metal-organic compounds

Bis[μ-1,2-bis(1,2,4-triazol-4-yl)ethane]-bis[diiodidozinc(II)]

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In the title dinuclear complex, $[Zn_2I_4(C_6H_8N_6)_2]$, two Zn^{II} atoms are bridged by two 1,2-bis(1,2,4-triazol-4-yl)ethane (btre) ligands, forming a centrosymmetric metallacycle. The coordination geometry of the Zn^{II} ion is distorted tetrahedral with the coordination sphere formed by two N atoms from the triazole rings of two symmetry-related btre ligands and two iodide ligands.

Related literature

For the isostructural zinc complexes $[Zn_2(btre)_2X_4]$, where X = Cl, Br, see: Habit *et al.* (2009). For other triazole coordination compounds, see: Haasnoot (2000); Li *et al.* (2003); Zhang *et al.* (2007); Zhu *et al.* (2004).
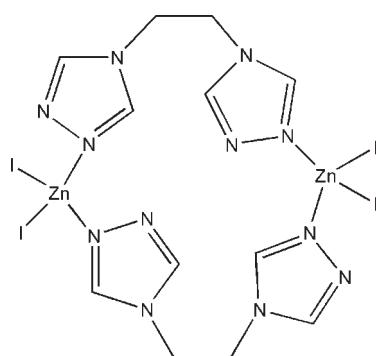
Experimental

Crystal data

$[Zn_2I_4(C_6H_8N_6)_2]$
M_r = 966.71
Monoclinic, $C2/c$
a = 20.241 (5) Å
b = 7.3847 (14) Å
c = 17.348 (4) Å
β = 97.375 (5)°
V = 2571.6 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 6.69 mm^{-1}
T = 293 K
$0.59 \times 0.21 \times 0.20$ mm

Data collection

Rigaku Mercury CCD diffractometer
Absorption correction: multi-scan (*REQAB*; Jacobson, 1998)
T_{min} = 0.110, T_{max} = 0.348
11703 measured reflections
2339 independent reflections
2063 reflections with $I > 2\sigma(I)$
R_{int} = 0.040

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.106
S = 1.07
2339 reflections
136 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.69 e Å^{-3}
$\Delta\rho_{min}$ = −1.31 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—N1	2.017 (5)	Zn1—I1	2.5479 (8)
Zn1—N4^i	2.019 (5)	Zn1—I2	2.5523 (9)
N1—Zn1—N4^i	103.68 (19)	N1—Zn1—I2	113.03 (14)
N1—Zn1—I1	108.78 (14)	N4^i—Zn1—I2	107.90 (14)
N4^i—Zn1—I1	112.08 (14)	I1—Zn1—I2	111.19 (3)

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

Data collection: *CrystalClear* (Rigaku, 2000); 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: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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supporting information

Bis[*µ*-1,2-bis(1,2,4-triazol-4-yl)ethane]bis[diiodidozinc(II)]

Yunfei Feng, Na Liang, Baolong Li and Haiyan Li

S1. Comment

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).

In our previous work, we synthesized several zinc^{II} complexes with 1,2-bis(1,2,4-triazol-1-yl)ethane (bte; Li *et al.*, 2003; Zhang *et al.*, 2007; Zhu *et al.*, 2004). 1,2-Bis(1,2,4-triazol-4-yl)ethane (btre) is an isomer of 1,2-bis(1,2,4-triazol-1-yl)ethane. In the present work, we report here the preparation and crystal structure of a dimeric zinc^{II} complex, namely, [Zn(btre)I$_2$]$_2$ (I).

The crystal structure of (I) is built up from a neutral dimeric metallacycle. The dimer is centrosymmetric. As shown in Fig.1, in each dimer, two zinc^{II} centres are connected by two btre lignads resulting in a discrete Zn$_2$(btre)$_2$ 18-membered binuclear metallacycle.

