metal-organic compounds

(Di-2-pyridyl sulfide-$\kappa^2 N$,N')diiodido-zinc(II)

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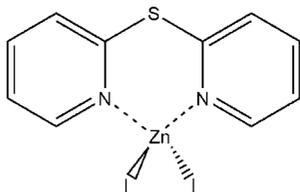Correspondence e-mail: mwriedt@ac.uni-kiel.de

The title compound, $[ZnI_2(C_{10}H_8N_2S)]$, contains a six-membered chelate ring adopting a boat conformation in which the Zn atom is coordinated by two iodide ions and by the two pyridyl N atoms of a single di-2-pyridyl sulfide ligand within a slightly distorted tetrahedron. The Zn, S and I atoms are located on a crystallographic mirror plane. As usual for this type of complex, the sulfide group does not participate in zinc coordination. The dihedral angle between the two pyridine rings is 60.1 (1)°.

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).

Experimental

Crystal data

$[ZnI_2(C_{10}H_8N_2S)]$	V = 1406.27 (18) Å³
M_r = 507.41	Z = 4
Orthorhombic, $Pnma$	Mo $K\alpha$ radiation
a = 13.9418 (8) Å	μ = 6.26 mm⁻¹
b = 10.9742 (10) Å	T = 170 (2) K
c = 9.1913 (6) Å	0.15 × 0.11 × 0.08 mm

Data collection

Stoe IPDS-1 diffractometer	11604 measured reflections
Absorption correction: numerical	1784 independent reflections
(*X-SHAPE*; Stoe, 1998*a*)	1535 reflections with $I > 2\sigma(I)$
T_{min} = 0.352, T_{max} = 0.464	R_{int} = 0.029

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029	80 parameters
$wR(F^2)$ = 0.074	H-atom parameters constrained
S = 1.02	$\Delta\rho_{max}$ = 0.90 e Å⁻³
1784 reflections	$\Delta\rho_{min}$ = −0.86 e Å⁻³

Table 1
Selected geometric parameters (Å, °).

Zn1—N1	2.063 (3)	Zn1—I2	2.5473 (6)
Zn1—I1	2.5447 (6)	C1—S1	1.775 (3)
N1—Zn1—N1ⁱ	93.85 (14)	N1—Zn1—I2	108.33 (8)
N1—Zn1—I1	113.69 (7)	I1—Zn1—I2	116.54 (2)

Symmetry code: (i) $x, -y + \frac{1}{2}, z$.

Data collection: *IPDS* (Stoe, 1998*b*); cell refinement: *IPDS*; data reduction: *IPDS*; 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*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2649).

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supporting information

(Di-2-pyridyl sulfide-κ^2N,N')diiodidozinc(II)

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S1. Comment

Recently, we are interested in the synthesis, structures and thermal properties of coordination polymers based on zinc(II) halides and N-donor ligands (Bhosekar *et al.*, 2007). We have found for example that most of the ligand rich compounds can be transformed into ligand deficient compounds on heating. Starting from these findings we have initiated systematic investigations on this topic. In these investigations we have reacted zinc(II) iodine with 2,2′-bipyridyldisulfide. In this reaction, simultaneously a cleavage of the S—S bond takes place leading to the formation of di-2'pyridyl sulfide (dps). In further reaction with zinc(II) iodine the title compound (I) has been formed. To identify this product in further reaction by X-ray powder diffraction, a structure determination was performed.

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 the 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 crystal structure the coordination geometry about the Zn(II) ion is almost tetrahedral with bonds being formed to two iodine ions and the two pyridyl nitrogen atoms of a single dps ligand (Fig. 1). These latter interactions result in the formation of a six-membered chelate ring, which is in a boat conformation. The angles at Zn(II) range from 93.85 to 108.33°, the largest being N—Zn—I. The Zn—I and Zn—N distances are in the range of 2.5447 (6)–2.5473 (6) and 2.063 (3) Å. The structural parameters in the dps molecule are quite regular. In particular the C—S bond, 1.775 Å, is in good agreement with those expected for C(sp^2)-S bonds (1.77 Å).

