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Bis[(1*S*,1′*S*)-1,1′-(4-amino-4*H*-1,2,4-triazole-3,5-diyl)diethanol-κN^1]bis(nitrato-κ*O*)zinc

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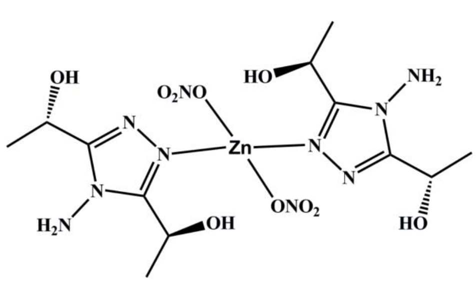
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.004 Å; R factor = 0.033; wR factor = 0.088; data-to-parameter ratio = 16.0.

In the title homochiral mononuclear compound, $[Zn(NO_3)_2(C_6H_{12}N_4O_2)_2]$, the Zn^{II} atom is located on a twofold rotation axis and coordinated by two N atoms from two ligands and two O atoms from two NO_3^- anions, adopting a distorted tetrahedral coordination geometry. The compound is enantiomerically pure and corresponds to the *S* diastereoisomer, with the optical activity originating from the chiral ligand. In the crystal, molecules are connected into three-dimensional supramolecular networks through O—H···O, O—H···N and N—H···O hydrogen bonds.

Related literature

For 4-amino-4*H*-1,2,4-triazole transition metal complexes, see: Zhai *et al.* (2006); Yi *et al.* (2004). For the non-linear optical properties of chiral coordination compounds, see: Evans & Lin (2002). For uses of chiral coordination compounds, see: Hang *et al.* (2011); Lin (2010).



Experimental

Crystal data

$[Zn(NO_3)_2(C_6H_{12}N_4O_2)_2]$
M_r = 533.78
Tetragonal, $P4_12_12$
a = 12.1252 (7) Å
c = 14.6108 (17) Å
V = 2148.1 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.22 mm^{-1}
T = 298 K
0.36 × 0.18 × 0.12 mm

Data collection

Bruker APEX DUO diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.767, T_{max} = 0.862
7446 measured reflections
2463 independent reflections
2154 reflections with $I > 2\sigma(I)$
R_{int} = 0.032

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.088
S = 1.05
2463 reflections
154 parameters
378 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Absolute structure: Flack (1983), 993 Friedel pairs
Flack parameter: −0.022 (15)

Table 1
Selected geometric parameters (Å, °).

Zn1—N1	2.0239 (19)	Zn1—O3	2.071 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2^{ii}	0.82	2.07	2.867 (3)	163
N4—H4*B*···O5^{ii}	0.89	2.51	3.142 (5)	129
O2—H2···N2^{iii}	0.82	2.13	2.943 (3)	174
N4—H4*C*···O4^{iv}	0.89	2.40	3.022 (4)	127

Symmetry codes: (ii) $x-\frac{1}{2}, -y+\frac{3}{2}, -z+\frac{7}{4}$; (iii) $-y+2, -x+2, -z+\frac{3}{2}$; (iv) $-x+2, -y+2, z-\frac{1}{2}$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT-Plus* (Bruker, 2000); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *DIAMOND* (Brandenburg & Putz, 2007); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FF2051).

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supplementary materials

Acta Cryst. (2012). E**68**, m191-m192 [**doi:10.1107/S1600536812001754**]

Bis[(1*S*,1'*S*)-1,1'-(4-amino-4*H*-1,2,4-triazole-3,5-diyl)diethanol-κN^1]bis(nitrato-κ*O*)zinc

X.-G. Liu, L. Shen, Q.-S. Cai and M. Luo

Comment

Chiral coordination complexes have received considerable attention due to their potential applications in the area of ferroelectrics, enantiopure catalysis and separation (Hang *et al.*, 2011; Lin *et al.*, 2010). Among the different approaches to synthesize chiral coordination compounds, the most effective synthetic strategy is to use optically pure chiral ligands. Herein, we report a chiral zinc coordination compound (S)-[Zn(deoatrz)$_2$(NO$_3$)$_2$], by using an enantiopure (1*S*,1'*S*)-1,1'-(4-amino-4*H*-1,2,4-triazole-3,5-diyl)diethanol (deoatrz), reacting with zinc salts. Furthermore, its structure is characterized.

