# metal-organic compounds

# Dibromido(di-2-pyridyl sulfide-$\kappa^2 N$,$N'$)-zinc(II)

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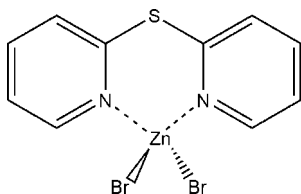Correspondence e-mail: mwriedt@ac.uni-kiel.de

The molecule of the title compound, [ZnBr$_2$(C$_{10}$H$_8$N$_2$S)], contains a six-membered chelate ring in a boat conformation in which the Zn atom is coordinated by two Br atoms and by the two pyridyl N atoms of a single di-2-pyridyl sulfide (dps) ligand within a slightly distorted tetrahedron. The dihedral angle between the pyridine rings is 52.7 (1)°. As is usual for this type of complex, the sulfide group does not participate in the zinc coordination.

## Related literature

For related literature, see: Anderson & Steel (1998); Bhosekar *et al.* (2007); Kondo *et al.* (1995); Nicolò *et al.* (1996); Teles *et al.* (1999); Tresoldi *et al.* (1991, 1992); Näther *et al.* (2003); Näther & Jess (2006)



## Experimental

### Crystal data

[ZnBr$_2$(C$_{10}$H$_8$N$_2$S)]
$M_r$ = 413.43
Monoclinic, $P2_1/c$
$a$ = 11.0385 (8) Å
$b$ = 8.9627 (5) Å
$c$ = 13.157 (1) Å
$\beta$ = 91.663 (9)°

$V$ = 1301.2 (2) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 8.16 mm$^{-1}$
$T$ = 170 (2) K
0.14 × 0.10 × 0.07 mm

### Data collection

Stoe IPDS-1 diffractometer
Absorption correction: numerical
($X$-$SHAPE$; Stoe, 1998)
$T_{min}$ = 0.285, $T_{max}$ = 0.394

14781 measured reflections
3105 independent reflections
2534 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.041

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.085
$S$ = 1.03
3105 reflections

146 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.15 e Å$^{-3}$
$\Delta\rho_{min}$ = −1.16 e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Zn1—N11 | 2.055 (3) | Zn1—Br2 | 2.3504 (6) |
| Zn1—N1 | 2.058 (3) | Zn1—Br1 | 2.3527 (5) |
| | | | |
| N11—Zn1—N1 | 94.66 (11) | N11—Zn1—Br1 | 107.43 (8) |
| N11—Zn1—Br2 | 115.35 (8) | N1—Zn1—Br1 | 108.56 (8) |
| N1—Zn1—Br2 | 109.76 (8) | Br2—Zn1—Br1 | 118.38 (2) |

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, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *CIFTAB* in *SHELXTL*.

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**supplementary materials**

## Dibromido(di-2-pyridyl sulfide-$\kappa^2N,N'$)zinc(II)

## M. Wriedt, I. Jess and C. Näther

### 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 precursur compounds (Näther *et al.* 2003; Näther & Je\&s, 2006). In further investigations we have reacted zinc(II) bromide with 2,2'-bipyridyldisulfide (dpds). In this reaction a cleavage of the S—S bond takes place leading to the formation of di-2-pyridyl sulfide (dps) which in a concomitant reaction with zinc(II) bromide forms the title chelate-complex.

In general, dps is a versatile ambidentate ligand that, due to its conformational flexibility, can act in N,*N*'-bidentate (Tresoldi *et al.*, 1992; Kondo *et al.*, 1995 and Nicolò *et al.*, 1996) or bridging (Tresoldi *et al.*, 1991 and Teles *et al.*, 1999) coordination modes toward many metals, resulting in complexes with different stereochemistry. When dps is connected to a metal atom as a chelate ligand, a six-membered ring in boat conformation is formed, differently from its rigid analogues 2,2'-bipyridine that generates a pentacyclic chelate in a planar arragement. In addition, in some cases dps can act as tridentate ligand in a N,*N,S*-coordination mode involving metal-sulfur interactions (Anderson & Steel, 1998).

