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Bis(4-aminobenzenesulfonamide- κ N⁴)-dichloridozincSabrina Benmebarek,^a Mhamed Boudraa,^a Sofiane Bouacida,^{a,b,*} Hocine Merazig^a and George Dénès^c

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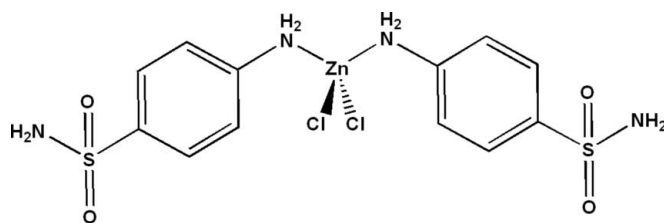
Received 1 December 2013; accepted 18 December 2013

Key indicators: single-crystal X-ray study; $T = 150$ K; mean $\sigma(\text{C}-\text{C}) = 0.008$ Å; R factor = 0.040; wR factor = 0.067; data-to-parameter ratio = 17.1.

In the title compound, $[\text{ZnCl}_2(\text{C}_6\text{H}_8\text{N}_2\text{O}_2\text{S})_2]$, the Zn^{II} ion lies on a twofold rotation axis and has a slightly distorted tetrahedral coordination geometry, involving two Cl atoms and two N atoms from the amino groups attached directly to the benzene rings [$\text{Zn}-\text{Cl} = 2.2288$ (16) Å and $\text{Zn}-\text{N} = 2.060$ (5) Å]. The dihedral angle between the benzene rings is 67.1 (3)°. The crystal packing can be describe as layers in a zigzag arrangement parallel to (001). The amine H atoms act as donor atoms and participate in intermolecular $\text{N}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen bonds, forming a three-dimensional network.

Related literature

For background to sulfanilamides and their applications, see: Wong & Giandomenico (1999); Ferrer *et al.* (1990); Supuran *et al.* (1998); Medina *et al.* (1999). For related structures, see: Benmebarek *et al.* (2012, 2013).



Experimental

Crystal data

$[\text{ZnCl}_2(\text{C}_6\text{H}_8\text{N}_2\text{O}_2\text{S})_2]$
 $M_r = 480.68$

Orthorhombic, *Ab*a2
 $a = 7.7957$ (15) Å

$b = 27.916$ (6) Å
 $c = 8.2701$ (17) Å
 $V = 1799.8$ (6) Å³
 $Z = 4$

Mo $K\alpha$ radiation
 $\mu = 1.92$ mm⁻¹
 $T = 150$ K
 $0.23 \times 0.19 \times 0.15$ mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2002)
 $T_{\text{min}} = 0.639$, $T_{\text{max}} = 0.746$

6151 measured reflections
2051 independent reflections
1563 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.075$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.067$
 $S = 1.00$
2051 reflections
120 parameters
3 restraints
H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\text{max}} = 0.38$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.40$ e Å⁻³
Absolute structure: Flack parameter determined using 601 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: 0.037 (18)

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1A}\cdots\text{Cl1}^{\text{i}}$	0.99	2.50	3.327 (5)	141
$\text{N2}-\text{H1N}\cdots\text{O2}^{\text{ii}}$	0.86 (5)	2.10 (6)	2.891 (8)	152 (5)
$\text{N2}-\text{H2N}\cdots\text{O1}^{\text{iii}}$	0.86 (5)	2.18 (6)	3.015 (8)	163 (5)

Symmetry codes: (i) $x + \frac{1}{2}, -y, z - \frac{1}{2}$; (ii) $-x + 1, -y + \frac{1}{2}, z - \frac{1}{2}$; (iii) $-x + \frac{3}{2}, y, z - \frac{1}{2}$.

Data collection: APEX2 (Bruker, 2011); cell refinement: SAINT (Bruker, 2011); data reduction: SAINT; program(s) used to solve structure: SIR2002 (Burla *et al.*, 2005); program(s) used to refine structure: SHELXL2013 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012) and DIAMOND (Brandenburg & Berndt, 2001); software used to prepare material for publication: WinGX (Farrugia, 2012).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH5676).

