

Bing-Yu Zhang, Tu-Gen Xu[‡] and
Duan-Jun Xu*Department of Chemistry, Zhejiang University,
People's Republic of China[‡] Department of Chemistry Hangzhou Teachers
College People's Republic of China

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

Key indicators

Single-crystal X-ray study

T = 295 K

Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$

R factor = 0.040

wR factor = 0.096

Data-to-parameter ratio = 17.0

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>. **μ -Aqua-bis(μ -4-methylbenzoato- $\kappa^2\text{O}:\text{O}'$)-
bis[(4-methylbenzoato- κO)(phenanthroline-
 $\kappa^2\text{N},\text{N}'$)cobalt(II)]**

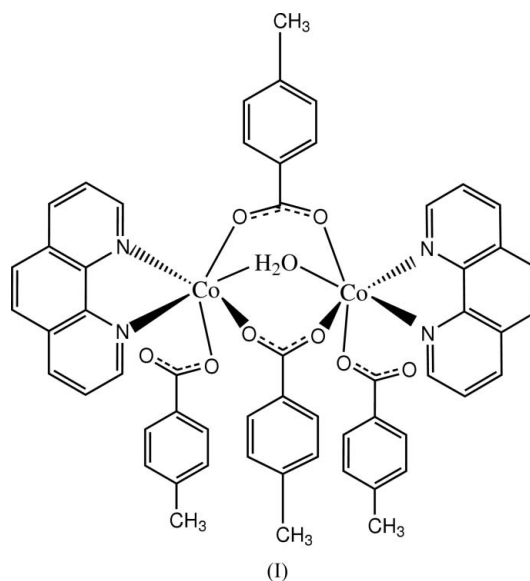
The title dinuclear Co^{II} complex, $[\text{Co}_2(\text{C}_8\text{H}_7\text{O}_2)_4(\text{C}_{12}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})]$, has C_2 symmetry with the coordinated water O atom located on a twofold axis. Two Co^{II} ions are bridged by two methylbenzoate (MBZ) anions and one water molecule. Each Co^{II} ion displays a distorted octahedral coordination geometry. π - π Stacking occurs between roughly parallel MBZ and phenanthroline (phen) ligands and between parallel phen ligands.

Received 10 August 2006

Accepted 11 August 2006

Comment

Over the past few years, we have paid much attention to π - π stacking in metal complexes (Chen *et al.*, 2003; Li *et al.*, 2005) because π - π stacking between aromatic rings is an important non-covalent interaction and is correlated with the electron-transfer process in some biological systems (Deisenhofer & Michel, 1989). As part of an investigation on the nature of π - π stacking, we prepared the title methylbenzoate complex of Co^{II} , (I), and present here its crystal structure.



The molecular structure of (I) is shown in Fig. 1. The dinuclear Co^{II} complex has C_2 symmetry; the coordinated water O atom O5 is located on a twofold axis and bridges two Co^{II} ions. The Co^{II} ion assumes a distorted octahedral coordination geometry (Table 1) formed by a phenanthroline (phen) ligand, a coordinated water molecule and three 4-methylbenzoate (MBZ) anions. One MBZ coordinates in monodentate mode to each Co^{II} ion, and other two MBZ anions bridge Co^{II} ions, forming the dinuclear molecule. Atom Co^{I} [symmetry code: (i) $1 - x, y, -z + \frac{3}{2}$] is displaced by