In the molecular structure the coordination geometry about the Zn atom is almost tetrahedral with bonds being formed to two Br atoms and the two pyridyl N atoms of a single dps ligand (Fig. 1). These interactions result in the formation of a six-membered chelate ring in a boat conformation. The $X$—Zn—$X$ angles ($X$ = Br, N) range from 94.7 (1) to 118.38 (2)°, the largest being Br—Zn—Br. The Zn—Br and Zn—N distances are in the range of 2.3504 (6)–2.3527 (5) and 2.055 (3)–2.058 (3) Å. The structural parameters in the bps molecule are quite regular. In particular the C—S bonds of 1.776 (4) Å (S1—C1) and 1.778 (4) Å (S1—C11) are in good agreement with those expected for C($sp^2$)—S bonds (1.77 Å, Tresoldi *et al.* 1992).

### Experimental

ZnBr$_2$ and 2,2'-bipyridyldisulfide was obtained from Alfa Aesar, methanol was obtained from Fluka. 0.125 mmol (28.1 mg) zinc(II) bromide, 0.0312 mmol (6.87 mg) 2,2'-bipyridyldisulfide and 3 ml of methanol were transfered into a test-tube, which was closed and heated to 110 °C for three days. On cooling colourless block-shaped single crystals of the title compound were obtained.

### Refinement

All H atoms were located from the difference Fourier map but were positioned with idealized geometry and were refined isotropically with $U_{eq}$(H) = 1.2 $U_{eq}$(C) of the parent atom using a riding model with C—H = 0.97 Å.
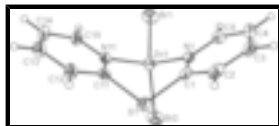
# supplementary materials

## Figures



Fig. 1. : Crystal structure of compound I showing the labelling scheme, and displacement ellipsoids drawn at the 50% probability level.

## Dibromido(di-2-pyridyl sulfide-$\kappa^2 N,N'$)zinc(II)

*Crystal data*

| | |
|---|---|
| [ZnBr$_2$(C$_{10}$H$_8$N$_2$S)] | $F_{000} = 792$ |
| $M_r = 413.43$ | $D_x = 2.111$ Mg m$^{-3}$ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation $\lambda = 0.71073$ Å |
| Hall symbol: -P 2ybc | Cell parameters from 8000 reflections |
| $a = 11.0385$ (8) Å | $\theta = 13.8–24.9°$ |
| $b = 8.9627$ (5) Å | $\mu = 8.16$ mm$^{-1}$ |
| $c = 13.157$ (1) Å | $T = 170$ (2) K |
| $\beta = 91.663$ (9)° | Block, colourless |
| $V = 1301.2$ (2) Å$^3$ | $0.14 \times 0.10 \times 0.07$ mm |
| $Z = 4$ | |

*Data collection*

| | |
|---|---|
| Stoe IPDS-1 diffractometer | 3105 independent reflections |
| Radiation source: fine-focus sealed tube | 2534 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{int} = 0.041$ |
| $T = 170(2)$ K | $\theta_{max} = 28.0°$ |
| Phi scans | $\theta_{min} = 2.8°$ |
| Absorption correction: numerical (X-SHAPE; Stoe, 1998) | $h = -14\rightarrow14$ |
| $T_{min} = 0.285$, $T_{max} = 0.394$ | $k = -11\rightarrow11$ |
| 14781 measured reflections | $l = -17\rightarrow17$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)] = 0.033$ | $w = 1/[\sigma^2(F_o^2) + (0.0528P)^2 + 0.9116P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.085$ | $(\Delta/\sigma)_{max} = 0.001$ |
| $S = 1.03$ | $\Delta\rho_{max} = 1.15$ e Å$^{-3}$ |
| 3105 reflections | $\Delta\rho_{min} = -1.15$ e Å$^{-3}$ |

146 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Extinction correction: SHELXL, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0076 (6)