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supporting information

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Bis(4-aminobenzenesulfonamide- κ N⁴)dichloridozinc

Sabrina Benmebarek, Mhamed Boudraa, Sofiane Bouacida, Hocine Merazig and George Dénès

S1. Comment

The use of metal complexes as pharmaceuticals has shown promise in recent years particularly as anticancer agents (Wong & Giandomenico, 1999). Recently, sulfadruugs and their complexes have applications as diuretic, antiglaucoma or antiepileptic drugs among others (Ferrer *et al.*, 1990; Supuran *et al.*, 1998). Furthermore, metal sulfanilamides have received attention owing to their antimicrobial activity (Medina *et al.*, 1999). As part of our ongoing studies on the synthesis, structures and biological activity of organometallic sulfanilamide complexes (Benmebarek *et al.* 2012, 2013) we have synthesized and determined the crystal structure of the title compound (I).

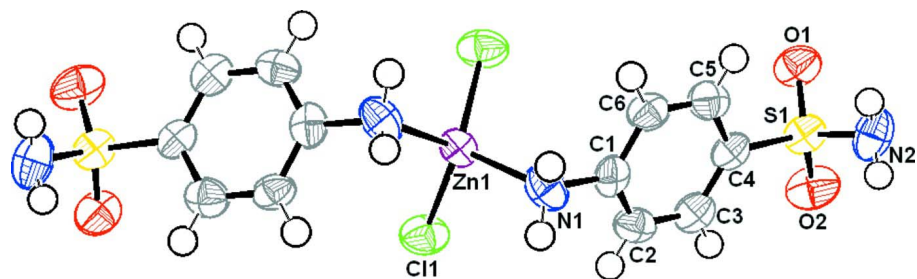
The molecular geometry and the atom-numbering scheme are shown in Fig 1. The title compound is a mononuclear zinc(II) complex in which the Zn^{II} ion is in a slightly distorted tetrahedral geometry involving two Cl atoms and two N atoms from the two amino groups of the sulfanilamide unit [Zn—Cl = 2.2288 (16) Å and Zn—N = 2.060 (5) Å]. The angles involving the Zn atom range from 104.38 (14) to 116.38 (11)°. The dihedral angle between the two benzene rings is 67.1 (3)°. The crystal packing can be describe by a interacting layers in zigzag parallel to (001) planes (Fig.2). The sulfonamidic nitrogen atoms, acting as donor, participate in intermolecular N—H···O and N—H···Cl hydrogen bonds forming a three-dimensional network (Table 1, Fig. 3).

S2. Experimental

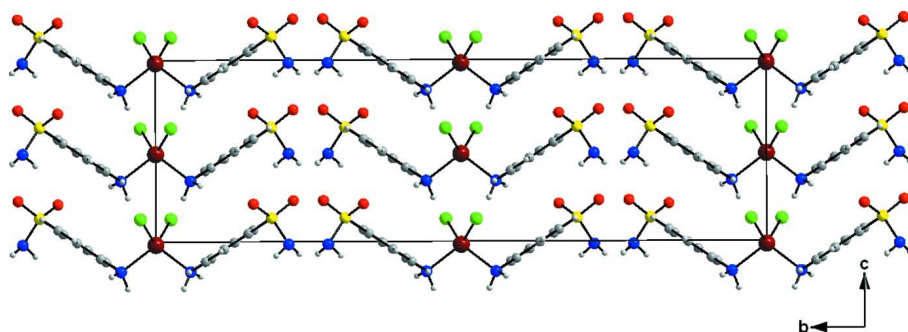
ZnCl₂ (0.1 mmol) and sulfanilamide (0.5 mmol) were dissolved in 15 ml solution of NaOH 0.01 N and heated, under continuous stirring, at 373 K for 15 min. The solution was transfered into a 23 ml teflon-lined stainless steel autoclave and heated at 453 K for 3 days. Then the autoclave was cooled to room temperature at 10K/h. Clear block-shaped crystal were collected, washed with ethanol and dried in air at ambient temperature.

S3. Refinement

All non-H atoms were refined with anisotropic atomic displacement parameters. Approximate positions for all H atoms were first obtained from the difference electron density map. However, the H atoms were situated into idealized positions and the H-atoms have been refined within the riding atom approximation. The applied constraints were as follows: C—H = 0.93 Å and N—H = 0.90 Å. $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C or N})$. The atoms H1N and H2N amino group were located in difference Fourier maps and included in the subsequent refinement with the constaint of N—H = 0.85 (2)Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{N})$.