Each zinc^{II} centre is four-coordinated by two N atoms of btre ligands and two I lignads (Table 1), forming a distorted tetrahedral geometry. Each btre exhibits a gauche conformation in (I). The N3—C5—C6—N6 torsion angle is 63.8 (7)°. The dihedral angle between the two triazole rings is 45.6 (2)°. The Zn···Zn separation via the bridging btre ligand is 7.755 (2) Å in (I), compared with the corresponding values of 7.8750 (2) Å in [Zn(btre)Cl$_2$]$_2$ and 7.7980 (5) Å in [Zn(btre)Br$_2$]$_2$ (Habit *et al.*, 2009).

S2. Experimental

10 ml of aqueous solution of ZnI$_2$ (1 mmol) was added to a tube, and 10 ml of MeOH solution of 1,2-bis(1,2,4-triazol-4-yl)ethane (btre) (1.0 mmol) was carefully added above the aqueous solution. Colourless crystals were obtained after about two weeks. Anal. Calcd. for C$_{12}$H$_{16}$I$_4$N$_{12}$Zn$_2$: C, 14.91; H, 1.67; N, 17.39%. Found: C, 14.82; H, 1.56; N, 17.31%.

S3. Refinement

H atom were placed in idealized positions and refined as riding, with C—H distances of 0.93 (triazole) and 0.97Å (ethane), and with U$_{iso}$(H) = 1.2U$_{eq}$(C).
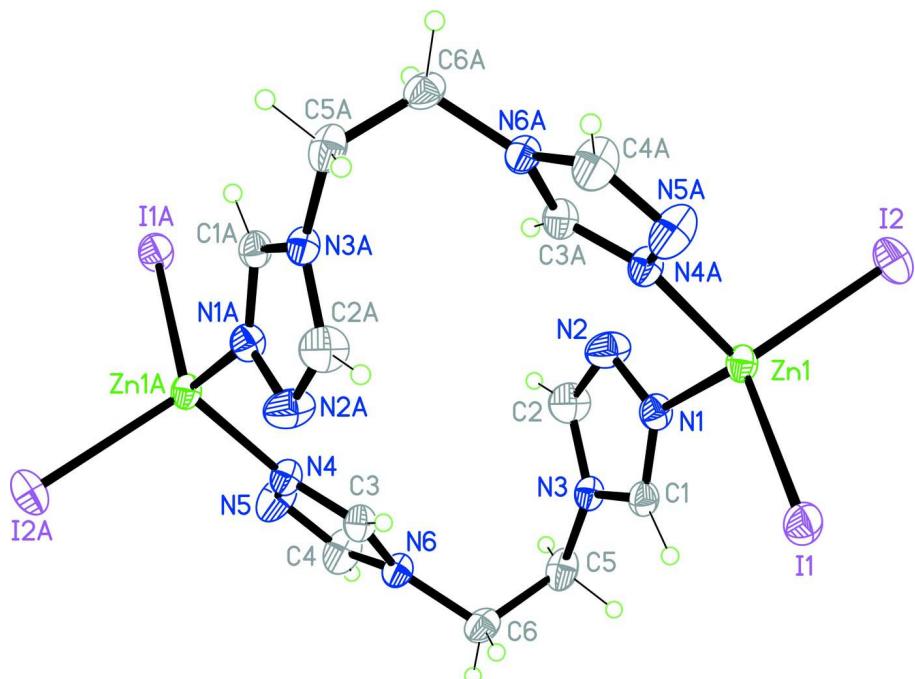
Figure 1

