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catena-Poly[[dibromidozinc(II)]- μ -4-(3-pyridyl)-4H-1,2,4-triazole]

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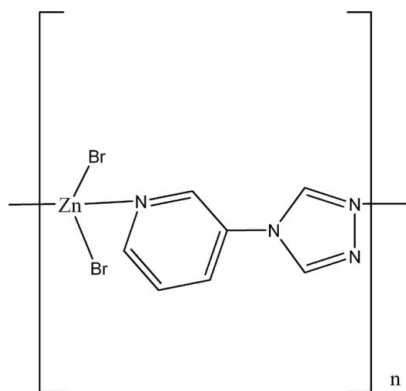
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 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.010$ Å;
 R factor = 0.039; wR factor = 0.090; data-to-parameter ratio = 14.9.

The title complex, $[\text{ZnBr}_2(\text{C}_7\text{H}_6\text{N}_4)]_n$, was formed under hydrothermal conditions using the ligand 4-(3-pyridyl)-4H-1,2,4-triazole (L). The unique Zn^{II} ion is coordinated by one triazole N atom, one pyridine N atom and two Br atoms in a slightly distorted tetrahedral coordination environment. Symmetry-related Zn^{II} ions are connected by bridging L ligands into chains parallel to $[001]$ in which the $\text{Zn} \cdots \text{Zn}$ separation is 8.643 (7) Å. In the crystal structure, weak intermolecular $\text{C}-\text{H} \cdots \text{Br}$ hydrogen bonds link the chains into a three-dimensional network.

Related literature

For the preparation of the ligand used to synthesize the title compound, see: Gioia *et al.* (1988). For background literature on supramolecular polymer chemistry, see: Lehn (1995); Ouahab (1997). For complexes incorporating 4-3-pyridyl-1,2,4-triazole ligands, see: Moulton & Zaworotko (2001); Pan *et al.* (2001); Prior & Rosseinsky (2001); Ma *et al.* (2001); Ding *et al.* (2006).



Experimental

Crystal data

 $[\text{ZnBr}_2(\text{C}_7\text{H}_6\text{N}_4)]$
 $M_r = 371.35$
 Monoclinic, $P2_1/c$
 $a = 6.787$ (6) Å
 $b = 18.769$ (15) Å
 $c = 8.643$ (7) Å
 $\beta = 101.316$ (11)°

 $V = 1079.6$ (15) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 9.64$ mm⁻¹
 $T = 293$ K
 $0.18 \times 0.12 \times 0.06$ mm

Data collection

 Bruker APEXII diffractometer
 Absorption correction: multi-scan
 (*SADABS*; Sheldrick, 1996)
 $T_{\text{min}} = 0.522$, $T_{\text{max}} = 1.000$

 5681 measured reflections
 1903 independent reflections
 1510 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.041$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.090$
 $S = 1.10$
 1903 reflections

 128 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.65$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.60$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{C}7-\text{H}7 \cdots \text{Br}1^{\text{i}}$	0.93	2.92	3.711 (7)	145
$\text{C}6-\text{H}6 \cdots \text{Br}2^{\text{ii}}$	0.93	2.93	3.779 (8)	153

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

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH5068).

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supporting information

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catena-Poly[[dibromidozinc(II)]- μ -4-(3-pyridyl)-4H-1,2,4-triazole]**Bin Ding and Hong-Ai Zou****S1. Comment**

Supramolecular polymer chemistry is a branch of modern science which is developing rapidly through the combination of polymer chemistry with supramolecular chemistry (Lehn, 1995; Ouahab, 1997). Recently, considerable efforts have been devoted to crystal engineering of supramolecular architecture sustained by coordination covalent bonding, hydrogen bonding or some molecular interaction and their combination. The compounds formed are of interest owing to their fascinating structural diversity and potential application in design of porous materials with novel inclusion or reactivity properties and in supramolecular devices such as sensors and indicators (Moulton & Zaworotko, 2001; Pan *et al.*, 2001; Prior & Rosseinsky, 2001; Ma *et al.*, 2001; Ding *et al.*, 2006). We report herein the crystal structure of the title complex.

A view of the coordination around the Zn^{II} ion of the title compound is shown in Fig. 1. The unique Zn^{II} ion is coordinated by one triazole nitrogen atom, one pyridine nitrogen atom and two bromine ligands in a slightly distorted tetrahedral coordination environment. Symmetry related Zn^{II} ions are connected by bridging *L* ligands to form one-dimensional chains (Fig. 2) in which the Zn \cdots Zn separation is 8.643 (7) Å. In the crystal structure, weak intermolecular C—H \cdots Br hydrogen bonds (Table 1) exist between *L* triazole rings and bromine atoms pairs of inversion related 1-D chains, which are further assembled through C—H \cdots Br interactions to form a 3-D network (see Fig. 3).

