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[(1-Azulenyl)methanethiolato-κS]-(1,4,8,12-tetraazacyclopentadecane-$\kappa^4 N$)zinc(II) perchlorate

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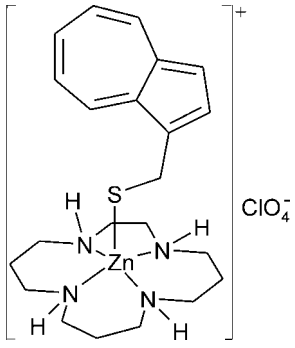
Key indicators: single-crystal X-ray study; T = 183 K; mean σ(C–C) = 0.008 Å; disorder in solvent or counterion; R factor = 0.049; wR factor = 0.138; data-to-parameter ratio = 19.9.

In the title compound, $[Zn(C_{11}H_{26}N_4)(C_{11}H_9S)]ClO_4$, the Zn^{II} atom is five-coordinated by four N atoms from a neutral 1,4,8,12-tetraazacyclopentadecane aza-macrocycle molecule, and one S atom from an azulenylmethanethiolate ligand. Only monomers are found in the crystal. The coordination geometry can be described as trigonal bipyramidal, with the thiolate group in an equatorial position. The Zn—N and Zn—S distances are in the usual ranges for this type of complex.

Related literature

For related literature, see: Notni, Görls *et al.* (2006); Notni, Schenk *et al.* (2006); Notni *et al.* (2007); Salter *et al.* (2005); Schenk *et al.* (2006).



Experimental

Crystal data

$[Zn(C_{11}H_{26}N_4)(C_{11}H_9S)]ClO_4$
M_r = 552.42
Orthorhombic, $P2_12_12_1$
a = 8.0795 (1) Å
b = 13.7163 (3) Å
c = 23.0913 (5) Å
V = 2559.00 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.18 mm^{-1}
T = 183 (2) K
0.06 × 0.06 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: none
18270 measured reflections
5858 independent reflections
4978 reflections with $I > 2\sigma(I)$
R_{int} = 0.060

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.138
S = 1.04
5858 reflections
295 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.73 e Å^{-3}
$\Delta\rho_{min}$ = −0.65 e Å^{-3}
Absolute structure: Flack (1983), 2541 Friedel pairs
Flack parameter: 0.002 (16)

Table 1
Selected geometric parameters (Å, °).

Zn—N4	2.134 (4)	Zn—N1	2.272 (4)
Zn—N2	2.139 (4)	Zn—S	2.2804 (10)
Zn—N3	2.235 (3)		
N4—Zn—N2	130.42 (16)	N3—Zn—N1	159.70 (15)
N4—Zn—N3	86.95 (15)	N4—Zn—S	118.88 (11)
N2—Zn—N3	85.81 (17)	N2—Zn—S	110.70 (12)
N4—Zn—N1	91.17 (15)	N3—Zn—S	99.13 (10)
N2—Zn—N1	80.05 (17)	N1—Zn—S	99.46 (11)

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens, 1990); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2083).

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supplementary materials

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[(1-Azulenyl)methanethiolato-κS](1,4,8,12-tetraazacyclopentadecane-$\kappa^4 N$)zinc(II) perchlorate

H. Görls, J. Notni and E. Anders

Comment

The title compound belongs to a series of zinc thiolate complexes with azamacrocyclic ligands (Notni, Görls *et al.*, 2006), which are potent model systems for a number of zinc enzymes (Schenk *et al.*, 2006). These compounds possess nucleophilic *p*-methylthiolate or phenylmethylthiolate residues, the nucleophilicity of which is influenced by the nature of the macrocyclic ligand (Notni, Schenk *et al.*, 2006; Notni *et al.*, 2007). In order to gain insight into the electronic properties of the sulfur atom, azulenylmethyl derivatives were believed to allow a qualitative estimation of electron density at the thiolate sulfur employing VIS spectroscopy. However, the project failed since most of the desired complexes were elusive due to degradation processes during synthesis.

