

The infinite double-stranded chain polymer *catena-poly*[[bis(dicyan-amido)zinc(II)]-di- μ -1,2-bis(1,2,4-triazol-1-yl)ethane- $\kappa^4 N^4:N^{4'}$]

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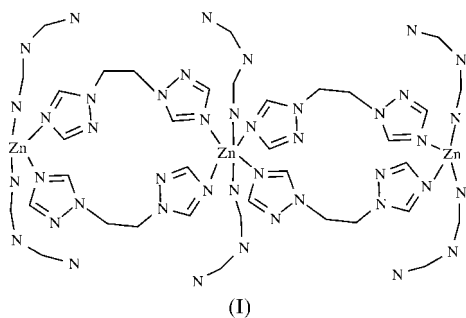
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The coordination geometry of the Zn^{II} atom in the title complex, [Zn(C₂N₃)₂(C₆H₈N₆)₂]_n or [Zn(dca)₂(bte)₂]_n, where bte is μ -1,2-bis(1,2,4-triazol-1-yl)ethane and dca is dicyanamide, is distorted compressed octahedral, in which the Zn^{II} atom lies on an inversion center and coordinates four N atoms from the triazole rings of four symmetry-related bte ligands and two N atoms from two symmetry-related monodentate dca ligands. The structure is polymeric, with 18-membered spiro-fused rings extending in the *b* direction and each 18-membered ring involving two inversion-related bte molecules.

Comment

The syntheses of new organic–inorganic polymers has been a rapidly developing area of research in recent years because of their unusual properties, such as electronic, optical, magnetic and catalytic properties (Batten & Robson, 1998; Blake *et al.*, 1999).



The design of coordination polymers is greatly influenced by several factors, such as the metal coordination preference, the structural characteristics of the polydentate organic ligand, the metal–ligand ratio, the solvent system and the counter-ion. The most widely used ligands are rigid rod-like organic building blocks, such as 4,4'-bipyridine (Fujita *et al.*, 1994) and

4,4'-azobispyridine (Li *et al.*, 2001), while flexible ligands have been studied relatively little. The flexible ligand 1,2-bis(1,2,4-triazol-1-yl)ethane (Torres *et al.*, 1988) is an excellent alternative for further research. The dicyanamide ligand, [N(CN)₂][−], is also a remarkably versatile building block for the construction of supramolecular architectures, since it can act in a mono-, bi- or tridentate manner (Riggio *et al.*, 2001; Li *et al.*, 2002). We report here the crystal structure of a novel infinite double-stranded chain polymer, *viz.* [Zn(dca)₂(bte)₂]_n, (I), which has been synthesized from a mixed-ligand system of 1,2-bis(1,2,4-triazol-1-yl)ethane (bte) and dicyanamide (dca).

Fig. 1 shows the local coordination about the zinc center in (I). The complex molecules have a center of symmetry and the Zn^{II} atom lies on an inversion center. The coordination geometry of the Zn^{II} atom is distorted compressed octahedral and the atom coordinates four N atoms from the triazole rings of four symmetry-related bte ligands and two N atoms from two symmetry-related monodentate dca ligands. The equatorial plane contains two N atoms from the triazole rings of two bte ligands [Zn1–N3 = 2.1948 (14) Å and Zn1–N3ⁱⁱⁱ = 2.1948 (14) Å; symmetry code: (iii) 1 – *x*, –*y*, 1 – *z*] and two N atoms from two dca ligands [Zn1–N7 = 2.1734 (16) Å and Zn1–N7ⁱⁱⁱ = 2.1734 (16) Å], and the axial positions are occupied by two triazole N atoms of two bte ligands [Zn1–N6ⁱ = 2.1263 (13) Å and Zn1–N6ⁱⁱ = 2.1263 (13) Å; symmetry codes: (i) *x*, *y* – 1, *z*; (ii) 1 – *x*, 1 – *y*, 1 – *z*]. The bte ligands exhibit a gauche conformation in (I). Zn^{II} atoms are linked by bte ligands *via* the N atoms in the 4-positions of two triazole rings, and a rhombic network of size 5.601 (2) × 6.687 (2) Å is formed. The diagonal lengths of the rhomb are 8.369 (2) Å for Zn1ⁱ···Zn1ⁱ and 9.063 (2) Å for C6ⁱⁱⁱ···C6ⁱ; the rhombic angles are 94.6 (2) and 85.4 (2)°.

Compound (I) has an infinite double-stranded chain structure (Fig. 1). The r.m.s. deviations of the triazole ring atoms from the mean planes of the rings containing atoms N3 and N6 are 0.0024 (9) and 0.0009 (8) Å, respectively, and the dihedral angle between the planes of the N3- and N6-triazole rings is 58.05 (6)°. The bte ligand is twisted during coordination and the N1–C5–C6–N4 torsion angle is 58.11 (16)°. Two strands of bte ligands are wrapped around one another and are held together by Zn^{II} atoms, forming an infinite double-stranded

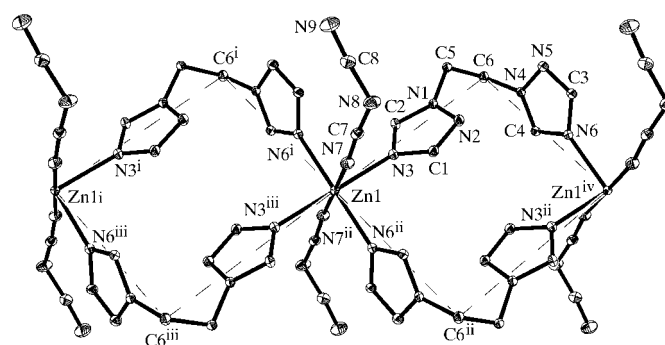


Figure 1

The coordination environment of the Zn atom of (I), showing displacement ellipsoids at the 30% probability level. [Symmetry codes: (i) *x*, –1 + *y*, *z*; (ii) 1 – *x*, 1 – *y*, 1 – *z*; (iii) 1 – *x*, –*y*, 1 – *z*; (iv) *x*, 1 + *y*, *z*.]

