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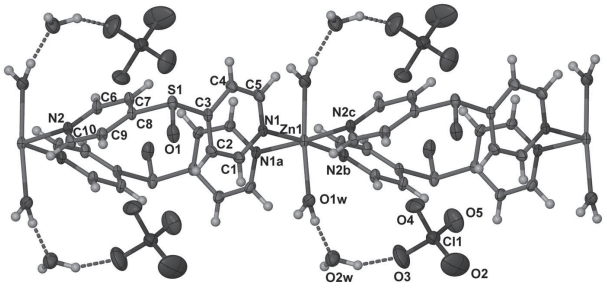
Crystal structure of poly[diaquabis(μ_2-4,4′-sulfinyldipyridine-κ^2*N*,*N*′)zinc(II)] diperchlorate dihydrate, $C_{20}H_{24}N_4O_{14}S_2Cl_2Zn$



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Abstract

$C_{20}H_{24}N_4O_{14}S_2Cl_2Zn$, monoclinic, *C*2/*c* (no.15), $a = 20.4949(9)$ Å, $b = 9.9752(3)$ Å, $c = 16.8927(6)$ Å, $\beta = 124.945(4)°$, $V = 2830.9(2)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0406$, $wR_{ref}(F^2) = 0.1135$, $T = 296$ K.

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Tables 1–3 contain details of the methods used and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

All reagents and solvents from commercial sources were used without further purification. 4-(Pyridin-4-ylsulfane)pyridine was purchased from J&K Chemical and used without further purification. 4-(Pyridin-4-ylsulfinyl)pyridine was synthesized according to a procedure in literature [1]. 3-Chlorobenzoperoxoic acid (72%, 500 mg, 2.1 mmol) dissolved in 20 mL of CH_2Cl_2 was added to a 10 mL CH_2Cl_2 containing 4-(pyridin-4-ylsulfane)pyridine (376 mg, 2 mmol) pre-cooled to 0°C. After stirring for 2 h at 0°C, the solution was treated with 30 mL saturated $Na_2S_2O_3$ solution, saturated $NaHCO_3$ solution (20 mL), and brine (15 mL) and dried over $MgSO_4$. The combined organic extract was concentrated to give a light-yellow solid, which was purified by column chromatography on silica gel using ethyl acetate/CH_2Cl_2 (1:1) as eluent to give 4-(pyridin-4-ylsulfinyl)pyridine as a white powder (228 mg). Yield: 56%. 4-(Pyridin-4-ylsulfinyl)pyridine (21 mg, 0.1 mmol) and $Zn(ClO_4)_2{\cdot}6H_2O$ (37.2 mg, 0.1 mmol) were dissolved in 6 ml ethanol. The mixture was stirred at room temperature for 3 h. After filtering, the the clear solution was left to stand in air. Colorless crystals (20.46 mg, 55% yield) of the title compound were obtained after two weeks.

Table 1: Data collection and handling.

Crystal:	Colorless, Block, size 0.38×0.40×0.55 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	12.80 cm^{-1}
Diffractometer, scan mode:	Bruker APEXII , ω scan
$2\theta_{max}$:	55.78°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	20101, 3369
$N(param)_{refined}$:	232
Programs:	SHELX [6], PLATON [7], Diamond [8]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1WA)	8*f*	−0.1077	0.7810	0.0452	0.052
H(1WB)	8*f*	−0.1478	0.8496	0.0707	0.052
H(1A)	8*f*	−0.0400	0.5775	0.1091	0.054
H(2A)	8*f*	0.0182	0.4054	0.0805	0.056
H(4A)	8*f*	0.2295	0.5249	0.3110	0.050
H(5A)	8*f*	0.1656	0.7000	0.3289	0.050
H(6A)	8*f*	0.0888	0.0756	0.3410	0.047
H(7A)	8*f*	0.1496	0.2519	0.3200	0.046
H(9A)	8*f*	0.1083	0.0652	0.0847	0.046
H(10A)	8*f*	0.0510	−0.1080	0.1147	0.046
H(2WB)	8*f*	−0.2548	1.0079	0.0048	0.079
H(2WA)	8*f*	−0.2803	0.8984	0.0377	0.079