*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 | 0.74601 (4) | 0.84740 (4) | 0.50911 (3) | 0.01791 (12) |
| Br1 | 0.72001 (4) | 1.08853 (4) | 0.57571 (3) | 0.03251 (13) |
| Br2 | 0.76278 (4) | 0.82087 (5) | 0.33235 (3) | 0.03579 (13) |
| N1 | 0.8929 (3) | 0.7499 (3) | 0.5825 (2) | 0.0174 (5) |
| C1 | 0.8968 (3) | 0.6003 (4) | 0.5939 (2) | 0.0187 (6) |
| C2 | 0.9955 (4) | 0.5287 (4) | 0.6405 (3) | 0.0258 (7) |
| H2 | 0.9973 | 0.4231 | 0.6461 | 0.031* |
| C3 | 1.0912 (4) | 0.6142 (5) | 0.6789 (3) | 0.0308 (8) |
| H3 | 1.1597 | 0.5677 | 0.7106 | 0.037* |
| C4 | 1.0854 (4) | 0.7682 (5) | 0.6702 (3) | 0.0323 (9) |
| H4 | 1.1491 | 0.8289 | 0.6973 | 0.039* |
| C5 | 0.9853 (3) | 0.8322 (4) | 0.6215 (3) | 0.0252 (7) |
| H5 | 0.9818 | 0.9377 | 0.6153 | 0.030* |
| S1 | 0.77889 (9) | 0.48727 (9) | 0.54086 (8) | 0.0262 (2) |
| N11 | 0.6206 (3) | 0.7109 (3) | 0.5746 (2) | 0.0173 (5) |
| C11 | 0.6435 (3) | 0.5653 (3) | 0.5880 (2) | 0.0175 (6) |
| C12 | 0.5613 (3) | 0.4683 (4) | 0.6314 (3) | 0.0247 (7) |
| H12 | 0.5790 | 0.3650 | 0.6384 | 0.030* |
| C13 | 0.4528 (4) | 0.5268 (4) | 0.6640 (3) | 0.0291 (8) |
| H13 | 0.3945 | 0.4635 | 0.6935 | 0.035* |
| C14 | 0.4303 (4) | 0.6768 (5) | 0.6535 (3) | 0.0311 (8) |
| H14 | 0.3569 | 0.7185 | 0.6767 | 0.037* |
| C15 | 0.5160 (3) | 0.7667 (4) | 0.6085 (3) | 0.0240 (7) |
| H15 | 0.5004 | 0.8705 | 0.6015 | 0.029* |

