Hong-Ru Fu*, Kai-Lu Wang and Xiao-Xiao Zhao

Crystal structure of poly[bis(1-methyl-[4,4'-bipyridin]-1-ium- κN)-tetrakis(μ_3 -sulfato- $\kappa^3 O:O':O''$)trizinc(II)], $C_{22}H_{22}Zn_3N_4O_{16}S_4$

Table 1: Data collection and handling.

Crystal:	Orange block
Size:	$0.17 \times 0.14 \times 0.12$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	2.74 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω -scans
$\theta_{\max}$, completeness:	25° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	11771, 5267, 0.026
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4664
$N(\text{param})_{\text{refined}}$:	444
Programs:	CrysAlis ^{PRO} [1], SHELX [2], OLEX2 [3]

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Abstract

$C_{22}H_{22}Zn_3N_4O_{16}S_4$, monoclinic, $P2_1/n$ (no. 14), $a = 9.2909(2)$ Å, $b = 16.8888(4)$ Å, $c = 19.3547(6)$ Å, $\beta = 98.924(3)^\circ$, $V = 3000.22(14)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0401$, $wR_{\text{ref}}(F^2) = 0.0942$, $T = 293(2)$ K.

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A part of the title crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

A mixture of 1,1-bis(4-carboxyphenyl)-(4,4-bipyridinium) dichloride (24 mg, 0.05 mmol), 1-(4-methyl)-4,4-bipyridinium chloride (17 mg, 0.10 mmol), $Zn(SO_4) \cdot 2H_2O$ (56 mg,

0.2 mmol) and *N,N*-dimethylformamide (5 mL) were added to water (0.5 mL) in a 25 mL Teflon-lined autoclave. The mixture was heated at 353 K for 2 days and then slowly cooled to room temperature. Colorless block crystals of the title compound were obtained.

Experimental details

The methyl groups were refined using rigid groups allowed to rotate about the C–C bond (AFIX 137 option of the SHELX program). The U_{iso} values of the hydrogen atoms of methyl groups and oxygen were set to $1.5 U_{\text{eq}}(\text{C}, \text{O})$.

Discussion

Coordination polymers (CPs) have attracted considerable attention because of their interesting structures and potential application as functional materials [4–6]. Structural motifs include one-dimensional chains and ladders, two-dimensional grids, three-dimensional networks and interpenetrated structures [7–9]. Viologens (1,1-disubstituted-4,4-bipyridinium) are well known for their photoelectrochromism, electron-accepting ability and redox activity [10, 11]. A series of ligands with varied coordination sites have been designed and synthesized based on 4,4-dipyridyl over the past few years [12].

The asymmetric unit of the title structure consists of three Zn(II) ions, four sulfate ions, two 1-(4-methyl)-4,4-bipyridinium cations. All sulfate ions adopt one kind of coordination mode: three oxygen atoms bridge three Zn(II) ions, and four sulfate ions connect three Zn(II) ions to form the

*Corresponding author: Hong-Ru Fu, College of Chemistry and Chemical Engineering, Henan Key Laboratory of Function-Oriented Porous Materials, Luoyang Normal University, Luoyang, Henan 471934, P.R. China, e-mail: hongrufu2015@163.com

Kai-Lu Wang and Xiao-Xiao Zhao: College of Chemistry and Chemical Engineering, Henan Key Laboratory of Function-Oriented Porous Materials, Luoyang Normal University, Luoyang, Henan 471934, P.R. China