Single crystal structural analysis reveals that the title compound crystallizes in the tetragonal system, chiral space group P4$_1$2$_1$2. The title compound is a mononuclear and its asymmetric unit consists of one Zn atom, two deoatrz ligands and two NO$_3$– anions (Fig. 1). The Zn atom is coordinated by two N atoms (N1, N1A) from two deoatrz ligands and two NO$_3$– anions (O3, O3A), adopting a distorted tetrahedral coordination geometry. The Zn—O and Zn—N bond lengths are 2.071 (2) and 2.024 (1) Å, respectively. The bond angles around Zn atom vary from 95.9 (8) to 143.5 (1)^o.

As shown in Fig. 2, the interesting H-bonds are observed in the title compound. The fundamentally units are one dimensional chiral hydrogen bond chains along *c* axis, and subsequently the chains are connected into three-dimensional chiral supramolecular networks through O—H···O, O—H···N and N—H···O hydrogen bond interactions.

Experimental

An 10 ml ethanol solution of (1*S*,1'*S*)-1,1'-(4-amino-4*H*-1,2,4-triazole -3,5-diyl)diethanol (0.2 mmol, 0.0344 g) and Zn(NO$_3$)$_2$.$_6$H$_2$O (0.10 mmol, 0.0298 g) was stirred for five minutes and then filtered. The filtrate was carefully layered with 10 ml ethyl ether. After one week, colorless needle-like crystals of the title compound were obtained. Yield: 45%.

Refinement

All H atoms were put in calculated positions. All H atoms were refined with U_{iso}(H) = 1.2U_{eq}(N and O) and U_{iso}(H) = 1.2 or 1.5U_{eq}(C).

Figures

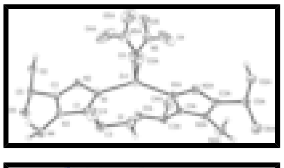

Fig. 1. Coordination geometry of Znic in the title compound with atomic labeling scheme. Thermal ellipsoids are at the 30% probability level. All H atoms except those attached to O and N atoms are omitted for clarity.

Fig. 2. The hydrogen-bonded chains in the title compound along the *c* axis.

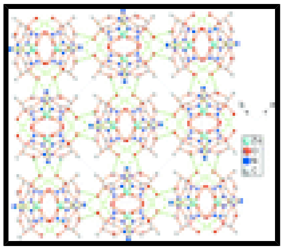

Fig. 3. Three dimensional hydrogen-bonded supramolecular networks in the title compound Viewed from c dimension.

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Crystal data

$[Zn(NO_3)_2(C_6H_{12}N_4O_2)_2]$	D_x = 1.651 Mg m^{-3}
M_r = 533.78	Mo *K*α radiation, λ = 0.71073 Å
Tetragonal, $P4_12_12$	Cell parameters from 7446 reflections
Hall symbol: P 4abw 2nw	θ = 1.7–27.5°
a = 12.1252 (7) Å	μ = 1.22 mm^{-1}
c = 14.6108 (17) Å	*T* = 298 K
V = 2148.1 (3) Å^3	Needle, colourless
Z = 4	0.36 × 0.18 × 0.12 mm
F(000) = 1104	

Data collection

Bruker APEX DUO diffractometer	2463 independent reflections
Radiation source: fine-focus sealed tube	2154 reflections with $I > 2\sigma(I)$
graphite	R_{int} = 0.032
φ and ω scans	θ_{max} = 27.5°, θ_{min} = 2.4°
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)	*h* = −15→9
T_{min} = 0.767, T_{max} = 0.862	*k* = −15→13
7446 measured reflections	*l* = −18→12

