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catena-Poly[[dichlorozinc(II)]-μ-*N*,*N*′-bis(4-pyridylmethyl)piperazine]

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The title compound, $[ZnCl_2(C_{16}H_{20}N_4)]_n$, was prepared from the reaction of *N*,*N*′-bis(4-pyridylmethyl)piperazine (bpmp) and $ZnCl_2$. The asymmetric unit contains one Cl atom, half a Zn^{II} ion and half a bmpb moiety. The Zn^{II} ion, which lies on a twofold axis, has a distorted tetrahedral coordination geometry, with the central piperazine group in bpmp bridging $ZnCl_2$ units to form a one-dimensional polymeric chain. The piperazine connector in bpmp adopts a stable chair conformation.

Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.006 Å
R factor = 0.043
wR factor = 0.116
Data-to-parameter ratio = 10.5

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

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Comment

The construction of coordination polymers has been a field of rapid growth in supramolecular chemistry and materials chemistry owing to the fascinating structures and potential applications of these compounds as functional materials (Blake *et al.*, 1999; Eddaoudi *et al.*, 2001; Hagrman *et al.*, 1999). The design of organic ligands containing appropriate coordination sites linked by a connector with specific positional orientation is especially crucial to the formation of directed supramolecular architectures (Blake *et al.*, 1999; Carlucci *et al.*, 2003; Wang *et al.*, 2004). Among various organic ligands, some of the most useful are neutral pyridyl-containing bidentate or multidentate ligands, because of their simple bridging mode and ability to form strong coordination compounds with transition metal ions (Hagrman *et al.*, 1999; Kitagawa & Konda,1998; MacGillivray *et al.*, 1994). Many rigid rod-like bipyridyl ligands have been employed for the rational design of solid-state architectures of coordination polymers. For example, Biradha and colleagues have designed a series of rigid bipyridyl ligands by increasing the number of phenyl rings between pyridyl rings, thereby obtaining two-dimensional square frameworks of different sizes through assembly of these ligands with metal ions (Biradha & Fujita, 2000; Biradha *et al.*, 2000). Flexible bridging ligands have received less attention than rigid ligands because of the difficulties inherent in predicting the structure of the final product, although flexibility and conformational freedom provide the probability of producing some unique frameworks with beautiful aesthetics and useful properties (Belcher *et al.*, 2002; Paz *et al.*, 2002). Hence, a great deal of work is required in order to establish a knowledge based on relevant structural types and functional properties from flexible bridging ligands.

In the design and synthesis of pyridyl-containing organic ligands, piperazine is an excellent connector. The flexibility and conformational freedom in *N*,*N*′-alkyl disubstituted piperazines can result in either a chair or a boat conformation, leading to supramolecular isomerism (Halfen *et al.*, 2000; Niu *et al.*, 2001; Ratilainen *et al.*, 1999). With the aim of investigating the effect of a disubstituted piperazine connector on

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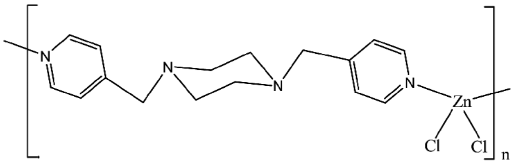
self-assembly, we have designed an exo-bidentate ligand, *N*,*N*′-bis(4-pyridylmethyl)piperazine (bpmp). We report here the synthesis and characterization of the title one-dimensional zigzag chain complex $[Zn(bpmp)Cl_2]_n$, (I).



(I)

Single-crystal X-ray analysis reveals that (I) crystallizes in the monoclinic space group *C*2/*c* and forms a one-dimensional zigzag chain through interconnection of $ZnCl_2$ units and bpmp. The polymeric chain structure is generated by the action of the crystallographic twofold axis. As shown in Fig. 1, each Zn^{II} ion is coordinated by two N atoms from different bpmp moieties and two terminal Cl^- ions in a distorted tetrahedral environment. The Zn—N and Zn—Cl bond distances are 2.061 (3) and 2.2139 (11) Å, respectively. The $Cl1—Zn—Cl^i$ (symmetry code as in Table 1) bond angle of 123.02 (7)° is larger than the $N1—Zn—N1^i$ bond angle of 102.13 (16)°, probably to minimize the Cl···Cl interaction. The dihedral angle between the two pyridyl rings attached to Zn^{II} is 82.4°, indicating that they are approximately perpendicular to one another. Bpmp behaves in an exo-bidentate mode, with the two pyridyl rings in bpmp being parallel to each other. The piperazine connector adopts a stable chair conformation. Thus, bpmp connects $ZnCl_2$ units into a one-dimensional polymeric chain (Fig. 2), with a Zn···Zn separation of 16.57 Å. There are no other noteworthy short contacts or weak interactions between adjacent chains (Fig. 3).

