

Cadmium binicotinate

Xiao-Chun Huang,^{a,b} Lin-Yun Zhang,^b Xiao-Ming Chen^b and Seik Weng Ng^{b,c*}

^aDepartment of Chemistry, Shantou University, Shantou 515063, People's Republic of China, ^bSchool of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, People's Republic of China, and ^cDepartment of Chemistry, University of Malaya, 50603, Kuala Lumpur, Malaysia

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

Key indicators

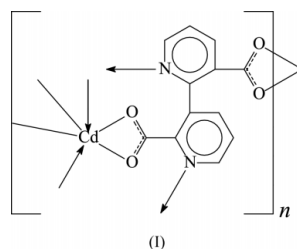
Single-crystal X-ray study
 T = 294 K
 Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
 R factor = 0.019
 wR factor = 0.045
 Data-to-parameter ratio = 15.1

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

The binicotinate dianion in cadmium binicotinate, $[\text{Cd}(\text{C}_{12}\text{H}_6\text{N}_2\text{O}_4)]$, lies on a special position of 2 symmetry; the Cd atom lies on another special position of 2 symmetry. The carboxy CO_2 unit chelates to the Cd atom [$\text{Cd}-\text{O}$ 2.304 (2) and 2.396 (2) \AA]; the Cd atom is linked to one N atom of another binicotinate group [$\text{Cd}-\text{N1}$ 2.315 (2) \AA] and to the N atom of a third binicotinate group in a six-coordinate, distorted octahedral environment.

Comment

The nicotinate (3-pyridylcarboxylate) monoanion forms a large number of complexes with metal ions; the related binicotinate (2,2'-bipyridyl-3,3'-dicarboxylate) dianion exemplifies the multidentate nature of a dicarboxylate in having two nicotinate units connected together. A check through the November 2002 version of the Cambridge Structural Database (Allen, 2002) lists only metal derivatives having water inside and outside the coordination sphere but no anhydrous complexes. For example, in the Co^{II} derivative, two N atoms and the O atoms of two carboxy CO_2 groups are coordinated to the metal atom, but the six-coordinate geometry results from the two coordinated water ligands (Wu *et al.*, 2003; Zhang *et al.*, 2002).



The binicotinate dianion in cadmium binicotinate (Fig. 1) lies on a special position of 2 symmetry (Wyckoff 2*f*); the Cd atom lies on another special position of 2 symmetry (Wyckoff 2*g*). The carboxy unit chelates to the Cd atom [$\text{Cd}-\text{O}$ 2.304 (2), 2.396 (2) \AA]; the Cd atom is linked to one N atom of another binicotinate group [$\text{Cd}-\text{N1}$ 2.315 (2) \AA] and to the N atom of a third binicotinate group in a six-coordinate, distorted octahedral environment. The two pyridyl rings are perpendicular to each other [dihedral angle 87.7 (1) $^\circ$] but the carboxy unit of the ring is coplanar with it [dihedral angle 3.8 (1) $^\circ$]. The μ_4 nature of the dinicotinate entity gives rise to the formation of layers (Fig. 2). The related cadmium bis(nicotinate) exists as tricadmium hexanicotinate tetrahydrate. It features chelating and monodentate carboxy groups, and the pyridyl N atoms are all involved in coordination (Chen, 2003).

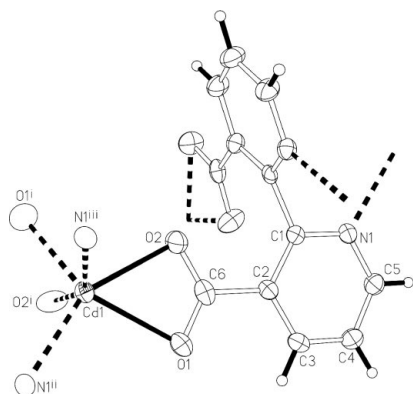


Figure 1
ORTEP (Johnson, 1976) plot (50% probability displacement ellipsoids), illustrating the coordination geometry of the Cd atom in cadmium binicotinate. H atoms are drawn as spheres of arbitrary radii. [Symmetry codes: (i) $\frac{3}{2} - y, \frac{3}{2} - x, \frac{3}{2} - z$; (ii) $x - 1, y, z$; (iii) $\frac{3}{2} - y, \frac{3}{2} - x, \frac{3}{2} - z$.]

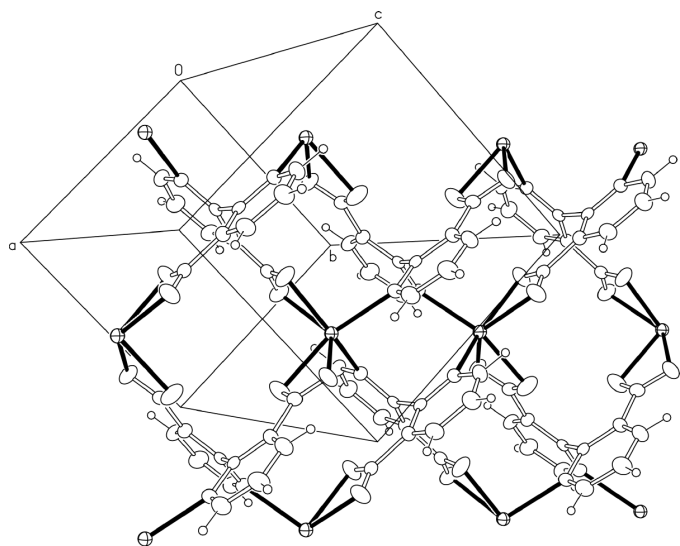


Figure 2
ORTEP (Johnson, 1976) plot (50% probability displacement ellipsoids), illustrating the layer structure of cadmium binicotinate. H atoms are drawn as spheres.