A dimeric structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level (symmetry code for atoms A: -x+1/2, -y+1/2, -z+1).
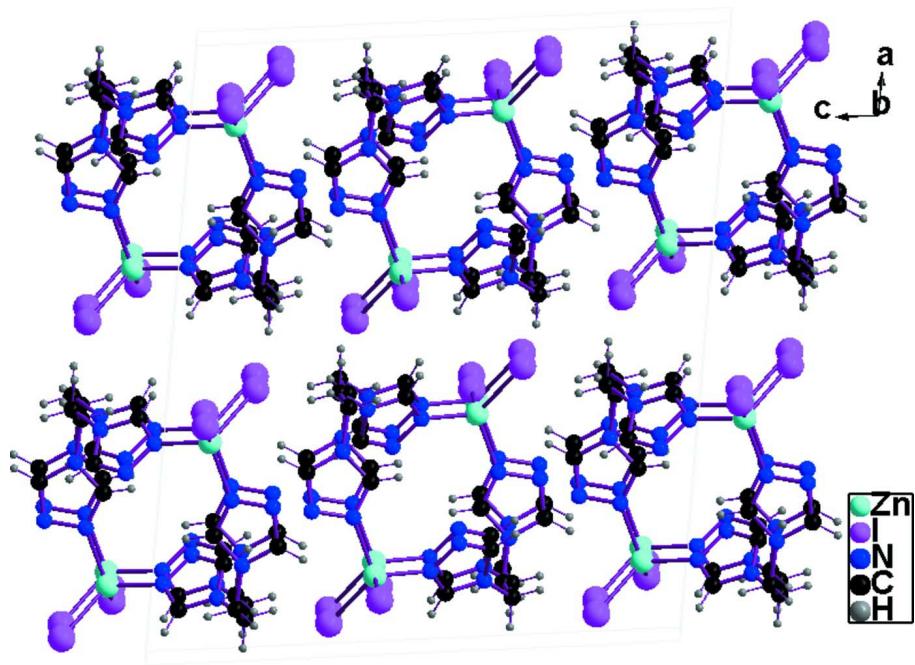
Figure 2

Crystal packing of the title compound viewed along the [010] direction.

Bis[μ-1,2-bis(1,2,4-triazol-4-yl)ethane]bis[diiodidozinc(II)]

Crystal data

$[Zn_2I_4(C_6H_8N_6)_2]$	$F(000) = 1776$
$M_r = 966.71$	$D_x = 2.497$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71070$ Å
Hall symbol: -c 2yc	Cell parameters from 4578 reflections
$a = 20.241$ (5) Å	$\theta = 3.1$–25.4°
$b = 7.3847$ (14) Å	$\mu = 6.69$ mm^{-1}
$c = 17.348$ (4) Å	$T = 293$ K
$\beta = 97.375$ (5)°	Block, yellow
$V = 2571.6$ (9) Å^3	0.59 × 0.21 × 0.20 mm
$Z = 4$	

Data collection

Rigaku Mercury CCD diffractometer	11703 measured reflections
Radiation source: fine-focus sealed tube	2339 independent reflections
Graphite monochromator	2063 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.040$
Absorption correction: multi-scan (REQAB; Jacobson, 1998)	$\theta_{max} = 25.3°$, $\theta_{min} = 3.1°$
	$h = -23 \rightarrow 24$
	$k = -8 \rightarrow 8$
$T_{min} = 0.110$, $T_{max} = 0.348$	$l = -20 \rightarrow 20$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.039$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.106$	
$S = 1.07$	H-atom parameters constrained
2339 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0585P)^2 + 4.1632P]$
136 parameters	where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	$(\Delta/\sigma)_{max} = 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.69$ e Å^{-3}
	$\Delta\rho_{min} = -1.31$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Zn1	0.13008 (3)	−0.08434 (9)	0.58428 (4)	0.0339 (2)
I1	0.05228 (2)	0.08983 (6)	0.66190 (3)	0.04764 (18)
I2	0.09753 (2)	−0.41797 (6)	0.57188 (3)	0.05286 (19)
N1	0.1311 (2)	0.0385 (7)	0.4806 (3)	0.0372 (11)