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.033	H-atom parameters constrained
$wR(F^2)$ = 0.088	$w = 1/[\sigma^2(F_o^2) + (0.0455P)^2 + 0.2512P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.05	$(\Delta/\sigma)_{max}$ = 0.001
2463 reflections	$\Delta\rho_{max}$ = 0.32 e Å^{-3}
154 parameters	$\Delta\rho_{min}$ = −0.23 e Å^{-3}
378 restraints	Absolute structure: Flack (1983), 993 Friedel pairs

Primary atom site location: structure-invariant direct methods	Flack parameter: −0.022 (15)

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.92340 (3)	0.92340 (3)	1.0000	0.03222 (13)
O1	0.72436 (18)	0.90461 (18)	0.95521 (12)	0.0417 (5)
H1	0.7021	0.8493	0.9817	0.063*
O2	1.13628 (15)	0.75723 (17)	0.67187 (13)	0.0336 (4)
H2	1.1479	0.8235	0.6777	0.050*
O3	1.09002 (17)	0.89583 (19)	1.02136 (13)	0.0464 (5)
O4	1.0802 (3)	1.0273 (3)	1.1173 (3)	0.1176 (14)
O5	1.2371 (2)	0.9742 (3)	1.0727 (2)	0.0758 (9)
N1	0.91797 (19)	0.85483 (18)	0.87379 (13)	0.0285 (5)
N2	1.00505 (19)	0.81575 (19)	0.82025 (13)	0.0279 (5)
N3	0.84957 (17)	0.80180 (17)	0.74473 (15)	0.0271 (4)
N4	0.7738 (2)	0.7823 (2)	0.67330 (16)	0.0427 (6)
H4B	0.7928	0.7208	0.6440	0.064*
H4C	0.7753	0.8388	0.6345	0.064*
N5	1.1372 (2)	0.9678 (2)	1.07029 (17)	0.0417 (6)
C1	0.8266 (2)	0.8474 (2)	0.82697 (16)	0.0273 (5)
C2	0.9608 (2)	0.7841 (2)	0.74215 (16)	0.0262 (5)
C3	0.7171 (2)	0.8883 (2)	0.85876 (17)	0.0332 (6)
H3	0.6595	0.8343	0.8446	0.040*
C4	0.6903 (3)	0.9988 (3)	0.8141 (2)	0.0467 (8)
H4D	0.6216	1.0261	0.8377	0.070*
H4E	0.6844	0.9892	0.7490	0.070*
H4F	0.7479	1.0507	0.8274	0.070*
C5	1.0219 (2)	0.7390 (2)	0.66148 (17)	0.0299 (6)
H5	0.9968	0.7776	0.6063	0.036*
C6	1.0044 (3)	0.6164 (3)	0.6482 (2)	0.0460 (8)
H6A	1.0389	0.5934	0.5923	0.069*
H6B	0.9268	0.6011	0.6452	0.069*
H6C	1.0363	0.5770	0.6987	0.069*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.03548 (17)	0.03548 (17)	0.02569 (18)	0.0024 (2)	0.00483 (13)	−0.00483 (13)
O1	0.0449 (12)	0.0468 (14)	0.0334 (9)	−0.0032 (10)	0.0117 (9)	0.0021 (9)
O2	0.0277 (10)	0.0310 (11)	0.0420 (9)	0.0005 (8)	0.0038 (8)	−0.0056 (9)
O3	0.0380 (12)	0.0514 (13)	0.0497 (10)	0.0025 (9)	−0.0045 (9)	−0.0172 (9)
O4	0.0629 (19)	0.112 (3)	0.178 (3)	0.0013 (19)	−0.005 (2)	−0.105 (3)
O5	0.0356 (15)	0.102 (2)	0.0901 (18)	0.0029 (14)	−0.0133 (13)	−0.0283 (17)
N1	0.0269 (11)	0.0310 (11)	0.0277 (9)	0.0003 (10)	0.0016 (9)	−0.0025 (8)
N2	0.0260 (11)	0.0307 (11)	0.0269 (9)	0.0038 (9)	−0.0002 (8)	−0.0031 (8)
N3	0.0242 (10)	0.0296 (10)	0.0275 (8)	−0.0036 (8)	−0.0028 (9)	−0.0012 (9)
N4	0.0409 (14)	0.0495 (16)	0.0378 (10)	−0.0041 (11)	−0.0161 (11)	−0.0046 (12)
N5	0.0369 (15)	0.0375 (14)	0.0508 (13)	0.0048 (11)	−0.0053 (11)	−0.0062 (12)
C1	0.0282 (13)	0.0250 (13)	0.0288 (10)	−0.0015 (10)	0.0020 (10)	0.0035 (10)
C2	0.0265 (11)	0.0248 (12)	0.0272 (10)	−0.0010 (9)	−0.0026 (10)	0.0020 (10)
C3	0.0265 (14)	0.0394 (15)	0.0336 (11)	−0.0004 (11)	0.0022 (10)	0.0016 (11)
C4	0.0406 (18)	0.0481 (19)	0.0515 (16)	0.0162 (15)	0.0033 (14)	0.0044 (15)
C5	0.0278 (13)	0.0339 (14)	0.0281 (10)	0.0028 (11)	−0.0015 (10)	−0.0028 (10)
C6	0.0423 (18)	0.0410 (18)	0.0546 (17)	−0.0048 (15)	0.0031 (15)	−0.0171 (14)

