

A coordination polymer of CdCl₂ with the novel zwitterionic dicarboxylate ligand 2,2'-(2-methylbenzimidazolium-1,3-diyl)diacetate (pda)

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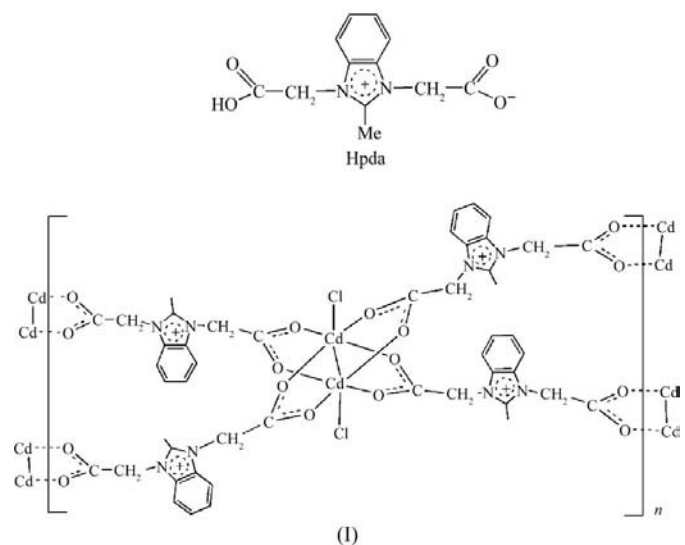
The title compound, poly[chlorido[μ_4 -2,2'-(2-methylbenzimidazolium-1,3-diyl)diacetato]cadmium(II)], [Cd(C₁₂H₁₁N₂O₄)Cl]_n, is an undulating two-dimensional polymer consisting of a paddlewheel Cd₂(CO₂)₄ cluster which lies on an inversion centre. These paddlewheel clusters act as four-connected square building units interlinked *via* bridging zwitterionic dicarboxylate ligands into a corrugated layer which is consolidated by π - π interactions between benzene rings of benzimidazole groups. Neighbouring layers are further assembled *via* interlayer π - π interactions into a three-dimensional supramolecular structure. The key feature of this study is the synthesis of a paddlewheel-based polymer constructed with a novel multifunctional zwitterionic dicarboxylate ligand.

Comment

Paddlewheel clusters of the type [M₂(CO₂R)₄], in which a metal dimer is bridged by four carboxylate groups, have been the subject of attention in the field of directed design and construction of metal-organic frameworks (MOFs) with desired topologies and specific properties, because of their known coordination properties and well defined shape (Abourahma *et al.*, 2003; Bourne *et al.*, 2001; Cotton *et al.*, 2002). When coordination occurs at the axial positions, the paddlewheel fragment may act as a ditopic linker to construct one-dimensional polymers, whereas the same cluster can act as a four-connected square unit when the linkage occurs at the equatorial sites through the use of polycarboxylate ligands. Yaghi and co-workers have described the behaviour of four-connected square moieties as building blocks in MOFs (Kim *et al.*, 2001). Some interesting topologies, such as discrete three-dimensional porous molecules (Cotton *et al.*, 2001; Ni *et al.*, 2005), interpenetration networks (Wang *et al.*, 2005), bowl-

shaped two-dimensional structures (Bourne *et al.*, 2001; Xue *et al.*, 2007), NbO-, PtS- or 4².8⁴ Ivt-type three-dimensional networks (Chen *et al.*, 2005; Wang *et al.*, 2005; Delgado-Friedrichs *et al.*, 2003), have been made, based on four-connected paddlewheel building blocks linked by linear dicarboxylate, angular dicarboxylate, tridirectional tricarboxylate or tetrahedral (square) carboxylate ligands. By controlling the features of the organic ligands, *viz.* size, shape, functionality, flexibility and symmetry, the topologies and properties of a large variety of coordination polymers can be finely tuned. Furthermore, it must be kept in mind that a variety of weak noncovalent interactions, such as hydrogen bonding, π - π interactions, van der Waals interactions and the like, also play an important role in the assembly of MOFs.

In studying the topologies and properties of MOFs based on the paddlewheel cluster, our efforts have been directed towards the synthesis of various supramolecular complexes based on multifunctional carboxylate ligands. In the present study, we used a long flexible zwitterionic dicarboxylate ligand, namely 2,2'-(2-methylbenzimidazolium-1,3-diyl)diacetate (pda) (Ni *et al.*, 2007), in which two carboxymethyl groups are attached to the two benzimidazole N atoms, giving the latter a positive charge. For charge balance in the free (monoprotonated) Hpda ligand, only one of the two carboxylate groups is protonated. The deprotonated pda ligand in the title compound, (I), contributes a single negative charge to the coordination framework. The flexibility of the ligand as a whole and the extended π conjugated system of benzimidazole are expected to play key roles in the topologies found for its metal complexes.



