Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Bis(4-formylbenzoato-κ^2O,O')(1,10-phenanthroline-κ^2N,N')cadmium(II)–bis(μ_2-4-formylbenzoato-κ^2O:O')bis[(4-formylbenzoato-κ^2O,O')(1,10-phenanthroline-κ^2N,N')cadmium(II)] (1/1)

Zhao-Peng Deng,[a] Shan Gao[a] and Seik Weng Ng[b]*

[a]College of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, People's Republic of China, and [b]Department of Chemistry, University of Malaya, Kuala Lumpur 50603, Malaysia

Correspondence e-mail: seikweng@um.edu.my

Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.006 Å
R factor = 0.033
wR factor = 0.069
Data-to-parameter ratio = 16.8

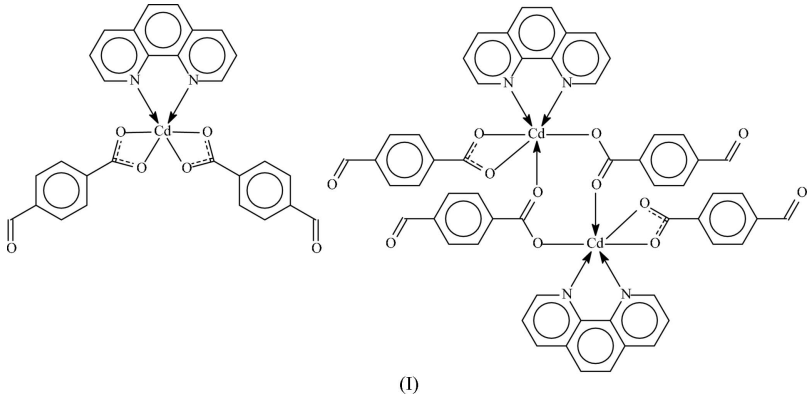
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 6 November 2006
Accepted 12 November 2006

The title compound, $[Cd(C_8H_5O_3)_2(C_{12}H_8N_2)][Cd_2(C_8H_5O_3)_4(C_{12}H_8N_2)_2]$, having the empirical formulation bis(4-formylbenzoato)(1,10-phenanthroline)cadmium(II), is a 1/1 cocrystal consisting of mononuclear and dinuclear molecules. In the monomeric molecule that lies on a special position of site symmetry 2, cadmium is chelated by the *N*-heterocycle as well as by both carboxylate units in a *cis*-octahedral geometry. The dimeric molecule lies on another special position of site symmetry 2 that relates two monomeric units; the octahedral Cd atom is chelated by one carboxylate group and the *N*-heterocycle; the other carboxylate group functions as a carboxylate bridge between the two metal atoms.

Comment

Cadmium bis(4-formylbenzoate) forms with imidazole a dimeric 1/2 adduct in which both carboxylate groups chelate the metal atom; the six-coordinate status is raised to a seven-coordinate pentagonal bipyramidal arrangement as the O atom of one of the carboxylate groups also interacts with metal atom of a symmetry-related monomeric molecule. The chelating group shows unambiguous short and long Cd–O bonds [2.367 (3), 2.573 (2) Å]. However, in the bridging group, the intra-monomer [2.434 (2), 2.494 (2) Å] and inter-monomer [2.441 (2) Å] bonds are of almost the same length (Deng *et al.*, 2006*a*). The coordination status of the metal in cadmium bis(4-formylbenzoate) adducts appear to be sensitive to the nature of the *N*-heterocycle; for example, in the adduct with the larger benzimidazole ligand, one carboxylate is chelating whereas the other is only monodentate. Moreover, sevenfold coordination is not achieved as a water molecule completes the coordination geometry (Deng *et al.*, 2006*b*). Curiously, 1,10-phenanthroline affords a 1/1 adduct, (I), that is made up of mononuclear and dinuclear molecules.



(I)

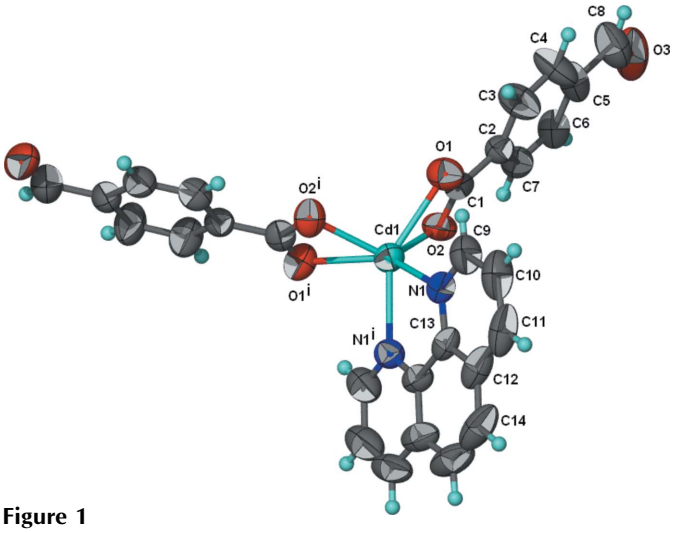


Figure 1
The structure of the mononuclear bis(4-formylbenzoato)(1,10-phenanthroline)cadmium molecule. Displacement ellipsoids are drawn at the 50% probability level, and H atoms are drawn as spheres of arbitrary radii. Symmetry code: (i) $2-x, 1-y, z$].

