Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

μ-Aqua-bis(*μ*-2′-carboxybiphenyl-2-carboxylato-κ^2O:O')bis[bis(2′-carboxybiphenyl-2-carboxylato-κO)(1,10-phenanthroline-κ^2N,N')-cobalt(II)]

Qian Miao,* Mao-Lin Hu and Fan Chen

Department of Chemistry and Materials Science, Wenzhou Normal College, Wenzhou 325027, People's Republic of China

Correspondence e-mail:
mq0577@yahoo.com.cn

Received 12 August 2004
Accepted 17 August 2004
Online 28 August 2004

In the title complex, $[Co_2(C_{14}H_9O_4)_4(C_{12}H_8N_2)_2(H_2O)]$, each Co^{2+} cation is surrounded by two N atoms from a 1,10-phenanthroline (phen) ligand and four O atoms [one from a water molecule, one from a monodentate 2′-carboxybiphenyl-2-carboxylate (Hbpdc) ligand and two from two bridging Hbpdc ligands), thus forming a distorted CoO_4N_2 octahedron. The two Co^{2+} cations are bridged by two Hbpdc anions *via* their carboxylate groups to produce an eight-membered dinuclear ring. The Co centres are also bridged by a water molecule, this latter species lying on a twofold axis.

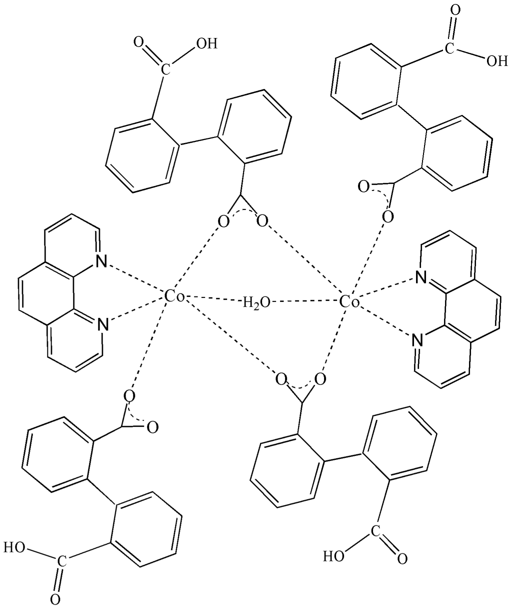
Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.014 Å
R factor = 0.117
wR factor = 0.247
Data-to-parameter ratio = 12.5

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

Comment

Carboxylate anions possess versatile binding modes to metal cations, such as monodentate, chelating bidentate, bridging bidentate and bridging tridentate, thereby generating varied and sometimes surprising molecular architectures (Zhang *et al.*, 1990). Therefore, metal complexes with carboxylate anions have been extensively studied (Hu *et al.*, 2003; Wang *et al.*, 2003), also including several 4,4′-biphenyldicarboxylate complexes (Almeida Paz *et al.*, 2002; Zhang *et al.*, 2004). However, complexes constructed from 2,2′-biphenyldicarboxylate anions and metal cations are still limited. Thus, we have selected the Co—Hbpdc–phen system (Hbpdc is 2′-carboxybiphenyl-2-carboxylate and phen is 1,10-phenanthroline) to extend this area of research and present here the crystal structure of $[Co_2(Hbpdc)_4(phen)_2(H_2O)]$, (I).



(I)

In (I), the Co centre possesses a distorted octahedral geometry (Fig. 1 and Table 1). The basal plane consists of two phen N atoms, one carboxylate O atom from an Hbpdc anion and one aqua O atom, while the two apical positions are filled with two carboxylate O atoms from two other Hbpdc anions. The mean deviation of the octahedral basal plane composed of atoms N1, N2, O5 and O9 is only 0.0330 Å. The axial Co1—O1 and Co1—O6^{i} (see Table 1 for symmetry code) bond distances are 2.150 (5) and 2.097 (5) Å, respectively. The Co—O and Co—N bond distances in (I) are within the ranges of those observed for related structures [*e.g.* Co—O$_c$ (c = carboxylate) = 2.024–2.155 Å and Co—N$_{\rm phen}$ = 2.093–2.155 Å (Hu *et al.*, 2004)]. The overall [Co_2(Hbpdc)$_4$(phen)$_2$(H_2O)] complex is generated by twofold symmetry; the two Co atoms are bridged by two Hbpdc anions *via* their carboxylate groups to produce an eight-membered dinuclear ring with a Co1$\cdots$Co1^{i} separation of 3.6615 (16) Å. The water molecule (O9) also bridges the Co atoms and lies on a twofold axis.

