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# The infinite one-dimensional chain polymer *catena*-poly[[bis[$\mu$-1,1′-ethane-1,2-diylbis(1,2,4-triazole)-$\kappa^2N^4:N^{4'}$]bis[azidozinc(II)]]-di-$\mu$-azido-$\kappa^4N^1:N^1$]

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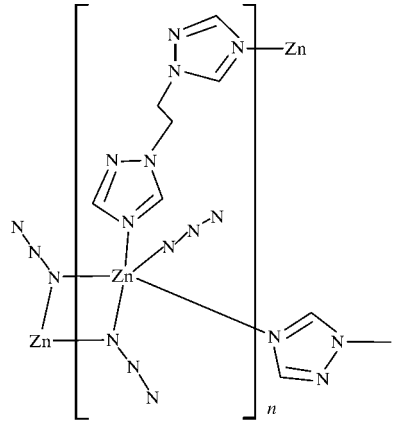
In the crystal structure of the title complex, $[Zn(N_3)_2(C_6H_8N_6)]_n$ or $[Zn(N_3)_2(bte)]_n$, where bte is $\mu$-1,2-bis(1,2,4-triazol-1-yl)ethane, each Zn atom is pentacoordinated in a distorted trigonal-bipyramidal coordination environment involving two N atoms from two bte ligands and three N atoms from three azide ligands. The Zn atoms are bridged by $\mu$-1,1-azide groups and bte ligands around a centre of inversion, forming an infinite one-dimensional chain containing both four-membered Zn($\mu$-1,1-$N_3$)$_2$Zn and 18-membered Zn(*gauche*-bte)$_2$Zn rings.

## Comment

Interest in the crystal engineering of coordinated frameworks stems not only from their potential applications as zeolite-like materials in molecular selection, ion exchange and catalysis but also from their intriguing variety of architectures and topologies (Robson *et al.*, 1992). The design of coordination polymers is highly 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 (Riggio *et al.*, 2001; Batten & Murray, 2003). 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). Relatively few studies of flexible ligands have been reported, but bis(1,2,4-triazol-1-yl)ethane (bte; Li, Xu *et al.*, 1999; Li, Zhou *et al.*, 1999; Li *et al.*, 2003) is an excellent flexible-ligand candidate for further research.

The pseudohalide azide has been demonstrated to be an extremely versatile ligand, which can provide end-to-end (EE or 1,3), end-on (EO or 1,1) or terminal coordination modes. Thus, a large number of azide-bridged polymers have been synthesized and magneto-structurally characterized (Ribas *et al.*, 1999). However, azide-bridged Zn polymers are relatively rare (Krischner *et al.*, 1986; Pan *et al.*, 1999; Chen & Chen, 2002). In the present work, we report the preparation and crystal structure of $[Zn(N_3)_2(bte)]_n$, (I), which exhibits a novel one-dimensional chain containing both four-membered Zn($\mu$-1,1-$N_3$)$_2$Zn and 18-membered Zn(*gauche*-bte)$_2$Zn rings.




(I)

The molecular structure of (I) is shown in Fig. 1 and Table 1 gives selected structural parameters. Each Zn atom is pentacoordinated in a distorted trigonal-bipyramidal coordination environment. The trigonal base plane is defined by two N atoms [N3 and N6$^{i}$; symmetry code: (i) $1-x$, $1-y$, $2-z$] from two bridging bte ligands and one N atom (N10) from an azide ligand. The Zn—$N_{bte}$ bond lengths are shorter than those found in $[Zn(dca)_2(bte)_2]_n$ (dca is dicyanamide; Li *et al.*, 2003). Two azide N atoms [N7 and N10$^{ii}$; symmetry code: (ii) $-x$, $1-y$, $2-z$] occupy the axial positions. Atoms Zn1, N7 and N10$^{ii}$ deviate from the trigonal base plane by 0.2809 (9), 2.287 (2) and −2.193 (2) Å, respectively. One azide ligand is monodentate; the other acts as a bridging ligand linking two Zn atoms in an end-on (EO or 1,1) coordination mode [Zn1—N10—Zn1$^{ii}$ = 105.32 (7)°], generating a four-membered Zn($\mu$-1,1-$N_3$)$_2$Zn ring, with an intra-ring Zn···Zn distance of 3.5830 (9) Å.

