

A new dinuclear Zn^{II} compound with a 1,4-benzenedicarboxylate bridge

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Key indicators

Single-crystal X-ray study
 $T = 292$ K
Mean $\sigma(\text{C}-\text{C}) = 0.006$ Å
 R factor = 0.052
 wR factor = 0.113
Data-to-parameter ratio = 14.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

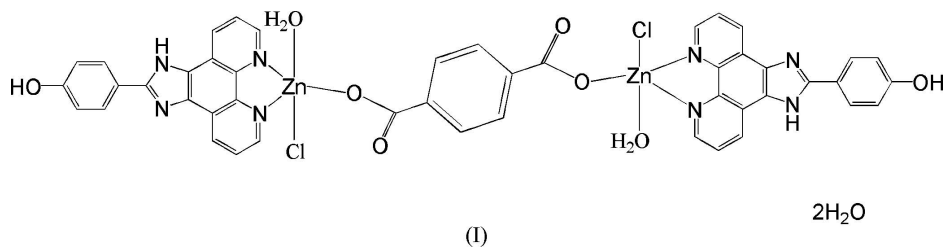
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In the compound μ_2 -1,4-benzenedicarboxylate- $\kappa^2 O, O'$ -bis-{aquachloro[4-(1*H*-1,3,7,8-tetraazacyclopenta[*l*]phenanthren-2-yl)phenol- $\kappa^2 N, N'$]zinc(II)} dihydrate, $[\text{Zn}_2\text{Cl}_2(1,4\text{-BDC})(L)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, where 1,4-BDC is the 1,4-benzenedicarboxylate dianion, $\text{C}_8\text{H}_4\text{O}_4^{2-}$, and *L* is 4-(1*H*-1,3,7,8-tetraazacyclopenta[*l*]phenanthren-2-yl)phenol, $\text{C}_{19}\text{H}_{12}\text{N}_4\text{O}$, the Zn^{II} atom is five-coordinated by two N atoms from one *L* ligand, one Cl^- ion, an O atom from a 1,4-BDC anion and one water molecule in an approximate trigonal-bipyramidal geometry. The complete 1,4-BDC ligand is generated by inversion symmetry; it bridges two Zn^{II} atoms to form a dinuclear complex. Neighbouring complexes interact through π - π contacts and various kinds of hydrogen bonds, leading to a two-dimensional supramolecular structure.

Comment

The synthesis and design of supramolecular compounds possessing novel structures and properties have attracted increasing interest (Eddaoudi *et al.*, 2001). 1,10-Phenanthroline (phen) or its derivatives have long been used in the construction of metal-organic complexes. The phen derivative 4-(1*H*-1,3,7,8-tetraazacyclopenta[*l*]phenanthren-2-yl)phenol (*L*) possesses an extended delocalized aromatic system. To date, only a handful of supramolecular architectures based on *L* molecules have been described (Che *et al.*, 2006). We selected 1,4-benzenedicarboxylic acid (1,4- H_2BDC) as a linker and *L* as a secondary ligand, generating a new coordination compound, $[\text{Zn}_2(1,4\text{-BDC})(L)_2(\text{Cl}_2)(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, (I), which is reported here.



In compound (I), the Zn^{II} atom is five-coordinated by two N atoms from one *L* ligand, one Cl^- ion, an O atom from a 1,4-BDC dianion and one water molecule (Fig. 1). Two Zn^{II} atoms are bridged by the centrosymmetric 1,4-BDC ligand to form a dinuclear complex. The $\text{Zn}-\text{N}$, $\text{Zn}-\text{Cl}$ and $\text{Zn}-\text{O}$ bond lengths are normal (Table 1). The $\text{ZnN}_2\text{O}_2\text{Cl}$ coordination polyhedron approximates a trigonal bipyramid, with atoms N1 and O1 in the axial positions. The carboxylate C—O bond lengths suggest that the bonding is largely localized.

It is notable that neighbouring dinuclear complexes interact through π - π contacts, leading to a two-dimensional supramolecular structure (Fig. 2). There are two types of π - π interactions: one exists between two *L* ligands (centroid separation = 3.45 Å), while the other exists between the *L* and 1,4-BDC ligands (centroid separation = 3.61 Å). Finally, various hydrogen bonds involving the water molecules, -NH-groups, Cl⁻ ions and carboxylate O atoms (Table 2) complete the crystal structure of (I).

Experimental

The ligand *L* was synthesized by the literature method of Steck & Day (1943). A methanol solution (6 ml) of *L* (0.5 mmol) was added slowly to an aqueous solution (12 ml) of ZnCl₂·H₂O (0.5 mmol) and 1,4-H₂BDC (1 mmol) with stirring. The resulting solution was filtered and the filtrate was allowed to stand in air at room temperature for several days, yielding pale-yellow crystals of (I) in 61% yield based on Zn.