Thus, the two independent Hbpdc anions in (I) show two different coordination modes: one is bridging bidentate and the other is monodentate. It is worth noting that monodentate coordination mode results in a larger dihedral angle [82.3 (3)°] between two benzene rings as compared with the smaller dihedral angle [59.4 (3)°] between those in the bridging bidentate coordination mode, indicating the flexible nature of the C—C single bond linking the benzene rings in the Hbpdc anion.

The crystal packing in (I) is stabilized by O—H$\cdots$O hydrogen bonds, as listed in Table 2, including Hbpdc–Hbpdc and water–Hbpdc links.

Experimental

Compound (I) was hydrothermally synthesized from a mixture of 2,2′-biphenyldicarboxylate (2 mmol, 0.48 g), $CoCl_2 \cdot 4H_2O$ (1 mmol, 0.20 g), 1,10-phenanthroline (3 mmol, 0.54 g) and water (20 ml) in a 30 ml Teflon-lined stainless steel reactor. The solution was heated to 420 K for 3 d. After the reaction system had been slowly cooled to room temperature, red block-shaped crystals were collected and washed with distilled water (yield: 68%).

Crystal data

[$Co_2(C_{14}H_9O_4)_4(C_{12}H_8N_2)_2(H_2O)$]
M_r = 1461.13
Monoclinic, $C2/c$
a = 32.2977 (7) Å
b = 10.2480 (3) Å
c = 22.6078 (7) Å
β = 117.237 (1)°
V = 6653.2 (3) Å^3
Z = 4
D_x = 1.459 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3246 reflections
θ = 2.5–23.6°
μ = 0.58 mm^{-1}
T = 298 (2) K
Block, red
0.41 × 0.16 × 0.14 mm

Data collection

Bruker SMART APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{\rm min}$ = 0.798, $T_{\rm max}$ = 0.924
16951 measured reflections
5871 independent reflections
5697 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.048
$\theta_{\rm max}$ = 25.0°
$h = -38 \rightarrow 37$
$k = -10 \rightarrow 12$
$l = -26 \rightarrow 26$

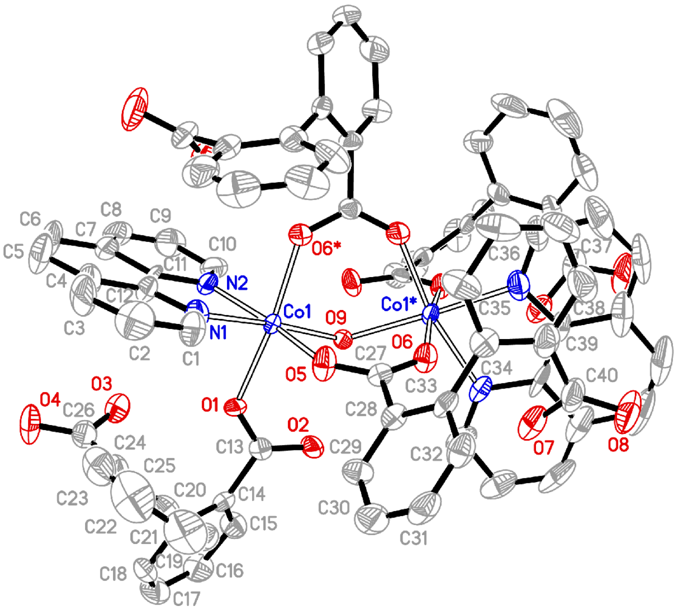


Figure 1
The molecular structure of (I), showing displacement ellipsoids at the 50% probability level. H atoms have been omitted for clarity. The Co1* and O6* species are generated by the symmetry code ($2 - x, y, \frac{1}{2} - z$).