In crystalline form, the title compound is air-stable for several months. The crystal structure of the title compound contains a monovalent zinc(II) complex cation and a discrete perchlorate anion as shown in Fig. 1. Within the cation, the Zn^{II} atom is coordinated by four N atoms and one S atom. Whether the coordination polyhedron can be assigned to tetragonal-pyramidal or trigonal-bipyramidal type is a question, which has been discussed in detail before (Notni, Görls *et al.*, 2006). Following the argumentation given therein, we consider the title structure being trigonal-bipyramidal since pairs of opposing short Zn—N bond lengths [2.134 (4) and 2.139 (4) Å] as well as long Zn—N bond lengths [2.235 (3) and 2.272 (4) Å] are found. This is the largest difference between short and long Zn—N bond distances found for this type of zinc complexes (Notni, Görls *et al.*, 2006; Salter *et al.*, 2005). The pair of long N—Zn—N bonds is considered the axis of the trigonal bipyramid, the thiolate group thus being found in the equatorial position. The Zn—S bond length of 2.280 (1)Å is within the usual range for this kind of compounds (2.27–2.32 Å). The N atoms in these complexes are chiral in nature and the absolute configuration could be determined. In analogy to similar zinc–thiolate complexes of 1,4,8,12-tetraazacyclopentadecane, the N-bound H atoms are found in (+ – – –) positions ('+' denotes the H atom being positioned at the thiolate side of the macrocycle and '–' at the opposite side).

Experimental

The title compound was prepared according to the published procedure (Notni, Görls *et al.*, 2006). A solution of zinc perchlorate hexahydrate (0.750 g, 2 mmol) and 1,4,8,12,tetraazacyclopentadecane (0.430 g, 2 mmol) in methanol (20 ml) was heated for 15 min. Then a solution of potassium hydroxide (0.112 g, 2 mmol) and 1-azulenylmethylthiol (0.350 g, 2 mmol) in methanol (5 ml) was added dropwise, whereupon a fine-crystalline precipitate of potassium perchlorate was obtained. This was filtered off, and from the remaining deep-blue solution, blue needle crystals of the title compound precipitated after 5 min which were collected on a filter funnel and dried in vacuum. Yield 66% (0.731 g). m. p. 473.5–475.5 K. Analysis, calculated for $C_{22}H_{35}ClN_4O_4SZn$: C 47.83, H 6.39, N 10.14, S 5.80, Cl 6.42%; Found: C 47.81, H 6.42, N 9.94, S 5.70, Cl 6.49%.

Refinement

H atoms were positioned geometrically and refined as riding, with C—H = 0.95Å (CH) and 0.99Å (CH_2), and N—H = 0.93Å and $U_{iso}(H) = 1.2U_{eq}(C, N)$. O atoms of the perchlorate group are disordered and they were refined isotropically.

Figures

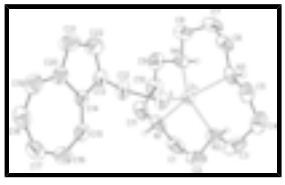


Fig. 1. Molecular structure of the title compound. Displacement ellipsoids are drawn at the 40% probability level. The perchlorate anion was omitted for clarity. H atoms have been omitted except those attached to N atoms.

[(1-Azulenyl)methanethiolato-κ*S*](1,4,8,12-tetraazacyclopentadecane-\ κ^4*N*)zinc(II) perchlorate

Crystal data

$[Zn(C_{11}H_{26}N_4)(C_{11}H_9S)]ClO_4$	$F_{000} = 1160$
$M_r = 552.42$	$D_x = 1.434$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 18270 reflections
$a = 8.0795$ (1) Å	$\theta = 2.3$–$27.5°$
$b = 13.7163$ (3) Å	$\mu = 1.18$ mm^{-1}
$c = 23.0913$ (5) Å	$T = 183$ (2) K
$V = 2559.00$ (8) Å^3	Prism, blue
$Z = 4$	0.06 × 0.06 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer	4978 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.060$
Monochromator: graphite	$\theta_{max} = 27.5°$
$T = 183(2)$ K	$\theta_{min} = 2.3°$
φ and ω scans	$h = -10 \rightarrow 9$
Absorption correction: none	$k = -17 \rightarrow 17$
18270 measured reflections	$l = -28 \rightarrow 29$
5858 independent reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.049$	$w = 1/[\sigma^2(F_o^2) + (0.0822P)^2 + 1.0799P]$