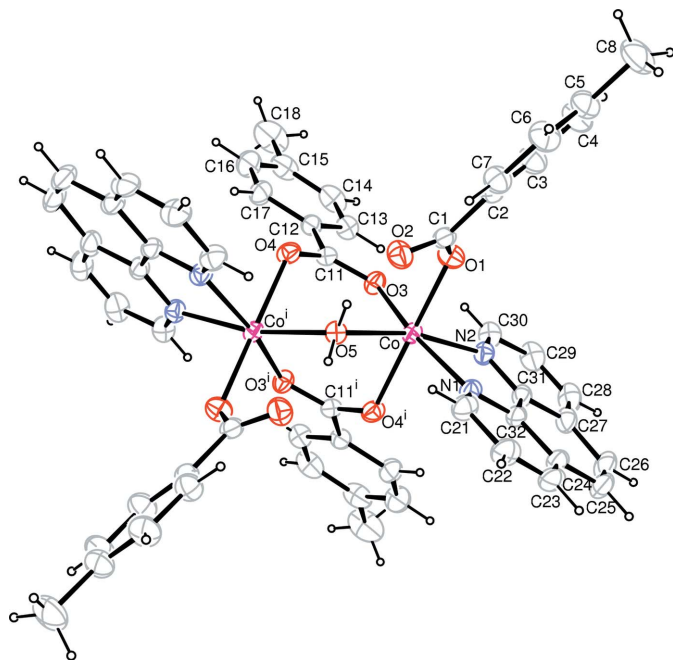


Figure 1
The molecular structure of (I) with 30% probability displacement ellipsoids (arbitrary spheres for H atoms) [symmetry code: (i) $1 - x, y, -z + \frac{3}{2}$].

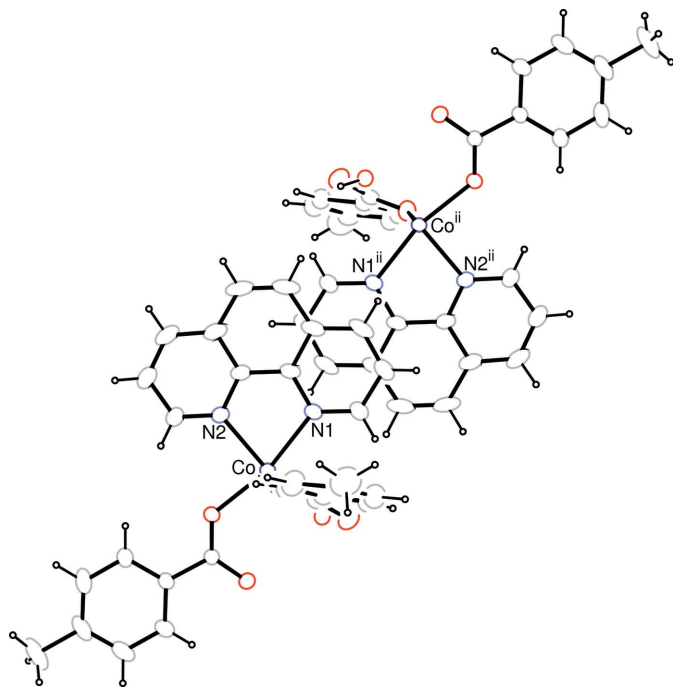


Figure 2
 π - π Stacking between parallel phen ligands [symmetry code: (ii) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$].

1.485 (6) Å from the C11-carboxyl plane whereas the Co atom is coplanar with the C11-carboxyl plane [deviation 0.021 (8) Å]. This implies a poor overlap between the atomic orbitals of atoms Coⁱ and O4. However, the Coⁱ—O4 bond distance is almost identical with the Co—O3 bond distance

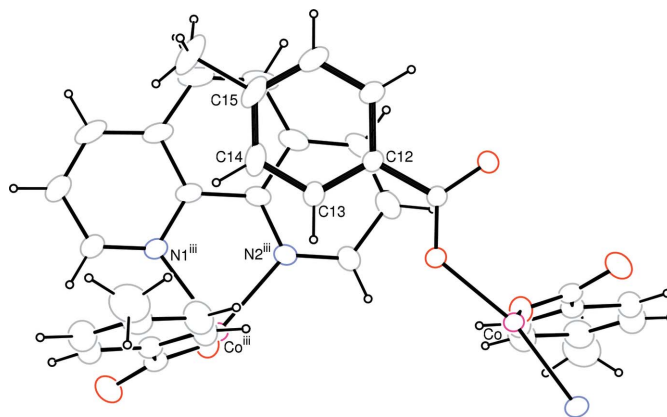


Figure 3
 π - π Stacking between roughly parallel phen and MBZ ligands [symmetry code: (iii) $1 - x, 1 - y, 1 - z$].

