

Bis(μ -benzene-1,2-dicarboxylato)-bis[aqua[2-(2-chloro-6-fluorophenyl)-1*H*-imidazo[4,5-*f*][1,10]phenanthroline]cadmium(II)} and its zinc(II) analogue

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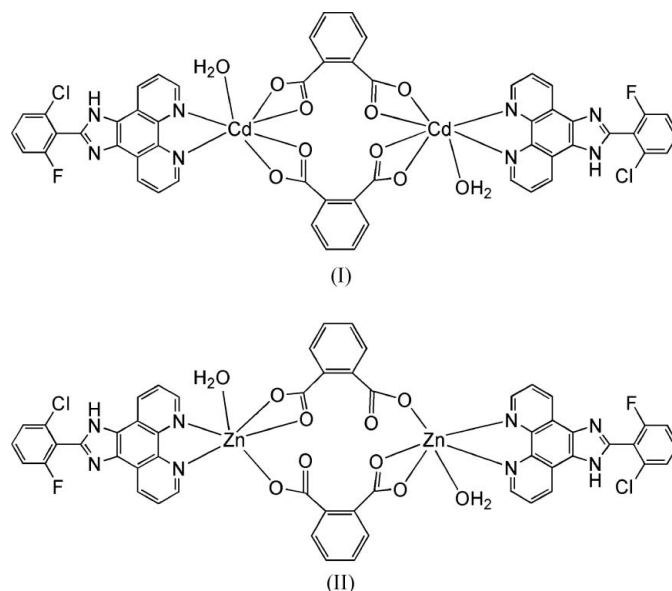
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In the isomorphous title compounds, $[\text{Cd}_2(\text{C}_8\text{H}_4\text{O}_4)_2(\text{C}_{19}\text{H}_{10}\text{ClFN}_4)_2(\text{H}_2\text{O})_2]$ and $[\text{Zn}_2(\text{C}_8\text{H}_4\text{O}_4)_2(\text{C}_{19}\text{H}_{10}\text{ClFN}_4)_2(\text{H}_2\text{O})_2]$, the Cd^{II} centre is seven-coordinated by two N atoms from one [2-(2-chloro-6-fluorophenyl)-1*H*-imidazo[4,5-*f*][1,10]phenanthroline (*L*) ligand, one water O atom and four carboxylate O atoms from two different benzene-1,2-dicarboxylate (1,2-bdc) ligands in a distorted pentagonal-bipyramidal coordination, while the Zn^{II} centre is six-coordinated by two N atoms from one *L* ligand, one water O atom and three carboxylate O atoms from two different 1,2-bdc ligands in a distorted octahedral coordination. Each pair of adjacent metal centres is bridged by two 1,2-bdc ligands to form a dimeric structure. In the dimer, each *L* ligand coordinates one metal centre. The dimer is centrosymmetric, with a crystallographic inversion centre midway between the two metal centres. The aromatic interactions lead the dimers to form a two-dimensional supramolecular architecture. Finally, O—H...O and N—H...O hydrogen bonds reinforce the two-dimensional structures of the two compounds.

Comment

The design and synthesis of discrete and polymeric metal-organic complexes is currently attracting considerable attention in view of their interesting structural topologies and properties (Eddaoudi *et al.*, 2001; Hagrman *et al.*, 1999; Ockwig *et al.*, 2005). These complexes can be specially designed by the careful selection of metal cations with preferred coordination geometries, considering also the nature of the anions, the structure of the connecting ligands and the reaction conditions (Wang *et al.*, 2008; Chen *et al.*, 2008). Usually, two different types of interactions, such as covalent bonds and noncovalent intermolecular forces, can be