	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.138$	$(\Delta/\sigma)_{max} = 0.038$
$S = 1.04$	$\Delta\rho_{max} = 0.73$ e Å^{-3}
5858 reflections	$\Delta\rho_{min} = -0.65$ e Å^{-3}
295 parameters	Extinction correction: none
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 2541 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: 0.002 (16)

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Zn	0.54052 (5)	0.85174 (3)	0.645222 (17)	0.03886 (13)	
S	0.38553 (14)	0.73185 (7)	0.60351 (5)	0.0489 (2)	
N1	0.5011 (5)	0.8137 (3)	0.74001 (15)	0.0618 (11)	
H1C	0.4144	0.7691	0.7400	0.074*	
N2	0.3875 (5)	0.9714 (3)	0.67100 (19)	0.0631 (10)	
H2C	0.4580	1.0237	0.6779	0.076*	
N3	0.5965 (5)	0.9402 (3)	0.56637 (15)	0.0554 (9)	
H3C	0.6522	0.9965	0.5776	0.067*	
N4	0.8012 (4)	0.8308 (3)	0.65356 (15)	0.0541 (9)	
H4C	0.8461	0.8926	0.6589	0.065*	
C1	0.4320 (9)	0.9025 (4)	0.7666 (2)	0.084 (2)	
H1A	0.5223	0.9492	0.7751	0.100*	
H1B	0.3767	0.8858	0.8035	0.100*	
C2	0.3087 (8)	0.9488 (5)	0.7257 (3)	0.0865 (19)	
H2A	0.2152	0.9035	0.7191	0.104*	
H2B	0.2643	1.0093	0.7432	0.104*	
C3	0.2676 (7)	1.0040 (6)	0.6259 (3)	0.095 (2)	
H3A	0.1984	1.0567	0.6423	0.113*	
H3B	0.1934	0.9488	0.6164	0.113*	
C4	0.3464 (8)	1.0407 (5)	0.5699 (3)	0.0880 (19)	
H4A	0.2574	1.0656	0.5444	0.106*	
H4B	0.4193	1.0964	0.5795	0.106*	
C5	0.4450 (8)	0.9681 (4)	0.5367 (2)	0.0724 (14)	
H5A	0.3767	0.9092	0.5301	0.087*	
H5B	0.4734	0.9959	0.4984	0.087*	
C6	0.7047 (7)	0.8838 (4)	0.5260 (2)	0.0691 (14)	
H6A	0.7189	0.9214	0.4897	0.083*	
H6B	0.6495	0.8216	0.5161	0.083*	
C7	0.8750 (7)	0.8621 (5)	0.5518 (2)	0.0780 (16)	
H7A	0.9470	0.8363	0.5206	0.094*	
H7B	0.9242	0.9241	0.5652	0.094*	
C8	0.8765 (7)	0.7925 (4)	0.6002 (2)	0.0718 (14)	
H8A	0.9925	0.7738	0.6084	0.086*	
H8B	0.8163	0.7329	0.5884	0.086*	
C9	0.8607 (6)	0.7707 (5)	0.7035 (2)	0.0704 (14)	
H9A	0.9831	0.7722	0.7043	0.084*	

