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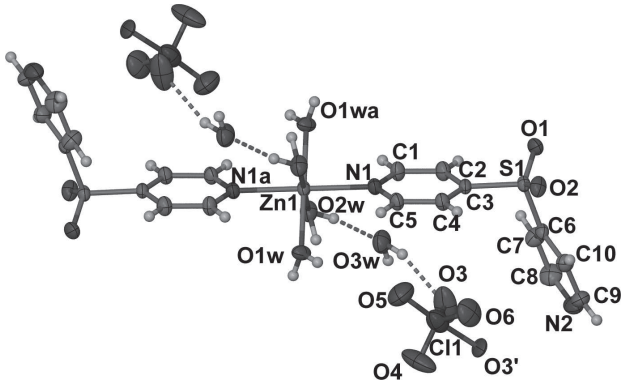
Crystal structure of *trans*-tetraaqua-bis(4,4′-sulfonyldipyridine-κ*N*)zinc(II) diperchlorate dihydrate, $C_{20}H_{28}Cl_2ZnN_4O_{18}S_2$



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Abstract

$C_{20}H_{28}Cl_2Zn_4O_{18}S_2$, monoclinic, $P2_1/c$ (no. 14), $a = 8.0835(16)$ Å, $b = 17.389(4)$ Å, $c = 11.576(2)$ Å, $\beta = 106.59(3)°$, $V = 1559.4(6)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0505$, $wR_{ref}(F^2) = 0.1511$, $T = 296$ K.

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The crystal structure is shown in the figure. Tables 1–3 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colorless, block, size 0.44×0.40×0.31 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	11.79 cm^{-1}
Diffractometer, scan mode:	Bruker Ape xII, ω scans
$2\theta_{max}$:	55.83°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	14967, 3719
$N(param)_{refined}$:	224
Programs:	SHELX [8], Diamond [9]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1A)	4*e*	1.4001	0.8713	0.1418	0.035
H(2A)	4*e*	1.3697	0.7400	0.1491	0.037
H(4A)	4*e*	1.5812	0.7226	−0.1248	0.034
H(5A)	4*e*	1.5932	0.8554	−0.1294	0.033
H(7A)	4*e*	1.1303	0.6358	0.0520	0.044
H(8A)	4*e*	0.8587	0.5995	−0.0617	0.053
H(9A)	4*e*	1.0463	0.4933	−0.2914	0.046
H(10A)	4*e*	1.3234	0.5331	−0.1925	0.039
H(1WA)	4*e*	1.7054	0.9812	0.2246	0.054
H(1WB)	4*e*	1.5675	1.0303	0.2370	0.054
H(2WB)	4*e*	1.1804	0.9624	0.0287	0.054
H(2WA)	4*e*	1.2106	0.9888	−0.0606	0.054
H(3WB)	4*e*	1.0114	0.8464	−0.0309	0.070
H(3WA)	4*e*	0.8900	0.8776	−0.0007	0.070

Source of material

All reagents and solvents were obtained from commercial sources and used without further purification. Di-4-pyridylsulfide was synthesized following the procedure reported [1], which (470 mg, 2.5 mmol) was disolved in glacial acetic acid (15 mL) and 30% w/w hydrogen peroxide (1.5 mL) at room temperature. After two weeks the resuted solution was treated with water (20 mL), leading to crystalline precipitate, which was filtered off and purified by chromatography over silica-gel by using ethyl acetate/CH_2Cl_2(3:2) as eluent. 4,4′-Sulfonyldipyridine was obtained as white powdery product 209 mg (yield 38%). At room temperature, 4,4′-sulfonyldipyridine (22 mg, 0.1 mmol) and zinc(II) perchlorate hexahydrate (20 mg, 0.05 mmol) were dissolved in 4 mL acetonitrile with stirring. After 3 hours, the colorless clear solution was filtrated and left to slowly evaporate in air. Colorless block-shaped crystals of the title complex (yield 20.3 mg, 50% based on ligand) were deposited after two weeks.

Experimental details

All hydrogen atoms were introduced at calculated positions. One oxygen atom of the perchlorate anion is disordered.