The asymmetric unit of (I) contains one pda ligand, one Cd²⁺ ion and one chloride anion. Each pair of Cd²⁺ ions is bridged by four carboxylate groups from four different pda ligands to form a paddlewheel cluster, Cd₂(CO₂)₄, which lies on an inversion centre (Fig. 1). The paddlewheels, acting as four-connected square building units, are bridged by pda to form a two-dimensional undulating sheet structure in which four adjacent paddlewheel units are linked to form a quadrilateral structural subunit. The void in the subunit is occupied

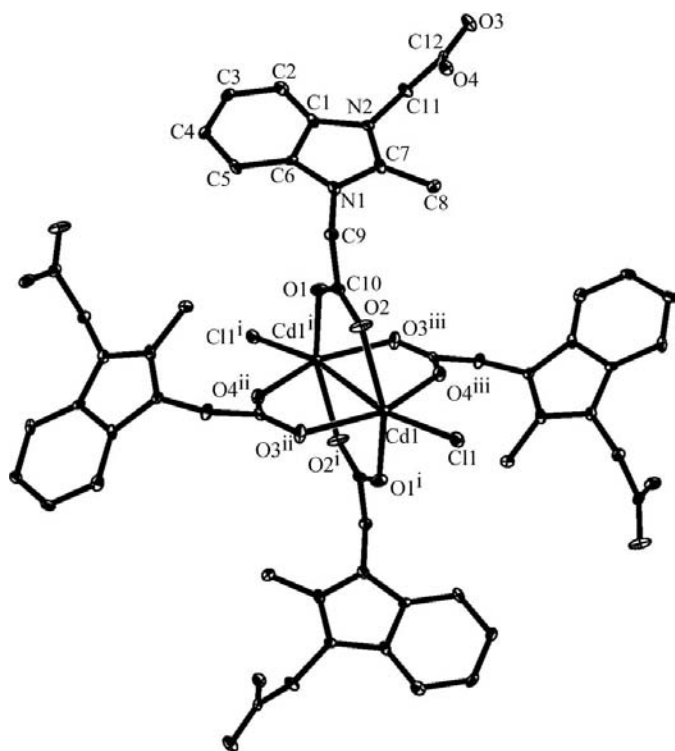


Figure 1

The molecular structure of (I), showing the atom-numbering scheme and the paddlewheel unit. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted. See Table 1 for symmetry codes.

by two benzene rings from two opposing ligands and two methyl groups from another two opposing ligands (Fig. 2). The axial positions of the paddlewheel cluster are occupied by chloride ions. The bond distances and angles around Cd^{2+} (Table 1) are comparable with those in other Cd paddlewheel units (Li & Mak, 1995). The two carboxylate groups of a given ligand lie on opposite sides of the benzimidazole plane. The dihedral angles between the carboxylate groups at C10 and C12 and the benzimidazole plane are $82.4(2)$ and $54.6(4)^\circ$, respectively, allowing neighbouring paddlewheel units to display pronounced canting relative to one another. The torsion angles C1-N2-C11-C12 and C6-N1-C9-C10 are $117.6(3)$ and $97.7(2)^\circ$, respectively. The carboxylate groups are tilted in such a way that one O atom of each is closer to the centroid of the positively charged imidazole ring [$\text{Cg}\cdots\text{O1} = 3.488(2)$ Å and $\text{Cg}\cdots\text{O4} = 3.476(3)$ Å; Cg represents the centroid of the imidazole ring].

One interesting feature of the pda ligand is the large conjugated π system of benzimidazole, which enables π - π interactions in the formation of MOFs (Hunter & Sanders, 1990; Wang *et al.*, 2008). In the crystal structure of (I), the benzene rings of the ligands at (x, y, z) and $(1-x, 2-y, -z)$, which are strictly parallel because they are related by inversion, have a perpendicular distance of $3.321(1)$ Å, a ring-centroid separation of $3.654(7)$ Å and a ring-centroid slippage of 1.523 Å. These π - π interactions play an important role in assembling the paddlewheel units into the undulating two-dimensional structure of (I), which is significantly different

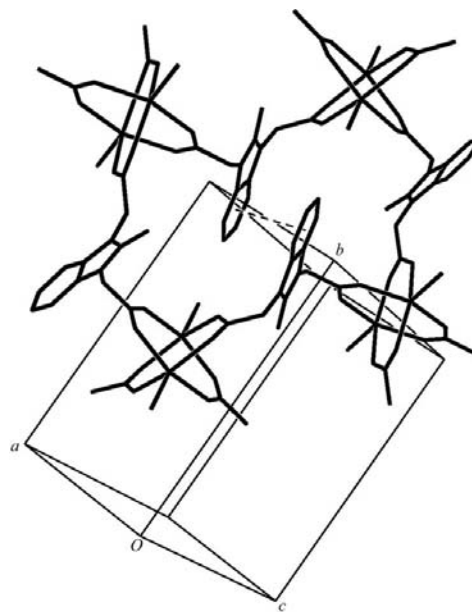


Figure 2

The undulating quadrilateral structural subunit of (I), with the π - π interaction shown as a dashed line.