used to construct varied supramolecular architectures (Wang *et al.*, 2007). To date, much research has focused on controlling motifs of metal-organic complexes through coordination bonds. However, less attention has been given to noncovalent π - π interactions (Yang *et al.*, 2009). The π - π interaction can be one of the most powerful noncovalent intermolecular interactions for directing supramolecular architectures (Yang *et al.*, 2007; Qiao *et al.*, 2009). In particular, conjugated π systems can strongly influence the physical properties of coordination compounds. Therefore, the design of versatile functional ligands that are capable of coordinating to a metal atom while providing the π -conjugated system for organizing their complexes into extended networks through π - π interactions is quite desirable. So far, the 1,10-phenanthroline ligand has been widely used to construct supramolecular architectures owing to its excellent coordinating ability and large conjugated system that can easily form π - π interactions. However, derivatives such as 2-(2-chloro-6-fluorophenyl)-1*H*-imidazo[4,5-*f*][1,10]phenanthroline (*L*), which is a good candidate for the construction of metal-organic supramolecular architectures, have received far less attention (Wang *et al.*, 2007). On the other hand, carboxylate-based ligands have been successfully employed in the generation of many interesting coordination compounds (Ockwig *et al.*, 2005). In this contribution, we selected benzene-1,2-dicarboxylate (1,2-bdc) as an organic linker and *L* as an N-donor chelating ligand, generating two isomorphous coordination compounds, $[\text{Cd}(1,2\text{-bdc})(\text{L})(\text{H}_2\text{O})_2]$, (I), and $[\text{Zn}(1,2\text{-bdc})(\text{L})(\text{H}_2\text{O})_2]$, (II).



Compounds (I) and (II) are isomorphous and, therefore, only the structure of (I) will be described in detail. Selected bond lengths and angles for the two compounds are given in Tables 1 and 3. As shown in Fig. 1, the Cd^{II} centre is seven-coordinated by two N atoms from one *L* ligand, one water O atom and four carboxylate O atoms from two different 1,2-bdc ligands, in a distorted pentagonal-bipyramidal coordination.

Four O atoms (O1, O2, O3ⁱ and O4ⁱ; symmetry code as in Fig. 1) from two 1,2-bdc anions and one N atom (N2) from the *L* ligand make up the equatorial plane, while the axial positions are occupied by one water O atom (O1W) and a second N atom (N1) from the *L* ligand. The Cd—O(carboxylate) distances range from 2.314 (2) to 2.484 (2) Å, which are comparable to those found in other crystallographically characterized Cd^{II} complexes (Qiao *et al.*, 2008). Each pair of adjacent Cd^{II} centres is bridged by two 1,2-bdc ligands to form a dimeric structure with a Cd···Cd separation of 4.987 (4) Å. In the dimer, each *L* ligand coordinates one metal centre. The dimer is centrosymmetric, with a crystallographic inversion centre midway between the two Cd^{II} centres. Notably, the *L* ligands are arranged in a parallel fashion at both sides of a dimer, leading to a structure capable of aromatic intercalation. Two types of aromatic interactions between neighbouring dimers have been found. One is a π – π interaction between the quinoline ring systems [N2/C4–C12 at (*x*, *y*, *z*) and (–*x*, –*y* + 1, –*z* + 1)] of the *L* ligands [with a centroid–centroid distance of 3.854 (3) Å, a face-to-face distance of 3.304 (2) Å and a dihedral angle of 0.607 (3)°], which leads the dimers to form a one-dimensional supramolecular chain along the *c* axis. The

second is a C–H··· π interaction between atom C23 of the 1,2-bdc ligand and a pyridine ring [N2/C6–C10 at (–*x*, *y* – $\frac{1}{2}$, –*z* + $\frac{3}{2}$)] of the *L* ligand [3.588 (5) Å; Fig. 2]. When these interactions are taken into account, the one-dimensional supramolecular chains become a two-dimensional supramolecular layer. Moreover, there are both N–H···O and O–H···O hydrogen bonds in (I). The N–H···O hydrogen bonds join the molecules into one-dimensional chains in the *c*-axis direction (along with the reported π – π interaction) (Tables 2 and 4). The supramolecular layers form a three-dimensional supramolecular architecture through the N–H···O and O–H···O hydrogen bonds.

Although compounds (I) and (II) are isostructural, their coordination is slightly different. In (I), the Cd^{II} centre is seven-coordinated by two N atoms from one *L* ligand, one water O atom and four carboxylate O atoms from two different 1,2-bdc ligands, in a distorted pentagonal-bipyramidal coordination. Conversely, in (II), the Zn^{II} centre is six-coordinated by three carboxylate O atoms from two different 1,2-bdc ligands, one water O atom and two N atoms from one *L* ligand, in a distorted octahedral coordination.

