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Dibromido(di-2-pyridyl disulfide- κ^2N,N')zinc(II)

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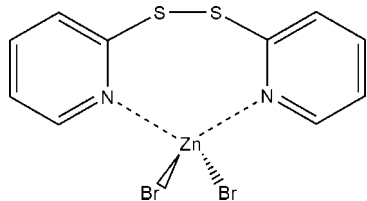
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 Key indicators: single-crystal X-ray study; $T = 170$ K; mean $\sigma(C-C) = 0.010$ Å; R factor = 0.046; wR factor = 0.120; data-to-parameter ratio = 16.8.

The molecular structure of the title compound, $[ZnBr_2(C_{10}H_8N_2S_2)]$, contains a seven-membered chelate ring in which the zinc atom is coordinated by two bromide ions and by the two pyridyl N atoms of a single 2,2'-dipyridyldisulfide (dpds) ligand within a slightly distorted tetrahedron. As is usual for this type of complex, the disulfide group does not participate in zinc coordination. The chelate complexes are connected *via* weak intermolecular $C-H \cdots Br$ hydrogen bonding into chains, which extend in the $[010]$ direction.

Related literature

For related literature, see: Bhosekar *et al.* (2007); Kinoshita *et al.* (2003); Kadooka *et al.* (1976); Kubo *et al.* (1998); Näther & Jess (2006); Näther *et al.* (2003); Pickardt *et al.* (2005); Raghavan & Seff (1977).



Experimental

Crystal data

 $[ZnBr_2(C_{10}H_8N_2S_2)]$
 $M_r = 445.49$

 Triclinic, $P\bar{1}$
 $a = 7.7610$ (8) Å

 $b = 8.2962$ (8) Å

 $c = 12.3576$ (13) Å

 $\alpha = 95.488$ (12)°

 $\beta = 107.161$ (12)°

 $\gamma = 112.950$ (11)°

 $V = 679.70$ (12) Å³
 $Z = 2$

 Mo $K\alpha$ radiation

 $\mu = 7.97$ mm⁻¹
 $T = 170$ (2) K

 $0.09 \times 0.09 \times 0.08$ mm

Data collection

Stoe IPDS-1 diffractometer

Absorption correction: none

6076 measured reflections

2609 independent reflections

 2167 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.054$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.120$
 $S = 1.06$

2609 reflections

155 parameters

H-atom parameters constrained

 $\Delta\rho_{max} = 1.31$ e Å⁻³
 $\Delta\rho_{min} = -1.43$ e Å⁻³
Table 1

Selected geometric parameters (Å, °).

Br1—Zn1	2.3897 (10)	Zn1—N11	2.042 (5)
Br2—Zn1	2.3664 (10)	Zn1—N1	2.091 (5)
N11—Zn1—N1	117.2 (2)	N11—Zn1—Br1	103.35 (15)
N11—Zn1—Br2	112.77 (15)	N1—Zn1—Br1	100.99 (15)
N1—Zn1—Br2	103.61 (14)	Br2—Zn1—Br1	119.06 (4)

Data collection: *IPDS Program Package* (Stoe, 1998); cell refinement: *IPDS Program Package*; data reduction: *IPDS Program Package*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP in SHELXTL* (Bruker, 1998); software used to prepare material for publication: *CIFTAB in SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2061).

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supporting information

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Dibromido(di-2-pyridyl disulfide- κ^2N,N')zinc(II)**Mario Wriedt, Inke Jess and Christian Näther****S1. Comment**

In our ongoing investigation on the synthesis, structures and properties of new coordination polymers based on zinc(II) halides and N-donor ligands (Bhosekar *et al.* 2007), we have started systematic investigation of their thermal behavior because we have demonstrated that new ligand-deficient coordination polymers can be conveniently prepared by thermal decomposition of suitable ligand-rich precursor compounds (Näther *et al.* 2003; Näther & Jess, 2006). In further investigations we have reacted zinc(II) bromine with 2,2'-bipyridyldisulfide (dpds). In this reaction the title chelate-complex has been formed by accident.

