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catena-Poly[[dichloridozinc(II)]- μ -2,5-di-4-pyridyl-1,3,4-thiadiazole- $\kappa^2N^2:N^5$]

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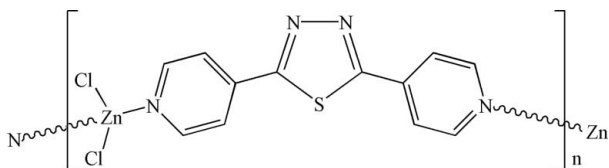
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 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(C-C) = 0.004$ Å; R factor = 0.038; wR factor = 0.089; data-to-parameter ratio = 17.4.

The title compound, $[ZnCl_2(C_{12}H_8N_4S)]_n$, was obtained by crystallization of 2,5-di-4-pyridyl-1,3,4-thiadiazole with $ZnCl_2$ in an MeOH/ $CHCl_3$ solvent system. The structure contains infinite chains of $ZnCl_2$ units connected by the bifunctional thiadiazole ligands, with Zn^{II} adopting a distorted tetrahedral coordination geometry. The dihedral angle between the two pyridyl rings in each ligand is $34.3(1)^\circ$, and the dihedral angles between the thiadiazole ring and the two pyridyl rings are $18.3(2)$ and $16.1(2)^\circ$. The shortest $Zn \cdots Zn$ distance within each polymeric chain is $11.862(3)$ Å, while the shortest interchain $Zn \cdots Zn$ distance is $7.057(3)$ Å.

Related literature

For related literature, see: Chen *et al.* (2007); Dong, Ma & Huang (2003); Dong, Ma, Huang, Guo & Smith (2003); Du *et al.* (2003); Fujita (1998); Huang *et al.* (2004); Inoue *et al.* (1996); Maekawam *et al.* (2000); Moulton & Zaworotko (2001); Xiong *et al.* (2001).



Experimental

Crystal data

$[ZnCl_2(C_{12}H_8N_4S)]$
 $M_r = 376.55$
 Monoclinic, $P2_1/n$
 $a = 12.9990(13)$ Å
 $b = 5.4039(5)$ Å
 $c = 20.195(2)$ Å
 $\beta = 101.459(4)^\circ$

$V = 1390.3(2)$ Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 2.29$ mm⁻¹
 $T = 293(2)$ K
 $0.20 \times 0.12 \times 0.04$ mm

Data collection

Rigaku Mercury CCD diffractometer
 Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2002)
 $T_{min} = 0.690$, $T_{max} = 0.912$

10073 measured reflections
 3155 independent reflections
 2688 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.089$
 $S = 1.03$
 3155 reflections

181 parameters
 H-atom parameters constrained
 $\Delta\rho_{max} = 0.43$ e Å⁻³
 $\Delta\rho_{min} = -0.38$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Zn1—N4 ⁱ	2.060 (2)	Zn1—Cl1	2.1939 (8)
Zn1—N1	2.060 (2)	Zn1—Cl2	2.2402 (8)
N4 ⁱ —Zn1—N1	103.11 (9)	N4 ⁱ —Zn1—Cl2	104.00 (7)
N4 ⁱ —Zn1—Cl1	107.44 (6)	N1—Zn1—Cl2	104.64 (6)
N1—Zn1—Cl1	107.78 (7)	Cl1—Zn1—Cl2	127.44 (3)

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

Data collection: *CrystalClear* (Rigaku, 2002); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXL97* and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: B12274).

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supporting information

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catena-Poly[[dichloridozinc(II)]- μ -2,5-di-4-pyridyl-1,3,4-thiadiazole- κ^2 N²:N⁵]

Li-Juan Chen, Ming-Xing Yang, Xiao-Hua Chen and Shen Lin

S1. Comment

Much current research activity of supramolecular coordination polymers with novel topologies and structural motifs is driven by their encouraging potential applications in the fields of nonlinear optics, catalysis and separation, magnetism and molecular recognition (Moulton & Zaworotko, 2001, Xiong *et al.*, 2001, Inoue *et al.*, 1996). Therefore, the discovery and rational design of such coordination polymers is an important and very active topic. One useful strategy for the discovery of novel coordination polymers has been the use of various spacer ligands as the building block (Du *et al.*, 2003, Chen *et al.*, 2007). So far, a wide range of infinite frameworks have already been generated with simple 4,4'-bi-pyridyl-based ligands (Maekawam *et al.*, 2000, Fujita, 1998).

