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Tris(allylthiourea-κ*S*)bromidozinc(II) bromide

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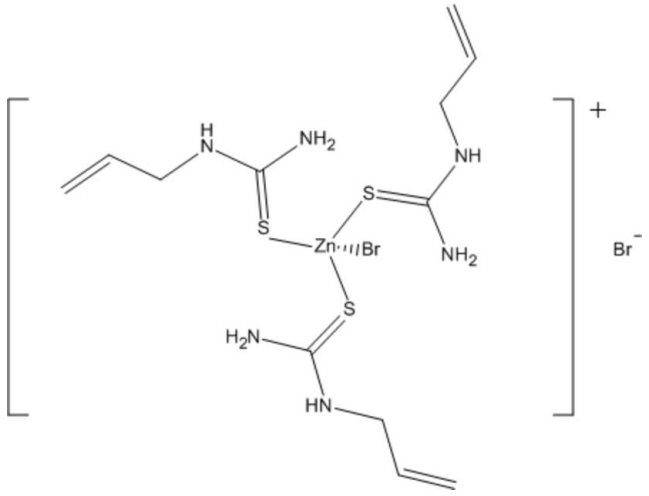
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.005 Å; R factor = 0.019; wR factor = 0.045; data-to-parameter ratio = 18.6.

In the title compound, $[ZnBr(C_4H_8N_2S)_3]Br$, the Zn^{II} atom is coordinated by one Br atom and the S atoms of three *N*-allylthiourea ligands in a distorted tetrahedral geometry. The Zn^{II} atom and the two Br atoms are located on a threefold axis.

Related literature

For transition metal complexes containing allylthiourea ligands, see: Gambino *et al.* (2002); Olijnyk *et al.* (2003). For similar structures of *N*-allylthiourea coordination compounds, see: Zhang *et al.* (1990); Yuan *et al.* (1990); Hou *et al.* (1993); Sun *et al.* (2004). For compounds that have similar Zn—Br bond lengths, see: Bermejo *et al.* (2000, 2001); Castineiras *et al.* (2000).



Experimental

Crystal data

$[ZnBr(C_4H_8N_2S)_3]Br$
M_r = 573.74
Trigonal, $R3$
a = 11.3591 (2) Å
c = 14.5172 (4) Å
V = 1622.19 (6) Å^3
Z = 3
Mo $K\alpha$ radiation
μ = 5.13 mm^{-1}
T = 296 K
0.35 × 0.32 × 0.32 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.265, T_{max} = 0.294
2605 measured reflections
1359 independent reflections
1305 reflections with $I > 2\sigma(I)$
R_{int} = 0.018

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.019
$wR(F^2)$ = 0.045
S = 0.95
1359 reflections
73 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}
Absolute structure: Flack (1983), 522 Friedel pairs
Flack parameter: 0.047 (8)

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL*; software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RN2081).

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supporting information

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Tris(allylthiourea-κS)bromidozinc(II) bromide

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S1. Comment

Coordination compounds with *N*-allylthiourea (abbreviated as ATU) ligands have many kinds of applications, such as electroplating (Gambino *et al.*, 2002), radiotherapeutic (Olijnyk *et al.*, 2003) and nonlinear optical materials(Zhang *et al.*, 1990; Yuan *et al.*, 1990; Hou *et al.*, 1993; Sun *et al.*, 2004).

The title compound consists of $[ZnBr(ATU)_3]^+$ and Br^- ions. The Zn^{II} atom is coordinated to a Br atom and three ATU ligands through their S atoms in a distorted tetrahedral arrangement. The bond angles around the Zn atom range from 101.64 (2)° to 116.038 (14)°, which show an obvious deviation from the ideal tetrahedral value of 109.5°. Zn and Br1 atoms lie on the threefold axis which is perpendicular to the plane of the three S atoms. The Br2 atom also lies on the axis(Fig.1). The Zn—Br1 distance [2.4640 (6) Å] is comparable with the average values reported in other complexes containing Zn—Br bonds, *e.g.* 2.4367 (9) and 2.445 (1)Å (Bermejo *et al.*, 2001), 2.4394 (8) and 2.4457 (7)Å (Castineiras *et al.*, 2000), 2.4207 (7) and 2.4654 (8)Å (Bermejo *et al.*, 2000).

S2. Experimental

To 2.252 g $ZnBr_2$ (0.01 mol) in 5 ml water, 3.486 g ATU (0.03 mol) in 10 ml water was slowly added with stirring. After standing for 1 h, the lower layer of oily solid was separated and dissolved in small volume of ethanol. Small single crystals of $Zn[Br(ATU)_3]Br$ were obtained by slow evaporation of this solution.

S3. Refinement

H atoms were placed geometrically (C—H = 0.93 - 0.97 Å, N—H = 0.86 Å) and refined using the riding model approximation, with $U_{iso} = 1.2U_{eq}$.