Compound (I) develops into an infinite one-dimensional chain extending along the *a* axis and constructed from the alternate interconnection of four-membered Zn($\mu$-1,1-$N_3$)$_2$Zn and 18-membered Zn(*gauche*-bte)$_2$Zn rings (Fig. 2). The bte ligands exhibit a *gauche* conformation. The two triazole ring planes, *viz*. C1/C2/N1–N3 and C3/C4/N4–N6, are planar, with r.m.s. deviations of 0.0019 (11) and 0.0006 (10) Å, respectively. The dihedral angle between these two triazole ring planes is 51.65 (6)°. The bte ligand is twisted, the N1—C5—C6—N4 torsion angle being 62.6 (2)°.

There are four potentially coordinating N atoms in the bte ligand, but only two, at the 4-positions of the triazole rings, coordinate to Zn atoms. Two bte ligands are thus held together by two Zn atoms, forming a Zn(*gauche*-bte)$_2$Zn ring around a centre of inversion, similar to that found in $[Zn(dca)_2(bte)_2]_n$

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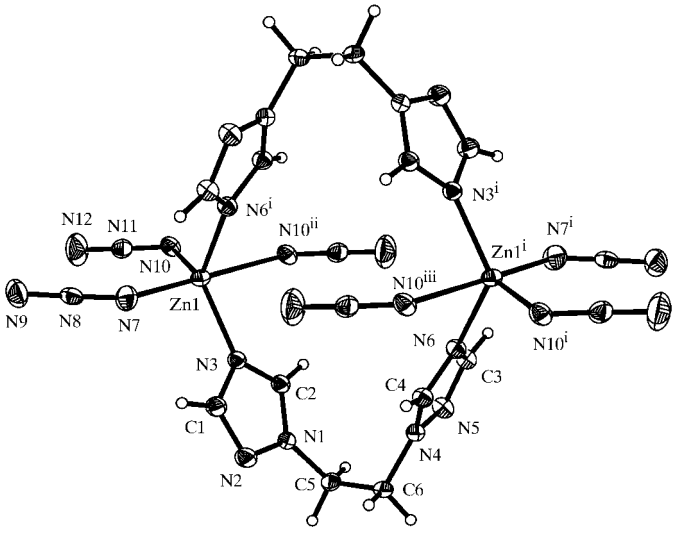


**Figure 1**
A view of (I), with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) $1-x, 1-y, 2-z$; (ii) $-x, 1-y, 2-z$; (iii) $1+x, y, z$.]

(Li *et al.*, 2003). The Zn···Zn separation across the 18-membered ring is 6.7220 (18) Å, which is obviously shorter than the 8.369 (4) Å separation in $[Zn(dca)_2(bte)_2]_n$. There are weak H···N interactions between the azide N atoms and alkane (triazole) H atoms of neighbouring chains [N8···H6*B*—C6$^{iv}$ (H···N = 2.50 Å) and N9···H4*A*—C4$^{v}$ (H···N = 2.27 Å); symmetry codes: (iv) $-1+x, y, -1+z$; (v) $1-x, 2-y, 2-z$], linking adjacent chains in the crystal.

One example of an azide-bridged Zn polymer is $[Zn(N_3)_2(4,4'\text{-bipy})]$ (Pan *et al.*, 1999; Martin *et al.*, 2001), in which the Zn–azide chain is an interesting combination of bridging types, incorporating four-membered $ZnN_2Zn$ rings, in which the azides bridge through one terminal atom, and six-membered rings, in which one of the azides coordinates to a pair of Zn atoms in an end-on fashion. Further examples are $[Zn(N_3)_2L]$ ($L$ is 2-methylpyridine, 3-methylpyridine, 4-methylpyridine, and 2,4-, 3,4- and 3,5-dimethylpyridine; Mautner *et al.*, 1987, 1988; Mautner & Kratky, 1988; Mautner & Krischner, 1992), in which each Zn atom is surrounded by four N atoms from different azide groups and one N atom from the pyridine in a distorted trigonal-bipyramidal fashion. The $ZnN_5$ polyhedra share common edges, thus forming chains. To our knowledge, a one-dimensional chain constructed from the alternate interconnection of four-membered and 18-membered rings is unusual. The structure of (I) is a successful example of the synthesis of a novel polymer using the flexible bis(1,2,4-triazol-1-yl)alkane ligand.

