

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

Dichlorido(di-2-pyridyl sulfide- κ^2N,N')-zinc(II)

Mario Wriedt,* Inke Jess and Christian Näther

Institut für Anorganische Chemie, Christian-Albrechts-Universität Kiel,
Olshausenstrasse 40, D-24098 Kiel, Germany
Correspondence e-mail: mwriedt@ac.uni-kiel.de

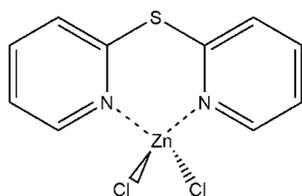
Received 21 November 2007; accepted 22 November 2007

Key indicators: single-crystal X-ray study; $T = 170$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å;
R factor = 0.036; wR factor = 0.096; data-to-parameter ratio = 20.1.

The crystal structure of the title compound, $[\text{ZnCl}_2(\text{C}_{10}\text{H}_8\text{N}_2\text{S})]$, consists of a six-membered chelate ring in which the Zn atom is approximately tetrahedrally coordinated by two chloride ions and by the two pyridyl N atoms of a single di-2-pyridyl sulfide ligand. 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 $50.4(1)^\circ$.

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

$[\text{ZnCl}_2(\text{C}_{10}\text{H}_8\text{N}_2\text{S})]$
 $M_r = 324.51$
Monoclinic, $P2_1/c$
 $a = 12.1944(12)$ Å
 $b = 7.6404(4)$ Å
 $c = 14.2572(15)$ Å
 $\beta = 110.426(12)^\circ$

$V = 1244.82(19)$ Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 2.54$ mm⁻¹
 $T = 170(2)$ K
 $0.14 \times 0.10 \times 0.07$ mm

Data collection

Stoe IPDSI diffractometer
Absorption correction: numerical
(*X-SHAPE*; Stoe & Cie, 1998)
 $T_{\min} = 0.751$, $T_{\max} = 0.852$

7272 measured reflections
2939 independent reflections
2297 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.036$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.096$
 $S = 1.00$
2939 reflections

146 parameters
H-atom parameters constrained
 $\Delta\rho_{\max} = 0.47$ e Å⁻³
 $\Delta\rho_{\min} = -0.60$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Zn1—N1	2.057 (2)	Zn1—Cl1	2.2192 (8)
Zn1—N11	2.061 (2)	Zn1—Cl2	2.2261 (8)
N1—Zn1—Cl1	109.32 (7)	N1—Zn1—Cl2	108.68 (7)
N11—Zn1—Cl1	115.66 (7)	N11—Zn1—Cl2	107.42 (7)

Data collection: *IPDS Program Package* (Stoe & Cie, 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*.

This work is supported by the state of Schleswig-Holstein and the Deutsche Forschungsgemeinschaft (Projekt No. NA 720/1–1). We are very grateful to Professor Dr. Wolfgang Bensch for the facility to use his experimental equipment.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2646).

References

- Anderson, R. J. & Steel, P. J. (1998). *Acta Cryst.* **C54**, 223–225.
Bhosekar, G., Jess, I. & Näther, C. (2007). *Inorg. Chem.* **43**, 6508–6515.
Bruker (1998). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Kondo, M., Kawata, S., Kitagawa, S., Kiso, H. & Munakata, M. (1995). *Acta Cryst.* **C51**, 567–569.
Nicolò, F., Bruno, G. & Tresoldi, G. (1996). *Acta Cryst.* **C52**, 2188–2191.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Stoe & Cie (1998). *X-SHAPE* (Version 1.03) and *IPDS Program Package* (Version 2.89). Stoe & Cie, Darmstadt, Germany.
Teles, W. M., Fernandes, N. G., Abras, A. & Filgueiras, C. A. L. (1999). *Transition Met. Chem.* **24**, 321–325.
Tresoldi, G., Piraino, P., Rotondo, E. & Faraone, F. (1991). *J. Chem. Soc. Dalton Trans.*, pp. 425–430.
Tresoldi, G., Rotondo, E., Piraino, P., Lanfranchi, M. & Tiripichio, A. (1992). *Inorg. Chim. Acta*, **194**, 233–241.

supporting information

Acta Cryst. (2008). E64, m10 [https://doi.org/10.1107/S1600536807062101]

Dichlorido(di-2-pyridyl sulfide- κ^2N,N')zinc(II)**Mario Wriedt, Inke Jess and Christian Näther****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) chloride 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) chloride the title compound (I) is 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 bonded to the metal 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 arrangement. 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 approximately tetrahedral with bonds being formed to two chloride 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 115.66°, the largest being N—Zn—Cl. The Zn—Cl and Zn—N distances are in the range of 2.057 (2)–2.061 (2) and 2.2192 (8)–2.2261 (8) Å. The structural parameters in the dps molecule are quite regular. In particular the C—S bonds, 1.782 (3) and 1.780 (3) Å, are in good agreement with those expected for $C(sp^2)$ -S bonds (1.77 Å).