**Figure 1**

The molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level. Only the the asymmetric unit is labelled. H atoms are represented as small spheres of arbitrary radii.

**Figure 2**

Packing of (I) viewed *via a* axis showing alternating layers in zigzag parallel to (001) planes.

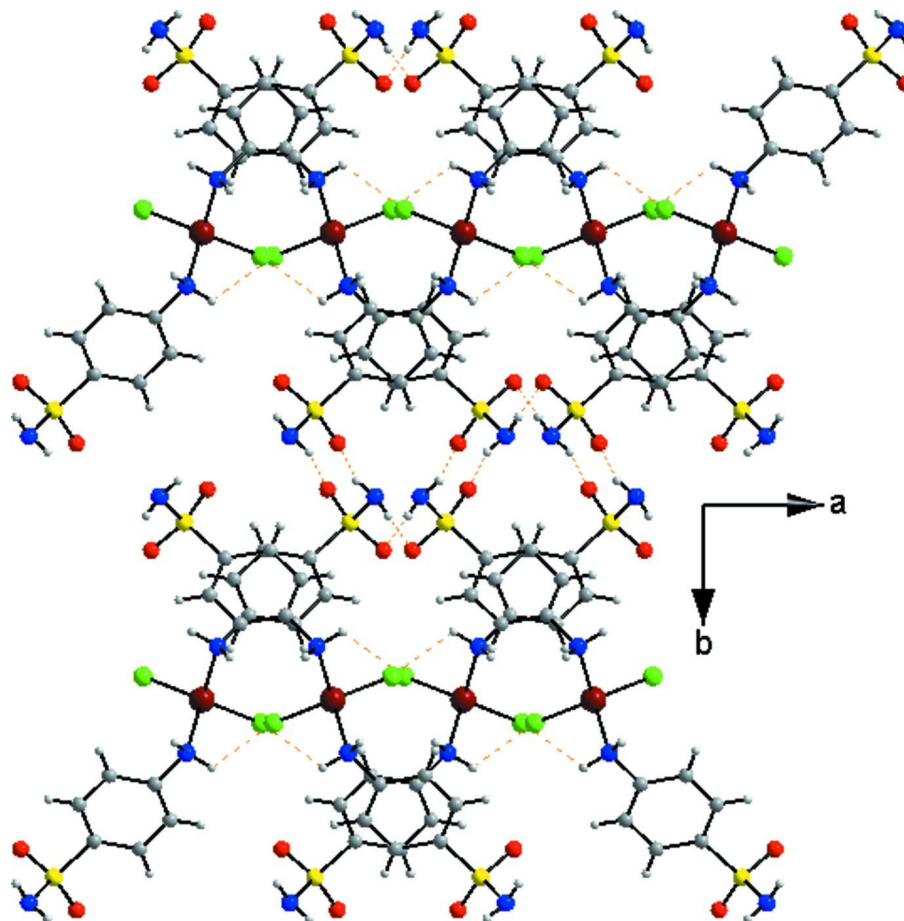


Figure 3

Packing of the title compound viewed along the c axis showing hydrogen bonds [N—H \cdots Cl and N—H \cdots O] as dashed lines

Bis(4-aminobenzenesulfonamide- κN^4)dichloridozinc

Crystal data

[ZnCl₂(C₆H₈N₂O₂S)₂]

$M_r = 480.68$

Orthorhombic, $Aba2$

$a = 7.7957$ (15) Å

$b = 27.916$ (6) Å

$c = 8.2701$ (17) Å

$V = 1799.8$ (6) Å³

$Z = 4$

$F(000) = 976$

$D_x = 1.774$ Mg m⁻³

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

Cell parameters from 805 reflections

$\theta = 2.9$ – 22.3°

$\mu = 1.92$ mm⁻¹

$T = 150$ K

Block, colourless

$0.23 \times 0.19 \times 0.15$ mm

Data collection

Bruker APEXII CCD

diffractometer

Radiation source: sealed tube

φ and ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2002)