S2. Experimental

The ligand *L* was prepared according to the previously reported literature methods (Gioia, *et al.*, 1988). A mixture of ZnBr₂ (22.5 mg, 0.1 mmol), *L* (14.6 mg, 0.1 mmol) and water (10 ml) was stirred for 5 h and filtered. The filtrate was kept in a CaCl₂ desiccator. Suitable single crystals for X-ray diffraction study were obtained after a few days, yield 23% (based on Zn(II) salts). Anal. Calc. for C₇H₆Br₂N₄Zn: C, 22.64%; H, 1.63%; N, 15.09%. Found: C, 22.75%; H, 1.87%; N, 15.14%. FT—IR (KBr): 3115 (w), 3050 (w), 2940(w), 1540(s), 1473(m), 1395(m), 1368(w), 1244(w), 1199(s), 1075(s), 1030(s), 978(w), 945(w), 869(s), 684(w), 640 (s), 489(m), 425 (w) cm⁻¹.

S3. Refinement

H atoms were positioned geometrically and were allowed to ride on their parent C atoms with C—H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

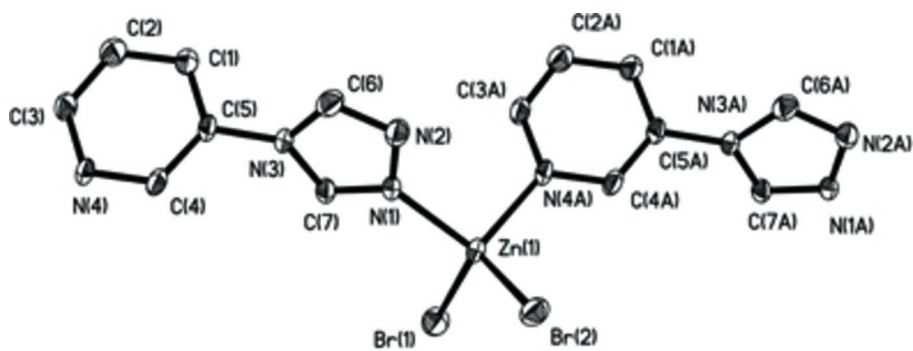


Figure 1

A view of the coordination around the Zn^{II} ion of the title 1-D compound [symmetry code: (A) $x, y, z - 1$].

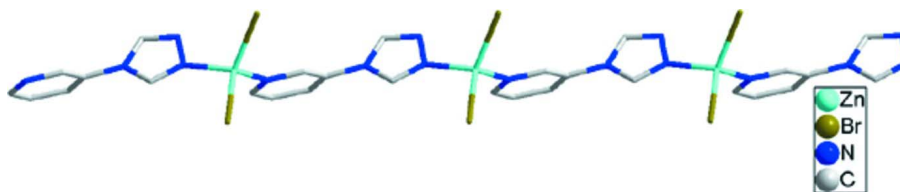


Figure 2

One-dimensional structure of the title compound

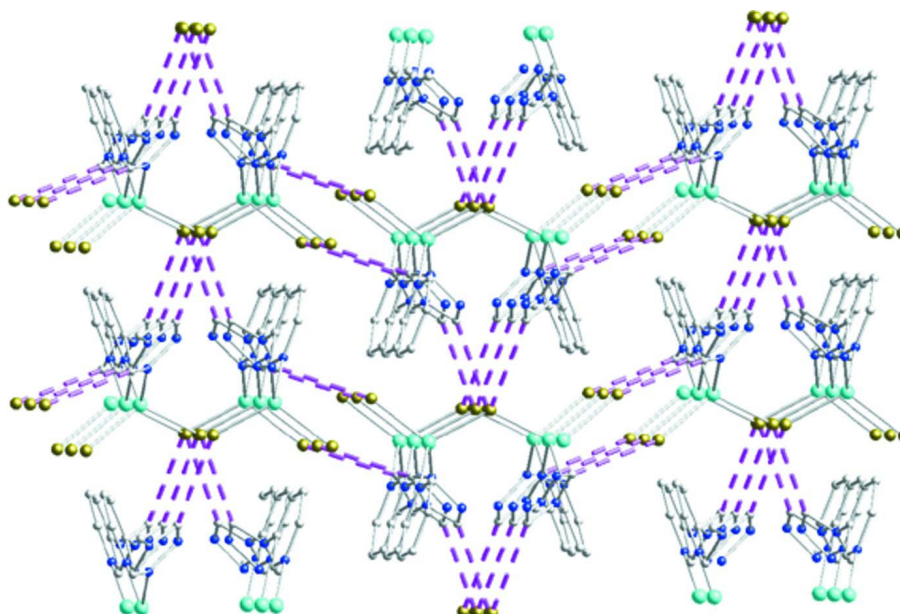


Figure 3

Part of the crystal structure of the title compound showing hydrogen bonds as dashed lines.