The versatile coordination properties of dpds enables a series of different chelate-complexes and coordination polymers. It can act in N,N'-bidentate (Kinoshita *et al.*, 2003; Kadooka *et al.* 1976 & Pickardt *et al.* 2005) or bridging (Kubo *et al.* 1998 & Kinoshita *et al.* 2003) coordination modes toward many metals. When dpds is connected to the metal atom as a chelate ligand, a seven-membered ring is formed.

The title compound is isotopic to that of the corresponding chloride compound reported by Pickardt *et al.* in 2005. In the crystal structure the coordination geometry about the Zn(II) ion is almost tetrahedral with bonds being formed to two bromine ions and the two pyridyl nitrogen atoms of a single dpds ligand (Fig. 1). These latter interactions result in the formation of a seven-membered chelate ring. As usual for this type of complexes, the disulfide group does not participate in zinc-coordination. Moreover the chelate-complexes form infinite weak C—H \cdots Br intermolecular hydrogen bonded chains along the [0 1 0] direction (C12—H12: 0.95 Å, H12 \cdots Br2ⁱ: 2.84 (2) Å, C12 \cdots Br2ⁱ: 3.74 (3), C12—H12 \cdots Brⁱ: 160 °, see Fig. 2). The Zn—Br and Zn—N distances are in the range of 2.3664 (10)–2.3897 (10) and 2.042 (5)–2.091 (5) Å. The angles at Zn(II) range from 100.99 (15) to 119.06 (4)°, the largest being Br—Zn—Br (Tab. 1). The structural parameters in the dpds molecule are quite regular. In particular the C—S bond, 1.784 (7)–1.783 (6) Å, is in good agreement with those expected for C(sp²)—S bonds (1.77 Å). The S—S bond length, 2.050 (3) Å, is somewhat longer than that found in the structure of the free ligand, 2.016 (2) Å (Raghavan & Seff, 1977).

S2. Experimental

ZnBr₂ and dpds was obtained from Alfa Aesar and methanol was obtained from Fluka. 0.125 mmol (28.15 mg) zinc(II) bromine, 0.125 mmol (27.5 mg) dpds and 3 ml of methanol were transferred in a test-tube, which were closed and heated to 110 °C for four days. On cooling colourless block-shaped single crystals of (I) were obtained.

S3. Refinement

All H atoms were located in difference map but were positioned with idealized geometry and were refined isotropic with $U_{eq}(H) = 1.2 U_{eq}(C)$ of the parent atom using a riding model with C—H = 0.95 Å.

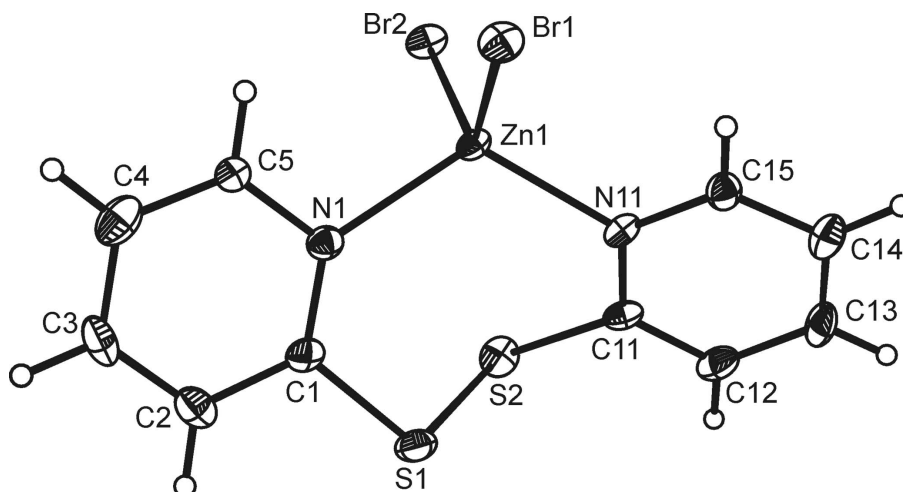


Figure 1

Molecular structure of the title compound with labelling and displacement ellipsoids drawn at the 50% probability level.