S2. Experimental

ZnI$_2$ and 2,2′-bipyridyldisulfide was obtained from Alfa Aesar and methanol was obtained from Fluka. 0.125 mmol (39.9 mg) zinc(II) iodine, 0.125 mmol (27.6 mg) 2,2′-bipyridyldisulfide and 3 ml of methanol were transfered in test-tube, which were closed and heated to 110 °C for four days. On cooling colourless block-shaped single crystals of (I) are 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.
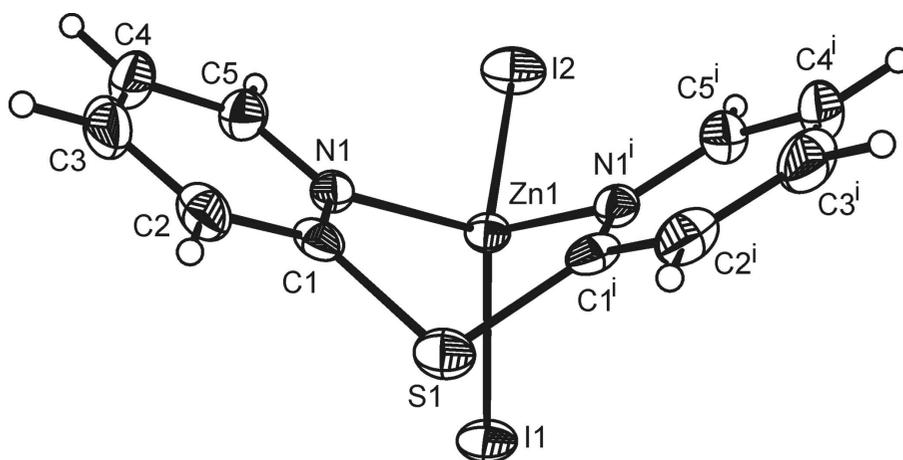
Figure 1

Crystal structure of compound I with labelling and displacement ellipsoids drawn at the 50% probability level. Symmetry code: i = x, -y + 1/2, z.

(Di-2-pyridyl sulfide-$\kappa^2 N,N'$)diiodidozinc(II)

Crystal data

[ZnI₂(C₁₀H₈N₂S)]	$D_x = 2.397$ Mg m⁻³
$M_r = 507.41$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Orthorhombic, $Pnma$	Cell parameters from 8000 reflections
$a = 13.9418$ (8) Å	$\theta = 11.2–26.1°$
$b = 10.9742$ (10) Å	$\mu = 6.26$ mm⁻¹
$c = 9.1913$ (6) Å	$T = 170$ K
$V = 1406.27$ (18) Å³	Block, colourless
$Z = 4$	$0.15 \times 0.11 \times 0.08$ mm
$F(000) = 936$	

Data collection

Stoe IPDS-1 diffractometer	11604 measured reflections
Radiation source: fine-focus sealed tube	1784 independent reflections
Graphite monochromator	1535 reflections with $I > 2\sigma(I)$
φ scans	$R_{int} = 0.029$
Absorption correction: numerical (*X-SHAPE*; Stoe, 1998a)	$\theta_{max} = 28.1°$, $\theta_{min} = 2.7°$
$T_{min} = 0.352$, $T_{max} = 0.464$	$h = -18 \rightarrow 16$
	$k = -14 \rightarrow 14$
	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.029$	$w = 1/[\sigma^2(F_o^2) + (0.0526P)^2 + 0.1693P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.074$	
$S = 1.03$	$(\Delta/\sigma)_{max} = 0.001$
1784 reflections	$\Delta\rho_{max} = 0.90$ e Å⁻³
80 parameters	$\Delta\rho_{min} = -0.86$ e Å⁻³
0 restraints	Extinction correction: *SHELXL*, Fc*=kFc[1+0.001xFc²λ³/sin(2θ)]⁻¹ᐟ⁴
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0034 (4)
Secondary atom site location: difference Fourier map	