H9B	0.8259	0.7023	0.6976	0.084*	
C10	0.7948 (7)	0.8062 (5)	0.7619 (2)	0.0766 (16)	
H10A	0.8712	0.7847	0.7929	0.092*	
H10B	0.7929	0.8784	0.7620	0.092*	
C11	0.6270 (9)	0.7697 (5)	0.7749 (2)	0.0811 (17)	
H11A	0.6247	0.6982	0.7688	0.097*	
H11B	0.6020	0.7821	0.8162	0.097*	
C12	0.4652 (7)	0.6230 (3)	0.6411 (2)	0.0608 (11)	
H12A	0.5863	0.6294	0.6465	0.073*	
H12B	0.4135	0.6182	0.6799	0.073*	
C13	0.4289 (5)	0.5323 (3)	0.60742 (18)	0.0495 (10)	
C14	0.2793 (5)	0.4818 (3)	0.60754 (16)	0.0422 (8)	
C15	0.1353 (6)	0.5078 (3)	0.63574 (18)	0.0547 (10)	
H15A	0.1418	0.5657	0.6582	0.066*	
C16	−0.0175 (7)	0.4616 (4)	0.6360 (2)	0.0653 (12)	
H16A	−0.1021	0.4942	0.6571	0.078*	
C17	−0.0651 (7)	0.3740 (4)	0.6098 (2)	0.0698 (13)	
H17A	−0.1756	0.3537	0.6169	0.084*	
C18	0.0282 (8)	0.3127 (4)	0.5746 (2)	0.0692 (13)	
H18A	−0.0273	0.2558	0.5614	0.083*	
C19	0.1875 (7)	0.3225 (4)	0.5565 (2)	0.0665 (13)	
H19A	0.2266	0.2723	0.5317	0.080*	
C20	0.2998 (6)	0.3947 (3)	0.5689 (2)	0.0546 (10)	
C21	0.4628 (8)	0.4009 (4)	0.5486 (3)	0.0780 (16)	
H21A	0.5143	0.3556	0.5232	0.094*	
C22	0.5374 (7)	0.4838 (4)	0.5715 (3)	0.0699 (13)	
H22A	0.6474	0.5042	0.5635	0.084*	
Cl	0.79877 (18)	0.11964 (9)	0.68485 (6)	0.0683 (3)	
O41	0.8208 (14)	0.2153 (8)	0.7006 (5)	0.091 (3)*	0.575 (13)
O42	0.6918 (15)	0.0533 (10)	0.7147 (5)	0.114 (4)*	0.575 (13)
O43	0.918 (3)	0.0559 (17)	0.6803 (12)	0.221 (9)*	0.575 (13)
O44	0.8335 (15)	0.0986 (8)	0.6292 (5)	0.122 (4)*	0.575 (13)
O41A	0.823 (3)	0.2011 (15)	0.7194 (9)	0.126 (7)*	0.425 (13)
O42A	0.6508 (15)	0.0964 (10)	0.7185 (5)	0.082 (3)*	0.425 (13)
O43A	0.961 (2)	0.0861 (11)	0.7227 (7)	0.120 (5)*	0.425 (13)
O44A	0.7107 (19)	0.1457 (11)	0.6300 (6)	0.116 (5)*	0.425 (13)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn	0.0422 (2)	0.0405 (2)	0.0338 (2)	−0.00398 (19)	−0.00309 (18)	−0.00221 (17)
S	0.0618 (6)	0.0410 (5)	0.0440 (5)	−0.0080 (4)	−0.0168 (5)	−0.0002 (4)
N1	0.079 (3)	0.069 (2)	0.0373 (17)	−0.025 (2)	0.0085 (17)	−0.0057 (17)
N2	0.054 (2)	0.056 (2)	0.079 (3)	−0.0016 (19)	0.008 (2)	−0.015 (2)
N3	0.071 (2)	0.059 (2)	0.0365 (17)	−0.0173 (19)	−0.0119 (16)	0.0113 (15)
N4	0.0449 (16)	0.069 (2)	0.0479 (19)	−0.0047 (17)	0.0017 (15)	−0.0041 (17)
C1	0.114 (5)	0.085 (4)	0.052 (3)	−0.037 (4)	0.032 (3)	−0.025 (3)
C2	0.070 (3)	0.094 (4)	0.096 (5)	−0.003 (3)	0.027 (3)	−0.033 (4)

