Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

A new two-dimensional supramolecule composed of μ-2,6-dimethylpyridine-3,5-dicarboxylato-$\kappa^4O^3,O^{3'}:O^5,O^{5'}$-bis[chloro(1,10-phenanthroline-κ^2N,N')zinc(II)]

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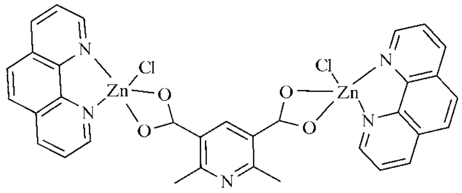
Received 10 November 2006
Accepted 28 February 2007
Online 17 March 2007

In the binuclear title molecule, $[Zn_2(C_9H_7NO_4)Cl_2(C_{12}H_8N_2)_2]$, the two metal centres are bridged by a 2,6-dimethylpyridine-3,5-dicarboxylate ligand. The binuclear unit is extended to form a two-dimensional supramolecular motif *via* π–π stacking interactions between neighbouring phenanthroline rings.

Comment

In the last decade, there has been a great upsurge in the publication of new metal–organic complexes, owing not only to their intriguing structural topologies but also to their potential applications in adsorption, ion exchange, catalysis, nonlinear optical and magnetic materials (Batten & Robson, 1998; Yaghi *et al.*, 1998; Hagrman *et al.*, 1999; Zhang *et al.*, 2003). One area of interest is in the construction of supramolecular architectures from N- and O-donor ligands (Doyle *et al.*, 2003; Go *et al.*, 2004; Zheng *et al.*, 2003). A number of studies show that, besides metal–ligand coordination bonding, supramolecular interactions such as hydrogen bonding and π–π stacking are important in the construction of supramolecular structures (Sreenivasulu & Vittal, 2004). Compared with benzenedicarboxylic acid, the coordination modes of pyridinedicarboxylic acid are more varied, so it is regarded as an excellent candidate for the self-assembly of metal–organic complexes. As an extension of our previous work (Huang, He, Niu *et al.*, 2006; Huang, He, Wang *et al.*, 2007), we report here the synthesis and crystal structure of the title binuclear compound, $[Zn(mpdc)Cl_2(phen)_2]$ (mpdc is 2,6-dimethylpyridine-3,5-dicarboxylate and phen is 1,10-phenanthroline), (I).



(I)

Compound (I) crystallizes in the space group *Pna*2$_1$. The crystal structure reveals that (I) consists of a neutral $[Zn(mpdc)Cl_2(phen)_2]$ unit. Compound (I) is stable in air and insoluble in common organic solvents such as methanol, ethanol, acetone and dimethylformamide. The assignment of the formula is supported by elemental analysis.

As shown in Fig. 1, (I) is a binuclear compound composed of one mpdc^{2-} anion, two phen ligands, two Cl$^-$ anions and two Zn^{II} cations. The two different Zn centres, Zn1 and Zn2, are bridged by the mpdc^{2-} anion acting as a V-shaped connector. Each Zn^{II} cation is primarily coordinated to two N atoms from a chelating phen ligand [Zn1—N2 = 2.087 (6) Å, Zn1—N3 = 2.061 (6) Å, Zn2—N4 = 2.101 (6) Å and Zn2—N5 = 2.067 (6) Å], one O atom from the mpdc^{2-} anion [Zn1—O1 = 1.985 (5) Å and Zn2—O3 = 1.944 (5) Å] and one Cl atom [Zn1—Cl1 = 2.218 (3) Å and Zn2—Cl2 = 2.206 (3) Å], to furnish a distorted trigonal–bipyramidal geometry. The other interactions between the Zn^{II} cations and the O atom of the

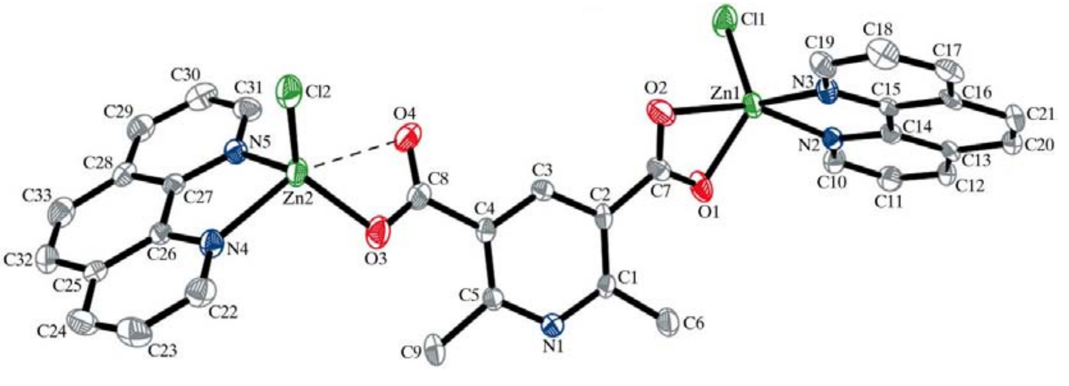


Figure 1
A view of the title complex, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