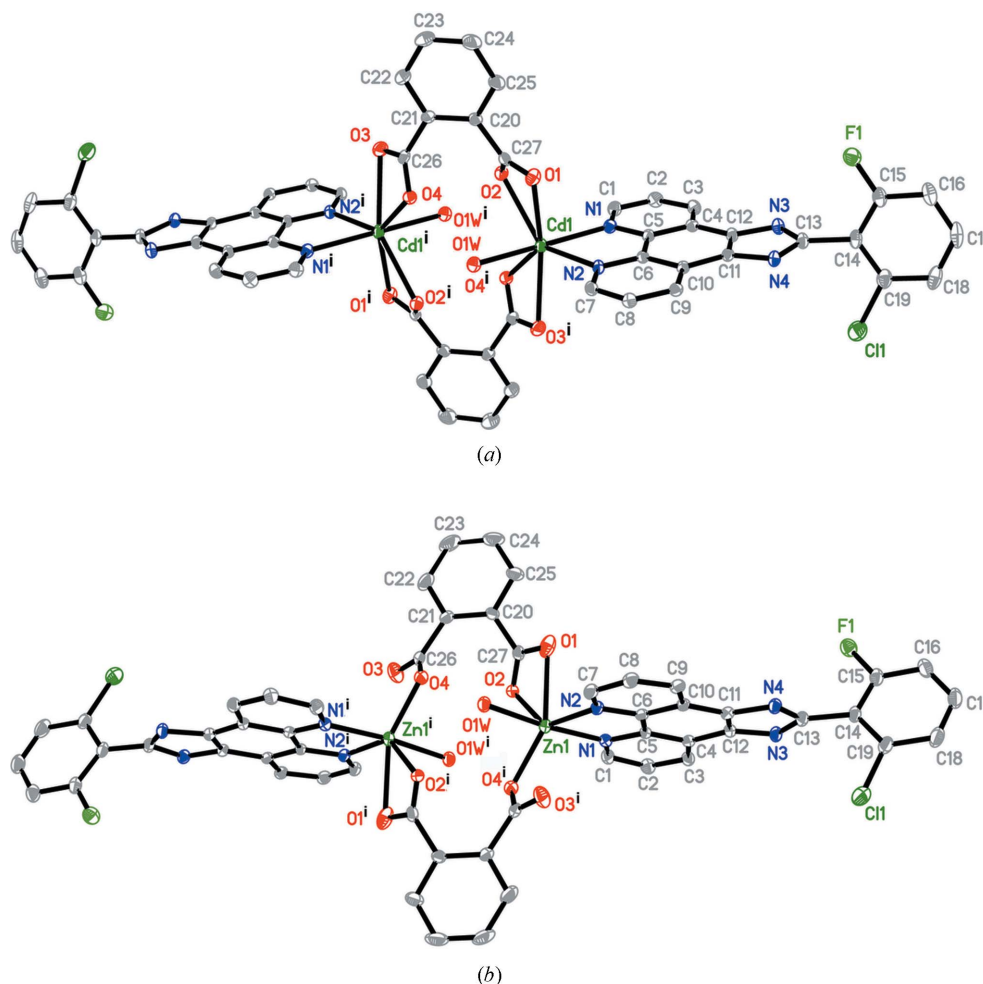
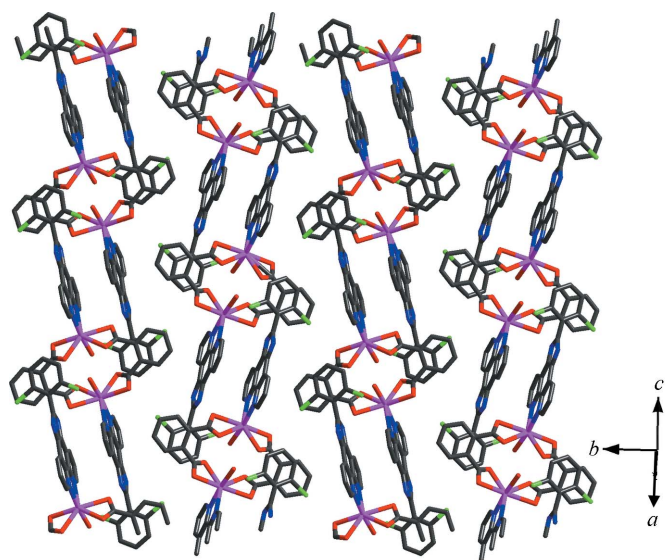


Figure 1

A view of the local coordination of the *M*^{II} cations in (a) (I) (*M* = Cd) and (b) (II) (*M* = Mn), showing the atom-numbering schemes. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity. [Symmetry code: (i) –*x*, –*y* + 1, –*z* + 2.]