$T_{\min} = 0.639$, $T_{\max} = 0.746$

6151 measured reflections

2051 independent reflections

1563 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.075$

$\theta_{\max} = 27.4^\circ$, $\theta_{\min} = 2.9^\circ$

$h = -10 \rightarrow 10$
 $k = -36 \rightarrow 35$

$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.067$
 $S = 1.00$
 2051 reflections
 120 parameters
 3 restraints
 Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2)]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.38 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.40 \text{ e } \text{\AA}^{-3}$
 Absolute structure: Flack parameter determined using 601 quotients $[(I^-)-(I^+)]/[(I^-)+(I^+)]$ (Parsons *et al.*, 2013)
 Absolute structure parameter: 0.037 (18)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.1797 (7)	0.0904 (2)	-0.0925 (8)	0.0181 (15)
C2	0.1224 (6)	0.1288 (2)	-0.0041 (9)	0.0202 (13)
H2	0.0028	0.1339	0.0093	0.024*
C3	0.2387 (8)	0.1598 (2)	0.0653 (8)	0.0205 (15)
H3	0.2002	0.1866	0.1263	0.025*
C4	0.4132 (7)	0.1514 (2)	0.0446 (8)	0.0182 (14)
C5	0.4705 (7)	0.1121 (2)	-0.0415 (9)	0.0214 (16)
H5	0.5901	0.1065	-0.0532	0.026*
C6	0.3546 (7)	0.0811 (2)	-0.1103 (7)	0.0188 (15)
H6	0.3928	0.0539	-0.1689	0.023*
N1	0.0594 (5)	0.05705 (19)	-0.1656 (7)	0.0221 (13)
H1A	0.1090	0.0447	-0.2676	0.026*
H1B	-0.0475	0.0744	-0.1929	0.026*
N2	0.6629 (6)	0.21766 (18)	-0.0154 (9)	0.0267 (12)
H1N	0.591 (6)	0.235 (2)	-0.069 (7)	0.032*
H2N	0.712 (7)	0.1973 (18)	-0.079 (7)	0.032*
O1	0.6944 (5)	0.15998 (16)	0.2073 (6)	0.0275 (12)
O2	0.4808 (6)	0.22535 (16)	0.2260 (6)	0.0312 (12)
S1	0.56714 (18)	0.18997 (6)	0.1307 (2)	0.0204 (3)
Cl1	-0.22591 (17)	0.02497 (6)	0.1242 (2)	0.0273 (4)
Zn1	0.0000	0.0000	-0.01787 (14)	0.0176 (2)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.023 (3)	0.019 (4)	0.012 (3)	-0.003 (3)	-0.004 (3)	0.007 (3)

C2	0.020 (3)	0.024 (3)	0.017 (4)	0.004 (2)	0.002 (3)	0.005 (4)
C3	0.027 (3)	0.020 (4)	0.015 (3)	0.001 (3)	-0.001 (3)	0.002 (3)
C4	0.025 (3)	0.016 (3)	0.014 (3)	0.001 (3)	-0.002 (3)	0.001 (3)
C5	0.021 (3)	0.024 (3)	0.019 (4)	0.002 (3)	0.005 (3)	0.004 (3)
C6	0.022 (3)	0.018 (4)	0.017 (4)	0.004 (3)	0.005 (3)	-0.002 (3)
N1	0.018 (2)	0.031 (3)	0.017 (3)	-0.004 (2)	-0.001 (2)	0.001 (3)
N2	0.039 (3)	0.023 (3)	0.019 (3)	-0.007 (2)	-0.002 (4)	0.003 (4)
O1	0.030 (3)	0.025 (3)	0.027 (3)	0.003 (2)	-0.011 (2)	0.000 (2)
O2	0.041 (3)	0.027 (3)	0.026 (3)	0.007 (2)	-0.006 (2)	-0.012 (2)
S1	0.0261 (7)	0.0209 (9)	0.0144 (8)	0.0013 (6)	-0.0036 (8)	-0.0010 (9)
Cl1	0.0259 (7)	0.0307 (9)	0.0252 (9)	0.0073 (7)	0.0086 (9)	0.0030 (10)
Zn1	0.0164 (4)	0.0218 (5)	0.0145 (5)	-0.0010 (5)	0.000	0.000

