Bis{2-[(dimethylamino-κN)methyl]-benzenethiolato-κS}zinc(II)

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In the title compound, $[Zn(C_9H_{12}NS)_2]$, the Zn^{II} center is located on a twofold rotation axis and is coordinated in a distorted tetrahedral environment in a bidentate fashion by anionic thiolate S and neutral amino N atoms of two 2-[(dimethylamino)methyl]benzenethiolate ligands. All the molecules are in the Δ form. The chosen crystal can thus be considered enantiomerically pure. Intermolecular C—H$\cdots\pi$ contacts connect the molecules into a two-dimensional network.

Related literature

A related structure was reported by Rijnberg et al. (1997). For related literature concerning the geometrical features see: Ernst et al. (1967); Evans & Boeyens (1989); Robinson et al. (1971).
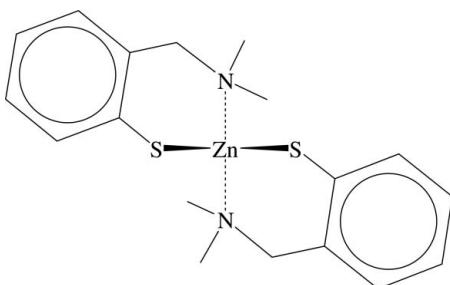
Experimental

Crystal data

[Zn(C_9H_{12}NS)_2]
$M_r = 397.88$
Orthorhombic, $P2_12_12$
$a = 10.1731 (2)$ Å
$b = 14.1431 (2)$ Å
$c = 6.4862 (1)$ Å

$V = 933.23 (3)$ Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 1.54$ mm^{-1}
$T = 150 (2)$ K
$0.36 \times 0.12 \times 0.09$ mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*MULABS* routine of *PLATON*; Spek, 2003)
$T_{min} = 0.82$, $T_{max} = 0.87$

11294 measured reflections
2143 independent reflections
2001 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.047$
$S = 1.06$
2143 reflections
107 parameters
H-atom parameters constrained

$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}
Absolute structure: Flack (1983), 880 Friedel pairs
Flack parameter: -0.013 (9)

Table 1

Selected geometric parameters (Å, °).

Zn1—N1	2.1129 (14)	S1—C1	1.7743 (17)
Zn1—S1	2.2811 (4)		
N1^i—Zn1—N1	119.76 (8)	S1^i—Zn1—S1	131.82 (2)
N1—Zn1—S1^i	102.41 (4)	C1—S1—Zn1	102.47 (5)
N1—Zn1—S1	101.24 (4)		

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

Table 2

C—H$\cdots\pi$ interaction (Å, °).

Cg is the centroid of the C1–C6 aromatic ring.

X—H$\cdots Cg$	X—H	H$\cdots Cg$	$X\cdots Cg$	X—H$\cdots Cg$
C8—H8C$\cdots Cg^i$	0.98	2.96	3.8324 (19)	149

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

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *HKL-2000* (Otwinowski & Minor, 1997); data reduction: *HKL-2000*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: manual editing of the *SHELXL97* output.

References

Ernst, R. E., O'Conner, M. J. & Holm, R. H. (1967). *J. Am. Chem. Soc.* **89**, 6104–6113.

Evans, D. G. & Boeyens, J. C. A. (1989). *Acta Cryst.* B**45**, 581–590.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Rijnberg, E., Hovestad, N. J., Kleij, A. W., Jastrzebski, J. T. B. H., Boersma, J., Janssen, M. D., Spek, A. L. & van Koten, G. (1997). *Organometallics*, **16**, 2847–2857.

Robinson, K., Gibbs, G. V. & Ribbe, P. H. (1971). *Science*, **172**, 567–570.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

supplementary materials

Bis{2-[(dimethylamino-*κN*)methyl]benzenethiolato-*κS*}zinc(II)

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Comment

The title compound, (I), crystallizes enantiomerically pure in space group $P2_12_12$. The absolute structure of the crystal chosen could be determined from the Flack parameter of −0.013 (9) (Flack, 1983). The unit cell consists of two chiral $Zn(C_9H_{12}NS)_2$ molecules, in which the Zn^{II} complex appears in the Δ form (Ernst *et al.*, 1967).

The Zn^{II} center occupies a special position, located on a twofold axis at [1/2, 0, *z*]. The coordination geometry at the Zn^{II} is defined by two monoanionic, S,N-bonded 2-[(dimethylamino)methyl]benzenethiolato ligands (Fig. 1). The ligand coordinates to the metal in a bidentate fashion *via* the anionic thiolato S1 [Zn1—S1 = 2.2811 (4) Å] and the neutral amino N1 [Zn1—N1 = 2.1129 (14) Å]. These distances compare well with those observed in the related $Zn(SC_6H_4CH(Me)NMe_2-2)_2$ complex reported by Rijnberg *et al.* (1997), with Zn—S of 2.284 (3) and 2.260 (2) Å, and Zn—N of 2.146 (8) and 2.096 (6) Å.