Geometric parameters (Å, °)

Zn1—N1	2.0239 (19)	N3—N4	1.410 (3)
Zn1—N1^{i}	2.0239 (19)	N4—H4B	0.8900
Zn1—O3	2.071 (2)	N4—H4C	0.8900
Zn1—O3^{i}	2.071 (2)	C1—C3	1.492 (4)
O1—C3	1.426 (3)	C2—C5	1.496 (4)
O1—H1	0.8200	C3—C4	1.525 (4)
O2—C5	1.412 (3)	C3—H3	0.9800
O2—H2	0.8200	C4—H4D	0.9600
O3—N5	1.265 (3)	C4—H4E	0.9600
O4—N5	1.212 (4)	C4—H4F	0.9600
O5—N5	1.215 (4)	C5—C6	1.514 (4)
N1—C1	1.305 (3)	C5—H5	0.9800
N1—N2	1.397 (3)	C6—H6A	0.9600
N2—C2	1.318 (3)	C6—H6B	0.9600
N3—C1	1.352 (3)	C6—H6C	0.9600
N3—C2	1.366 (3)		
N1—Zn1—N1^{i}	143.46 (13)	N2—C2—C5	125.9 (2)
N1—Zn1—O3	95.90 (8)	N3—C2—C5	124.6 (2)
N1^{i}—Zn1—O3	104.96 (8)	O1—C3—C1	107.4 (2)
N1—Zn1—O3^{i}	104.96 (8)	O1—C3—C4	108.4 (2)
N1^{i}—Zn1—O3^{i}	95.90 (8)	C1—C3—C4	110.4 (2)
O3—Zn1—O3^{i}	109.73 (13)	O1—C3—H3	110.2
C3—O1—H1	109.5	C1—C3—H3	110.2