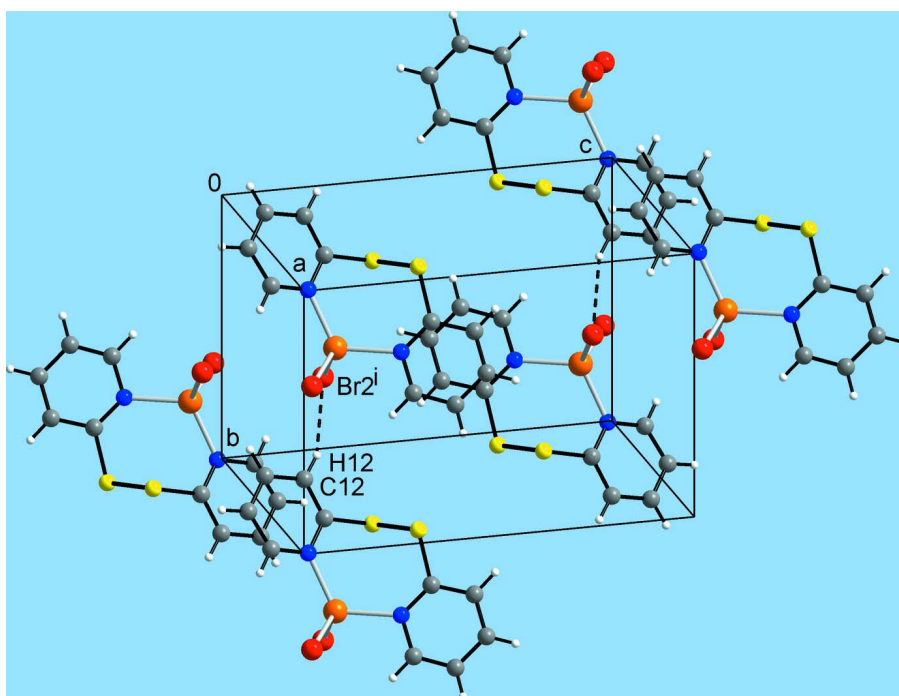


Figure 2

Crystal structure of the title compound with view along the [0 1 0] direction. Intermolecular C—H...Br hydrogen bonding is shown as dashed lines. Symmetry code: $i = x, -1 + y, z$.

Dibromido(di-2-pyridyl disulfide- κ^2N,N')zinc(II)

Crystal data

$[\text{ZnBr}_2(\text{C}_{10}\text{H}_8\text{N}_2\text{S}_2)]$

$M_r = 445.49$

Triclinic, $P\bar{1}$

$a = 7.7610(8) \text{ \AA}$

$b = 8.2962(8) \text{ \AA}$

$c = 12.3576(13) \text{ \AA}$

$\alpha = 95.488(12)^\circ$

$\beta = 107.161(12)^\circ$

$\gamma = 112.950(11)^\circ$

$V = 679.70(12) \text{ \AA}^3$

$Z = 2$
 $F(000) = 428$
 $D_x = 2.177 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 8000 reflections

$\theta = 2.9\text{--}28.1^\circ$
 $\mu = 7.97 \text{ mm}^{-1}$
 $T = 170 \text{ K}$
 Block, colourless
 $0.09 \times 0.09 \times 0.08 \text{ mm}$

Data collection

STOE IPDS-1
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 Phi scans
 6076 measured reflections
 2609 independent reflections

