Gaoxiang Meng*, Zhou Li and Yongming Yang

A new polymorph of tetrakis(dimethylammonium) catena-poly[tetrakis(μ_2 -sulfato- $\kappa^2 O:O'$)dizinc(II)], $\text{Zn}_2\text{C}_8\text{H}_{32}\text{N}_4\text{O}_{16}\text{S}_4$

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Abstract

$\text{Zn}_2\text{C}_8\text{H}_{32}\text{N}_4\text{O}_{16}\text{S}_4$, triclinic, $P\bar{1}$ (no. 2), $a = 9.0313(9)$ Å, $b = 9.6075(14)$ Å, $c = 15.3044(15)$ Å, $\alpha = 89.933(2)^\circ$, $\beta = 78.579(1)^\circ$, $\gamma = 68.878(1)^\circ$, $V = 1210.6(2)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0323$, $wR_{\text{ref}}(F^2) = 0.1043$, $T = 100(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

*Corresponding author: Gaoxiang Meng, School of Advanced Materials and Mechatronic Engineering, Hubei Minzu University, Enshi, 445000, Hubei, PR China, E-mail: gaoxiang_meng@126.com
Zhou Li and Yongming Yang, School of Advanced Materials and Mechatronic Engineering, Hubei Minzu University, Enshi, 445000, Hubei, PR China

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.20 × 0.08 × 0.06 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	2.41 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	32.2°, 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	13782, 7660, 0.028
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 6626
$N(\text{param})_{\text{refined}}$:	339
Programs:	Bruker [1], SHELX [2, 3], Diamond [4], Olex2 [5]

Source of material

$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.297 g, 1.0 mmol), 3-cyanopyridine (0.104 g, 1.0 mmol), sodium azide (0.066 g, 1.0 mmol) and deoxidized DMF (10.0 mL) were sealed in a 25.0 mL polytetrafluoroethylene reactor. The mixed solution was stirred at room temperature for 30 min and then placed in an oven at 120 °C for three days. After slow cooling to room temperature at a rate of 5 °C/min, we have unexpectedly obtained colorless block-shaped crystals of compound (I), which were very easily moisturized in air within several minutes.

Experimental details

Hydrogen atoms bonded to methyl carbon atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms with C–H = 0.98 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C (methyl)})$. Hydrogen atoms bonded to nitrogen atoms were initially found from the difference maps and refined with the restraint of N–H = 0.86(1) Å by using the command DFIX and their thermal factors being set 1.2 times of the parent atoms.

Comment

In recent years, the design and synthesis of ion-conductive crystalline materials has become increasingly more

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.77707 (3)	0.22177 (2)	0.26211 (2)	0.00958 (6)
Zn2	0.26927 (3)	0.28270 (2)	0.23727 (2)	0.00957 (6)
S1	0.96162 (6)	0.31733 (5)	0.38046 (3)	0.00880 (9)
S2	0.46388 (6)	0.47842 (5)	0.22888 (3)	0.01034 (9)
S3	0.57211 (6)	0.03252 (5)	0.26918 (3)	0.00973 (9)
S4	0.09154 (6)	0.18167 (5)	0.12167 (3)	0.00919 (9)
O1	0.88008 (18)	0.21093 (16)	0.36486 (9)	0.0123 (3)
O2	0.90468 (18)	0.44968 (16)	0.33146 (9)	0.0137 (3)
O3	1.14135 (17)	0.23509 (16)	0.34579 (9)	0.0116 (3)
O4	0.93404 (18)	0.35267 (16)	0.47632 (9)	0.0136 (3)
O5	0.58752 (18)	0.40675 (17)	0.28378 (10)	0.0172 (3)
O6	0.30936 (18)	0.45844 (17)	0.27339 (10)	0.0156 (3)
O7	0.4363 (2)	0.63724 (17)	0.23000 (11)	0.0193 (3)
O8	0.5180 (2)	0.40590 (17)	0.13866 (10)	0.0179 (3)
O9	0.73833 (18)	0.03969 (16)	0.24105 (11)	0.0170 (3)
O10	0.47624 (18)	0.11401 (17)	0.20302 (9)	0.0156 (3)
O11	0.49608 (19)	0.10674 (17)	0.35843 (10)	0.0166 (3)
O12	0.58686 (19)	−0.12316 (16)	0.26399 (10)	0.0168 (3)
O13	0.15541 (18)	0.30117 (16)	0.13965 (9)	0.0126 (3)
O14	0.13229 (18)	0.14370 (16)	0.02524 (9)	0.0131 (3)
O15	−0.08988 (18)	0.25040 (17)	0.15091 (9)	0.0141 (3)
O16	0.15670 (19)	0.05409 (16)	0.17241 (9)	0.0142 (3)
N1	0.8129 (2)	0.60289 (19)	0.18058 (11)	0.0131 (3)
H1A	0.834 (3)	0.5245 (19)	0.2089 (16)	0.016*
H1B	0.724 (2)	0.672 (2)	0.2080 (16)	0.016*
C1	0.9434 (3)	0.6605 (2)	0.18324 (15)	0.0194 (4)
H1C	1.0469	0.5895	0.1490	0.029*
H1D	0.9519	0.6729	0.2454	0.029*
H1E	0.9181	0.7574	0.1571	0.029*
C2	0.8016 (3)	0.5700 (2)	0.08817 (13)	0.0180 (4)
H2A	0.7883	0.6594	0.0550	0.027*
H2B	0.7080	0.5404	0.0898	0.027*
H2C	0.9011	0.4882	0.0586	0.027*
N2	0.2254 (2)	0.89922 (19)	0.32797 (11)	0.0123 (3)
H2D	0.310 (2)	0.837 (2)	0.2932 (15)	0.015*
H2E	0.208 (3)	0.9809 (18)	0.3018 (16)	0.015*
C3	0.2471 (3)	0.9055 (3)	0.42067 (14)	0.0232 (5)
H3A	0.1506	0.9818	0.4574	0.035*
H3B	0.3426	0.9310	0.4215	0.035*
H3C	0.2627	0.8078	0.4447	0.035*
C4	0.0879 (3)	0.8520 (2)	0.32192 (14)	0.0173 (4)
H4A	0.1101	0.7510	0.3419	0.026*
H4B	0.0750	0.8524	0.2598	0.026*
H4C	−0.0121	0.9217	0.3600	0.026*
N3	0.2760 (2)	0.3345 (2)	0.48768 (11)	0.0131 (3)
H3D	0.186 (2)	0.410 (2)	0.4961 (18)	0.016*
H3E	0.286 (3)	0.299 (3)	0.4347 (9)	0.016*
C5	0.4106 (3)	0.3872 (3)	0.48980 (15)	0.0200 (4)
H5A	0.3979	0.4305	0.5500	0.030*
H5B	0.4084	0.4634	0.4469	0.030*
H5C	0.5145	0.3027	0.4739	0.030*
C6	0.2677 (3)	0.2217 (2)	0.55241 (14)	0.0195 (4)
H6A	0.3657	0.1311	0.5361	0.029*
H6B	0.1718	0.1969	0.5515	0.029*
H6C	0.2602	0.2622	0.6126	0.029*