N2	0.1752 (3)	−0.0096 (9)	0.4306 (3)	0.0571 (15)
N3	0.1084 (2)	0.2012 (7)	0.3770 (2)	0.0340 (10)
N4	0.2741 (2)	0.5707 (6)	0.3664 (3)	0.0375 (11)
N5	0.2601 (3)	0.6027 (9)	0.2874 (3)	0.0580 (17)
N6	0.1672 (2)	0.5550 (7)	0.3363 (3)	0.0365 (11)
C1	0.0918 (3)	0.1627 (8)	0.4480 (3)	0.0361 (13)
H1A	0.0573	0.2171	0.4702	0.043*
C2	0.1604 (4)	0.0924 (10)	0.3697 (4)	0.0543 (19)
H2A	0.1831	0.0903	0.3264	0.065*
C3	0.2178 (3)	0.5456 (8)	0.3934 (3)	0.0389 (14)
H3A	0.2135	0.5241	0.4453	0.047*
C4	0.1964 (4)	0.5905 (10)	0.2722 (4)	0.057 (2)
H4A	0.1732	0.6044	0.2227	0.069*
C5	0.0761 (3)	0.3322 (10)	0.3219 (3)	0.0466 (16)
H5A	0.0282	0.3217	0.3209	0.056*
H5B	0.0867	0.3030	0.2704	0.056*
C6	0.0963 (3)	0.5244 (9)	0.3406 (4)	0.0441 (15)
H6A	0.0702	0.6049	0.3045	0.053*
H6B	0.0867	0.5535	0.3926	0.053*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0336 (4)	0.0388 (4)	0.0292 (4)	−0.0052 (3)	0.0042 (3)	0.0017 (3)
I1	0.0509 (3)	0.0455 (3)	0.0502 (3)	−0.00351 (19)	0.0210 (2)	−0.00607 (18)
I2	0.0723 (4)	0.0381 (3)	0.0476 (3)	−0.01108 (19)	0.0055 (2)	−0.00284 (17)
N1	0.042 (3)	0.040 (3)	0.031 (2)	−0.002 (2)	0.011 (2)	0.002 (2)
N2	0.057 (4)	0.071 (4)	0.047 (3)	0.020 (3)	0.020 (3)	0.015 (3)
N3	0.033 (2)	0.040 (3)	0.028 (2)	−0.005 (2)	0.0016 (19)	0.004 (2)
N4	0.035 (3)	0.047 (3)	0.030 (2)	−0.004 (2)	0.004 (2)	0.004 (2)
N5	0.042 (3)	0.102 (5)	0.029 (3)	−0.005 (3)	0.002 (2)	0.010 (3)
N6	0.031 (2)	0.046 (3)	0.032 (2)	−0.002 (2)	0.002 (2)	0.008 (2)
C1	0.037 (3)	0.038 (3)	0.035 (3)	−0.004 (3)	0.010 (3)	0.001 (3)
C2	0.066 (4)	0.067 (5)	0.034 (3)	0.008 (4)	0.019 (3)	0.010 (3)
C3	0.041 (3)	0.044 (3)	0.032 (3)	−0.004 (3)	0.007 (3)	0.001 (3)
C4	0.050 (4)	0.089 (6)	0.031 (3)	−0.007 (4)	−0.001 (3)	0.017 (3)
C5	0.037 (3)	0.068 (4)	0.032 (3)	−0.012 (3)	−0.007 (3)	0.009 (3)
C6	0.034 (3)	0.058 (4)	0.040 (3)	0.007 (3)	0.003 (3)	0.016 (3)

Geometric parameters (Å, º)

Zn1—N1	2.017 (5)	N5—C4	1.285 (9)
Zn1—N4[i]	2.019 (5)	N6—C3	1.333 (7)
Zn1—I1	2.5479 (8)	N6—C4	1.351 (8)
Zn1—I2	2.5523 (9)	N6—C6	1.463 (7)
N1—C1	1.296 (7)	C1—H1A	0.9300
N1—N2	1.369 (7)	C2—H2A	0.9300
N2—C2	1.301 (8)	C3—H3A	0.9300