As previously reported (Dong, Ma & Huang, 2003, Huang *et al.*, 2004), oxadiazole-containing ligands can take versatile bonding modes (it can act as mono-, bi-, tri- and even tetradentate ligand) and the structural geometries of the ligands themselves are also variable. On the other hand, d¹⁰ transition metal-containing complexes often show interesting optical properties. Our interest in the supramolecular coordination polymers lead us to use 2,5-di-4-pyridyl-1,3,4-thiadiazole (*L*) and ZnCl₂ as precursors to generate the title compound.

Crystallization of *L* and ZnCl₂ in MeOH/CHCl₃ mixed solvent system at room temperature yield the title compound, [Zn(C₁₂H₈N₄S)Cl₂]_n. The crystal structure is composed of 1-D zigzag chains with ZnCl₂ units connected to each other by the N-donor bifunctional ligands. As shown in Fig. 1, the Zn^{II} center adopts a distorted tetrahedral coordination geometry, defined by two N donors from two 2,5-di-4-pyridyl-1,3,4- thiadiazole ligands (*L*) and terminal chloride ligands. Both Zn—N bond distances are 2.060 (2) Å, and the two Zn—Cl bond distances are 2.1938 (8) and 2.2402 (8) Å, respectively. The greatest angular distortion from tetrahedral geometry is exhibited by the Cl—Zn—Cl angle of 127.44 (3) ° and by the N—Zn—N angle of 103.11 (9) °. All these values compare well to those reported in other [Zn(4,4'-bipy)] compounds (Dong, Ma, Huang, Guo *et al.*, 2003). The two pyridyl ring groups in each ligand are not coplanar, and the dihedral angle between them is 34.3 (1) °. The dihedral angles between the thiadiazole ring and the two pyridyl ring groups in each ligand are 18.3 (2) ° and 16.1 (2) °. The intrachain Zn···Zn distance is 11.862 (3) Å, while the shortest interchain Zn···Zn distance is 7.057 (3) Å.

In the crystal, the 1-D zigzag chains stack along crystallographic β axis. In the *ac* plane (Fig. 2), neighboring chains are arranged in opposite directions, and are stacked either in a shoulder-to-shoulder or a staggered fashion.

S2. Experimental

A solution of ZnCl₂ (22.7 mg, 0.05 mmol) in MeOH (5 ml) was carefully layered on a solution of 2,5-di-4-pyridyl-1,3,4-thiadiazole (12 mg, 0.05 mmol) in CHCl₃ (5 ml) in a straight glass tube. After one week, colorless single crystals were obtained (yield *ca* 25% based on Zn).

S3. Refinement

H atoms were placed geometrically with C—H = 0.93 Å and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

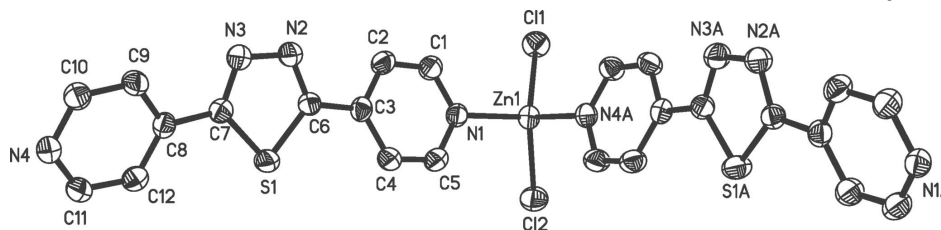


Figure 1

Molecular structure of the title compound showing 30% probability displacement ellipsoids (H atoms are omitted).

catena-Poly[[dichloridozinc(II)]- μ -2,5-di-4-pyridyl-1,3,4-thiadiazole- $\kappa^2\text{N}^2:\text{N}^5$]

Crystal data

[ZnCl₂(C₁₂H₈N₄S)]

$M_r = 376.55$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 12.9990$ (13) Å

$b = 5.4039$ (5) Å

$c = 20.195$ (2) Å

$\beta = 101.459$ (4)°

$V = 1390.3$ (2) Å³

$Z = 4$

$F(000) = 752$

$D_x = 1.799$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2905 reflections

$\theta = 3.9$ – 27.5 °

$\mu = 2.29$ mm⁻¹

$T = 293$ K

Prism, white

$0.20 \times 0.12 \times 0.04$ mm

Data collection

Rigaku Mercury CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: multi-scan

(*CrystalClear*; Rigaku, 2002)

$T_{\text{min}} = 0.690$, $T_{\text{max}} = 0.912$

10073 measured reflections

3155 independent reflections

2688 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

$\theta_{\text{max}} = 27.5$ °, $\theta_{\text{min}} = 3.9$ °

$h = -14 \rightarrow 16$

$k = -7 \rightarrow 6$

$l = -26 \rightarrow 26$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.089$