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Table 3: Atomic displacement parameters (Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn(1)	2*b*	1.5	1.0	0.0	0.0244(3)	0.0177(3)	0.0286(3)	0.0013(2)	0.0071(2)	0.0010(2)
S(1)	4*e*	1.46522(9)	0.61589(4)	0.02273(6)	0.0220(4)	0.0178(3)	0.0295(4)	−0.0002(2)	0.0075(3)	0.0022(2)
O(1)	4*e*	1.5807(3)	0.5836(1)	−0.0377(2)	0.026(1)	0.027(1)	0.049(1)	0.0023(8)	0.0162(9)	−0.0032(9)
O(2)	4*e*	1.4858(3)	0.5991(1)	0.1476(2)	0.041(1)	0.027(1)	0.030(1)	−0.0040(9)	0.0050(9)	0.0077(8)
N(1)	4*e*	1.4980(3)	0.8757(1)	0.0052(2)	0.029(1)	0.021(1)	0.028(1)	0.0004(9)	0.008(1)	0.0017(8)
N(2)	4*e*	0.9277(4)	0.5428(2)	−0.1863(3)	0.029(1)	0.044(2)	0.045(2)	−0.007(1)	−0.000(1)	0.006(1)
C(1)	4*e*	1.4344(4)	0.8409(2)	0.0867(3)	0.038(2)	0.022(1)	0.033(2)	0.001(1)	0.016(1)	0.000(1)
C(2)	4*e*	1.4171(4)	0.7623(2)	0.0928(3)	0.036(2)	0.025(1)	0.035(2)	−0.001(1)	0.016(1)	0.002(1)
C(3)	4*e*	1.4728(3)	0.7179(2)	0.0124(2)	0.024(1)	0.016(1)	0.027(1)	−0.0004(9)	0.005(1)	0.0008(9)
C(4)	4*e*	1.5416(4)	0.7520(2)	−0.0710(3)	0.035(2)	0.022(1)	0.028(1)	0.002(1)	0.012(1)	0.002(1)
C(5)	4*e*	1.5497(4)	0.8317(2)	−0.0722(3)	0.035(2)	0.021(1)	0.028(1)	−0.000(1)	0.012(1)	0.003(1)
C(6)	4*e*	1.2537(4)	0.5895(2)	−0.0600(2)	0.024(1)	0.020(1)	0.031(1)	−0.002(1)	0.008(1)	0.001(1)
C(7)	4*e*	1.1155(4)	0.6083(2)	−0.0191(3)	0.030(2)	0.042(2)	0.042(2)	−0.003(1)	0.014(1)	−0.008(1)
C(8)	4*e*	0.9538(4)	0.5850(2)	−0.0867(3)	0.027(2)	0.052(2)	0.056(2)	−0.004(2)	0.017(2)	−0.000(2)
C(9)	4*e*	1.0640(5)	0.5236(2)	−0.2227(3)	0.040(2)	0.036(2)	0.033(2)	−0.005(1)	−0.000(1)	−0.004(1)
C(10)	4*e*	1.2309(4)	0.5463(2)	−0.1637(3)	0.033(2)	0.031(1)	0.033(2)	0.002(1)	0.009(1)	−0.002(1)
O(1W)	4*e*	1.6017(3)	0.9984(1)	0.1873(2)	0.030(1)	0.036(1)	0.026(1)	0.0089(8)	0.0021(9)	−0.0035(8)
O(2W)	4*e*	1.2483(3)	1.0031(1)	0.0258(2)	0.028(1)	0.031(1)	0.050(1)	−0.0009(8)	0.016(1)	0.0010(9)
O(3W)	4*e*	1.0037(3)	0.8847(2)	0.0184(2)	0.044(2)	0.033(1)	0.062(2)	0.003(1)	0.016(1)	−0.003(1)
Cl(1)	4*e*	0.9803(2)	0.77683(6)	−0.26054(9)	0.0698(7)	0.0510(6)	0.0418(5)	0.0144(5)	0.0203(5)	0.0054(4)
O(5)[a]	4*e*	1.114(1)	0.8373(5)	−0.2188(7)	0.127(6)	0.137(6)	0.145(6)	−0.035(5)	0.003(5)	−0.030(5)
O(3')[b]	4*e*	0.856(3)	0.707(1)	−0.305(2)	0.12(2)	0.06(1)	0.14(2)	−0.07(1)	−0.05(2)	0.03(1)
O(4)	4*e*	0.8858(6)	0.8099(4)	−0.3625(5)	0.075(3)	0.243(7)	0.142(4)	0.023(4)	0.019(3)	0.113(4)
O(3)	4*e*	0.906(1)	0.7697(3)	−0.1696(5)	0.269(8)	0.107(4)	0.152(5)	0.019(4)	0.165(5)	0.020(3)
O(6)	4*e*	1.0863(8)	0.7168(3)	−0.2764(5)	0.145(5)	0.109(4)	0.146(5)	0.050(3)	0.063(4)	−0.015(3)

[a]Occupancy factor: 0.8; [b]Occupancy factor: 0.2.

Discussion

Coordination chemistry of di-4-pyridylsulfide and its positional isomers have been widely explored in the past decades [2–4]. However, only silver(I) complexes with 4-(pyridin-4-ylsulfinyl)pyridine a ligand bearing an angular-SO-moiety derived from di-4-pyridylsulfide were reported [5]. Herein, we report a zinc(II) complex with a ligand with an angular-SO_2-moiety derived from di-4-pyridylsulfide. In the title complex the Zn^{2+} is located on an inversion center with a slightly distorted N_2O_4 octahedral coordination sphere comprising N atoms from two monodentate *trans*-related organic ligands and four aqua ligands (see the figure). The two perchlorate anions are linked to the O2w of the mononuclear complex molecule through water O—H···O hydrogen bonding interactions (O3w···O3 2.895(2) Å, O3w···O2w 2.840(2) Å) (shown in the figure). The Zn1—N1 bond length is 2.162(3) Å. The ligand adopts an angular shape with the C3—S1—C6 angle of 105.65(12)°, which is comparable to that value of 104.05(8)° in a related Ag(I) complex [7].

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