzimidazole ligands, as shown in Fig. 2. A three-centered hydrogen bond occurs between benzimidazole atom $\text{N}31$ and the carboxyl groups (see Table 2). The molecular packing diagram is illustrated in Fig. 3. No π - π stacking is observed between benzimidazole rings in the crystal.

Experimental

An ethanol solution (10 ml) of benzimidazole (0.47 g, 4 mmol) was mixed with an aqueous solution (10 ml) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.24 g,

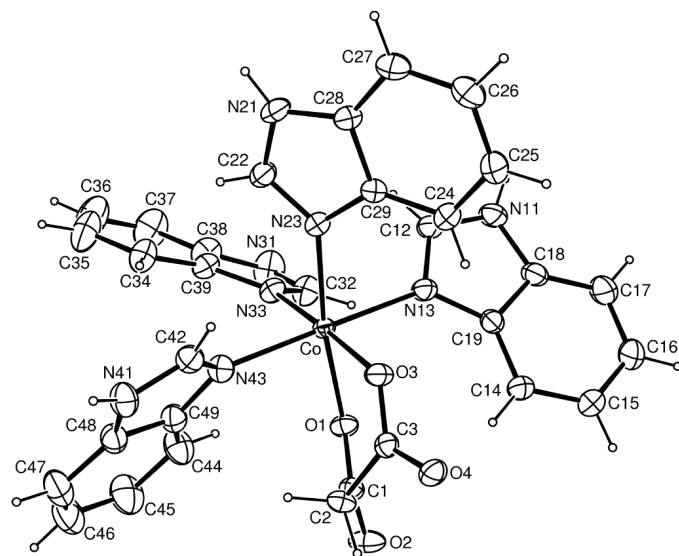


Figure 1
The structure of (I), showing 30% probability displacement ellipsoids.

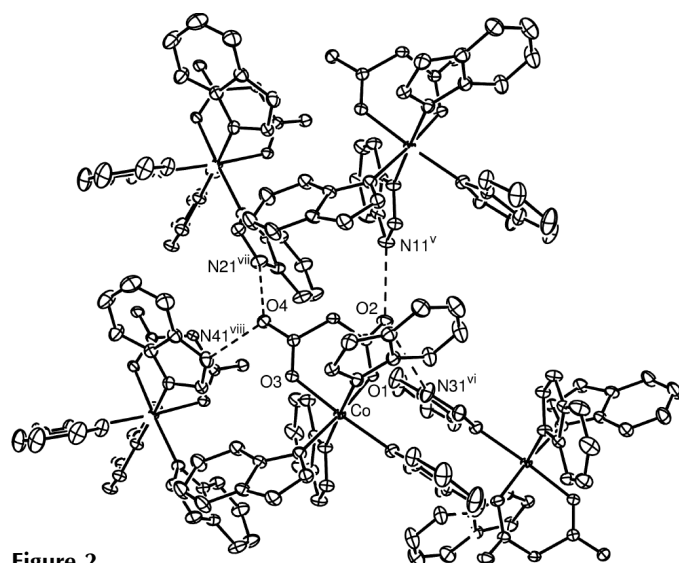


Figure 2
A diagram showing the hydrogen bonding between uncoordinated carboxyl O atoms and benzimidazole ligands. [Symmetric codes: (v) $x - 1, y, z$; (vi) $1 - x, -y, 1 - z$; (vii) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$; (viii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$].

1 mmol) at room temperature. An aqueous solution (6 ml) containing malonic acid (0.10 g, 1 mmol) and Na_2CO_3 (0.11 g, 1 mmol) was added to the above solution with stirring at room temperature. Then the mixture was refluxed for 1 h and filtered. Blue single crystals were obtained after 3 d.