Table 2: (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N4	0.3217 (2)	0.8367 (2)	−0.01619 (11)	0.0158 (3)
H4D	0.259 (3)	0.9290 (14)	−0.0149 (18)	0.019*
H4E	0.336 (4)	0.806 (3)	−0.0708 (9)	0.019*
C7	0.2295 (3)	0.7568 (3)	0.03922 (14)	0.0206 (4)
H7A	0.2023	0.7960	0.1018	0.031*
H7B	0.2957	0.6497	0.0342	0.031*
H7C	0.1293	0.7716	0.0184	0.031*
C8	0.4745 (3)	0.8199 (3)	0.01206 (17)	0.0265 (5)
H8A	0.5433	0.7136	0.0077	0.040*
H8B	0.4494	0.8614	0.0740	0.040*
H8C	0.5319	0.8737	−0.0268	0.040*

important [6], among which ammonium-related organic cationic compounds were seldom observed because of their large volumes and shape anisotropies. The study of the characteristics of these compounds, such as their macroscopical crystallization conditions, microscopical molecular and/or atomic arrangements is a meaningful research avenue. As part of our continuing studies on metal-tetrazole compounds [7], we have unexpectedly obtained a new polymer compound as a potential ion-conductive material, $\{[\text{Zn}_2(\text{SO}_4)_4] \cdot (\text{C}_2\text{H}_8\text{N})_4\}_n$, namely catena-[tetrakis(dimethylammonium) tetrakis(μ_2 -sulfato)-di-zinc(II)], (I). Compound (I) is a new polymorph of an early reported compound (CSD Recode: USAKOQ). Herein, the crystal structure of (I) was reported in this paper.

The title compound crystallizes in the triclinic $P\bar{1}$ space group. Its asymmetric unit is composed of two Zn(II) cations, four sulfate anions and four dimethyl ammonium cations. All the component ions are crystallographically independent. The two Zn(II) cations are bridged by two sulfate anions and the other two sulfate anions similarly link the two metal centers with the adjacent symmetry-related Zn(II) ions (c.f. the Figure). All the four sulfate groups in (I) are in the μ_2 -bridging mode, resulting in the basic $[-(\text{SO}_4)-\text{Zn}(\text{SO}_4)_2\text{Zn}-(\text{SO}_4)-]^{4-}$ unit. Both Zn(II) cations are tetra-coordinated by four oxygen atoms from four different sulfate anions with the $\text{Zn} \cdots \text{O}$ bond lengths ranging from 1.9426(15) to 1.9802(14) Å; the bond lengths in USAKOQ span from 1.953(2) to 1.962(2) Å. USAKOQ was crystallized in the monoclinic $C2/m$ space group with only half of the component ions of (I) in its asymmetric unit. Their $\text{Zn} \cdots \text{Zn}$ distances separated by two sulfate groups in both polymorphs are also distinctively different from each other, 4.503(2)/4.632(2) Å in (I) and 4.513(2)/4.702(2) Å in USAKOQ [6]. The formation of polymorph (I) may be mainly ascribed to the crystallization condition such as the temperature [120 °C for (I) and 70 °C for USAKOQ].

In the crystal packing, Zn(II) cations are tetrahedrally coordinated by four different sulfate oxygen atoms in the μ_2 -bridging modes, forming a one-dimensional coordination polymer along the [100] axis. Adjacent [100] chain polymers are linked by extensive N–H...O hydrogen bonds, resulting in the final three-dimensional network.

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