C3	0.055 (3)	0.107 (5)	0.121 (5)	0.022 (3)	−0.019 (3)	−0.033 (4)
C4	0.089 (4)	0.080 (4)	0.095 (5)	0.007 (3)	−0.035 (4)	0.015 (3)
C5	0.085 (4)	0.073 (3)	0.059 (3)	0.001 (3)	−0.017 (3)	0.018 (2)
C6	0.083 (3)	0.088 (4)	0.037 (2)	−0.004 (3)	0.014 (2)	0.003 (2)
C7	0.066 (3)	0.117 (5)	0.051 (3)	−0.017 (3)	0.015 (2)	−0.014 (3)
C8	0.062 (3)	0.089 (4)	0.064 (3)	−0.005 (3)	0.012 (2)	−0.008 (3)
C9	0.054 (3)	0.082 (3)	0.075 (3)	0.003 (3)	−0.024 (2)	0.008 (3)
C10	0.083 (4)	0.092 (4)	0.055 (3)	0.003 (3)	−0.032 (3)	0.001 (3)
C11	0.111 (5)	0.086 (4)	0.047 (3)	−0.019 (4)	−0.007 (3)	0.014 (3)
C12	0.086 (3)	0.044 (2)	0.053 (2)	−0.009 (2)	−0.025 (3)	0.0027 (18)
C13	0.057 (2)	0.0449 (19)	0.046 (2)	−0.0006 (18)	−0.0149 (18)	0.0022 (17)
C14	0.055 (2)	0.0375 (18)	0.0337 (17)	0.0030 (17)	−0.0042 (16)	0.0017 (15)
C15	0.075 (3)	0.050 (2)	0.038 (2)	0.008 (2)	0.002 (2)	0.0029 (18)
C16	0.067 (3)	0.075 (3)	0.054 (3)	0.004 (3)	0.012 (2)	0.005 (2)
C17	0.065 (3)	0.077 (3)	0.067 (3)	−0.011 (3)	0.007 (2)	0.017 (3)
C18	0.083 (3)	0.059 (3)	0.066 (3)	−0.022 (3)	−0.007 (3)	−0.002 (2)
C19	0.075 (3)	0.052 (2)	0.073 (3)	−0.007 (2)	−0.004 (3)	−0.012 (2)
C20	0.068 (3)	0.044 (2)	0.052 (2)	0.001 (2)	0.001 (2)	−0.0080 (18)
C21	0.064 (3)	0.067 (3)	0.103 (4)	−0.006 (3)	0.016 (3)	−0.032 (3)
C22	0.056 (2)	0.068 (3)	0.086 (3)	−0.005 (3)	−0.003 (3)	−0.005 (3)
Cl	0.0732 (7)	0.0494 (6)	0.0825 (8)	−0.0190 (5)	0.0227 (7)	−0.0145 (6)

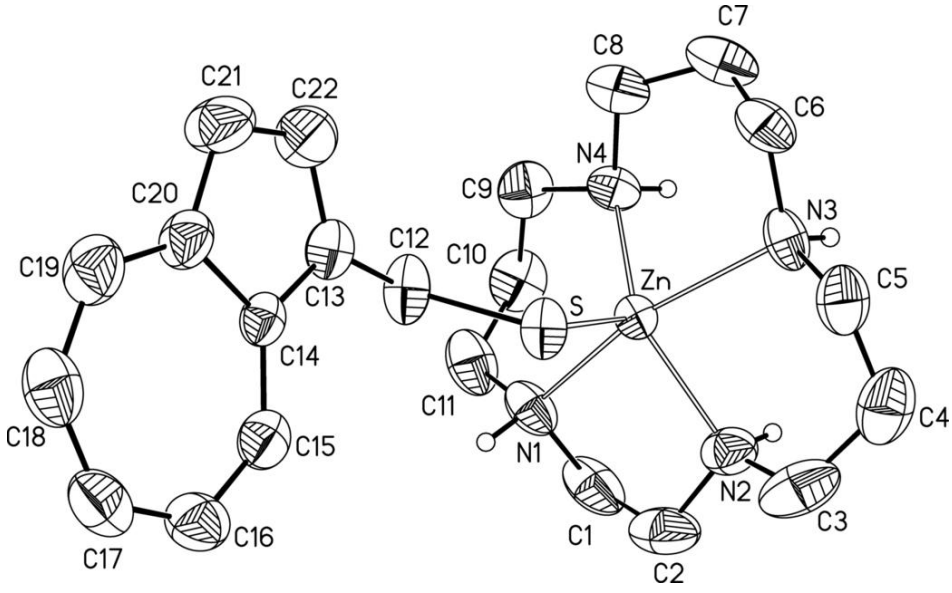
Geometric parameters (Å, °)