**Figure 2**

A view of the two-dimensional supramolecular structure of (I) constructed by two types of aromatic interactions: π - π interactions between quinoline ring systems of *L* ligands [N2/C4-C12 at (*x*, *y*, *z*) and ($-x$, $-y + 1$, $-z + 1$)] and C-H... π interactions between atom C23 of the 1,2-bdc ligand and a pyridine ring of the *L* ligand [N2/C6-C10 at ($-x$, $y - \frac{1}{2}$, $-z + \frac{3}{2}$)].

It should be pointed out that the related compound [Cd(1,2-bdc)(H₂O)] displays a two-dimensional layer structure, where neighbouring Cd^{II} centres are bridged by carboxylate O atoms of 1,2-bdc ligands (Wang *et al.*, 2003). Clearly, the *L* ligand plays an important role in the formation of the dimeric structure. It is also noteworthy that the structure of (I) is different from the related structure [Cd(1,2-bdc)(*L'*)₃]_{*n*} (*L'* = benzimidazole; Cui *et al.*, 2006). In this compound, the Cd^{II} centre is seven-coordinated by four O atoms from two 1,2-bdc ligands and three N atoms from three *L'* ligands, resulting in a distorted pentagonal-bipyramidal geometry. The 1,2-bdc ligands bridge the Cd^{II} centres to form an extended helical chain structure. Neighbouring chains interact through π - π interactions, yielding a two-dimensional structure.

Experimental

CdCl₂·2.5H₂O (0.5 mmol), 1,2-H₂bdc (0.5 mmol) and *L* (0.5 mmol) were dissolved in distilled water (12 ml), and then triethylamine (0.01 mol) was added until the pH value of the system was adjusted to about 5.5. The resulting solution was stirred for about 1 h at room temperature, sealed in a 23 ml Teflon-lined stainless steel autoclave and heated at 458 K for 6 d under autogenous pressure. The reaction system was subsequently cooled slowly to room temperature. Pale-yellow block-shaped crystals of (I) suitable for single-crystal X-ray diffraction analysis were collected from the final reaction system by filtration, washed several times with distilled water and dried in air at ambient temperature (yield 67%, based on Cd^{II}). Compound (II) was prepared in the same way as (I), using ZnCl₂·2H₂O as the metal source. Pale-yellow crystals were obtained (yield 71%, based on Zn^{II}).

Compound (I)

Crystal data

[Cd₂(C₈H₄O₄)₂(C₁₉H₁₀ClFN₄)₂·(H₂O)₂]
M_r = 1286.58
 Monoclinic, *P*2₁/*c*
a = 8.7749 (7) Å
b = 21.8204 (17) Å
c = 13.5740 (11) Å

β = 105.479 (1)°
V = 2504.8 (3) Å³
Z = 2
 Mo *K*α radiation
 μ = 1.03 mm⁻¹
T = 293 K
 0.27 × 0.22 × 0.20 mm

Data collection

Bruker APEX diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.752, *T_{max}* = 0.811

13862 measured reflections
 4944 independent reflections
 3703 reflections with *I* > 2σ(*I*)
R_{int} = 0.030

Refinement

R [*F*² > 2σ(*F*²)] = 0.037
wR [*F*²] = 0.087
S = 1.00
 4944 reflections
 360 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}}$ = 0.68 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -0.23 e Å⁻³

Table 1

Selected geometric parameters (Å, °) for (I).

Cd1—N1	2.295 (3)	Cd1—O1W	2.330 (3)
Cd1—N2	2.320 (2)	Cd1—O4 ⁱ	2.314 (2)
Cd1—O1	2.439 (2)	Cd1—O3 ⁱ	2.481 (2)
Cd1—O2	2.484 (2)		
N1—Cd1—O4 ⁱ	101.66 (8)	O4 ⁱ —Cd1—O3 ⁱ	54.42 (8)
N1—Cd1—N2	72.53 (9)	N2—Cd1—O3 ⁱ	84.12 (8)
O4 ⁱ —Cd1—N2	136.75 (8)	O1W—Cd1—O3 ⁱ	81.25 (11)
N1—Cd1—O1W	171.31 (9)	O1—Cd1—O3 ⁱ	153.51 (9)
O4 ⁱ —Cd1—O1W	86.69 (9)	N1—Cd1—O2	96.92 (9)
N2—Cd1—O1W	99.77 (9)	O4 ⁱ —Cd1—O2	89.23 (7)
N1—Cd1—O1	96.46 (9)	N2—Cd1—O2	133.69 (8)
O4 ⁱ —Cd1—O1	139.74 (8)	O1W—Cd1—O2	85.48 (9)
N2—Cd1—O1	82.97 (8)	O1—Cd1—O2	52.82 (7)
O1W—Cd1—O1	78.30 (11)	O3 ⁱ —Cd1—O2	141.72 (7)
N1—Cd1—O3 ⁱ	101.57 (9)		

Symmetry code: (i) $-x, -y + 1, -z + 2$.