*Atomic displacement parameters ($Å^2$)*

|  | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|

| | | | | | |
|---|---|---|---|---|---|
| Zn1 | 0.0211 (2) | 0.01532 (19) | 0.01722 (19) | −0.00099 (14) | −0.00055 (14) | 0.00326 (13) |
| Br1 | 0.0418 (3) | 0.01468 (17) | 0.0407 (2) | 0.00437 (14) | −0.00482 (17) | −0.00135 (13) |
| Br2 | 0.0492 (3) | 0.0418 (2) | 0.01642 (18) | −0.01221 (18) | 0.00179 (15) | 0.00378 (14) |
| N1 | 0.0158 (14) | 0.0174 (12) | 0.0192 (13) | 0.0002 (10) | 0.0023 (10) | −0.0007 (10) |
| C1 | 0.0196 (17) | 0.0198 (15) | 0.0171 (15) | 0.0046 (12) | 0.0062 (12) | −0.0003 (11) |
| C2 | 0.026 (2) | 0.0284 (17) | 0.0238 (17) | 0.0106 (14) | 0.0068 (14) | 0.0047 (13) |
| C3 | 0.0200 (19) | 0.049 (2) | 0.0232 (17) | 0.0120 (16) | 0.0013 (14) | 0.0013 (15) |
| C4 | 0.0188 (19) | 0.047 (2) | 0.0313 (19) | 0.0016 (16) | −0.0014 (15) | −0.0104 (17) |
| C5 | 0.0214 (19) | 0.0282 (17) | 0.0261 (18) | −0.0005 (14) | 0.0007 (14) | −0.0044 (14) |
| S1 | 0.0246 (5) | 0.0165 (4) | 0.0380 (5) | −0.0023 (3) | 0.0090 (4) | −0.0081 (3) |
| N11 | 0.0172 (14) | 0.0191 (12) | 0.0157 (12) | −0.0031 (10) | −0.0003 (10) | 0.0008 (10) |
| C11 | 0.0208 (18) | 0.0151 (13) | 0.0164 (14) | −0.0039 (12) | −0.0003 (12) | −0.0008 (11) |
| C12 | 0.0234 (19) | 0.0238 (16) | 0.0270 (18) | −0.0072 (14) | 0.0021 (14) | 0.0013 (13) |
| C13 | 0.027 (2) | 0.0340 (19) | 0.0269 (18) | −0.0118 (16) | 0.0030 (15) | 0.0007 (14) |
| C14 | 0.0142 (18) | 0.041 (2) | 0.038 (2) | −0.0009 (15) | 0.0047 (15) | −0.0051 (16) |
| C15 | 0.0164 (18) | 0.0251 (16) | 0.0305 (18) | 0.0017 (13) | 0.0014 (13) | −0.0014 (13) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Zn1—N11 | 2.055 (3) | C4—H4 | 0.9500 |
| Zn1—N1 | 2.058 (3) | C5—H5 | 0.9500 |
| Zn1—Br2 | 2.3504 (6) | S1—C11 | 1.778 (4) |
| Zn1—Br1 | 2.3527 (5) | N11—C11 | 1.340 (4) |
| N1—C5 | 1.348 (4) | N11—C15 | 1.347 (5) |
| N1—C1 | 1.350 (4) | C11—C12 | 1.391 (5) |
| C1—C2 | 1.391 (5) | C12—C13 | 1.387 (6) |
| C1—S1 | 1.776 (4) | C12—H12 | 0.9500 |
| C2—C3 | 1.388 (6) | C13—C14 | 1.373 (6) |
| C2—H2 | 0.9500 | C13—H13 | 0.9500 |
| C3—C4 | 1.386 (6) | C14—C15 | 1.388 (5) |
| C3—H3 | 0.9500 | C14—H14 | 0.9500 |
| C4—C5 | 1.385 (5) | C15—H15 | 0.9500 |
| N11—Zn1—N1 | 94.66 (11) | N1—C5—H5 | 118.9 |
| N11—Zn1—Br2 | 115.35 (8) | C4—C5—H5 | 118.9 |
| N1—Zn1—Br2 | 109.76 (8) | C1—S1—C11 | 104.63 (15) |
| N11—Zn1—Br1 | 107.43 (8) | C11—N11—C15 | 118.6 (3) |
| N1—Zn1—Br1 | 108.56 (8) | C11—N11—Zn1 | 120.5 (2) |
| Br2—Zn1—Br1 | 118.38 (2) | C15—N11—Zn1 | 120.8 (2) |
| C5—N1—C1 | 118.6 (3) | N11—C11—C12 | 122.7 (3) |
| C5—N1—Zn1 | 121.6 (2) | N11—C11—S1 | 119.7 (2) |
| C1—N1—Zn1 | 119.8 (2) | C12—C11—S1 | 117.5 (3) |
| N1—C1—C2 | 122.0 (3) | C13—C12—C11 | 118.0 (3) |
| N1—C1—S1 | 120.1 (3) | C13—C12—H12 | 121.0 |
| C2—C1—S1 | 117.8 (3) | C11—C12—H12 | 121.0 |
| C3—C2—C1 | 118.9 (3) | C14—C13—C12 | 119.7 (3) |
| C3—C2—H2 | 120.5 | C14—C13—H13 | 120.2 |
| C1—C2—H2 | 120.5 | C12—C13—H13 | 120.2 |
| C4—C3—C2 | 119.2 (3) | C13—C14—C15 | 119.1 (4) |
| C4—C3—H3 | 120.4 | C13—C14—H14 | 120.4 |

| | | | |
|---|---|---|---|
| C2—C3—H3 | 120.4 | C15—C14—H14 | 120.4 |
| C5—C4—C3 | 119.0 (4) | N11—C15—C14 | 121.8 (3) |
| C5—C4—H4 | 120.5 | N11—C15—H15 | 119.1 |
| C3—C4—H4 | 120.5 | C14—C15—H15 | 119.1 |
| N1—C5—C4 | 122.3 (3) | | |

**Fig. 1**