Geometric parameters (Å, °)

C1—C2	1.371 (8)	N1—Zn1	2.060 (5)
C1—C6	1.396 (7)	N1—H1A	0.9900
C1—N1	1.454 (7)	N1—H1B	0.9900
C2—C3	1.380 (8)	N2—S1	1.617 (6)
C2—H2	0.9500	N2—H1N	0.86 (3)
C3—C4	1.391 (8)	N2—H2N	0.86 (3)
C3—H3	0.9500	O1—S1	1.444 (4)
C4—C5	1.382 (8)	O2—S1	1.432 (5)
C4—S1	1.763 (6)	Cl1—Zn1	2.2288 (16)
C5—C6	1.374 (8)	Zn1—N1 ⁱ	2.060 (5)
C5—H5	0.9500	Zn1—Cl1 ⁱ	2.2288 (16)
C6—H6	0.9500		
C2—C1—C6	121.3 (6)	Zn1—N1—H1A	108.9
C2—C1—N1	120.8 (5)	C1—N1—H1B	108.9
C6—C1—N1	117.9 (6)	Zn1—N1—H1B	108.9
C1—C2—C3	119.9 (5)	H1A—N1—H1B	107.8
C1—C2—H2	120.1	S1—N2—H1N	110 (4)
C3—C2—H2	120.1	S1—N2—H2N	110 (4)
C2—C3—C4	119.0 (6)	H1N—N2—H2N	110 (7)
C2—C3—H3	120.5	O2—S1—O1	118.8 (3)
C4—C3—H3	120.5	O2—S1—N2	107.4 (3)
C5—C4—C3	120.9 (6)	O1—S1—N2	106.7 (3)
C5—C4—S1	118.2 (4)	O2—S1—C4	108.9 (3)
C3—C4—S1	120.8 (5)	O1—S1—C4	106.9 (3)
C6—C5—C4	120.0 (5)	N2—S1—C4	107.7 (3)
C6—C5—H5	120.0	N1 ⁱ —Zn1—N1	107.2 (3)
C4—C5—H5	120.0	N1 ⁱ —Zn1—Cl1 ⁱ	104.38 (14)
C5—C6—C1	118.8 (6)	N1—Zn1—Cl1 ⁱ	112.14 (13)
C5—C6—H6	120.6	N1 ⁱ —Zn1—Cl1	112.14 (13)
C1—C6—H6	120.6	N1—Zn1—Cl1	104.38 (14)
C1—N1—Zn1	113.2 (4)	Cl1 ⁱ —Zn1—Cl1	116.38 (11)
C1—N1—H1A	108.9		

C6—C1—C2—C3	1.9 (10)	N1—C1—C6—C5	-179.7 (6)
N1—C1—C2—C3	179.5 (6)	C2—C1—N1—Zn1	-91.0 (6)
C1—C2—C3—C4	-0.3 (10)	C6—C1—N1—Zn1	86.8 (6)
C2—C3—C4—C5	-1.2 (10)	C5—C4—S1—O2	-174.7 (5)
C2—C3—C4—S1	-180.0 (5)	C3—C4—S1—O2	4.1 (6)
C3—C4—C5—C6	1.1 (10)	C5—C4—S1—O1	-45.2 (6)
S1—C4—C5—C6	179.9 (5)	C3—C4—S1—O1	133.6 (5)
C4—C5—C6—C1	0.5 (10)	C5—C4—S1—N2	69.1 (6)
C2—C1—C6—C5	-2.0 (10)	C3—C4—S1—N2	-112.0 (5)

Symmetry code: (i) $-x, -y, z$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A \cdots Cl1 ⁱⁱ	0.99	2.50	3.327 (5)	141
N2—H1N \cdots O2 ⁱⁱⁱ	0.86 (5)	2.10 (6)	2.891 (8)	152 (5)
N2—H2N \cdots O1 ^{iv}	0.86 (5)	2.18 (6)	3.015 (8)	163 (5)

Symmetry codes: (ii) $x+1/2, -y, z-1/2$; (iii) $-x+1, -y+1/2, z-1/2$; (iv) $-x+3/2, y, z-1/2$.