Experimental

The bpmp ligand was synthesized according to the method of Niu *et al.* (2001). A solution of $ZnCl_2$ (0.034 g, 0.25 mmol) in H_2O (10 ml) was added slowly to a solution of bpmp (0.067 g, 0.25 mmol) in MeOH (10 ml), with stirring, producing a white precipitate. The reaction mixture was heated to 333 K and added dropwise to dimethylformamide (about 1 ml) until the precipitate dissolved. The resulting solution was filtered and kept in air for two weeks at room temperature; colorless crystals suitable for X-ray diffraction were obtained.

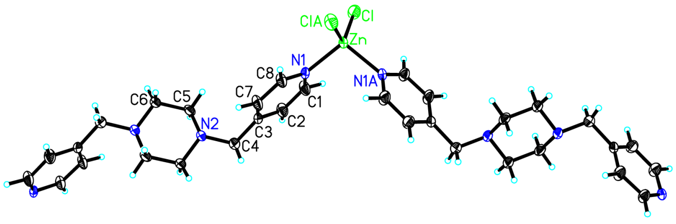


Figure 1
View of molecular structure Displacement ellipsoids are plotted at the 30% probability level. Atom N1*A* is generated by the symmetry operation $-x, y, \frac{1}{2} - z$.

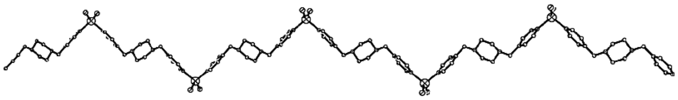


Figure 2
View of the one-dimensional zigzag chain.

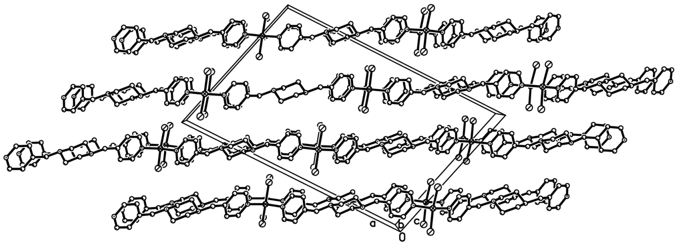


Figure 3
Packing diagram for (I), viewed along the *b* axis.

Crystal data

$[ZnCl_2(C_{16}H_{20}N_4)]$
$M_r = 404.63$
Monoclinic, *C*2/*c*
$a = 22.167$ (2) Å
$b = 5.8534$ (4) Å
$c = 14.2600$ (12) Å
$\beta = 105.629$ (3)°
$V = 1781.9$ (3) Å^3
$Z = 4$
$D_x = 1.508$ Mg m$^{-3$}
Mo *Kα* radiation
Cell parameters from 2306 reflections
$\theta = 3.0–25.1°$
$\mu = 1.68$ mm^{-1}
$T = 173$ (2) K
Rod, colorless
0.38 × 0.16 × 0.10 mm

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.724$, $T_{max} = 1.000$
2306 measured reflections
1525 independent reflections
1306 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 25.1°$
$h = -26 \rightarrow 8$
$k = -6 \rightarrow 6$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.116$
$S = 1.10$
1525 reflections
145 parameters
All H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0624P)^2 + 3.1799P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.67$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn—N1	2.061 (3)	Zn—Cl	2.2139 (11)
$N1^i$—Zn—N1	102.13 (16)	N1—Zn—Cl	110.79 (9)
$N1^i$—Zn—Cl	104.15 (8)	Cl—Zn—Cl^i	123.02 (7)

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

All H atoms were positioned geometrically (C—H = 0.96 Å), assigned isotropic displacement parameters and allowed to ride on their respective parent C atoms before the final cycle of least-squares refinement.

Data collection: *SMART* (Siemens, 1994); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1994); program(s) used to solve structure: *SHELXTL*/*PC* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*/*PC*; molecular graphics: *SHELXTL*/*PC*; software used to prepare material for publication: *SHELXTL*/*PC*.

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