Experimental

Binicotinic acid was synthesized using a reported procedure (Wimmer & Wimmer, 1983). Cadmium diacetate tetrahydrate (0.30 g, 1.0 mmol), 2,2'-bipyridine-3,3'-dicarboxylic acid (0.24 g, 1.0 mmol), triethylamine (excess, 1 ml) and water (10 ml) were mixed together and the mixture then transferred into a 23 ml Teflon Parr bomb. The bomb was heated to 433 K for 80 h. The oven was cooled to room temperature at a rate of 5 K h⁻¹. Pale-yellow, needle-shaped crystals were obtained in about 30% yield. CH&N elemental analysis (calc./found) for C₁₂H₆CdN₂O₄: C 40.65 (40.71), H 1.71 (2.01), N 7.90% (7.83%).

Crystal data

[Cd(C₁₂H₆N₂O₄)]
M_r = 354.59
Tetragonal, *P* $\bar{4}$ n2
a = 8.1791 (6) Å
c = 16.420 (1) Å
V = 1098.4 (1) Å³
Z = 4
D_x = 2.144 Mg m⁻³

Mo K α radiation
Cell parameters from 2772 reflections
 θ = 3.5–28.2°
 μ = 2.00 mm⁻¹
T = 294 (2) K
Needle, yellow
0.30 × 0.10 × 0.10 mm

Data collection

Bruker SMART APEX area-detector diffractometer
 φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2001)
T_{min} = 0.678, T_{max} = 0.825
4888 measured reflections

1314 independent reflections
1276 reflections with $I > 2\sigma(I)$
R_{int} = 0.020
 θ_{\max} = 28.2°
h = -10 → 10
k = -9 → 8
l = -21 → 15

Refinement

Refinement on F²
R[F² > 2 σ (F²)] = 0.019
wR(F²) = 0.045
S = 1.05
1314 reflections
87 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0236P)^2 + 0.1528P]$
where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ)_{max} = 0.001
 $\Delta\rho_{\max} = 0.37 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.35 \text{ e } \text{Å}^{-3}$
Absolute structure: Flack (1983),
548 Friedel pairs
Flack parameter = -0.01 (3)

Table 1

Selected geometric parameters (Å, °).

Cd1—O1	2.396 (2)	Cd1—N1 ⁱⁱ	2.315 (2)
Cd1—O2	2.304 (2)	Cd1—N1 ⁱⁱⁱ	2.315 (2)
O1—Cd1—O1 ⁱ	135.0 (1)	O2—Cd1—O2 ⁱ	94.7 (1)
O1—Cd1—O2	55.9 (1)	O2—Cd1—N1 ⁱⁱ	152.0 (1)
O1—Cd1—O2 ⁱ	92.5 (1)	O2—Cd1—N1 ⁱⁱⁱ	90.0 (1)
O1—Cd1—N1 ⁱⁱ	96.4 (1)	N1 ⁱⁱ —Cd1—N1 ⁱⁱⁱ	98.7 (1)
O1—Cd1—N1 ⁱⁱⁱ	112.8 (1)		

Symmetry codes: (i) $\frac{3}{2} - y, \frac{3}{2} - x, \frac{3}{2} - z$; (ii) $x - 1, y, z$; (iii) $\frac{3}{2} - y, \frac{3}{2} - x, \frac{3}{2} - z$.

The three H atoms were placed at calculated positions in the riding model approximation (C—H = 0.93 Å), with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$ of the parent atoms.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEPII (Johnson, 1976); software used to prepare material for publication: SHELXL97.

The authors thank the National Natural Science Foundation of China (grant No. 20131020), the Natural Science Foundation of Guangdong Province (grant No. 036601) and the University of Malaya for the generous support of this work.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
Bruker (2001). SADABS, SAINT and SMART. Bruker AXS Inc., Madison, Wisconsin, USA.
Chen, H.-J. (2003). *Acta Cryst.* **C59**, m371–m372.
Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
Johnson, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA.
Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.
Wimmer, F. L. & Wimmer, S. (1983). *Org. Prep. Proc. Int.* **15**, 368–369.
Wu, B.-L., Zhang, H.-Q., Zhang, H.-Y., Wu, Q.-A., Hou, H.-W., Zhu, Y. & Wang, X.-Y. (2003). *Aust. J. Chem.* **56**, 335–338.
Zhang, G. H., Wei, Y. G., Wang, P. & Gua, H. Y. (2002). *Acta Cryst.* **C58**, m605–m607.