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	0.51405 (4)	0.2500	0.14382 (5)	0.02090 (14)
I1	0.33175 (2)	0.2500	0.15746 (4)	0.03580 (13)
I2	0.58755 (3)	0.2500	−0.10991 (4)	0.03770 (13)
N1	0.57748 (16)	0.3873 (2)	0.2632 (3)	0.0221 (5)
C1	0.5819 (2)	0.3762 (3)	0.4090 (4)	0.0235 (6)
C2	0.6253 (2)	0.4633 (3)	0.4967 (4)	0.0330 (7)
H2	0.6262	0.4543	0.5995	0.040*
C3	0.6670 (3)	0.5630 (3)	0.4311 (5)	0.0413 (9)
H3	0.6969	0.6239	0.4887	0.050*
C4	0.6652 (3)	0.5741 (3)	0.2819 (5)	0.0421 (9)
H4	0.6946	0.6418	0.2355	0.050*
C5	0.6195 (3)	0.4844 (3)	0.2005 (4)	0.0318 (7)
H5	0.6180	0.4919	0.0976	0.038*
S1	0.52435 (9)	0.2500	0.49261 (12)	0.0301 (3)

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0163 (3)	0.0259 (3)	0.0205 (2)	0.000	−0.00265 (17)	0.000
I1	0.01489 (17)	0.0493 (2)	0.0432 (2)	0.000	−0.00252 (12)	0.000
I2	0.0333 (2)	0.0592 (2)	0.02065 (18)	0.000	0.00223 (11)	0.000
N1	0.0176 (12)	0.0218 (11)	0.0268 (13)	0.0006 (9)	−0.0008 (10)	−0.0019 (10)
C1	0.0157 (14)	0.0288 (14)	0.0259 (15)	0.0046 (11)	−0.0004 (11)	−0.0062 (12)
C2	0.0242 (16)	0.0354 (17)	0.0393 (19)	0.0040 (13)	−0.0057 (15)	−0.0157 (14)
C3	0.0300 (18)	0.0322 (17)	0.062 (3)	0.0007 (14)	−0.0065 (17)	−0.0214 (18)
C4	0.0347 (19)	0.0209 (15)	0.071 (3)	−0.0038 (13)	0.0040 (19)	−0.0020 (16)
C5	0.0303 (17)	0.0251 (14)	0.0400 (19)	0.0002 (13)	0.0018 (15)	0.0039 (13)
S1	0.0313 (6)	0.0379 (6)	0.0210 (5)	0.000	0.0053 (4)	0.000

Geometric parameters (Å, °)

Zn1—N1	2.063 (3)	C2—C3	1.378 (6)
Zn1—N1[i]	2.063 (3)	C2—H2	0.9500
Zn1—I1	2.5447 (6)	C3—C4	1.377 (7)
Zn1—I2	2.5473 (6)	C3—H3	0.9500
N1—C5	1.346 (4)	C4—C5	1.391 (5)

N1—C1	1.347 (4)	C4—H4	0.9500
C1—C2	1.389 (4)	C5—H5	0.9500
C1—S1	1.775 (3)	S1—C1[i]	1.775 (3)
N1—Zn1—N1[i]	93.85 (14)	C3—C2—H2	120.8
N1—Zn1—I1	113.69 (7)	C1—C2—H2	120.8
N1[i]—Zn1—I1	113.69 (7)	C4—C3—C2	120.0 (3)
N1—Zn1—I2	108.33 (8)	C4—C3—H3	120.0
N1[i]—Zn1—I2	108.33 (8)	C2—C3—H3	120.0
I1—Zn1—I2	116.54 (2)	C3—C4—C5	118.7 (3)
C5—N1—C1	118.6 (3)	C3—C4—H4	120.6
C5—N1—Zn1	122.5 (2)	C5—C4—H4	120.6
C1—N1—Zn1	118.8 (2)	N1—C5—C4	122.0 (4)
N1—C1—C2	122.3 (3)	N1—C5—H5	119.0
N1—C1—S1	118.8 (2)	C4—C5—H5	119.0
C2—C1—S1	118.8 (3)	C1—S1—C1[i]	102.5 (2)
C3—C2—C1	118.4 (3)		

Symmetry code: (i) x, $-y+1/2$, z.