Zn—N4	2.134 (4)	C9—C10	1.530 (8)
Zn—N2	2.139 (4)	C9—H9A	0.9900
Zn—N3	2.235 (3)	C9—H9B	0.9900
Zn—N1	2.272 (4)	C10—C11	1.476 (9)
Zn—S	2.2804 (10)	C10—H10A	0.9900
S—C12	1.843 (4)	C10—H10B	0.9900
N1—C11	1.431 (8)	C11—H11A	0.9900
N1—C1	1.474 (7)	C11—H11B	0.9900
N1—H1C	0.9300	C12—C13	1.496 (6)
N2—C2	1.448 (8)	C12—H12A	0.9900
N2—C3	1.491 (8)	C12—H12B	0.9900
N2—H2C	0.9300	C13—C22	1.379 (7)
N3—C5	1.454 (7)	C13—C14	1.393 (6)
N3—C6	1.494 (7)	C14—C15	1.380 (6)
N3—H3C	0.9300	C14—C20	1.500 (6)
N4—C8	1.472 (6)	C15—C16	1.388 (7)
N4—C9	1.496 (6)	C15—H15A	0.9500
N4—H4C	0.9300	C16—C17	1.400 (8)
C1—C2	1.512 (10)	C16—H16A	0.9500
C1—H1A	0.9900	C17—C18	1.390 (8)
C1—H1B	0.9900	C17—H17A	0.9500
C2—H2A	0.9900	C18—C19	1.360 (8)
C2—H2B	0.9900	C18—H18A	0.9500
C3—C4	1.527 (10)	C19—C20	1.374 (7)
C3—H3A	0.9900	C19—H19A	0.9500

C3—H3B	0.9900	C20—C21	1.401 (8)
C4—C5	1.488 (10)	C21—C22	1.392 (7)
C4—H4A	0.9900	C21—H21A	0.9500
C4—H4B	0.9900	C22—H22A	0.9500
C5—H5A	0.9900	Cl—O43	1.31 (2)
C5—H5B	0.9900	Cl—O44	1.345 (12)
C6—C7	1.529 (8)	Cl—O41	1.373 (11)
C6—H6A	0.9900	Cl—O41A	1.39 (2)
C6—H6B	0.9900	Cl—O42	1.432 (12)
C7—C8	1.469 (8)	Cl—O42A	1.461 (11)
C7—H7A	0.9900	Cl—O44A	1.496 (15)
C7—H7B	0.9900	Cl—O43A	1.640 (16)
C8—H8A	0.9900	O43—O44	1.48 (3)
C8—H8B	0.9900		
N4—Zn—N2	130.42 (16)	N4—C9—H9A	109.0
N4—Zn—N3	86.95 (15)	C10—C9—H9A	109.0
N2—Zn—N3	85.81 (17)	N4—C9—H9B	109.0
N4—Zn—N1	91.17 (15)	C10—C9—H9B	109.0
N2—Zn—N1	80.05 (17)	H9A—C9—H9B	107.8
N3—Zn—N1	159.70 (15)	C11—C10—C9	113.0 (5)
N4—Zn—S	118.88 (11)	C11—C10—H10A	109.0
N2—Zn—S	110.70 (12)	C9—C10—H10A	109.0
N3—Zn—S	99.13 (10)	C11—C10—H10B	109.0
N1—Zn—S	99.46 (11)	C9—C10—H10B	109.0
C12—S—Zn	101.15 (14)	H10A—C10—H10B	107.8
C11—N1—C1	112.6 (5)	N1—C11—C10	113.3 (4)
C11—N1—Zn	122.7 (3)	N1—C11—H11A	108.9
C1—N1—Zn	105.3 (3)	C10—C11—H11A	108.9
C11—N1—H1C	104.9	N1—C11—H11B	108.9
C1—N1—H1C	104.9	C10—C11—H11B	108.9
Zn—N1—H1C	104.9	H11A—C11—H11B	107.7
C2—N2—C3	112.8 (5)	C13—C12—S	111.1 (3)
C2—N2—Zn	109.4 (4)	C13—C12—H12A	109.4
C3—N2—Zn	114.3 (4)	S—C12—H12A	109.4
C2—N2—H2C	106.6	C13—C12—H12B	109.4
C3—N2—H2C	106.6	S—C12—H12B	109.4
Zn—N2—H2C	106.6	H12A—C12—H12B	108.0
C5—N3—C6	109.5 (4)	C22—C13—C14	108.2 (4)
C5—N3—Zn	110.9 (3)	C22—C13—C12	126.1 (4)
C6—N3—Zn	110.2 (3)	C14—C13—C12	125.7 (4)
C5—N3—H3C	108.7	C15—C14—C13	127.1 (4)
C6—N3—H3C	108.7	C15—C14—C20	125.4 (4)
Zn—N3—H3C	108.7	C13—C14—C20	107.4 (4)
C8—N4—C9	108.4 (4)	C14—C15—C16	129.4 (4)
C8—N4—Zn	112.4 (3)	C14—C15—H15A	115.3
C9—N4—Zn	117.4 (3)	C16—C15—H15A	115.3
C8—N4—H4C	105.9	C15—C16—C17	129.3 (5)
C9—N4—H4C	105.9	C15—C16—H16A	115.3
Zn—N4—H4C	105.9	C17—C16—H16A	115.3