DOI: 10.1107/S0108270107009663

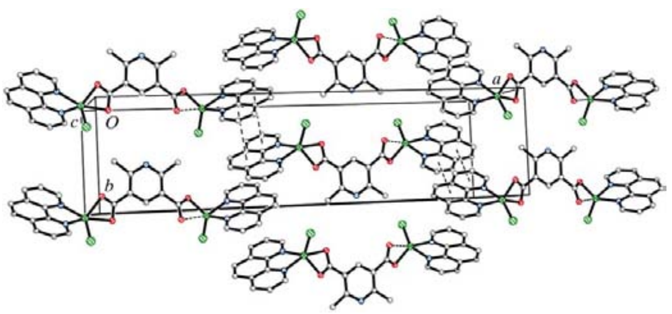


Figure 2
The packing of the title complex, extended to show the two-dimensional supramolecular motif formed *via* π–π stacking.

mpdc^{2-} anion are weaker [Zn1—O2 = 2.414 (5) Å and Zn2—O4 = 2.627 (5) Å]. All the O atoms of the mpdc^{2-} anion coordinate to a Zn centre, while the N atom does not. Each phen ligand acts as a terminal group, chelating one Zn^{II} cation *via* its two N atoms (Fig. 1).

There are two types of π–π stacking interactions between phen ligands in compound (I), and all aromatic rings of the phen ligand participate in the π–π stacking. For the first type of π–π stacking (dashed lines on the left-hand side of Fig. 2), the distance between two approximately parallel planes defined by the two rings of the phen ligands is 3.38 Å, the centroid-to-centroid distance is 3.575 Å and the displacement angle is 18.5°. For the second type of π–π stacking (dashed lines on the right-hand side of Fig. 2), the distance between the two approximately parallel planes defined by the two rings of the phen ligands is also 3.38 Å, but the centroid-to-centroid distance is 3.749 Å and the displacement angle is 25.3°. Each phen ligand interacts with phen ligands from two adjacent complexes through these two types of π–π stacking. In this way, a two-dimensional supramolecular architecture is generated from the discrete molecular complexes.

Experimental

A solution of H_2O (1 ml) and EtOH (10 ml) containing H_2mpdc (0.2 mmol, 46 mg), 1,10-phenanthroline (0.2 mmol, 40 mg), $ZnCl_2$ (0.2 mmol, 28 mg) and Et_3N (0.04 ml) was sealed in a 23 ml Teflon-lined stainless steel container and heated at 393 K for 72 h, then cooled to room temperature. The colourless crystals which formed were washed with ethanol (3 × 3 ml) to give compound (I) (yield 60%). Elemental analysis for $C_{33}H_{23}Cl_2N_5O_4Zn_2$ calculated: C 52.48, H 3.07, N 9.27%; found: C 52.50, H 3.06, N 9.26%.

Crystal data

$[Zn_2(C_9H_7NO_4)Cl_2(C_{12}H_8N_2)_2]$
$M_r = 755.20$
Orthorhombic, $Pna2_1$
$a = 31.578$ (14) Å
$b = 8.006$ (4) Å
$c = 12.006$ (6) Å
$V = 3035$ (2) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 1.81$ mm^{-1}
$T = 298$ (2) K
0.26 × 0.15 × 0.08 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.651$, $T_{max} = 0.869$
15087 measured reflections
5169 independent reflections
3397 reflections with $I > 2\sigma(I)$
$R_{int} = 0.061$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.089$
$S = 1.03$
5169 reflections
415 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.39$ e Å^{-3}
Absolute structure: Flack (1983), with 2817 Friedel pairs
Flack parameter: 0.24 (2)

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H = 0.90–0.96 Å and $U_{iso}(H) = 1.2–1.5U_{eq}(C)$.

Data collection and cell refinement: *SMART* (Siemens, 1996); data reduction: *SAINT* (Siemens, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics and publication material: *SHELXTL* (Sheldrick, 1997*b*).

This work was supported by the Natural Science Fund Council of China (NSFC; grant Nos. 20671011, 20331010, 90406002 and 90406024) and the Key Laboratory of Structural Chemistry Foundation (KLSCF; grant No. 060017).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3026). Services for accessing these data are described at the back of the journal.

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