Table 2

Hydrogen-bond geometry (Å, °) for (I).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N4—H4A...O1 ⁱⁱ	0.86	1.92	2.727 (3)	155
O1W—HW11...O2 ⁱ	0.77 (4)	2.11 (4)	2.815 (4)	153 (4)
O1W—HW12...O4	0.83 (4)	1.98 (5)	2.748 (4)	154 (4)

Symmetry codes: (i) $-x, -y + 1, -z + 2$; (ii) $-x, -y + 1, -z + 1$.

Compound (II)

Crystal data

[Zn₂(C₈H₄O₄)₂(C₁₉H₁₀ClFN₄)₂·(H₂O)₂]
M_r = 1192.52
 Monoclinic, *P*2₁/*c*
a = 8.695 (3) Å
b = 21.720 (6) Å
c = 13.211 (4) Å

β = 104.655 (5)°
V = 2413.8 (12) Å³
Z = 2
 Mo *K*α radiation
 μ = 1.19 mm⁻¹
T = 293 K
 0.29 × 0.24 × 0.22 mm

Data collection

Bruker APEX diffractometer	13479 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	4772 independent reflections
$T_{\min} = 0.703$, $T_{\max} = 0.772$	3026 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.044$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.116$	
$S = 1.01$	$\Delta\rho_{\text{max}} = 0.40 \text{ e } \text{\AA}^{-3}$
4772 reflections	$\Delta\rho_{\text{min}} = -0.43 \text{ e } \text{\AA}^{-3}$
360 parameters	

Table 3

Selected geometric parameters (\AA , $^\circ$) for (II).

Zn1—O1	2.364 (4)	Zn1—O4 ⁱ	2.094 (2)
Zn1—O2	2.377 (3)	Zn1—N1	2.092 (3)
Zn1—O1W	2.135 (3)	Zn1—N2	2.105 (3)
N1—Zn1—O4 ⁱ	96.55 (10)	N2—Zn1—O1	83.76 (10)
N1—Zn1—N2	79.08 (11)	O1W—Zn1—O1	81.60 (12)
O4 ⁱ —Zn1—N2	132.58 (10)	N1—Zn1—O2	91.86 (11)
N1—Zn1—O1W	174.69 (11)	O4 ⁱ —Zn1—O2	90.61 (10)
O4 ⁱ —Zn1—O1W	88.76 (11)	N2—Zn1—O2	136.36 (10)
N2—Zn1—O1W	97.48 (11)	O1W—Zn1—O2	87.88 (11)
N1—Zn1—O1	93.95 (11)	O1—Zn1—O2	54.10 (9)
O4 ⁱ —Zn1—O1	143.48 (9)		

Symmetry code: (i) $-x, -y + 1, -z + 2$.

Table 4

Hydrogen-bond geometry (\AA , $^\circ$) for (II).

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N4—H4A \cdots O1 ⁱⁱ	0.86	1.95	2.738 (4)	152
O1W—H11 \cdots O2 ⁱ	0.83 (4)	2.06 (4)	2.807 (4)	150 (4)
O1W—H12 \cdots O4	0.89 (4)	1.93 (4)	2.753 (4)	153 (4)

Symmetry codes: (i) $-x, -y + 1, -z + 2$; (ii) $-x, -y + 1, -z + 1$.

For both compounds, the water H atoms were located in a difference Fourier map and thereafter refined freely. All other H atoms were positioned geometrically ($N-H = 0.86 \text{ \AA}$ and $C-H =$

0.93 \AA) and refined as riding, with $U_{\text{iso}}(\text{H})$ values set at 1.2 times $U_{\text{eq}}(\text{carrier})$.

For both compounds, data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL-Plus* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3340). Services for accessing these data are described at the back of the journal.

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