The four coordinated Zn^{II} atom has a distorted-tetrahedral geometry, which is apparent from the S—Zn—N angles of 101.76 (8) and 102.41 (4)°. This can also be seen from the values for the quadratic elongation of 1.052 and for the angle variance of 168.05 Deg^2 (Robinson *et al.*, 1971). A conformational analysis of the ring puckering results in a coefficient of 92.6% for the cosine form of the six membered N1—Zn1—S1—C1—C2—C7 chelate ring (Evans & Boeyens, 1989). Therefore the ring is best described as a boat conformation.

The C1—S1—Zn1 angle of 102.47 (5)° indicates a distorted-tetrahedral geometry of the S atom, the distance C1—S1 is 1.7743 (17)Å and again agrees well with the C—S distance found in the $Zn(SC_6H_4CH(Me)NMe_2-2)_2$ complex with C—S = 1.76 (1)Å (Rijnberg *et al.*, 1997). The geometry of the amino N atom is tetrahedral, with angles ranging from 107.63 (13) [C9—N1—C7] to 111.70 (11)° [C9—N1—Zn1].

There is an intermolecular C—H···π contact of H8C to the C1—C6 aromatic ring (centroid *Cg*), with H8C···*Cg*^{i} = 2.96Å [symmetry code (i) 1 − *x*, −*y*, *z*], which connects the molecules into a two dimensional network perpendicular to c (Fig. 2).

Experimental

In order to synthesize mixed zinc complexes with isopropyllactate and aminoarenethiolate ligands, the title compound, (I), was formed by disproportionation of the mixed zinc compound.

To a mixture of 2.8 mMol $EtZn(SC_6H_4CMe_2NMe_2-2)$ and 2.8 mMol (*L*)-isopropyllactate was added dry diethyl ether. The reaction mixture was stirred for 1 h. At the bottom of the reaction vessel a sticky solid was deposed. After removal of the clear solution, this solid was dried in vacuo. Yellow, needle shaped crystals for data collection were obtained by recrystallization from $C_6D_6/CDCl_3$ (ratio 1:1).

supplementary materials

Refinement

All hydrogen atoms were introduced in geometrically idealized positions (C—H = 0.95–0.99 Å) and refined with a riding model. Methyl hydrogen atoms where refined to behave as a rigid rotator using the *SHELXL97* (Sheldrick, 1997) command AFIX 137. The isotropic displacement parameters of the hydrogen atoms were constrained with $U_{iso}(H) = 1.2U_{eq}(C)$ for H atoms of CH and CH_2 moieties and with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms.

Figures
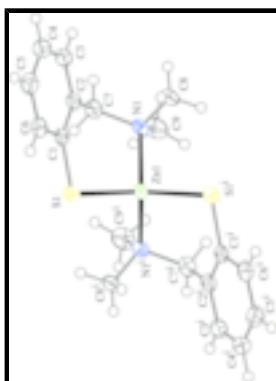
Fig. 1. : Displacement ellipsoid plot and atomic numbering scheme of (I). Ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $1 - x, -y, z$]
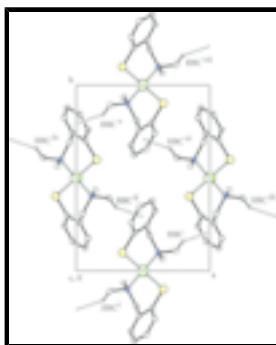
Fig. 2. : C—H···π interaction in (I), view along the crystallographic *c* axis. The C—H···π contacts are shown as dashed lines. [Symmetry codes: (i) $1 - x, -y, z$; (ii) $x - 1/2, 1/2 - y, 1 - z$; (iii) $1/2 + x, 1/2 - y, -z$; (iv) $1/2 - x, 1/2 + y, -z$; (v) $1 - x, 1 - y, z$; (vi) $3/2 - x, 1/2 + y, 1 - z$; (vii) $x, 1 + y, z$]

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Crystal data

[Zn(C$_9$H$_{12}$NS)$_2$]	$F_{000} = 416$
$M_r = 397.88$	$D_x = 1.416$ Mg m^{-3}
Orthorhombic, $P2_12_12$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: P 2 2ab	Cell parameters from 10982 reflections
$a = 10.1731$ (2) Å	$\theta = 1.0–27.5º$
$b = 14.1431$ (2) Å	$\mu = 1.54$ mm^{-1}
$c = 6.4862$ (1) Å	$T = 150$ (2) K
$V = 933.23$ (3) Å^3	Needle, yellow
$Z = 2$	$0.36 \times 0.12 \times 0.09$ mm