catena-Poly[[dibromidozinc(II)]- μ -4-(3-pyridyl)-4*H*-1,2,4-triazole]

Crystal data

[ZnBr₂(C₇H₆N₄)]

$M_r = 371.35$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 6.787 (6) \text{ \AA}$

$b = 18.769 (15) \text{ \AA}$

$c = 8.643 (7) \text{ \AA}$
 $\beta = 101.316 (11)^\circ$
 $V = 1079.6 (15) \text{ \AA}^3$
 $Z = 4$
 $F(000) = 704$
 $D_x = 2.285 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 1387 reflections
 $\theta = 2.6\text{--}24.1^\circ$
 $\mu = 9.64 \text{ mm}^{-1}$
 $T = 293 \text{ K}$
 Block, colorless
 $0.18 \times 0.12 \times 0.06 \text{ mm}$

Data collection

Bruker APEXII
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.522, T_{\max} = 1.000$

5681 measured reflections
 1903 independent reflections
 1510 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.041$
 $\theta_{\max} = 25.0^\circ, \theta_{\min} = 2.2^\circ$
 $h = -7 \rightarrow 8$
 $k = -22 \rightarrow 22$
 $l = -10 \rightarrow 7$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.090$
 $S = 1.10$
 1903 reflections
 128 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods
 Secondary atom site location: difference Fourier
 map

Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0105P)^2 + 4.1488P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.65 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.60 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97 (Sheldrick,
 2008)
 Extinction coefficient: 0.00010 (0)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.39470 (11)	0.63872 (4)	0.68138 (8)	0.0337 (2)
Br1	0.61578 (12)	0.54147 (4)	0.76801 (9)	0.0506 (3)
Br2	0.54852 (11)	0.74575 (4)	0.62834 (9)	0.0469 (2)
N1	0.2184 (8)	0.6476 (3)	0.8432 (5)	0.0334 (12)
N2	0.0687 (8)	0.6990 (3)	0.8251 (6)	0.0435 (14)
N3	0.0872 (8)	0.6435 (3)	1.0539 (5)	0.0324 (12)
N4	0.1730 (8)	0.6178 (3)	1.4833 (5)	0.0339 (12)
C1	-0.1373 (10)	0.5977 (4)	1.2212 (8)	0.0419 (17)

H1	-0.2388	0.5907	1.1332	0.050*
C2	-0.1642 (11)	0.5823 (4)	1.3737 (8)	0.0513 (19)
H2	-0.2868	0.5653	1.3907	0.062*
C3	-0.0079 (10)	0.5926 (4)	1.4974 (8)	0.0415 (17)
H3	-0.0279	0.5815	1.5980	0.050*
C4	0.2014 (10)	0.6340 (3)	1.3381 (7)	0.0373 (15)
H4	0.3248	0.6520	1.3251	0.045*
C5	0.0513 (10)	0.6243 (3)	1.2085 (7)	0.0333 (15)
C6	-0.0101 (11)	0.6954 (4)	0.9528 (8)	0.0451 (17)
H6	-0.1155	0.7235	0.9722	0.054*
C7	0.2253 (9)	0.6162 (3)	0.9792 (7)	0.0322 (14)
H7	0.3142	0.5799	1.0188	0.039*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0344 (4)	0.0455 (5)	0.0238 (4)	-0.0007 (3)	0.0122 (3)	0.0026 (3)
Br1	0.0527 (5)	0.0476 (4)	0.0534 (5)	0.0094 (4)	0.0153 (4)	0.0096 (3)
Br2	0.0419 (4)	0.0489 (4)	0.0529 (5)	-0.0042 (3)	0.0168 (3)	0.0093 (3)
N1	0.033 (3)	0.047 (3)	0.021 (2)	0.002 (3)	0.007 (2)	0.003 (2)
N2	0.042 (4)	0.055 (4)	0.036 (3)	0.011 (3)	0.015 (3)	0.012 (3)
N3	0.033 (3)	0.045 (3)	0.022 (2)	0.000 (2)	0.010 (2)	0.002 (2)
N4	0.041 (3)	0.042 (3)	0.023 (3)	-0.001 (3)	0.015 (2)	0.002 (2)
C1	0.038 (4)	0.057 (4)	0.031 (3)	-0.006 (3)	0.009 (3)	-0.002 (3)
C2	0.044 (5)	0.067 (5)	0.045 (4)	-0.014 (4)	0.014 (4)	0.002 (4)
C3	0.044 (4)	0.054 (4)	0.029 (3)	-0.010 (3)	0.013 (3)	0.006 (3)
C4	0.041 (4)	0.047 (4)	0.029 (3)	-0.002 (3)	0.019 (3)	0.002 (3)
C5	0.042 (4)	0.039 (3)	0.021 (3)	-0.002 (3)	0.013 (3)	-0.003 (3)
C6	0.041 (4)	0.052 (4)	0.046 (4)	0.011 (3)	0.019 (3)	0.006 (3)
C7	0.036 (4)	0.038 (3)	0.023 (3)	0.003 (3)	0.008 (3)	0.000 (3)