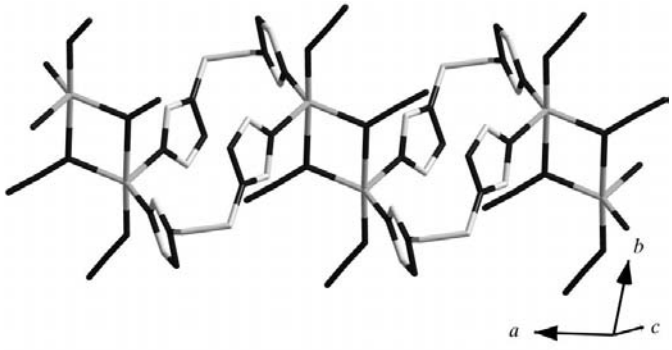


**Figure 2**
The infinite one-dimensional chain of (I).

## Experimental

A water/methanol (1:1 *v*/*v*) solution (25 ml) of 1,2-bis(1,2,4-triazol-1-yl)ethane (0.082 g, 0.5 mmol) was added to one leg of an H-shaped tube, and a water/methanol (1:1 *v*/*v*) solution (25 ml) of $NaN_3$ (0.078 g, 1.2 mmol) and $Zn(NO_3)_2\cdot 6H_2O$ (0.149 g, 0.5 mmol) was added to the other leg of the tube. Colourless crystals suitable for X-ray analysis were obtained after about three months. Analysis found: C 22.87, H 2.61, N 53.58%; calculated for $C_6H_8N_{12}Zn$: C 22.98, H 2.57, N 53.61%.

*Crystal data*

| | |
|---|---|
| $[Zn(N_3)_2(C_6H_8N_6)]$ | $Z = 2$ |
| $M_r = 313.61$ | $D_x = 1.805$ Mg m$^{-3}$ |
| Triclinic, $P\overline{1}$ | Mo $K\alpha$ radiation |
| $a = 7.646$ (3) Å | Cell parameters from 2938 reflections |
| $b = 8.690$ (3) Å | $\theta = 3.1$–$27.5°$ |
| $c = 9.266$ (3) Å | $\mu = 2.14$ mm$^{-1}$ |
| $\alpha = 95.430$ (5)° | $T = 193.2$ K |
| $\beta = 105.054$ (6)° | Block, colourless |
| $\gamma = 100.884$ (5)° | 0.50 × 0.35 × 0.21 mm |
| $V = 577.1$ (3) Å$^3$ | |

*Data collection*

| | |
|---|---|
| Rigaku Mercury CCD diffractometer | 2575 independent reflections |
| $\omega$ scans | 2488 reflections with $I > 2\sigma(I)$ |
| Absorption correction: multi-scan (North *et al.*, 1968) | $R_{int} = 0.023$ |
| $T_{min} = 0.412$, $T_{max} = 0.638$ | $\theta_{max} = 27.5°$ |
| 6341 measured reflections | $h = -9 \rightarrow 9$ |
| | $k = -11 \rightarrow 10$ |
| | $l = -12 \rightarrow 12$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0293P)^2 + 0.4081P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $R(F) = 0.025$ | $(\Delta/\sigma)_{max} = 0.001$ |
| $wR(F^2) = 0.063$ | $\Delta\rho_{max} = 0.29$ e Å$^{-3}$ |
| $S = 1.06$ | $\Delta\rho_{min} = -0.41$ e Å$^{-3}$ |
| 2575 reflections | |
| 172 parameters | |
| H-atom parameters constrained | |

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Zn1—N3 | 2.0222 (15) | Zn1—N10 | 1.9964 (17) |
| Zn1—N7 | 2.0344 (18) | Zn1—N10$^{ii}$ | 2.4943 (17) |
| Zn1—N6$^{i}$ | 2.0476 (15) | | |
| | | | |
| N3—Zn1—N7 | 93.69 (7) | N10—Zn1—N3 | 124.15 (7) |
| N3—Zn1—N6$^{i}$ | 121.68 (6) | N10—Zn1—N6$^{i}$ | 108.40 (6) |
| N3—Zn1—N10$^{ii}$ | 85.78 (6) | N10—Zn1—N7 | 107.44 (7) |
| N6$^{i}$—Zn1—N10$^{ii}$ | 85.28 (6) | N10—Zn1—N10$^{ii}$ | 74.68 (7) |
| N7—Zn1—N6$^{i}$ | 93.08 (7) | Zn1—N10—Zn1$^{ii}$ | 105.32 (7) |
| N7—Zn1—N10$^{ii}$ | 177.67 (6) | | |

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

H atoms were placed in idealized positions and refined as riding, with C—H distances of 0.95 (triazole) and 0.99 Å (ethane).

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL* and *DIAMOND* (Brandenburg, 2000).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1078). Services for accessing these data are described at the back of the journal.

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