N3—C2	1.342 (8)	C4—H4A	0.9300
N3—C1	1.350 (7)	C5—C6	1.502 (9)
N3—C5	1.455 (8)	C5—H5A	0.9700
N4—C3	1.301 (7)	C5—H5B	0.9700
N4—N5	1.384 (7)	C6—H6A	0.9700
N4—Zn1ⁱ	2.019 (5)	C6—H6B	0.9700
N1—Zn1—N4ⁱ	103.68 (19)	N3—C1—H1A	125.2
N1—Zn1—I1	108.78 (14)	N2—C2—N3	111.8 (5)
N4ⁱ—Zn1—I1	112.08 (14)	N2—C2—H2A	124.1
N1—Zn1—I2	113.03 (14)	N3—C2—H2A	124.1
N4ⁱ—Zn1—I2	107.90 (14)	N4—C3—N6	110.5 (5)
I1—Zn1—I2	111.19 (3)	N4—C3—H3A	124.7
C1—N1—N2	108.7 (5)	N6—C3—H3A	124.7
C1—N1—Zn1	129.1 (4)	N5—C4—N6	112.3 (6)
N2—N1—Zn1	122.1 (4)	N5—C4—H4A	123.9
C2—N2—N1	105.3 (5)	N6—C4—H4A	123.9
C2—N3—C1	104.5 (5)	N3—C5—C6	113.5 (5)
C2—N3—C5	128.9 (5)	N3—C5—H5A	108.9
C1—N3—C5	126.6 (5)	C6—C5—H5A	108.9
C3—N4—N5	107.7 (5)	N3—C5—H5B	108.9
C3—N4—Zn1ⁱ	133.9 (4)	C6—C5—H5B	108.9
N5—N4—Zn1ⁱ	118.4 (4)	H5A—C5—H5B	107.7
C4—N5—N4	105.3 (5)	N6—C6—C5	112.1 (5)
C3—N6—C4	104.2 (5)	N6—C6—H6A	109.2
C3—N6—C6	128.2 (5)	C5—C6—H6A	109.2
C4—N6—C6	127.5 (5)	N6—C6—H6B	109.2
N1—C1—N3	109.6 (5)	C5—C6—H6B	109.2
N1—C1—H1A	125.2	H6A—C6—H6B	107.9
N4ⁱ—Zn1—N1—C1	−131.9 (5)	C1—N3—C2—N2	0.9 (8)
I1—Zn1—N1—C1	−12.5 (5)	C5—N3—C2—N2	−178.9 (6)
I2—Zn1—N1—C1	111.5 (5)	N5—N4—C3—N6	1.5 (7)
N4ⁱ—Zn1—N1—N2	51.5 (5)	Zn1ⁱ—N4—C3—N6	177.6 (4)
I1—Zn1—N1—N2	171.0 (4)	C4—N6—C3—N4	−0.9 (7)
I2—Zn1—N1—N2	−65.0 (5)	C6—N6—C3—N4	176.2 (6)
C1—N1—N2—C2	1.0 (8)	N4—N5—C4—N6	0.9 (8)
Zn1—N1—N2—C2	178.2 (5)	C3—N6—C4—N5	−0.1 (8)
C3—N4—N5—C4	−1.4 (7)	C6—N6—C4—N5	−177.1 (6)
Zn1ⁱ—N4—N5—C4	−178.3 (5)	C2—N3—C5—C6	−101.4 (8)
N2—N1—C1—N3	−0.4 (7)	C1—N3—C5—C6	78.8 (7)
Zn1—N1—C1—N3	−177.4 (4)	C3—N6—C6—C5	−93.3 (7)
C2—N3—C1—N1	−0.3 (7)	C4—N6—C6—C5	83.1 (8)
C5—N3—C1—N1	179.6 (5)	N3—C5—C6—N6	63.8 (7)
N1—N2—C2—N3	−1.2 (9)		

Symmetry code: (i) −x+1/2, −y+1/2, −z+1.