Geometric parameters (Å, °)

Zn1—N1	2.018 (5)	N4—Zn1 ⁱⁱ	2.083 (5)
Zn1—N4 ⁱ	2.083 (5)	C1—C2	1.396 (9)
Zn1—Br2	2.3502 (18)	C1—C5	1.397 (9)
Zn1—Br1	2.3880 (17)	C1—H1	0.9300
N1—C7	1.308 (7)	C2—C3	1.364 (9)
N1—N2	1.388 (7)	C2—H2	0.9300
N2—C6	1.319 (8)	C3—H3	0.9300
N3—C7	1.339 (8)	C4—C5	1.370 (9)
N3—C6	1.386 (8)	C4—H4	0.9300
N3—C5	1.450 (7)	C6—H6	0.9300
N4—C4	1.341 (7)	C7—H7	0.9300
N4—C3	1.343 (8)		
N1—Zn1—N4 ⁱ	98.9 (2)	C3—C2—C1	119.0 (6)
N1—Zn1—Br2	114.26 (15)	C3—C2—H2	120.5

N4 ⁱ —Zn1—Br2	106.11 (14)	C1—C2—H2	120.5
N1—Zn1—Br1	105.51 (15)	N4—C3—C2	124.2 (6)
N4 ⁱ —Zn1—Br1	114.96 (15)	N4—C3—H3	117.9
Br2—Zn1—Br1	116.02 (7)	C2—C3—H3	117.9
C7—N1—N2	108.1 (5)	N4—C4—C5	120.9 (6)
C7—N1—Zn1	131.6 (4)	N4—C4—H4	119.5
N2—N1—Zn1	120.0 (4)	C5—C4—H4	119.5
C6—N2—N1	106.1 (5)	C4—C5—C1	121.9 (6)
C7—N3—C6	104.9 (5)	C4—C5—N3	119.2 (6)
C7—N3—C5	127.6 (5)	C1—C5—N3	118.9 (5)
C6—N3—C5	127.6 (5)	N2—C6—N3	110.0 (6)
C4—N4—C3	117.8 (6)	N2—C6—H6	125.0
C4—N4—Zn1 ⁱⁱ	120.9 (4)	N3—C6—H6	125.0
C3—N4—Zn1 ⁱⁱ	121.1 (4)	N1—C7—N3	110.9 (6)
C2—C1—C5	116.1 (6)	N1—C7—H7	124.6
C2—C1—H1	122.0	N3—C7—H7	124.6
C5—C1—H1	122.0		
N4 ⁱ —Zn1—N1—C7	127.0 (6)	N4—C4—C5—N3	179.0 (5)
Br2—Zn1—N1—C7	-120.8 (5)	C2—C1—C5—C4	0.6 (10)
Br1—Zn1—N1—C7	7.9 (6)	C2—C1—C5—N3	-178.1 (6)
N4 ⁱ —Zn1—N1—N2	-59.6 (5)	C7—N3—C5—C4	61.5 (9)
Br2—Zn1—N1—N2	52.7 (5)	C6—N3—C5—C4	-116.6 (7)
Br1—Zn1—N1—N2	-178.7 (4)	C7—N3—C5—C1	-119.8 (7)
C7—N1—N2—C6	-0.7 (7)	C6—N3—C5—C1	62.1 (9)
Zn1—N1—N2—C6	-175.6 (4)	N1—N2—C6—N3	0.8 (8)
C5—C1—C2—C3	-1.1 (10)	C7—N3—C6—N2	-0.6 (7)
C4—N4—C3—C2	0.1 (10)	C5—N3—C6—N2	177.8 (6)
Zn1 ⁱⁱ —N4—C3—C2	175.4 (6)	N2—N1—C7—N3	0.3 (7)
C1—C2—C3—N4	0.8 (11)	Zn1—N1—C7—N3	174.4 (4)
C3—N4—C4—C5	-0.7 (9)	C6—N3—C7—N1	0.2 (7)
Zn1 ⁱⁱ —N4—C4—C5	-176.0 (5)	C5—N3—C7—N1	-178.3 (6)
N4—C4—C5—C1	0.4 (10)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C7—H7 \cdots Br1 ⁱⁱⁱ	0.93	2.92	3.711 (7)	145
C6—H6 \cdots Br2 ^{iv}	0.93	2.93	3.779 (8)	153

Symmetry codes: (iii) $-x+1, -y+1, -z+2$; (iv) $x-1, -y+3/2, z+1/2$.