2167 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.054$
 $\theta_{\text{max}} = 26.0^\circ$, $\theta_{\text{min}} = 2.9^\circ$
 $h = -9 \rightarrow 9$
 $k = -10 \rightarrow 10$
 $l = -15 \rightarrow 15$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.120$
 $S = 1.06$
 2609 reflections
 155 parameters
 0 restraints
 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
 $w = 1/[\sigma^2(F_o^2) + (0.0684P)^2 + 2.046P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 1.31 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -1.43 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL*,
 $F_c^* = kFc[1 + 0.001x\text{Fc}^2\lambda^3/\sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.0071 (16)

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.99364 (9)	0.75728 (8)	0.23015 (6)	0.0193 (2)
Br2	0.38203 (9)	0.48414 (9)	0.12968 (6)	0.0197 (2)
Zn1	0.70460 (10)	0.50584 (9)	0.22904 (6)	0.0143 (2)
S1	0.7276 (3)	0.2365 (2)	0.44635 (15)	0.0223 (4)
N1	0.7378 (8)	0.5577 (7)	0.4048 (5)	0.0167 (11)
C2	0.7679 (9)	0.5176 (10)	0.5987 (6)	0.0222 (14)
H2	0.7685	0.4418	0.6517	0.027*
C5	0.7566 (10)	0.7263 (9)	0.4404 (5)	0.0190 (13)
H5	0.7473	0.7974	0.3850	0.023*
C1	0.7414 (9)	0.4556 (9)	0.4828 (5)	0.0166 (13)

C3	0.7933 (10)	0.6913 (10)	0.6347 (6)	0.0248 (15)
H3	0.8134	0.7373	0.7131	0.030*
C4	0.7888 (10)	0.7975 (10)	0.5545 (7)	0.0263 (15)
H4	0.8077	0.9175	0.5777	0.032*
S2	0.5117 (2)	0.1119 (2)	0.28313 (15)	0.0213 (4)
N11	0.7411 (7)	0.2888 (7)	0.1671 (5)	0.0151 (10)
C15	0.8390 (9)	0.2991 (9)	0.0928 (5)	0.0183 (13)
H15	0.9064	0.4133	0.0785	0.022*
C11	0.6512 (9)	0.1280 (8)	0.1897 (5)	0.0156 (12)
C14	0.8465 (10)	0.1511 (10)	0.0359 (6)	0.0237 (15)
H14	0.9146	0.1632	-0.0175	0.028*
C13	0.7523 (10)	-0.0148 (9)	0.0587 (6)	0.0225 (14)
H13	0.7544	-0.1189	0.0209	0.027*
C12	0.6535 (10)	-0.0270 (9)	0.1385 (6)	0.0227 (14)
H12	0.5899	-0.1386	0.1570	0.027*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0160 (3)	0.0134 (4)	0.0251 (4)	0.0025 (3)	0.0079 (3)	0.0054 (2)
Br2	0.0136 (3)	0.0182 (4)	0.0257 (4)	0.0065 (3)	0.0050 (3)	0.0070 (3)
Zn1	0.0137 (4)	0.0105 (4)	0.0198 (4)	0.0056 (3)	0.0067 (3)	0.0045 (3)
S1	0.0257 (9)	0.0218 (9)	0.0254 (9)	0.0145 (7)	0.0097 (7)	0.0113 (7)
N1	0.015 (3)	0.018 (3)	0.019 (3)	0.008 (2)	0.006 (2)	0.006 (2)
C2	0.016 (3)	0.035 (4)	0.017 (3)	0.013 (3)	0.006 (3)	0.007 (3)
C5	0.025 (3)	0.018 (3)	0.017 (3)	0.012 (3)	0.008 (3)	0.005 (3)
C1	0.011 (3)	0.021 (3)	0.021 (3)	0.009 (3)	0.005 (2)	0.007 (3)
C3	0.022 (3)	0.038 (4)	0.013 (3)	0.013 (3)	0.006 (3)	0.001 (3)
C4	0.020 (3)	0.021 (4)	0.040 (4)	0.010 (3)	0.013 (3)	0.006 (3)
S2	0.0147 (8)	0.0164 (8)	0.0303 (9)	0.0024 (6)	0.0108 (7)	0.0054 (7)
N11	0.012 (2)	0.011 (3)	0.021 (3)	0.005 (2)	0.004 (2)	0.003 (2)
C15	0.016 (3)	0.020 (3)	0.020 (3)	0.009 (3)	0.008 (3)	0.005 (3)
C11	0.009 (3)	0.014 (3)	0.021 (3)	0.005 (2)	0.001 (2)	0.006 (2)
C14	0.020 (3)	0.026 (4)	0.028 (4)	0.014 (3)	0.009 (3)	0.003 (3)
C13	0.023 (3)	0.023 (4)	0.018 (3)	0.013 (3)	0.003 (3)	-0.006 (3)
C12	0.025 (4)	0.015 (3)	0.025 (3)	0.010 (3)	0.004 (3)	0.004 (3)