Crystal data

$[\text{Co}(\text{C}_3\text{H}_2\text{O}_4)(\text{C}_7\text{H}_6\text{N}_2)_4]$	$D_x = 1.396 \text{ Mg m}^{-3}$
$M_r = 633.53$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 18608 reflections
$a = 9.2068 (12) \text{ \AA}$	$\theta = 2.0\text{--}25.0^\circ$
$b = 25.0492 (16) \text{ \AA}$	$\mu = 0.62 \text{ mm}^{-1}$
$c = 13.8555 (13) \text{ \AA}$	$T = 295 (2) \text{ K}$
$\beta = 109.444 (15)^\circ$	Prism, blue
$V = 3013.2 (6) \text{ \AA}^3$	$0.22 \times 0.15 \times 0.10 \text{ mm}$
$Z = 4$	

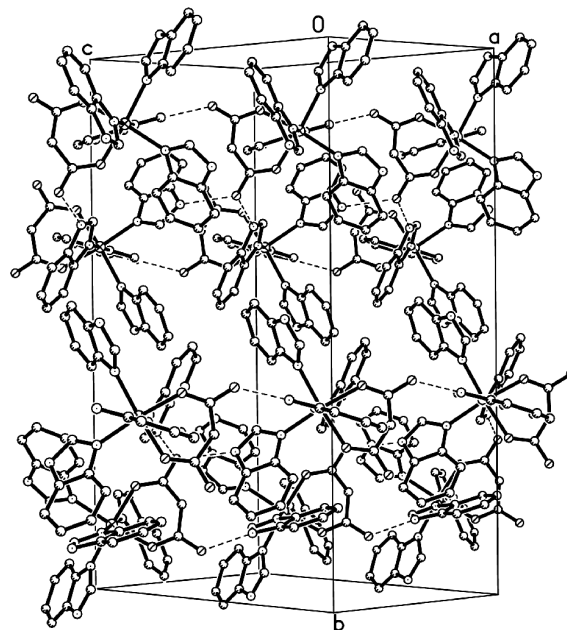


Figure 3
The molecular packing diagram.

Data collection

Rigaku R-Axis RAPID diffractometer	5357 independent reflections
ω scans	4289 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$R_{\text{int}} = 0.051$
$T_{\text{min}} = 0.868, T_{\text{max}} = 0.932$	$\theta_{\text{max}} = 25.2^\circ$
20267 measured reflections	$h = -11 \rightarrow 10$
	$k = -30 \rightarrow 30$
	$l = -14 \rightarrow 16$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0381P)^2 + 1.1717P]$
$R[F^2 > 2\sigma(F^2)] = 0.045$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.092$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.09$	$\Delta\rho_{\text{max}} = 0.29 \text{ e \AA}^{-3}$
5357 reflections	$\Delta\rho_{\text{min}} = -0.29 \text{ e \AA}^{-3}$
397 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters ($\text{\AA}, ^\circ$).

Co—O3	2.0684 (18)	Co—N23	2.122 (2)
Co—O1	2.0741 (17)	Co—N13	2.129 (2)
Co—N43	2.098 (2)	Co—N33	2.138 (2)
C12—N13—Co	122.45 (19)	C32—N33—Co	120.99 (19)
C19—N13—Co	133.02 (17)	C39—N33—Co	134.97 (17)
C22—N23—Co	128.66 (19)	C42—N43—Co	125.23 (18)
C29—N23—Co	126.61 (16)	C49—N43—Co	129.37 (18)

Table 2

Hydrogen-bonding geometry ($\text{\AA}, ^\circ$).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
N11—H11 \cdots O2 ⁱ	0.86	1.86	2.709 (3)	169
N21—H21 \cdots O4 ⁱⁱ	0.86	1.93	2.764 (3)	162
N31—H31 \cdots O1 ⁱⁱⁱ	0.86	2.06	2.870 (3)	156
N31—H31 \cdots O2 ⁱⁱⁱ	0.86	2.31	3.045 (3)	143
N41—H41 \cdots O4 ^{iv}	0.86	1.98	2.741 (3)	147

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

H atoms were included in the riding-model approximation, with C—H distances of 0.93 Å (benzimidazole) or 0.97 Å (malonate) and N—H distances of 0.86 Å, and were allowed for in the final cycles of refinement in the riding mode, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$ of the parent atom.

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

The authors thank Dr Jian-Ming Gu for assistance with the data collection.

References

- Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
- 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.
- Rigaku (1998). *PROCESS-AUTO*. Version 1.06. Rigaku Corporation, Tokyo, Japan.
- Rigaku/MS & Rigaku (2002). *CrystalStructure*. Version 3.00. Rigaku/MS, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA, and Rigaku Corporation, Akishima, Tokyo, Japan.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.