S2. Experimental

ZnCl₂ and 2,2'-bipyridyldisulfide was obtained from Alfa Aesar and methanol was obtained from Fluka. 0.0313 mmol (4.3 mg) zinc(II) chloride, 0.125 mmol (27.5 mg) 2,2'-bipyridyldisulfide and 3 ml of methanol were transferred in test-tube, which were closed and heated to 110 °C for three 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 $U_{eq}(H) = 1.2U_{eq}(C)$ of the parent atom using a riding model with C—H = 0.97 Å.

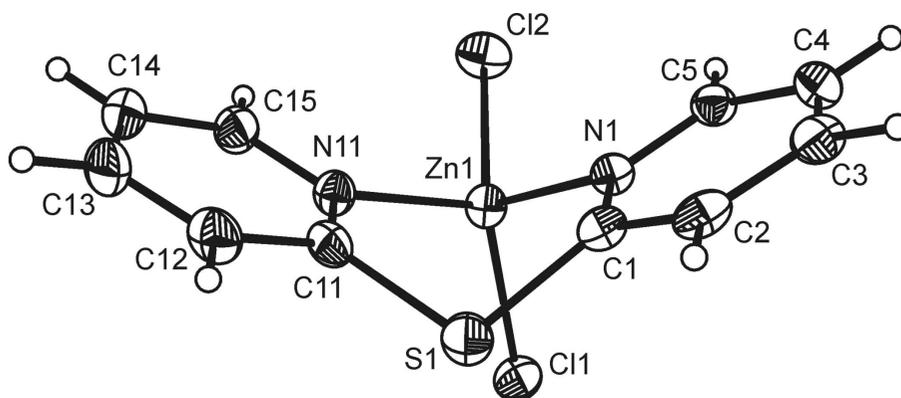


Figure 1

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

Dichlorido(di-2-pyridyl sulfide- κ^2N,N')zinc(II)

Crystal data

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

$M_r = 324.51$

Monoclinic, $P2_1/c$

$a = 12.1944$ (12) Å

$b = 7.6404$ (4) Å

$c = 14.2572$ (15) Å

$\beta = 110.426$ (12)°

$V = 1244.82$ (19) Å³

$Z = 4$

$F(000) = 648$

$D_x = 1.732$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 7174 reflections

$\theta = 3\text{--}28.1^\circ$

$\mu = 2.54$ mm⁻¹

$T = 170$ K

Block, colourless

$0.14 \times 0.10 \times 0.07$ mm

Data collection

Stoe IPDSI
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Phi scans

Absorption correction: numerical
(*X-SHAPE*; Stoe & Cie, 1998)

$T_{\min} = 0.751$, $T_{\max} = 0.852$

7272 measured reflections

2939 independent reflections

2297 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.036$

$\theta_{\max} = 28.1^\circ$, $\theta_{\min} = 3.0^\circ$

$h = -16 \rightarrow 15$

$k = -8 \rightarrow 10$

$l = -15 \rightarrow 18$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.096$

$S = 1.00$

2939 reflections

146 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

$w = 1/[\sigma^2(F_o^2) + (0.0636P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.47$ e Å⁻³

$\Delta\rho_{\min} = -0.60$ e Å⁻³

Extinction correction: *SHELXL*,

$F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0121 (14)

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.75122 (3)	0.38978 (4)	0.21941 (2)	0.02084 (13)
Cl1	0.85027 (6)	0.14097 (10)	0.23692 (6)	0.02808 (18)
Cl2	0.71512 (7)	0.54386 (11)	0.07932 (6)	0.03121 (19)
N11	0.59754 (19)	0.3765 (3)	0.24881 (19)	0.0218 (5)
C11	0.5996 (2)	0.3642 (4)	0.3433 (2)	0.0225 (6)
C12	0.4973 (3)	0.3575 (4)	0.3656 (3)	0.0304 (7)
H12	0.5007	0.3458	0.4329	0.036*
C13	0.3906 (3)	0.3682 (4)	0.2884 (3)	0.0346 (8)
H13	0.3198	0.3626	0.3021	0.042*
C14	0.3878 (3)	0.3870 (4)	0.1910 (3)	0.0329 (7)
H14	0.3154	0.3970	0.1371	0.039*
C15	0.4925 (2)	0.3910 (4)	0.1739 (2)	0.0272 (6)
H15	0.4909	0.4044	0.1072	0.033*
N1	0.83245 (18)	0.5499 (3)	0.33969 (18)	0.0202 (5)
C1	0.8192 (2)	0.5231 (4)	0.4286 (2)	0.0214 (5)
C2	0.8775 (2)	0.6216 (4)	0.5128 (2)	0.0250 (6)
H2	0.8654	0.6015	0.5742	0.030*
C3	0.9546 (2)	0.7517 (4)	0.5049 (2)	0.0289 (7)
H3	0.9974	0.8194	0.5618	0.035*
C4	0.9679 (2)	0.7808 (4)	0.4139 (3)	0.0292 (6)
H4	1.0199	0.8684	0.4071	0.035*
C5	0.9039 (2)	0.6795 (4)	0.3328 (2)	0.0229 (6)
H5	0.9107	0.7025	0.2696	0.027*
S1	0.73529 (6)	0.34212 (11)	0.44428 (6)	0.02965 (19)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.02206 (18)	0.0255 (2)	0.01652 (18)	−0.00095 (12)	0.00868 (12)	−0.00111 (13)
Cl1	0.0294 (3)	0.0284 (4)	0.0268 (4)	0.0042 (3)	0.0101 (3)	−0.0009 (3)
Cl2	0.0438 (4)	0.0333 (4)	0.0195 (4)	0.0018 (3)	0.0148 (3)	0.0042 (3)
N11	0.0207 (10)	0.0244 (12)	0.0216 (12)	−0.0007 (9)	0.0090 (9)	0.0001 (10)
C11	0.0245 (12)	0.0212 (14)	0.0248 (14)	−0.0028 (10)	0.0123 (11)	0.0008 (11)
C12	0.0327 (15)	0.0324 (17)	0.0335 (17)	−0.0010 (12)	0.0210 (13)	0.0041 (14)
C13	0.0250 (14)	0.0336 (18)	0.050 (2)	−0.0013 (12)	0.0196 (14)	0.0035 (15)
C14	0.0227 (13)	0.0330 (17)	0.0390 (19)	−0.0019 (12)	0.0056 (13)	0.0073 (15)