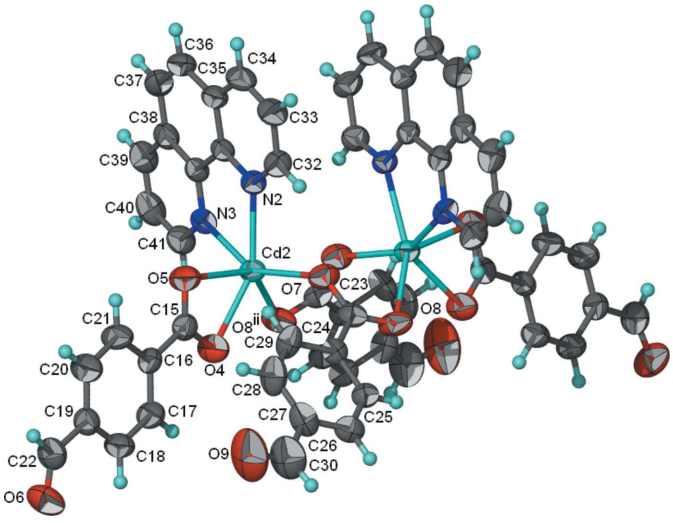


Figure 2
The structure of the dinuclear bis[bis(4-formylbenzoato)(1,10-phenanthroline)cadmium] molecule. Displacement ellipsoids are drawn at the 50% probability level, and H atoms are drawn as spheres of arbitrary radii [symmetry code: (ii) $1-x, 1-y, z$].

The mononuclear molecule, lying on a special position of site symmetry 2, shows chelation by both carboxylate groups and also by the *N*-heterocycle in a *cis*-octahedral geometry (Fig. 1). The dinuclear molecule, which lies on another special position of site symmetry 2, is chelated by only one carboxylate group and by the *N*-heterocycle; the other carboxylate group functions as a bridge between the metal centers (Fig. 2).

Experimental

Cadmium diacetate trihydrate (0.14 g, 0.5 mmol) was added to a 1:1 aqueous ethanol solution (20 ml) of 4-formylbenzoic acid (0.15 g, 1 mmol) and 1,10-phenanthroline (0.10 g, 0.5 mmol). Sodium hydroxide solution was added to the solution to a pH of about 5. The filtered solution was set aside for a few days for the colorless prismatic crystals to separate. C, H and N elemental analysis: Calculated for $C_{84}H_{54}Cd_3N_6O_{18}$: C 56.92, H 3.07, N 4.74%; found: C 56.95, H 3.03, N 4.76%.

Crystal data

$[Cd(C_8H_5O_3)_2(C_{12}H_8N_2)]$-$[Cd_2(C_8H_5O_3)_4(C_{12}H_8N_2)_2]$
M_r = 1772.53
Orthorhombic, $P2_12_12$
a = 16.082 (3) Å
b = 23.602 (5) Å
c = 9.710 (2) Å
V = 3685.6 (13) Å^3
Z = 2
D_x = 1.597 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.94 mm^{-1}
T = 295 (2) K
Prism, colorless
0.36 × 0.25 × 0.18 mm

Data collection

Rigaku R-AXIS RAPID IP diffractometer
ω scan
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.585, T_{max} = 0.850
35764 measured reflections
8434 independent reflections
6532 reflections with $I > 2\sigma(I)$
R_{int} = 0.042
θ_{max} = 27.5°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.069
S = 0.99
8434 reflections
502 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0353P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Absolute structure: Flack (1983), 3774 Friedel pairs
Flack parameter: 0.30 (2)

Table 1
Selected bond lengths (Å).

Cd1—O1	2.410 (3)	Cd2—O7	2.316 (2)
Cd1—O2	2.256 (3)	Cd2—O8^{ii}	2.301 (2)
Cd1—N1	2.298 (3)	Cd2—N2	2.335 (3)
Cd2—O4	2.317 (3)	Cd2—N3	2.345 (3)
Cd2—O5	2.432 (3)		

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

Carbon-bound H atoms were positioned geometrically (C—H = 0.93 Å) and were included in the refinement in the riding-model approximation, with U_{iso}(H) set to 1.2U_{eq}(C). The crystal is an inversion twin, the second twin component refining to 0.30 (2). The vibration of the C, N and O atoms was restrained to be nearly isotropic.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2006).

We thank the Heilongjiang Province Natural Science Foundation (No. B200501), the Scientific Fund for Remarkable Teachers of Heilongjiang Province (No. 1054 G036) and the University of Malaya for supporting this study.

References

Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
Deng, Z.-P., Gao, S. & Ng, S. W. (2006*a*). *Acta Cryst.* E**62**, m3249–m3250.
Deng, Z.-P., Gao, S. & Ng, S. W. (2006*b*). *Acta Cryst.* E**62**, m3251–m3253.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Rigaku (1998). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
Rigaku/MSC (2002). *CrystalStructure*. Rigaku/MSC Inc., The Woodlands, Texas, USA.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Westrip, S. P. (2006). *publCIF*. International Union of Crystallography, Chester, England.