C5—O2—H2	109.5	C4—C3—H3	110.2
N5—O3—Zn1	114.52 (17)	C3—C4—H4D	109.5
C1—N1—N2	108.94 (19)	C3—C4—H4E	109.5
C1—N1—Zn1	122.26 (18)	H4D—C4—H4E	109.5
N2—N1—Zn1	128.68 (16)	C3—C4—H4F	109.5
C2—N2—N1	106.0 (2)	H4D—C4—H4F	109.5
C1—N3—C2	107.0 (2)	H4E—C4—H4F	109.5
C1—N3—N4	126.3 (2)	O2—C5—C2	110.2 (2)
C2—N3—N4	126.6 (2)	O2—C5—C6	107.8 (2)
N3—N4—H4B	109.2	C2—C5—C6	113.0 (2)
N3—N4—H4C	109.2	O2—C5—H5	108.6
H4B—N4—H4C	109.5	C2—C5—H5	108.6
O4—N5—O5	120.9 (3)	C6—C5—H5	108.6
O4—N5—O3	118.2 (3)	C5—C6—H6A	109.5
O5—N5—O3	120.8 (3)	C5—C6—H6B	109.5
N1—C1—N3	108.6 (2)	H6A—C6—H6B	109.5
N1—C1—C3	124.7 (2)	C5—C6—H6C	109.5
N3—C1—C3	126.6 (2)	H6A—C6—H6C	109.5
N2—C2—N3	109.4 (2)	H6B—C6—H6C	109.5

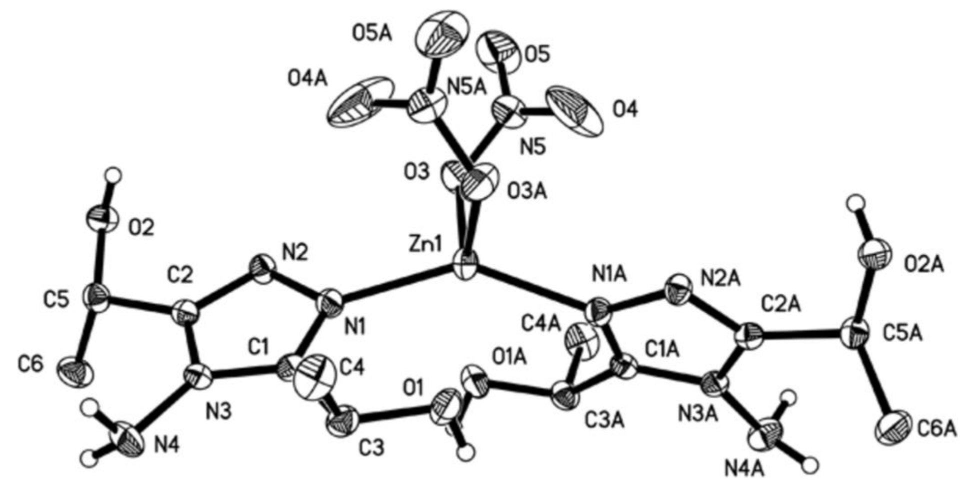
Symmetry codes: (i) y, x, $-z+2$.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2^{ii}	0.82	2.07	2.867 (3)	163.
N4—H4B···O5^{ii}	0.89	2.51	3.142 (5)	129.
O2—H2···N2^{iii}	0.82	2.13	2.943 (3)	174.
N4—H4C···O4^{iv}	0.89	2.40	3.022 (4)	127.

Symmetry codes: (ii) $x-1/2$, $-y+3/2$, $-z+7/4$; (iii) $-y+2$, $-x+2$, $-z+3/2$; (iv) $-x+2$, $-y+2$, $z-1/2$.

Fig. 1


O5A
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C2A
C5
N1
C4A
C5A
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Fig. 2

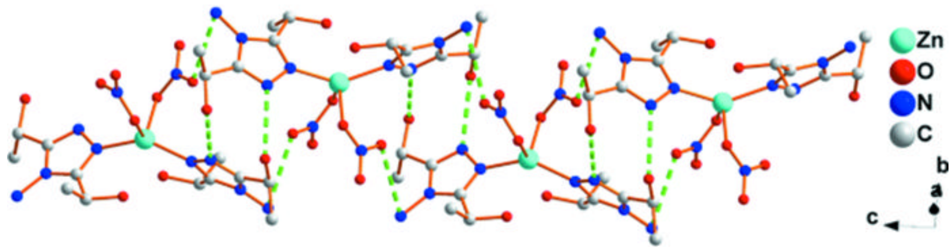

Fig. 3