Data collection

Nonius KappaCCD diffractometer	2143 independent reflections
Radiation source: rotating anode	2001 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.037$
$T = 150(2)$ K	$\theta_{max} = 27.5°$
φ and ω scans	$\theta_{min} = 2.5°$
Absorption correction: multi-scan (MULABS routine of PLATON; Spek, 2003)	$h = -12 \rightarrow 13$
$T_{min} = 0.82$, $T_{max} = 0.87$	$k = -12 \rightarrow 18$
11294 measured reflections	$l = -8 \rightarrow 8$

Refinement

Refinement on F^2	Hydrogen site location: difference Fourier map
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.020$	$w = 1/[\sigma^2(F_o^2) + (0.0182P)^2 + 0.1166P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.047$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.06$	$\Delta\rho_{max} = 0.20$ e Å^{-3}
2143 reflections	$\Delta\rho_{min} = -0.18$ e Å^{-3}
107 parameters	Extinction correction: none
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 880 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: −0.013 (9)

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	0.5000	0.0000	0.11091 (3)	0.02267 (8)
S1	0.34728 (4)	0.09804 (3)	0.25447 (7)	0.02740 (10)
N1	0.61791 (13)	0.09749 (11)	−0.0526 (2)	0.0260 (3)
C1	0.43649 (15)	0.20488 (12)	0.2857 (2)	0.0232 (3)
C2	0.52665 (15)	0.23934 (12)	0.1408 (2)	0.0256 (4)

C3	0.59119 (17)	0.32491 (12)	0.1791 (3)	0.0331 (4)
H3	0.6530	0.3480	0.0816	0.040*
C4	0.56685 (18)	0.37667 (13)	0.3565 (3)	0.0382 (5)
H4	0.6122	0.4343	0.3814	0.046*
C5	0.47595 (18)	0.34349 (13)	0.4964 (3)	0.0351 (4)
H5	0.4577	0.3789	0.6175	0.042*
C6	0.41102 (17)	0.25888 (13)	0.4619 (3)	0.0291 (4)
H6	0.3482	0.2372	0.5594	0.035*
C7	0.54904 (17)	0.19101 (13)	−0.0639 (2)	0.0294 (4)
H7A	0.4628	0.1815	−0.1314	0.035*
H7B	0.6012	0.2338	−0.1528	0.035*
C8	0.74530 (16)	0.10835 (13)	0.0541 (3)	0.0344 (4)
H8A	0.7935	0.0484	0.0491	0.052*
H8B	0.7300	0.1261	0.1981	0.052*
H8C	0.7970	0.1577	−0.0142	0.052*
C9	0.6432 (2)	0.06543 (15)	−0.2681 (3)	0.0419 (5)
H9A	0.7097	0.1063	−0.3315	0.063*
H9B	0.5615	0.0690	−0.3479	0.063*
H9C	0.6749	0.0000	−0.2664	0.063*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.01809 (12)	0.02763 (14)	0.02228 (12)	−0.00127 (13)	0.000	0.000
S1	0.0215 (2)	0.0304 (2)	0.0303 (2)	−0.00084 (18)	0.00561 (18)	−0.00021 (19)
N1	0.0218 (7)	0.0309 (8)	0.0253 (7)	−0.0020 (6)	0.0054 (5)	0.0016 (6)
C1	0.0199 (7)	0.0251 (9)	0.0245 (8)	0.0039 (7)	−0.0040 (6)	0.0046 (7)
C2	0.0217 (9)	0.0271 (9)	0.0282 (8)	0.0037 (7)	−0.0020 (6)	0.0056 (7)
C3	0.0252 (9)	0.0305 (11)	0.0435 (10)	0.0017 (8)	0.0024 (7)	0.0086 (9)
C4	0.0308 (10)	0.0285 (10)	0.0552 (12)	−0.0001 (8)	−0.0053 (9)	−0.0055 (9)
C5	0.0356 (12)	0.0327 (10)	0.0370 (10)	0.0066 (8)	−0.0043 (8)	−0.0059 (8)
C6	0.0271 (9)	0.0335 (10)	0.0267 (8)	0.0074 (8)	−0.0020 (7)	0.0021 (8)
C7	0.0281 (8)	0.0348 (10)	0.0255 (9)	0.0012 (8)	0.0025 (7)	0.0100 (7)
C8	0.0195 (8)	0.0350 (11)	0.0487 (11)	−0.0043 (8)	−0.0013 (8)	0.0065 (9)
C9	0.0400 (11)	0.0532 (13)	0.0325 (10)	−0.0058 (10)	0.0172 (9)	−0.0035 (9)

Geometric parameters (Å, °)

