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A novel dimeric zinc(II) complex: bis[μ-1,2-bis(1*H*-1,2,4-triazol-1-yl)-ethane-$\kappa^2N^4:N^{4'}$]bis[diisothiocyanato-zinc(II)]

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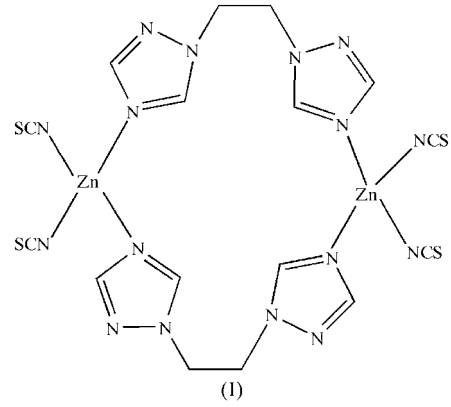
The coordination geometry of the Zn^{II} atom in the title complex, $[Zn_2(NCS)_4(C_6H_8N_6)_2]$, is that of a distorted tetrahedron, in which the Zn^{II} atom is coordinated by four N atoms from the triazole rings of two symmetry-related 1,2-bis(1,2,4-triazol-1-yl)ethane ligands and two thiocyanate ligands. Two Zn^{II} atoms are bridged by two organic ligands to form a dimer. The dimer lies about an inversion center.

Comment

1,2,4-Triazole and its derivatives are very interesting ligands, because they combine the coordination geometry of both pyrazole and imidazole with regard to the arrangement of their three heteroatoms. A large number of mononuclear, oligonuclear and polynuclear transition metal complexes of 1,2,4-triazole derivatives have been synthesized and characterized because of their magnetic properties and novel topologies (Haasnoot, 2000). However, complexes of the flexible bis(triazole) ligand have not been well explored (Haasnoot, 2000; van Albada *et al.*, 2000; Zhao *et al.*, 2002; Meng *et al.*, 2004; Li *et al.*, 2005).

In our previous studies, we synthesized several coordination polymers with the flexible ligand 1,2-bis(1,2,4-triazol-1-yl)-ethane (bte; Li *et al.*, 1999, 2003; Zhu *et al.*, 2004; Wang *et al.*, 2005). In order to extend our work, we report here the preparation and crystal structure of a novel dimeric Zn^{II} complex, *viz*. $[Zn(NCS)_2(bte)]_2$, (I).

The crystal structure of (I) is built up from a neutral dimeric metallocycle. The dimer is centrosymmetric. As shown in Fig. 1, in each dimer, two zinc(II) centers are connected by two bte ligands, resulting in a discrete $Zn_2(bte)_2$ 18-membered binuclear metallocycle. Wilke (1978) reported many binuclear complexes containing 3-, 4-, 5-, 7-, 9-, 11-, 12-, 13- and 14-membered binuclear metallocycles. Previously, we synthesized a dimeric copper(II) complex, *viz*. $\{[Cu(TTA)_2]_2(bte)\}$, in which bte acts as a bridge, linking two $Cu(TTA)_2$ units and forming a dimer structure [TTA is 1,1,1-trifluoro-3-(2-thenoyl)-acetone; Li *et al.*, 1999]. Complex (I) is the second dimer complex constructed from bte.



(I)

Each zinc(II) center is four-coordinated by two N atoms of bte ligands and two N atoms of two thiocyanate ligands (Table 1), forming a distorted tetrahedral geometry. The Zn—N(triazole) bond lengths in (I) are shorter than those in the similar compounds $[Zn(N_3)_2(bte)]_n$ (Zhu *et al.*, 2004) and $[Zn(dca)_2(bte)_2]_n$ (dca is dicyanamide; Li *et al.*, 2003). The N—Zn—N bond angles are in the range 102.35 (11)–116.53 (9)°. The monodentate N-bound NCS^- ligands are almost linear (Table 1).

However, the zinc(II) centers have different coordination geometries in the previously reported bte complexes. For example, the coordination environment of the zinc(II) center is distorted octahedral in $[Zn(dca)_2(bte)_2]_n$, which has a one-dimensional double chain containing a $Zn_2(bte)_2$ 18-membered metallocycle (Li *et al.*, 2003). The coordination environment of the zinc(II) center is distorted trigonal bipyramidal in $[Zn(N_3)_2(bte)]_n$, which forms an infinite one-dimensional chain containing both 18-membered $Zn_2(bte)_2$ and four-membered $Zn_2(\mu\text{-}1,1\text{-}N_3)_2$ rings (Zhu *et al.*, 2004).

Each bte ligand exhibits a *gauche* conformation in (I) and the above two cited compounds, in contrast to the *anti* conformation of the free bte molecule (Li *et al.*, 2004). The N1—C5—C6—N4 torsion angle is 69.1 (3)° in (I), 58.1 (2)° in $[Zn(dca)_2(bte)_2]_n$ (Li *et al.*, 2003) and 62.6 (2)° in [Zn-

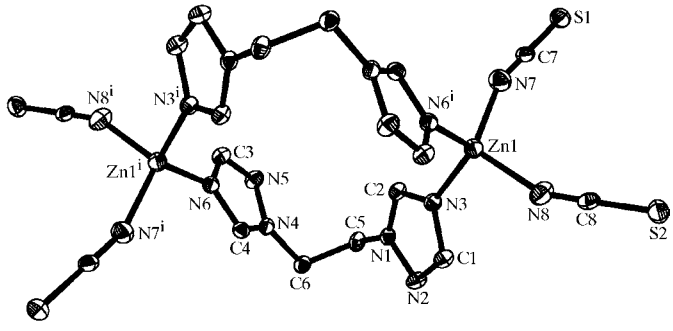


Figure 1
The dimeric structure of (I), with displacement ellipsoids drawn at the 30% probability level. H atoms have been omitted for clarity. [Symmetry code: (i) $-x+1, -y, -z+1$.]