$S = 1.04$

3155 reflections

181 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

$w = 1/[\sigma^2(F_o^2) + (0.0439P)^2 + 0.6049P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 0.43$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.38$ e Å⁻³

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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	1.45602 (2)	1.18961 (6)	0.680619 (15)	0.03305 (12)
S1	1.23784 (6)	0.24683 (15)	0.42060 (4)	0.04195 (19)
Cl1	1.34567 (6)	1.43843 (14)	0.71674 (4)	0.04576 (19)
Cl2	1.59540 (6)	1.29522 (15)	0.63700 (4)	0.0476 (2)
N1	1.37010 (17)	0.9563 (4)	0.60991 (10)	0.0325 (5)
N2	1.10437 (18)	0.3373 (5)	0.49394 (11)	0.0374 (5)
N3	1.06015 (18)	0.1586 (5)	0.45020 (12)	0.0385 (6)
N4	1.01683 (17)	-0.4543 (4)	0.25889 (10)	0.0320 (5)
C1	1.2665 (2)	0.9276 (5)	0.60620 (14)	0.0376 (6)
H1A	1.2329	1.0288	0.6325	0.045*
C2	1.2081 (2)	0.7546 (6)	0.56503 (14)	0.0370 (6)
H2A	1.1362	0.7423	0.5630	0.044*
C3	1.2576 (2)	0.5981 (5)	0.52646 (12)	0.0321 (6)
C4	1.3644 (2)	0.6283 (6)	0.53025 (14)	0.0397 (7)
H4A	1.4002	0.5273	0.5052	0.048*
C5	1.4169 (2)	0.8089 (6)	0.57142 (14)	0.0403 (7)
H5A	1.4883	0.8300	0.5727	0.048*
C6	1.1964 (2)	0.4066 (5)	0.48470 (12)	0.0308 (6)
C7	1.1201 (2)	0.0891 (5)	0.40919 (13)	0.0314 (6)
C8	1.0874 (2)	-0.1003 (5)	0.35760 (13)	0.0317 (6)
C9	1.0054 (2)	-0.2613 (5)	0.36310 (14)	0.0360 (6)
H9A	0.9736	-0.2536	0.4004	0.043*
C10	0.9723 (2)	-0.4310 (5)	0.31285 (13)	0.0364 (6)
H10A	0.9165	-0.5344	0.3165	0.044*
C11	1.0960 (2)	-0.3019 (5)	0.25406 (14)	0.0390 (7)
H11A	1.1278	-0.3178	0.2169	0.047*
C12	1.1329 (2)	-0.1232 (6)	0.30118 (14)	0.0389 (6)
H12A	1.1875	-0.0193	0.2954	0.047*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.03407 (19)	0.0322 (2)	0.03165 (17)	-0.00116 (13)	0.00357 (13)	0.00049 (13)
S1	0.0336 (4)	0.0522 (5)	0.0429 (4)	-0.0112 (3)	0.0145 (3)	-0.0163 (3)
Cl1	0.0474 (4)	0.0385 (4)	0.0521 (4)	0.0064 (3)	0.0115 (3)	-0.0035 (3)
Cl2	0.0436 (4)	0.0520 (5)	0.0500 (4)	-0.0069 (3)	0.0159 (3)	0.0043 (4)