Zn1—N1[i]	2.1128 (14)	C4—C5	1.378 (3)
Zn1—N1	2.1129 (14)	C4—H4	0.9500
Zn1—S1[i]	2.2811 (4)	C5—C6	1.385 (2)
Zn1—S1	2.2811 (4)	C5—H5	0.9500
S1—C1	1.7743 (17)	C6—H6	0.9500
N1—C8	1.477 (2)	C7—H7A	0.9900
N1—C9	1.492 (2)	C7—H7B	0.9900
N1—C7	1.499 (2)	C8—H8A	0.9800
C1—C6	1.398 (2)	C8—H8B	0.9800
C1—C2	1.401 (2)	C8—H8C	0.9800

C2—C3	1.399 (2)	C9—H9A	0.9800
C2—C7	1.510 (2)	C9—H9B	0.9800
C3—C4	1.386 (2)	C9—H9C	0.9800
C3—H3	0.9500		
N1^i—Zn1—N1	119.76 (8)	C4—C5—C6	120.53 (17)
N1^i—Zn1—S1^i	101.23 (4)	C4—C5—H5	119.7
N1—Zn1—S1^i	102.41 (4)	C6—C5—H5	119.7
N1^i—Zn1—S1	102.41 (4)	C5—C6—C1	121.03 (17)
N1—Zn1—S1	101.24 (4)	C5—C6—H6	119.5
S1^i—Zn1—S1	131.82 (2)	C1—C6—H6	119.5
C1—S1—Zn1	102.47 (5)	N1—C7—C2	115.27 (13)
C8—N1—C9	108.61 (14)	N1—C7—H7A	108.5
C8—N1—C7	109.96 (14)	C2—C7—H7A	108.5
C9—N1—C7	107.63 (13)	N1—C7—H7B	108.5
C8—N1—Zn1	109.33 (11)	C2—C7—H7B	108.5
C9—N1—Zn1	111.70 (11)	H7A—C7—H7B	107.5
C7—N1—Zn1	109.58 (10)	N1—C8—H8A	109.5
C6—C1—C2	118.66 (16)	N1—C8—H8B	109.5
C6—C1—S1	117.63 (13)	H8A—C8—H8B	109.5
C2—C1—S1	123.67 (13)	N1—C8—H8C	109.5
C3—C2—C1	119.26 (15)	H8A—C8—H8C	109.5
C3—C2—C7	118.49 (15)	H8B—C8—H8C	109.5
C1—C2—C7	122.08 (15)	N1—C9—H9A	109.5
C4—C3—C2	121.38 (17)	N1—C9—H9B	109.5
C4—C3—H3	119.3	H9A—C9—H9B	109.5
C2—C3—H3	119.3	N1—C9—H9C	109.5
C5—C4—C3	119.12 (18)	H9A—C9—H9C	109.5
C5—C4—H4	120.4	H9B—C9—H9C	109.5
C3—C4—H4	120.4		
N1^i—Zn1—S1—C1	−154.00 (7)	S1—C1—C2—C3	179.43 (12)
N1—Zn1—S1—C1	−29.82 (7)	C6—C1—C2—C7	−173.28 (15)
S1^i—Zn1—S1—C1	88.32 (5)	S1—C1—C2—C7	4.3 (2)
N1^i—Zn1—N1—C8	−141.01 (12)	C1—C2—C3—C4	−0.6 (3)
S1^i—Zn1—N1—C8	−30.18 (11)	C7—C2—C3—C4	174.74 (15)
S1—Zn1—N1—C8	107.53 (11)	C2—C3—C4—C5	−0.8 (3)
N1^i—Zn1—N1—C9	−20.77 (10)	C3—C4—C5—C6	0.9 (3)
S1^i—Zn1—N1—C9	90.06 (12)	C4—C5—C6—C1	0.4 (3)
S1—Zn1—N1—C9	−132.23 (11)	C2—C1—C6—C5	−1.8 (2)
N1^i—Zn1—N1—C7	98.41 (10)	S1—C1—C6—C5	−179.50 (13)
S1^i—Zn1—N1—C7	−150.76 (10)	C8—N1—C7—C2	−56.26 (18)
S1—Zn1—N1—C7	−13.05 (10)	C9—N1—C7—C2	−174.41 (15)
Zn1—S1—C1—C6	−143.07 (11)	Zn1—N1—C7—C2	63.93 (16)
Zn1—S1—C1—C2	39.38 (14)	C3—C2—C7—N1	114.67 (17)
C6—C1—C2—C3	1.9 (2)	C1—C2—C7—N1	−70.1 (2)

Symmetry codes: (i) −*x*+1, −*y*, *z*.

Table 2

C—H···π interaction (Å, °)

X—H···*Cg*	*X*—H	H···*Cg*	*X*···*Cg*	*X*—H···*Cg*
C8—H8C···*Cg*[i]	0.98	2.96	3.8324 (19)	149

Cg is the centroid of the C1–C6 aromatic ring. [Symmetry code: (i) $1 - x$, $-y$, z]

Fig. 1

Fig. 2