N1—C1—C2	109.7 (4)	C18—C17—C16	128.6 (5)
N1—C1—H1A	109.7	C18—C17—H17A	115.7
C2—C1—H1A	109.7	C16—C17—H17A	115.7
N1—C1—H1B	109.7	C19—C18—C17	129.3 (5)
C2—C1—H1B	109.7	C19—C18—H18A	115.4
H1A—C1—H1B	108.2	C17—C18—H18A	115.4
N2—C2—C1	110.2 (5)	C18—C19—C20	129.2 (5)
N2—C2—H2A	109.6	C18—C19—H19A	115.4
C1—C2—H2A	109.6	C20—C19—H19A	115.4
N2—C2—H2B	109.6	C19—C20—C21	126.5 (5)
C1—C2—H2B	109.6	C19—C20—C14	128.7 (5)
H2A—C2—H2B	108.1	C21—C20—C14	104.8 (4)
N2—C3—C4	114.8 (5)	C22—C21—C20	109.2 (5)
N2—C3—H3A	108.6	C22—C21—H21A	125.4
C4—C3—H3A	108.6	C20—C21—H21A	125.4
N2—C3—H3B	108.6	C13—C22—C21	110.4 (5)
C4—C3—H3B	108.6	C13—C22—H22A	124.8
H3A—C3—H3B	107.5	C21—C22—H22A	124.8
C5—C4—C3	116.0 (5)	O43—Cl—O44	68.0 (13)
C5—C4—H4A	108.3	O43—Cl—O41	124.5 (12)
C3—C4—H4A	108.3	O44—Cl—O41	115.5 (7)
C5—C4—H4B	108.3	O43—Cl—O41A	119.0 (15)
C3—C4—H4B	108.3	O44—Cl—O41A	133.9 (10)
H4A—C4—H4B	107.4	O41—Cl—O41A	19.9 (9)
N3—C5—C4	112.5 (5)	O43—Cl—O42	93.4 (11)
N3—C5—H5A	109.1	O44—Cl—O42	116.7 (7)
C4—C5—H5A	109.1	O41—Cl—O42	123.9 (8)
N3—C5—H5B	109.1	O41A—Cl—O42	108.6 (11)
C4—C5—H5B	109.1	O43—Cl—O42A	120.1 (11)
H5A—C5—H5B	107.8	O44—Cl—O42A	129.2 (7)
N3—C6—C7	112.6 (4)	O41—Cl—O42A	100.0 (8)
N3—C6—H6A	109.1	O41A—Cl—O42A	89.0 (11)
C7—C6—H6A	109.1	O42—Cl—O42A	27.3 (6)
N3—C6—H6B	109.1	O43—Cl—O44A	116.3 (14)
C7—C6—H6B	109.1	O44—Cl—O44A	48.9 (6)
H6A—C6—H6B	107.8	O41—Cl—O44A	93.2 (8)
C8—C7—C6	115.5 (5)	O41A—Cl—O44A	111.1 (11)
C8—C7—H7A	108.4	O42—Cl—O44A	105.8 (7)
C6—C7—H7A	108.4	O42A—Cl—O44A	96.5 (7)
C8—C7—H7B	108.4	O43—Cl—O43A	42.8 (11)
C6—C7—H7B	108.4	O44—Cl—O43A	106.4 (8)
H7A—C7—H7B	107.5	O41—Cl—O43A	91.3 (8)
C7—C8—N4	113.7 (5)	O41A—Cl—O43A	78.9 (11)
C7—C8—H8A	108.8	O42—Cl—O43A	92.7 (7)
N4—C8—H8A	108.8	O42A—Cl—O43A	107.9 (7)
C7—C8—H8B	108.8	O44A—Cl—O43A	154.0 (8)
N4—C8—H8B	108.8	Cl—O43—O44	57.3 (11)
H8A—C8—H8B	107.7	Cl—O44—O43	54.7 (10)
N4—C9—C10	113.1 (5)		

Fig. 1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