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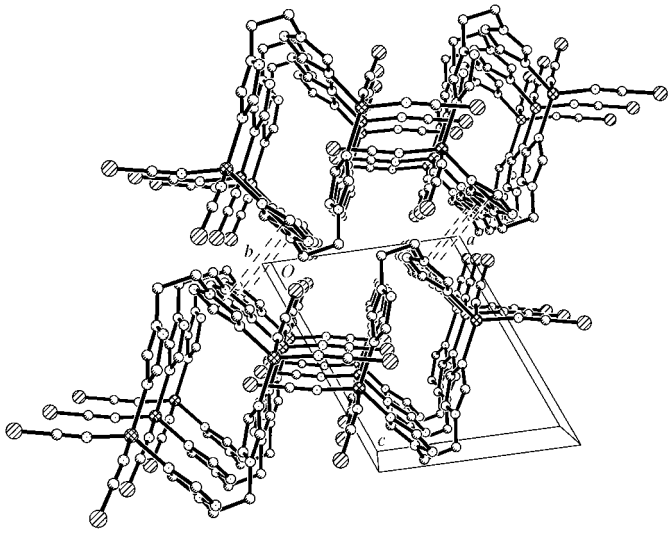

Figure 2
The cell packing of (I) along [010], showing π–π stacking interactions as dashed lines.

$(N_3)_2(bte)]_n$ (Zhu *et al.*, 2004). The dihedral angle between the two triazole ring is 60.03 (10)° in (I), 58.05 (6)° in $[Zn(dca)_2(bte)_2]_n$ and 51.65 (6)° in $[Zn(N_3)_2(bte)]_n$. The Zn···Zn separation *via* the bridging bte ligand is 7.268 (2) Å in (I), compared with the corresponding values of 8.369 (4) Å in $[Zn(dca)_2(bte)_2]_n$ and 6.722 (2) Å in $[Zn(N_3)_2(bte)]_n$.

Weak hydrogen-bonding and π–π stacking interactions play an important role in the formation of the crystal structure. The dimers superpose together along [010] and form channels with the dimensions 6.4 × 5.5 Å. The S atoms of adjacent dimers along [100] insert into the channels. The N4–N6/C3/C4 triazole ring and its symmetry equivalent at $(2 - x, -y, -z)$ are parallel, with a centroid-to-centroid distance of 4.048 Å and a perpendicular distance of 3.723 Å, exhibiting obvious π–π stacking interactions (Fig. 2). There are weak C—H···S hydrogen-bonding interactions between the H atoms of the bte molecules and the S atoms of thiocyanate groups of adjacent dimers (Table 2).

Experimental

A 25 ml water/methanol solution (1:1 *v*/*v*) of $Zn(NO_3)_2{\cdot}6H_2O$ (0.5 mmol) was added to one leg of a H-shaped tube, and a 25 ml water/methanol solution (1:1 *v*/*v*) of bte (0.5 mmol) and KSCN (1.0 mmol) was added to the other leg of the tube. Colorless crystals were obtained after about two months. Analysis calculated for $C_{16}H_{16}N_{16}S_4Zn_2$: C 27.79, H 2.33, N 32.42%; found: C 27.75, H 2.31, N 32.36%.

Crystal data

$[Zn_2(NCS)_4(C_6H_8N_6)_2]$
M_r = 691.51
Triclinic, $P\overline{1}$
a = 8.3859 (14) Å
b = 8.7715 (19) Å
c = 10.0402 (10) Å
α = 80.784 (13)°
β = 68.195 (11)°
γ = 87.373 (14)°
V = 676.8 (2) Å^3
Z = 1
D_x = 1.697 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 2.12 mm^{-1}
T = 193 (2) K
Block, colorless
0.30 × 0.24 × 0.14 mm

Data collection

Rigaku Mercury CCD diffractometer
ω scans
Absorption correction: multi-scan (Jacobson, 1998)
T_{min} = 0.546, T_{max} = 0.748
6769 measured reflections
2462 independent reflections
2192 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
θ_{max} = 25.3°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.083
S = 1.01
2462 reflections
172 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0453P)^2 + 0.3766P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.55 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—N7	1.935 (3)	Zn1—N3	1.994 (2)
Zn1—N8	1.945 (3)	Zn1—N6^{i}	2.009 (2)
N7—Zn1—N8	110.66 (12)	N3—Zn1—N6^{i}	116.53 (9)
N7—Zn1—N3	112.05 (11)	C7—N7—Zn1	159.1 (3)
N8—Zn1—N3	105.54 (11)	C8—N8—Zn1	156.4 (3)
N7—Zn1—N6^{i}	109.15 (10)	N7—C7—S1	179.3 (3)
N8—Zn1—N6^{i}	102.35 (11)	N8—C8—S2	179.2 (3)

Symmetry code: (i) $-x+1, -y, -z+1$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1···S1^{ii}	0.95	2.95	3.853 (3)	159
C2—H2···S1^{iii}	0.95	2.82	3.525 (3)	131
C4—H4···S2^{iv}	0.95	2.79	3.574 (3)	140
C6—H6*B*···S2^{iv}	0.99	2.95	3.819 (3)	148

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

H atoms were placed in idealized positions and refined as riding, with C—H distances of 0.95 (triazole) and 0.99 Å (ethane), and with $U_{iso}(H) = 1.2U_{eq}(C)$.

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); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3065). Services for accessing these data are described at the back of the journal.

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