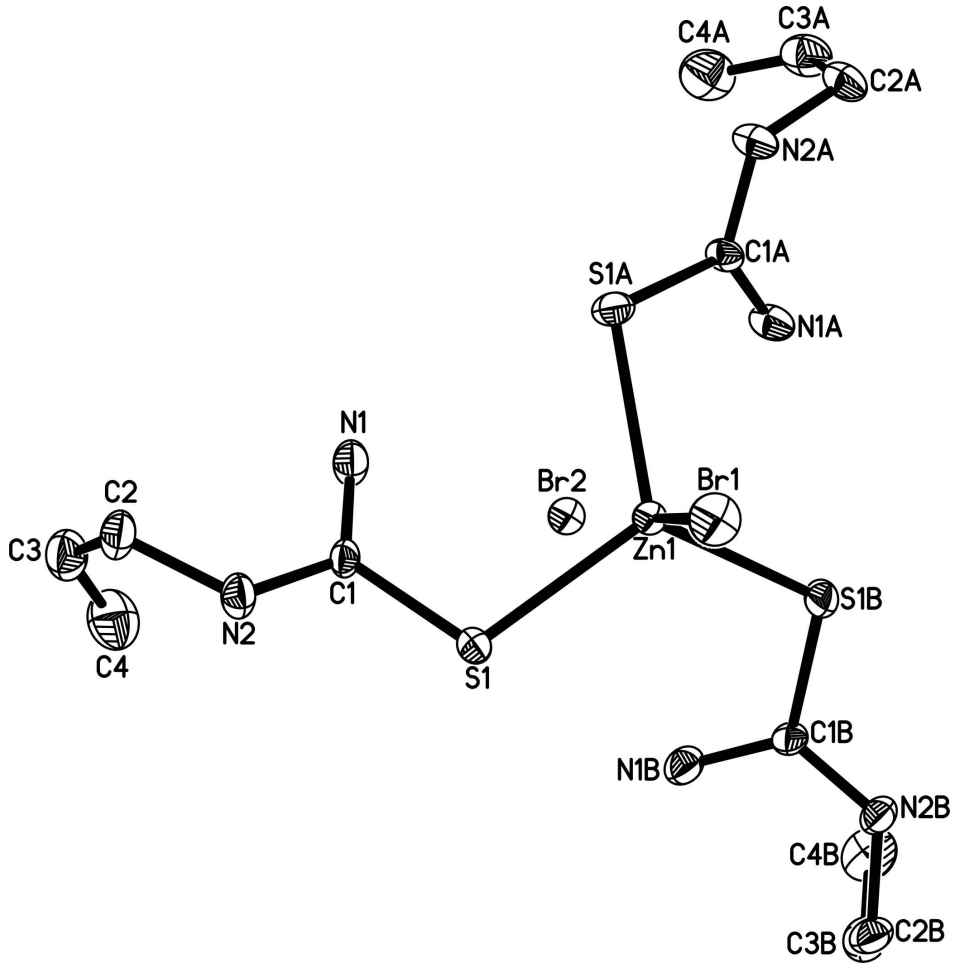

Figure 1

The molecule structure of ATZB with 30% displacement ellipsoids. H atoms are omitted for clarity. [Symmetry codes: (A)-*y* + 1, *x*-*y*, *z*; (B)-*x* + *y*+1, -*x* + 1, *z*]

Tris(allylthiourea-*κS*)bromidozinc(II) bromide

Crystal data

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M_r = 573.74
Trigonal, *R*3
a = 11.3591 (2) Å
c = 14.5172 (4) Å
V = 1622.19 (6) Å^3
Z = 3
F(000) = 858
D_x = 1.762 Mg m^{-3}
Mo *Kα* radiation, λ = 0.71073 Å
Cell parameters from 2071 reflections
θ = 2.5–27.5°
μ = 5.13 mm^{-1}
T = 296 K
Block, colourless
0.35 × 0.32 × 0.32 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.265, T_{max} = 0.294
2605 measured reflections
1359 independent reflections

1305 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$
$\theta_{max} = 27.5°$, $\theta_{min} = 2.5°$
$h = -13 \rightarrow 14$
$k = -14 \rightarrow 10$
$l = -15 \rightarrow 18$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.019$
$wR(F^2) = 0.045$
$S = 0.95$
1359 reflections
73 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ e Å^{-3}
Absolute structure: Flack (1983), 522 Friedel pairs
Absolute structure parameter: 0.047 (8)