Geometric parameters (Å, °)

Br1—Zn1	2.3897 (10)	C3—H3	0.9500
Br2—Zn1	2.3664 (10)	C4—H4	0.9500
Zn1—N11	2.042 (5)	S2—C11	1.783 (6)
Zn1—N1	2.091 (5)	N11—C11	1.343 (8)
S1—C1	1.784 (7)	N11—C15	1.344 (8)
S1—S2	2.050 (3)	C15—C14	1.385 (9)
N1—C1	1.344 (8)	C15—H15	0.9500
N1—C5	1.362 (8)	C11—C12	1.387 (9)
C2—C3	1.385 (10)	C14—C13	1.386 (11)

C2—C1	1.401 (9)	C14—H14	0.9500
C2—H2	0.9500	C13—C12	1.406 (10)
C5—C4	1.385 (10)	C13—H13	0.9500
C5—H5	0.9500	C12—H12	0.9500
C3—C4	1.389 (11)		
N11—Zn1—N1	117.2 (2)	C5—C4—C3	119.2 (6)
N11—Zn1—Br2	112.77 (15)	C5—C4—H4	120.4
N1—Zn1—Br2	103.61 (14)	C3—C4—H4	120.4
N11—Zn1—Br1	103.35 (15)	C11—S2—S1	104.0 (2)
N1—Zn1—Br1	100.99 (15)	C11—N11—C15	118.2 (5)
Br2—Zn1—Br1	119.06 (4)	C11—N11—Zn1	121.2 (4)
C1—S1—S2	106.7 (2)	C15—N11—Zn1	120.3 (4)
C1—N1—C5	118.1 (5)	N11—C15—C14	123.2 (6)
C1—N1—Zn1	131.4 (4)	N11—C15—H15	118.4
C5—N1—Zn1	110.4 (4)	C14—C15—H15	118.4
C3—C2—C1	118.8 (6)	N11—C11—C12	122.8 (6)
C3—C2—H2	120.6	N11—C11—S2	118.3 (4)
C1—C2—H2	120.6	C12—C11—S2	118.8 (5)
N1—C5—C4	122.2 (6)	C15—C14—C13	118.5 (6)
N1—C5—H5	118.9	C15—C14—H14	120.8
C4—C5—H5	118.9	C13—C14—H14	120.8
N1—C1—C2	122.5 (6)	C14—C13—C12	119.1 (6)
N1—C1—S1	121.5 (5)	C14—C13—H13	120.5
C2—C1—S1	115.9 (5)	C12—C13—H13	120.5
C2—C3—C4	119.1 (6)	C11—C12—C13	118.3 (6)
C2—C3—H3	120.5	C11—C12—H12	120.9
C4—C3—H3	120.5	C13—C12—H12	120.9