N1	0.0314 (11)	0.0336 (13)	0.0313 (11)	0.0002 (9)	0.0032 (9)	-0.0022 (10)
N2	0.0351 (12)	0.0412 (14)	0.0370 (12)	-0.0051 (10)	0.0094 (10)	-0.0086 (11)
N3	0.0344 (12)	0.0436 (14)	0.0377 (12)	-0.0044 (11)	0.0075 (10)	-0.0077 (11)
N4	0.0343 (12)	0.0300 (12)	0.0309 (10)	0.0007 (9)	0.0045 (9)	0.0001 (9)
C1	0.0335 (14)	0.0388 (16)	0.0396 (14)	0.0016 (12)	0.0054 (12)	-0.0069 (13)
C2	0.0287 (14)	0.0399 (16)	0.0415 (15)	0.0031 (12)	0.0048 (12)	-0.0050 (13)
C3	0.0323 (13)	0.0339 (15)	0.0287 (12)	-0.0026 (11)	0.0024 (10)	0.0031 (11)
C4	0.0347 (15)	0.0472 (17)	0.0382 (14)	-0.0017 (13)	0.0096 (12)	-0.0131 (13)
C5	0.0291 (14)	0.0494 (19)	0.0424 (15)	-0.0044 (12)	0.0069 (12)	-0.0086 (14)
C6	0.0298 (13)	0.0323 (14)	0.0302 (12)	0.0016 (11)	0.0056 (10)	-0.0008 (11)
C7	0.0306 (13)	0.0315 (14)	0.0318 (12)	-0.0011 (11)	0.0054 (11)	0.0022 (11)
C8	0.0300 (13)	0.0326 (14)	0.0307 (12)	0.0009 (11)	0.0012 (10)	-0.0016 (11)
C9	0.0380 (15)	0.0404 (16)	0.0315 (13)	-0.0054 (12)	0.0119 (12)	-0.0001 (12)
C10	0.0379 (15)	0.0356 (16)	0.0365 (14)	-0.0072 (12)	0.0097 (12)	0.0005 (12)
C11	0.0371 (15)	0.0463 (18)	0.0361 (14)	-0.0061 (13)	0.0134 (12)	-0.0080 (13)
C12	0.0322 (14)	0.0443 (16)	0.0416 (15)	-0.0082 (13)	0.0106 (12)	-0.0040 (13)

Geometric parameters (Å, °)

Zn1—N4 ⁱ	2.060 (2)	C2—H2A	0.930
Zn1—N1	2.060 (2)	C3—C4	1.384 (4)
Zn1—C11	2.1939 (8)	C3—C6	1.466 (4)
Zn1—C12	2.2402 (8)	C4—C5	1.373 (4)
S1—C7	1.727 (3)	C4—H4A	0.930
S1—C6	1.729 (3)	C5—H5A	0.930
N1—C5	1.341 (3)	C7—C8	1.462 (4)
N1—C1	1.343 (3)	C8—C12	1.390 (4)
N2—C6	1.302 (3)	C8—C9	1.397 (4)
N2—N3	1.357 (3)	C9—C10	1.372 (4)
N3—C7	1.301 (3)	C9—H9A	0.930
N4—C10	1.337 (3)	C10—H10A	0.930
N4—C11	1.337 (3)	C11—C12	1.374 (4)
C1—C2	1.375 (4)	C11—H11A	0.930
C1—H1A	0.930	C12—H12A	0.930
C2—C3	1.391 (4)		
N4 ⁱ —Zn1—N1	103.11 (9)	C3—C4—H4A	120.3
N4 ⁱ —Zn1—C11	107.44 (6)	N1—C5—C4	123.0 (3)
N1—Zn1—C11	107.78 (7)	N1—C5—H5A	118.5
N4 ⁱ —Zn1—C12	104.00 (7)	C4—C5—H5A	118.5
N1—Zn1—C12	104.64 (6)	N2—C6—C3	122.0 (2)
C11—Zn1—C12	127.44 (3)	N2—C6—S1	113.3 (2)
C7—S1—C6	86.95 (13)	C3—C6—S1	124.68 (19)
C5—N1—C1	117.7 (2)	N3—C7—C8	122.0 (2)
C5—N1—Zn1	121.31 (18)	N3—C7—S1	113.6 (2)
C1—N1—Zn1	120.60 (18)	C8—C7—S1	124.45 (19)
C6—N2—N3	113.2 (2)	C12—C8—C9	117.7 (3)
C7—N3—N2	113.0 (2)	C12—C8—C7	122.4 (2)

C10—N4—C11	117.7 (2)	C9—C8—C7	119.9 (2)
C10—N4—Zn1 ⁱⁱ	121.41 (18)	C10—C9—C8	119.3 (2)
C11—N4—Zn1 ⁱⁱ	120.52 (18)	C10—C9—H9A	120.3
N1—C1—C2	122.6 (3)	C8—C9—H9A	120.3
N1—C1—H1A	118.7	N4—C10—C9	122.9 (3)
C2—C1—H1A	118.7	N4—C10—H10A	118.6
C1—C2—C3	119.4 (3)	C9—C10—H10A	118.6
C1—C2—H2A	120.3	N4—C11—C12	123.4 (2)
C3—C2—H2A	120.3	N4—C11—H11A	118.3
C2—C3—C4	117.9 (3)	C12—C11—H11A	118.3
C2—C3—C6	119.5 (2)	C11—C12—C8	118.9 (3)
C4—C3—C6	122.6 (2)	C11—C12—H12A	120.5
C5—C4—C3	119.3 (3)	C8—C12—H12A	120.5
C5—C4—H4A	120.3		

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