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.117
$wR(F^2)$ = 0.247
S = 1.43
5871 reflections
470 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0582P)^2 + 63.3018P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.001
$\Delta\rho_{\rm max}$ = 0.57 e Å^{-3}
$\Delta\rho_{\rm min}$ = −1.04 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—O5	2.049 (5)	Co1—N2	2.145 (6)
Co1—O6^{i}	2.097 (5)	Co1—O9	2.150 (4)
Co1—N1	2.115 (6)	Co1—O1	2.150 (5)
O5—Co1—O6^{i}	96.5 (2)	N1—Co1—O9	175.9 (2)
O5—Co1—N1	90.5 (2)	N2—Co1—O9	102.8 (2)
O6^{i}—Co1—N1	92.0 (2)	O5—Co1—O1	93.2 (2)
O5—Co1—N2	168.5 (2)	O6^{i}—Co1—O1	170.3 (2)
O6^{i}—Co1—N2	84.1 (2)	N1—Co1—O1	88.1 (2)
N1—Co1—N2	77.9 (3)	N2—Co1—O1	86.4 (2)
O5—Co1—O9	88.75 (18)	O9—Co1—O1	87.96 (18)
O6^{i}—Co1—O9	92.07 (17)	Co1^{i}—O9—Co1	116.8 (3)

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O3—H3$\cdots$O1	0.82	1.87	2.684 (7)	173
O7—H7$\cdots$O6	0.82	1.93	2.745 (7)	172
O9—H9$A\cdots$O2^{i}	0.92 (8)	1.68 (8)	2.590 (6)	174 (8)
O9—H9$A\cdots$O1^{i}	0.92 (8)	2.47 (8)	2.986 (5)	116 (7)

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

Acta Cryst. (2004). E**60**, m1314–m1316 Miao *et al.* • [$Co_2(C_{14}H_9O_4)_4(C_{12}H_8N_2)_2(H_2O)$] **m1315**

Water H atoms were located from difference density maps and were refined without constraints. The other H atoms were positioned geometrically and allowed to ride on their parent atoms at distances of 0.93 (C—H) and 0.82 Å (O—H), and with $U_{\mathrm{iso}} = 1.2U_{\mathrm{eq}}$(parent atom).

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Bruker, 2002); software used to prepare material for publication: *SHELXL*97.

We acknowledge financial support by the Zhejiang Provincial Technology Project Foundation of China (No. 2004 C32088) and the Zhejiang Provincial Natural Science Foundation of China (No. 202137).

References

Almeia Paz, F. A., Khimyak, Y. Z., Bond, A. D., Rocha, J. & Klinowki J. (2002). *Eur. J. Inorg. Chem.* pp. 2823–2828.

Bruker (2002). *SADABS* (Version 2.03), *SAINT* (Version 6.02), *SMART* (Version 5.62) and *XP*. Bruker AXS Inc., Madison, Wisconsin, USA.

Hu, M. L., Xiao, H. P., Wang, S. & Li, X. H. (2003). *Acta Cryst.* C**59**, m454–m455.

Hu, M. L., Yuan, J. X., Xiao, H. P. & Chen, F. (2004). *Acta Cryst.* C**60**, m235–m237.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Wang, M., Xia, J., Jin, L., Cai, G. & Lu, S. (2003). *J. Mol. Struct.* **655**, 443–449.

Zhang, D. L., Huang, C. H. & Xu, G. X. (1990). *Chin. J. Chem.* **8**, 529–535.

Zhang, S. Y., Yu, M. X. & Zhu, L. G. (2004). *J. Mol. Struct.* **699**, 101–104.

m1316 Miao *et al.* • $[\mathrm{Co_2(C_{14}H_9O_4)_4(C_{12}H_8N_2)_2(H_2O)}]$ *Acta Cryst.* (2004). E**60**, m1314–m1316