Crystal data

[Zn₂Cl₂(C₈H₄O₄)(C₁₉H₁₂N₄O)₂·(H₂O)₂]₂·2H₂O
M_r = 1062.47
 Triclinic, *P* $\bar{1}$
a = 9.1608 (18) Å
b = 9.4769 (19) Å
c = 13.334 (3) Å
 α = 109.24 (3)°
 β = 90.66 (3)°
 γ = 104.02 (3)°
V = 1055.1 (5) Å³
Z = 1
D_x = 1.672 Mg m⁻³
 Mo *K* α radiation
 μ = 1.34 mm⁻¹
T = 292 (2) K
 Block, yellow
 0.29 × 0.25 × 0.21 mm

Data collection

Rigaku R-Axis RAPID diffractometer
 ω scans
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
T_{min} = 0.684, *T_{max}* = 0.758
 10429 measured reflections
 4780 independent reflections
 3065 reflections with *I* > 2 σ (*I*)
R_{int} = 0.059
 θ_{max} = 27.5°

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.052
wR (*F*²) = 0.113
S = 1.03
 4780 reflections
 321 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0392P)^2 + 0.7847P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.74 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{min} = -0.43 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Zn1—O1	2.049 (3)	Zn1—Cl1	2.2885 (14)
Zn1—O1W	2.080 (3)	C20—O2	1.237 (4)
Zn1—N1	2.150 (3)	C20—O1	1.263 (4)
Zn1—N2	2.072 (3)		
O1—Zn1—N2	90.17 (11)	O1W—Zn1—N1	89.60 (13)
O1—Zn1—O1W	87.43 (13)	O1—Zn1—Cl1	98.97 (10)
N2—Zn1—O1W	124.01 (13)	N2—Zn1—Cl1	118.99 (9)
O1—Zn1—N1	163.57 (12)	O1W—Zn1—Cl1	116.62 (11)
N2—Zn1—N1	78.13 (12)	N1—Zn1—Cl1	96.81 (9)

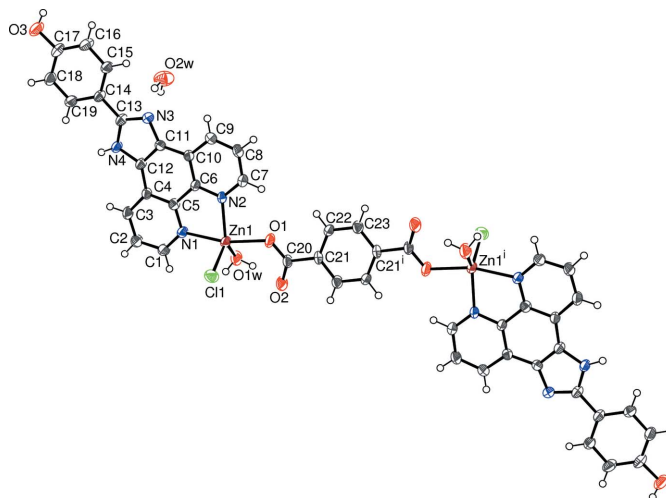


Figure 1

A view of (I). Displacement ellipsoids are drawn at the 50% probability level (arbitrary spheres for H atoms). [Symmetry code: (i) 1 - *x*, -*y*, 1 - *z*.]

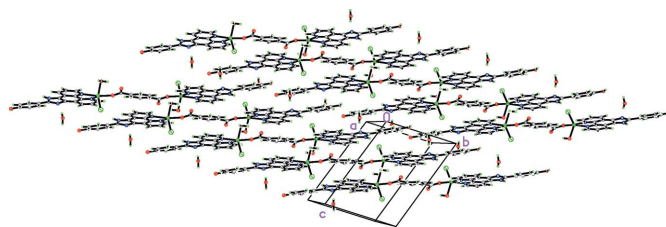


Figure 2

A view of the two-dimensional supramolecular structure of (I) formed via π - π interactions. H atoms have been omitted.

Table 2

Hydrogen-bond geometry (Å, °).

<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>
O1W—HW12...O2	0.87 (5)	1.95 (6)	2.774 (5)	158 (4)
O1W—HW11...O2 ⁱ	0.83 (6)	1.88 (6)	2.700 (5)	172 (6)
O3—H3A...O2W ⁱⁱ	0.82	1.90	2.713 (5)	173
N4—H4...Cl1 ⁱⁱⁱ	0.86	2.48	3.318 (4)	165
O2W—HW21...N3	0.88 (4)	2.01 (2)	2.884 (5)	172 (6)
O2W—HW22...Cl1 ^{iv}	0.94 (2)	2.85 (4)	3.571 (4)	134 (5)

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

The H atoms of the water molecules were located in difference maps and their positions were freely refined; O—H distances are included in Table 2. For HW11 and HW12, *U_{iso}* was freely refined; for HW21 and HW22, the constraint *U_{iso}*(H) = 1.5*U_{eq}*(O2W) was applied. The alcohol OH and all C- and N-bound H atoms were positioned geometrically (O—H = 0.82 Å, N—H = 0.86 Å and C—H = 0.93 Å) and refined as riding, with *U_{iso}*(H) = 1.2*U_{eq}*(carrier).

Data collection: PROCESS-AUTO (Rigaku, 1998); cell refinement: PROCESS-AUTO; data reduction: PROCESS-AUTO; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL-Plus (Sheldrick, 1990); software used to prepare material for publication: SHELXL97.

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