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	0.3333	0.6667	0.59387 (3)	0.02676 (12)
Br2	0.3333	0.6667	0.33457 (3)	0.03334 (12)
Br1	0.3333	0.6667	0.76360 (3)	0.04428 (15)
S1	0.19315 (8)	0.43514 (7)	0.56132 (5)	0.03569 (18)
N2	0.2489 (3)	0.2409 (2)	0.53827 (17)	0.0356 (5)
H2	0.1781	0.1993	0.5727	0.043*
N1	0.3941 (3)	0.4382 (2)	0.46202 (16)	0.0380 (6)
H1A	0.4379	0.4009	0.4402	0.046*
H1B	0.4190	0.5211	0.4483	0.046*
C2	0.3134 (3)	0.1641 (3)	0.5097 (2)	0.0397 (7)
H2A	0.2822	0.0861	0.5501	0.048*
H2B	0.4107	0.2207	0.5188	0.048*
C1	0.2880 (3)	0.3680 (3)	0.51681 (16)	0.0280 (5)
C3	0.2890 (4)	0.1143 (4)	0.4121 (2)	0.0526 (9)
H3	0.3323	0.0673	0.3931	0.063*
C4	0.2152 (5)	0.1295 (4)	0.3523 (3)	0.0690 (11)
H4A	0.1697	0.1757	0.3677	0.083*
H4B	0.2069	0.0943	0.2932	0.083*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.02154 (17)	0.02154 (17)	0.0372 (3)	0.01077 (8)	0.000	0.000
Br2	0.03343 (18)	0.03343 (18)	0.0332 (2)	0.01672 (9)	0.000	0.000
Br1	0.0489 (2)	0.0489 (2)	0.0351 (2)	0.02443 (11)	0.000	0.000
S1	0.0256 (4)	0.0211 (3)	0.0567 (4)	0.0089 (3)	0.0086 (3)	−0.0029 (3)
N2	0.0387 (14)	0.0236 (12)	0.0457 (11)	0.0164 (11)	0.0132 (11)	0.0082 (10)
N1	0.0420 (15)	0.0247 (12)	0.0473 (12)	0.0166 (12)	0.0169 (11)	0.0073 (10)
C2	0.0461 (19)	0.0288 (15)	0.0507 (15)	0.0236 (14)	0.0055 (14)	0.0045 (13)
C1	0.0317 (15)	0.0225 (14)	0.0312 (11)	0.0146 (12)	−0.0006 (11)	−0.0038 (10)
C3	0.061 (2)	0.0367 (18)	0.063 (2)	0.0268 (18)	0.0123 (18)	−0.0036 (16)
C4	0.079 (3)	0.058 (2)	0.059 (2)	0.026 (2)	−0.005 (2)	−0.0069 (18)

Geometric parameters (Å, º)

Zn1—S1^{i}	2.3426 (7)	N1—H1A	0.8600
Zn1—S1	2.3426 (7)	N1—H1B	0.8600
Zn1—S1^{ii}	2.3426 (7)	C2—C3	1.499 (5)
Zn1—Br1	2.4640 (6)	C2—H2A	0.9700
S1—C1	1.727 (3)	C2—H2B	0.9700
N2—C1	1.318 (4)	C3—C4	1.278 (6)
N2—C2	1.452 (4)	C3—H3	0.9300
N2—H2	0.8600	C4—H4A	0.9300
N1—C1	1.327 (3)	C4—H4B	0.9300
S1^{i}—Zn1—S1	116.038 (14)	N2—C2—H2A	108.2
S1^{i}—Zn1—S1^{ii}	116.038 (14)	C3—C2—H2A	108.2
S1—Zn1—S1^{ii}	116.038 (13)	N2—C2—H2B	108.2
S1^{i}—Zn1—Br1	101.64 (2)	C3—C2—H2B	108.2
S1—Zn1—Br1	101.64 (2)	H2A—C2—H2B	107.4
S1^{ii}—Zn1—Br1	101.64 (2)	N2—C1—N1	120.5 (3)
C1—S1—Zn1	110.33 (10)	N2—C1—S1	116.9 (2)
C1—N2—C2	126.6 (3)	N1—C1—S1	122.6 (2)
C1—N2—H2	116.7	C4—C3—C2	127.0 (4)
C2—N2—H2	116.7	C4—C3—H3	116.5
C1—N1—H1A	120.0	C2—C3—H3	116.5
C1—N1—H1B	120.0	C3—C4—H4A	120.0
H1A—N1—H1B	120.0	C3—C4—H4B	120.0
N2—C2—C3	116.3 (3)	H4A—C4—H4B	120.0
S1^{i}—Zn1—S1—C1	141.40 (9)	C2—N2—C1—S1	−179.4 (2)
S1^{ii}—Zn1—S1—C1	−0.08 (10)	Zn1—S1—C1—N2	145.88 (19)
Br1—Zn1—S1—C1	−109.34 (9)	Zn1—S1—C1—N1	−35.4 (2)
C1—N2—C2—C3	−75.8 (4)	N2—C2—C3—C4	−1.8 (6)
C2—N2—C1—N1	1.8 (4)		

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