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
Zn1	0.50141(5)	0.20515(3)	0.73754(3)	0.02148(13)
Zn2	−0.09834(5)	0.30132(3)	0.72793(3)	0.02138(13)
Zn3	0.92816(5)	0.06720(3)	0.75027(3)	0.02313(14)
S1	0.77088(11)	0.16841(6)	0.84509(6)	0.0207(2)
S2	0.71728(11)	0.15664(7)	0.63104(6)	0.0239(2)
S3	0.59021(11)	0.38443(6)	0.75877(6)	0.0219(2)
S4	0.19224(11)	0.18012(7)	0.74929(7)	0.0285(3)
O15	0.7896(4)	0.2334(2)	0.64564(18)	0.0380(8)
O8	0.4881(3)	0.31928(18)	0.73479(18)	0.0317(8)
O7	0.7238(3)	0.37522(19)	0.72804(16)	0.0298(7)
O10	0.8018(4)	0.1827(2)	0.91952(17)	0.0382(8)
O12	0.8308(4)	0.0899(2)	0.83052(18)	0.0399(8)
O5	0.5168(3)	0.45709(19)	0.72917(18)	0.0325(7)
O16	0.8159(4)	0.0921(2)	0.66089(18)	0.0399(9)
O1	0.0815(3)	0.2316(2)	0.7157(2)	0.0399(9)
O11	0.8305(4)	0.2282(2)	0.8043(2)	0.0481(9)
O6	0.6173(4)	0.3883(2)	0.83411(18)	0.0428(9)
O9	0.6112(3)	0.1646(2)	0.82432(18)	0.0410(9)
O14	0.6798(3)	0.1441(2)	0.55701(17)	0.0398(9)
N1	0.0290(4)	0.3733(2)	0.80547(19)	0.0253(8)
O13	0.5836(4)	0.1538(2)	0.66307(19)	0.0438(9)
O4	0.3046(4)	0.1659(2)	0.7064(2)	0.0490(10)
O3	0.2625(4)	0.2136(2)	0.8168(2)	0.0525(10)
N3	−0.0276(4)	0.3805(2)	0.6494(2)	0.0265(8)
O2	0.1272(4)	0.1020(2)	0.7617(2)	0.0465(9)
N2	0.4390(4)	0.6607(2)	1.01417(19)	0.0284(9)
N4	0.4077(4)	0.6213(2)	0.4678(2)	0.0304(9)
C5	−0.0282(5)	0.4134(3)	0.8540(2)	0.0352(12)
H5	−0.1231	0.4019	0.8603	0.042*
C12	0.0384(5)	0.3510(3)	0.5980(2)	0.0307(11)
H12	0.0298	0.2971	0.5886	0.037*
C8	0.2724(5)	0.5515(3)	0.9302(2)	0.0260(10)
C1	0.1668(5)	0.3910(3)	0.7978(3)	0.0310(11)
H1	0.2096	0.3635	0.7647	0.037*
C14	0.1365(5)	0.4767(3)	0.5732(2)	0.0258(10)
C9	0.4229(5)	0.5567(3)	0.9320(3)	0.0333(11)
H9	0.4693	0.5228	0.9047	0.040*
C7	0.2099(5)	0.6047(3)	0.9709(3)	0.0343(11)
H7	0.1095	0.6042	0.9700	0.041*
C3	0.1876(5)	0.4898(3)	0.8873(2)	0.0251(10)
C17	0.2307(5)	0.5272(3)	0.5356(2)	0.0265(10)
C4	0.0463(5)	0.4711(3)	0.8951(2)	0.0341(12)
H4	0.0015	0.4976	0.9282	0.041*
C16	−0.0178(5)	0.4580(3)	0.6601(3)	0.0311(11)
H16	−0.0684	0.4800	0.6933	0.037*
C22	0.5028(5)	0.6718(3)	0.4315(3)	0.0408(13)
H22A	0.4438	0.7035	0.3969	0.061*
H22B	0.5663	0.6389	0.4092	0.061*
H22C	0.5600	0.7058	0.4649	0.061*
C6	0.2940(5)	0.6586(3)	1.0127(3)	0.0336(11)
H6	0.2502	0.6936	1.0402	0.040*
C10	0.5027(5)	0.6118(3)	0.9739(2)	0.0331(11)
H10	0.6028	0.6151	0.9742	0.040*

Table 2 (continued)

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
C15	0.0635(5)	0.5078(3)	0.6248(3)	0.0314(11)
H15	0.0694	0.5616	0.6353	0.038*
C11	0.5302(6)	0.7165(3)	1.0612(3)	0.0386(12)
H11A	0.4827	0.7671	1.0598	0.058*
H11B	0.6232	0.7223	1.0461	0.058*
H11C	0.5436	0.6964	1.1081	0.058*
C13	0.1178(5)	0.3963(3)	0.5587(2)	0.0300(10)
H13	0.1589	0.3735	0.5227	0.036*
C2	0.2464(5)	0.4481(3)	0.8371(3)	0.0328(11)
H2	0.3410	0.4588	0.8297	0.039*
C21	0.2787(5)	0.6008(3)	0.5621(3)	0.0371(12)
H21	0.2510	0.6192	0.6034	0.045*
C18	0.2761(5)	0.5037(3)	0.4740(2)	0.0331(11)
H18	0.2470	0.4547	0.4547	0.040*
C20	0.3669(5)	0.6464(3)	0.5274(3)	0.0386(12)
H20	0.3987	0.6954	0.5457	0.046*
C19	0.3634(5)	0.5516(3)	0.4410(3)	0.0349(11)
H19	0.3918	0.5350	0.3993	0.042*

secondary building units, then, the secondary building units connect each other to form a two dimensional layer. Among three zinc ions, Zn2 ions are coordinated to two nitrogen atoms belonging to two 4-mbipy ligands, thus, 4-mbipy is a terminal ligand. The Zn–N bond lengths are in the range of 2.140(4)–2.200(4) Å, and the Zn–O bond length is 1.921(4)–2.110(4) Å.

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