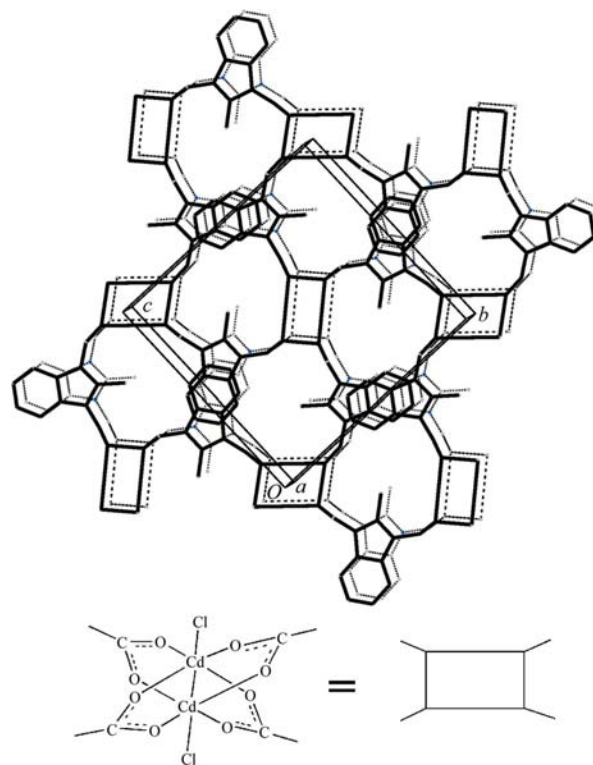


Figure 3

Schematic diagram of the three-dimensional supramolecular structure of (I), stabilized by interlayer π - π interactions. For clarity, the paddlewheel building block is simplified as a four-connected node.

from those of phenyldicarboxylate-containing paddlewheel polymers. Furthermore, the benzene rings involved in these intralayer π - π interactions occupy what would otherwise be voids in the polymer, obviating the possibility of molecular interpenetration, although the ligand is likely long enough to

form part of an interpenetrated structure. Similarly, a π - π interaction is observed between the benzene rings of the molecules at (x, y, z) and $(-x, 2 - y, -z)$ [perpendicular distance = 3.329 (2) Å, ring-centroid separation = 3.785 (3) Å and ring-centroid slippage = 1.799 Å].

The interlayer π - π interactions mediate a parallel assembly along the a axis, completing the three-dimensional supra-molecular structure (Fig. 3). Neighbouring layers are closely packed, with a nearest interlayer Cd...Cd distance of just 5.829 (4) Å. As a consequence of the efficient packing, the structure possesses a solvent-accessible volume of only 4.54% of the unit cell, as calculated by *PLATON* (Spek, 2003). No crystalline solvent is encapsulated in this compound.

Isostructural frameworks associated with CuCl₂, ZnCl₂ and MnCl₂ are also constructed by this ligand. Its flexibility, positively charged imidazole and large π -conjugated system bestow advantages on this ligand for the formation of extended MOFs.

Experimental

The pH of a 4:1 (v/v) ethanol-water solution (10 ml) containing CdCl₂·2H₂O (0.0658 g, 0.3 mmol) and Hpda (0.0498 g, 0.2 mmol) was adjusted to 7 using triethylamine. The solution was sealed in a Teflon-lined steel bomb (25 ml) and heated at 413 K for 2 d. Colourless block-shaped crystals were collected (yield 16%). Elemental analysis calculated for C₁₂H₁₁CdClN₂O₄: C 36.46, H 2.78, N 7.09%; found: C 36.62, H 2.92, N 7.35%.

Crystal data

[Cd(C ₁₂ H ₁₁ N ₂ O ₄)Cl]	$V = 1265.1 (3) \text{ \AA}^3$
$M_r = 395.08$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 7.2418 (9) \text{ \AA}$	$\mu = 1.95 \text{ mm}^{-1}$
$b = 13.4867 (17) \text{ \AA}$	$T = 173 (2) \text{ K}$
$c = 12.9531 (16) \text{ \AA}$	$0.40 \times 0.28 \times 0.16 \text{ mm}$
$\beta = 90.229 (2)^\circ$	