C15	0.0246 (13)	0.0304 (16)	0.0240 (15)	-0.0021 (11)	0.0053 (11)	0.0035 (13)
N1	0.0213 (10)	0.0208 (12)	0.0186 (11)	0.0014 (9)	0.0072 (9)	0.0003 (9)
C1	0.0229 (12)	0.0239 (14)	0.0176 (13)	0.0042 (10)	0.0075 (10)	0.0009 (11)
C2	0.0286 (13)	0.0290 (16)	0.0161 (13)	0.0099 (11)	0.0060 (11)	-0.0001 (12)
C3	0.0328 (15)	0.0212 (15)	0.0255 (15)	0.0056 (11)	0.0011 (12)	-0.0086 (12)
C4	0.0284 (14)	0.0204 (14)	0.0350 (17)	-0.0009 (11)	0.0064 (12)	-0.0025 (13)
C5	0.0237 (13)	0.0219 (14)	0.0230 (14)	0.0012 (10)	0.0081 (11)	0.0033 (12)
S1	0.0296 (4)	0.0375 (4)	0.0206 (4)	-0.0047 (3)	0.0073 (3)	0.0094 (3)

Geometric parameters (Å, °)

Zn1—N1	2.057 (2)	C14—H14	0.9500
Zn1—N11	2.061 (2)	C15—H15	0.9500
Zn1—C11	2.2192 (8)	N1—C5	1.345 (4)
Zn1—C12	2.2261 (8)	N1—C1	1.349 (4)
N11—C11	1.342 (4)	C1—C2	1.384 (4)
N11—C15	1.355 (4)	C1—S1	1.780 (3)
C11—C12	1.392 (4)	C2—C3	1.399 (4)
C11—S1	1.782 (3)	C2—H2	0.9500
C12—C13	1.382 (5)	C3—C4	1.381 (5)
C12—H12	0.9500	C3—H3	0.9500
C13—C14	1.384 (5)	C4—C5	1.384 (4)
C13—H13	0.9500	C4—H4	0.9500
C14—C15	1.382 (4)	C5—H5	0.9500
N1—Zn1—N11	93.85 (9)	N11—C15—H15	118.8
N1—Zn1—C11	109.32 (7)	C14—C15—H15	118.8
N11—Zn1—C11	115.66 (7)	C5—N1—C1	118.3 (3)
N1—Zn1—C12	108.68 (7)	C5—N1—Zn1	120.83 (19)
N11—Zn1—C12	107.42 (7)	C1—N1—Zn1	120.83 (19)
C11—Zn1—C12	118.90 (3)	N1—C1—C2	122.6 (3)
C11—N11—C15	118.5 (2)	N1—C1—S1	119.9 (2)
C11—N11—Zn1	120.53 (18)	C2—C1—S1	117.2 (2)
C15—N11—Zn1	120.8 (2)	C1—C2—C3	118.2 (3)
N11—C11—C12	121.8 (3)	C1—C2—H2	120.9
N11—C11—S1	120.3 (2)	C3—C2—H2	120.9
C12—C11—S1	117.7 (2)	C4—C3—C2	119.5 (3)
C13—C12—C11	119.1 (3)	C4—C3—H3	120.2
C13—C12—H12	120.5	C2—C3—H3	120.2
C11—C12—H12	120.5	C3—C4—C5	118.5 (3)
C12—C13—C14	119.5 (3)	C3—C4—H4	120.7
C12—C13—H13	120.3	C5—C4—H4	120.7
C14—C13—H13	120.3	N1—C5—C4	122.8 (3)
C15—C14—C13	118.5 (3)	N1—C5—H5	118.6
C15—C14—H14	120.7	C4—C5—H5	118.6
C13—C14—H14	120.7	C1—S1—C11	103.75 (13)
N11—C15—C14	122.5 (3)		