chain structure. Each chain consists of 18-membered spiro-fused rings, in which two Zn^{II} atoms are joined *via* two bte molecules. The chains extend along the *b* axis, and all of the Zn atoms in one chain are on the axial line. The Zn···Zn separation across the bridging bte ligand is equal to the *b*-axis translation [8.369 (4) Å], which is shorter than the inter-metallic distance found for [Cu(TTA)₂]₂(bte) [TTA is 1,1,1-trifluoro-3-(2-thenoyl)acetone], which exhibits *M*(*anti*-bte)*M* bridging [12.473 (2) Å; Li *et al.*, 1999]. The dicyanamide ligands are coordinated to the metal atoms in a monodentate manner *via* the nitrile N atom. Free dicyanamide ligands possess *C*_{2v} symmetry, while the dicyanamide ligand in (I) possesses pseudo-*C*_{2v} symmetry, with nitrile C–N bond distances of 1.156 (2) and 1.154 (2) Å (Table 1). There are weak N2···H5A–C5^v and N9···H2A–C2^{vi} interactions [symmetry codes: (v) $-x, -y + 1, -z + 1$; (vi) $-x, -y, -z + 1$] between triazole (dca) N atoms and alkane (triazole) H atoms of neighboring chains [N2···H5A–C5^v = 2.51 Å and N9···H2A–C2^{vi} = 2.54 Å]. There is also a weak interaction between a nitrile N atom and a triazole H atom of a neighboring chain [N9···H4A–C4^{vii} = 2.44 (3) Å; symmetry code: (vii) $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$]. Adjacent chains are linked *via* these weak interactions in the solid state in (I). Although many one-dimensional chain polymers have been reported (Dong *et al.*, 1999; Claramunt *et al.*, 2000), double-stranded chain polymers are rare (Zhao *et al.*, 2002). The synthesis of (I) is a successful example of the synthesis of novel polymers using the flexible bis(1,2,4-triazol-1-yl)alkane ligand.

Experimental

An aqueous solution (10 ml) of NaN(CN)₂ (1 mmol, 0.090 g) was mixed with an aqueous solution (10 ml) of Zn(NO₃)₂·6H₂O (0.5 mmol, 0.149 g) and the resulting mixture stirred for 20 min. A methanol solution (10 ml) of 1,2-bis(1,2,4-triazol-1-yl)ethane (0.082 g, 0.5 mmol) was then added slowly. The mixture was stirred at room temperature for 30 min and the resulting solution filtered. After the filtrate had been allowed to stand in air at room temperature for two weeks, well shaped colorless single crystals of (I) were obtained. The product was stable under ambient atmospheric conditions and insoluble in most common inorganic and organic solvents. Analysis found: C 36.46, H 2.98, N 47.73%; calculated for C₁₆H₁₆N₁₈Zn: C 36.55, H 3.07, N 47.98%.

Crystal data

[Zn(C₂N₃)₂(C₆H₈N₆)₂]
M_r = 525.84
 Monoclinic, *P*₂₁/*n*
a = 8.501 (4) Å
b = 8.369 (4) Å
c = 15.403 (6) Å
 β = 92.463 (6)°
V = 1094.8 (8) Å³
Z = 2

D_x = 1.595 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 3445 reflections
 θ = 3.5–27.5°
 μ = 1.17 mm⁻¹
T = 193.2 K
 Chunk, colorless
 0.55 × 0.39 × 0.20 mm

Data collection

Rigaku CCD diffractometer
 ω scans
 Absorption correction: multi-scan
 (*CrystalClear*; Rigaku, 2000)
T_{min} = 0.612, *T_{max}* = 0.802
 8103 measured reflections
 2386 independent reflections

2296 reflections with *I* > 2σ(*I*)
R_{int} = 0.023
 θ_{max} = 27.5°
h = –11 → 10
k = –10 → 10
l = –19 → 18

Table 1

Selected geometric parameters (Å, °).

Zn1–N6 ⁱ	2.1263 (13)	N8–C7	1.300 (2)
Zn1–N7	2.1734 (16)	N8–C8	1.314 (2)
Zn1–N3	2.1948 (14)	N9–C8	1.154 (2)
N7–C7	1.156 (2)		
N6 ⁱ –Zn1–N7	91.19 (5)	C7–N8–C8	119.49 (15)
N6 ⁱ –Zn1–N3	87.41 (5)	N7–C7–N8	173.85 (16)
N7–Zn1–N3	86.13 (5)	N9–C8–N8	174.38 (19)

Symmetry codes: (i) *x, y – 1, z*.

Refinement

Refinement on *F*²
R(*F*) = 0.028
wR(*F*²) = 0.063
S = 1.04
 2386 reflections
 160 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0313P)^2 + 0.5747P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.26 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.24 \text{ e } \text{Å}^{-3}$

Compound (I) crystallized in the monoclinic system and space group *P*₂₁/*n* was assigned from the systematic absences. H atoms were placed in idealized positions and refined as riding, with C–H distances of 0.93 (triazole) and 0.97 Å (ethane).

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1645). Services for accessing these data are described at the back of the journal.

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