(Table 1), suggesting some element of electrostatic interaction in the Co—O bonding.

The face-to-face separation of 3.334 (5) Å between parallel, partially overlapped N1-phen and N1ⁱⁱ-phen [symmetry code: (ii) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$] ligands clearly indicates the existence of π - π stacking (Fig. 2). In addition, a partially overlapped arrangement is observed between roughly parallel [dihedral angle 8.56 (10)°] phen and MBZ ligands (Fig. 3). The distances of MBZ atoms to the N1ⁱⁱⁱ-phen mean plane are 3.416 (2) (C12), 3.259 (2) (C13), 3.301 (3) (C14) and 3.485 (3) Å (C15). These short separations suggest the existence of π - π stacking between phen and MBZ ligands in the crystal structure of (I).

The coordinated water molecule is hydrogen bonded with the adjacent uncoordinated carboxyl atom O2 (Table 2).

Experimental

An acetonitrile/water (1:1) solution (20 ml) containing 4-methylbenzoic acid (1.36 g, 10 mmol), NaOH (0.40 g, 10 mmol), phen (1.98 g, 10 mmol) and CoCl₂·6H₂O (2.37 g, 1 mmol) was refluxed for 4 h and then filtered. Single crystals of (I) were obtained from the filtrate after 4 d.

Crystal data

[Co₂(C₈H₇O₂)₄(C₁₂H₈N₂)₂(H₂O)]
 $M_r = 1036.83$
 Monoclinic, C2/c
 $a = 23.3452$ (15) Å
 $b = 15.5790$ (13) Å
 $c = 15.5765$ (12) Å
 $\beta = 121.746$ (12)°
 $V = 4817.5$ (9) Å³

$Z = 4$
 $D_x = 1.430$ Mg m⁻³
 Mo K α radiation
 $\mu = 0.75$ mm⁻¹
 $T = 295$ (2) K
 Prism, red
 $0.32 \times 0.24 \times 0.20$ mm

Data collection

Rigaku R-AXIS RAPID
 diffractometer
 ω scans
 Absorption correction: multi-scan
 ABCOR (Higashi, 1995)
 $T_{\min} = 0.778, T_{\max} = 0.862$

22736 measured reflections
 5479 independent reflections
 4441 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.030$
 $\theta_{\text{max}} = 27.4^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.096$
 $S = 1.11$
 5479 reflections
 323 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0492P)^2 + 2.0407P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.30 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.47 \text{ e } \text{\AA}^{-3}$

Table 1

Selected bond lengths (\AA).

Co—N1	2.1633 (16)	Co—O3	2.0732 (13)
Co—N2	2.1342 (16)	Co—O4 ⁱ	2.0838 (13)
Co—O1	2.0755 (14)	Co—O5	2.1708 (11)

Symmetry code: (i) $-x + 1, y, -z + \frac{3}{2}$.

Table 2

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O5—H5A ⁱ ··O2 ⁱ	0.85	1.77	2.570 (2)	156

Symmetry code: (i) $-x + 1, y, -z + \frac{3}{2}$.

Methyl H atoms were placed in calculated positions with C—H = 0.96 \AA and torsion angles were refined to fit the electron density,

$U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. Aromatic H atoms were placed in calculated positions with C—H = 0.93 \AA , and refined in riding mode with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The water H atom was located in a difference Fourier map and refined as riding in its as-found relative position, $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

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

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.
- Chen, Z., Xu, D.-J., Li, Z.-Y., Wu, J.-Y. & Chiang, M. Y. (2003). *J. Coord. Chem.* **56**, 253–259.
- Deisenhofer, J. & Michel, H. (1989). *EMBO J.* **8**, 2149–2170.
- 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.
- Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
- Rigaku/MSK and Rigaku (2002). *CrystalStructure*. Version 3.00. Rigaku/MSK, The Woodlands, TX 77381-5209, USA.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.