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Table 3: Fractional coordinates and atomic displacement parameters (Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn(1)	4*e*	0	0.81418(4)	0.25	0.0445(3)	0.0227(2)	0.0425(3)	0.0	0.0300(2)	0.0
S(1)	8*f*	0.18083(5)	0.31300(7)	0.17836(6)	0.0519(5)	0.0284(3)	0.0584(5)	−0.0019(3)	0.0426(4)	−0.0038(3)
O(1)	8*f*	0.1494(2)	0.3059(2)	0.0745(2)	0.092(2)	0.043(1)	0.065(2)	−0.008(1)	0.062(2)	−0.008(1)
O(1W)	8*f*	−0.0971(1)	0.8245(2)	0.0972(2)	0.051(1)	0.041(1)	0.039(1)	0.0050(9)	0.026(1)	−0.0039(9)
N(1)	8*f*	0.0570(1)	0.6565(2)	0.2213(2)	0.040(1)	0.025(1)	0.041(1)	−0.0019(9)	0.024(1)	−0.0029(9)
N(2)	8*f*	0.0633(2)	−0.0330(2)	0.2297(2)	0.047(1)	0.026(1)	0.038(1)	−0.003(1)	0.028(1)	−0.0018(9)
C(1)	8*f*	0.0150(2)	0.5678(3)	0.1494(2)	0.037(2)	0.036(2)	0.049(2)	0.002(1)	0.017(1)	−0.010(1)
C(2)	8*f*	0.0491(2)	0.4634(3)	0.1322(2)	0.047(2)	0.036(2)	0.046(2)	−0.003(1)	0.020(2)	−0.014(1)
C(3)	8*f*	0.1299(2)	0.4473(3)	0.1934(2)	0.045(2)	0.025(1)	0.041(2)	−0.002(1)	0.031(1)	−0.001(1)
C(4)	8*f*	0.1747(2)	0.5350(3)	0.2686(2)	0.037(2)	0.038(2)	0.049(2)	−0.001(1)	0.023(1)	−0.009(1)
C(5)	8*f*	0.1355(2)	0.6391(3)	0.2790(2)	0.042(2)	0.037(2)	0.044(2)	−0.005(1)	0.023(2)	−0.014(1)
C(6)	8*f*	0.0929(2)	0.0737(3)	0.2889(2)	0.058(2)	0.029(1)	0.039(2)	−0.003(1)	0.032(2)	−0.001(1)
C(7)	8*f*	0.1289(2)	0.1806(3)	0.2768(2)	0.054(2)	0.027(1)	0.041(2)	−0.005(1)	0.030(2)	−0.004(1)
C(8)	8*f*	0.1335(2)	0.1785(2)	0.1984(2)	0.040(2)	0.024(1)	0.044(2)	0.001(1)	0.029(1)	0.001(1)
C(9)	8*f*	0.1047(2)	0.0692(3)	0.1371(2)	0.051(2)	0.032(1)	0.045(2)	0.002(1)	0.036(2)	−0.002(1)
C(10)	8*f*	0.0703(2)	−0.0341(3)	0.1556(2)	0.052(2)	0.029(1)	0.044(2)	−0.005(1)	0.033(2)	−0.008(1)
O(2W)	8*f*	−0.2451(2)	0.9202(3)	0.0251(2)	0.059(2)	0.058(2)	0.083(2)	0.005(1)	0.042(2)	0.004(1)
Cl(1)	8*f*	−0.14363(5)	1.25433(9)	−0.02419(6)	0.0508(5)	0.0551(5)	0.0447(4)	−0.0027(4)	0.0284(4)	−0.0004(4)
O(2)	8*f*	−0.1967(8)	1.354(1)	−0.0995(9)	0.093(8)	0.121(9)	0.098(7)	0.009(6)	0.054(6)	0.034(6)
O(3)	8*f*	−0.188(2)	1.146(2)	−0.054(2)	0.23(2)	0.077(9)	0.24(2)	−0.08(1)	0.18(2)	−0.10(1)
O(4)	8*f*	−0.0703(6)	1.1818(9)	0.0322(6)	0.047(4)	0.084(5)	0.064(5)	0.032(4)	0.024(4)	0.017(4)
O(5)	8*f*	−0.123(1)	1.330(2)	0.060(1)	0.14(1)	0.114(9)	0.068(6)	−0.072(8)	0.084(8)	−0.036(5)
O(2')	8*f*	−0.1633(8)	1.304(1)	−0.1098(6)	0.16(1)	0.20(1)	0.100(5)	0.046(8)	0.100(6)	0.080(6)
O(3')	8*f*	−0.1952(7)	1.149(1)	−0.0373(9)	0.098(6)	0.093(8)	0.109(6)	−0.039(5)	0.054(6)	0.018(6)
O(4')	8*f*	−0.0735(6)	1.239(2)	−0.019(1)	0.078(5)	0.20(1)	0.21(1)	−0.057(7)	0.099(8)	−0.15(1)
O(5')	8*f*	−0.1438(8)	1.341(1)	0.037(1)	0.121(7)	0.105(6)	0.124(9)	0.038(6)	0.065(7)	−0.040(5)

Experimental details

The perchlorate anion is disordered at two positions, which is treated as two parts with occupancy factors of 0.42:0.58. The disorder is not shown in the figure for clarity. The U_{iso} values of the hydrogen atoms of methyl groups were set to $1.5U_{eq}$(C) and the U_{iso} values of all other hydrogen atons were set to $1.2U_{eq}$(C, N).

Discussion

Sulfoxides have been widely studied due to their biological activity [2], their behavior as intermediates in homogeneous catalytic processes [3], their sterochemistry and their role as versatile precursors in inorganic synthesis [4]. The Zn(II) center takes a N_4O_2-octahedral coordination geometry with four pyridyl N and two aqua ligands (O1w). The Zn-N bond lengths lie within 2.151(2)-2.173(2) Å. Each 4-(pyridin-4-ylsulfinyl)pyridine functions as angular-shaped linker to bridge adjacent Zn(II) in a μ_2-bridging mode. The S1 = O1 bond length of 1.485(3) Å is in good agreement with the average value of 1.49 Å in analogous sulfoxide complexes [5]. An infinite double-bridged chain is furnished with the Zn(II) ions and the bridging 4-(pyridin-4-ylsulfinyl)pyridine ligands (Figure). The O2w water molecule links the coordinated O1w and the perchlorate anion through H-bonding interactions.

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