Data collection

Bruker SMART CCD area-detector diffractometer	5847 measured reflections
Absorption correction: multi-scan (<i>SADABS</i> ; Bruker, 1998)	2693 independent reflections
$T_{\min} = 0.555, T_{\max} = 0.732$	2241 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$	181 parameters
$wR(F^2) = 0.125$	H-atom parameters constrained
$S = 1.21$	$\Delta\rho_{\text{max}} = 1.04 \text{ e \AA}^{-3}$
2693 reflections	$\Delta\rho_{\text{min}} = -0.82 \text{ e \AA}^{-3}$

All H atoms were generated geometrically, with C—H distances of 0.95 (aromatic), 0.99 (methylene) or 0.98 Å (methyl) and with $U_{\text{iso}}(\text{H})$ values of 1.2 $U_{\text{eq}}(\text{C})$ for aromatic and methylene H atoms and 1.5 $U_{\text{eq}}(\text{C})$ for methyl H atoms.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINTE* (Bruker, 1998); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine

Table 1

Selected geometric parameters (Å, °).

Cd1—Cd1 ⁱ	3.3217 (7)	Cd1—Cl1	2.4395 (12)
Cd1—O2	2.241 (4)	O1—C10	1.238 (6)
Cd1—O1 ⁱ	2.245 (3)	O2—C10	1.237 (7)
Cd1—O3 ⁱⁱ	2.249 (4)	O3—C12	1.245 (6)
Cd1—O4 ⁱⁱⁱ	2.305 (3)	O4—C12	1.243 (6)
O2—Cd1—O1 ⁱ	151.50 (15)	O3 ⁱⁱ —Cd1—O4 ⁱⁱⁱ	152.39 (13)
O2—Cd1—O3 ⁱⁱ	84.42 (15)	O2—Cd1—Cl1	104.95 (11)
O1 ⁱ —Cd1—O3 ⁱⁱ	88.81 (14)	O1 ⁱ —Cd1—Cl1	103.33 (10)
O2—Cd1—O4 ⁱⁱⁱ	86.92 (14)	O3 ⁱⁱ —Cd1—Cl1	110.93 (10)
O1 ⁱ —Cd1—O4 ⁱⁱⁱ	86.42 (14)	O4 ⁱⁱⁱ —Cd1—Cl1	96.63 (9)

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

structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3164). Services for accessing these data are described at the back of the journal.

References

- Abourahma, H., Bodwell, G. J., Lu, J., Moulton, B., Pottie, I. R., Walsh, R. B. & Zaworotko, M. J. (2003). *Cryst. Growth Des.* **3**, 513–519.
- Bourne, S. A., Lu, J., Mondal, A., Moulton, B. & Zaworotko, M. J. (2001). *Angew. Chem. Int. Ed.* **40**, 2111–2113.
- Brandenburg, K. (1999). *DIAMOND*. Version 2.1e. Crystal Impact GbR, Bonn, Germany.
- Bruker (1998). *SMART, SAINT and SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Chen, B., Ockwig, N. W., Fronczek, F. R., Contreras, D. S. & Yaghi, O. M. (2005). *Inorg. Chem.* **44**, 181–183.
- Cotton, F. A., Lin, C. & Murillo, C. A. (2001). *Acc. Chem. Res.* **34**, 759–771.
- Cotton, F. A., Lin, C. & Murillo, C. A. (2002). *Proc. Natl Acad. Sci. USA*, **99**, 4810–4813.
- Delgado Friedrichs, O., O'Keeffe, M. & Yaghi, O. M. (2003). *Acta Cryst.* **A59**, 515–525.
- Hunter, C. A. & Sanders, J. K. M. (1990). *J. Am. Chem. Soc.* **112**, 5525–5534.
- Kim, J., Chen, B., Reineke, T. M., Li, H., Eddaoudi, M., Moler, D. B., O'Keeffe, M. & Yaghi, O. M. (2001). *J. Am. Chem. Soc.* **123**, 8239–8247.
- Li, S.-L. & Mak, T. C. W. (1995). *J. Chem. Soc. Dalton Trans.* pp. 1519–1524.
- Ni, Q.-L., Li, F.-S., Jin, L.-L., He, P.-X. & Wang, X.-J. (2007). *Chem. Res. Appl.* **20**, 1181–1184.
- Ni, Z., Yassar, A., Antoun, T. & Yaghi, O. M. (2005). *J. Am. Chem. Soc.* **127**, 12752–12753.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Wang, X.-J., Gui, L.-C., Ni, Q.-L., Liao, Y.-F., Jiang, X.-F., Tang, L.-H., Zhang, Z. & Wu, Q. (2008). *CrystEngComm*, **10**, 1003–1010.
- Wang, X.-L., Qin, C., Wang, E. B., Li, Y.-G. & Su, Z.-M. (2005). *Chem. Commun.* pp. 5450–5452.
- Xue, D.-X., Lin, Y.-Y., Cheng, X.-N. & Chen, X.-M. (2007). *Cryst. Growth Des.* **7**, 1332–1336.