Crystal structure of tetrakis(acetonitrile)zinc(II) sulfate, $\text{Zn}(\text{C}_2\text{H}_3\text{N})_4\text{SO}_4$

H.-L. Yang^I, F. Yang^{II} and H.-L. Zhu^{*,III}^I Xiangfan University, Department of Chemistry, Xiangfan, Hubei, 441000 P. R. China^{II} Wuhan University of Science and Engineering, Department of Chemistry, Wuhan, 430073 P. R. China^{III} Fuyang Normal College, Department of Chemistry, Fuyang, Anhui, 236041 P. R. China

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Abstract

$\text{C}_8\text{H}_{12}\text{N}_4\text{O}_4\text{SZn}$, orthorhombic, $Pna2_1$ (no. 33), $a = 24.25(1)$ Å, $b = 8.456(3)$ Å, $c = 20.743(8)$ Å, $V = 4253.9$ Å³, $Z = 12$, $R_{\text{gt}}(F) = 0.050$, $wR_{\text{ref}}(F^2) = 0.131$, $T = 298$ K.

Source of material

All reagents and solvents were used as purchased without further purification. C, H and N elemental analyses were performed on a Perkin-Elmer elemental analyzer.

An aqua-acetonitrile solution of $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ was poured into a Teflon vessel till 30 % of its volume was filled. Then the vessel was placed in a stainless steel tank to perform hydrothermal treatment. The crystallization reaction was performed at 160 °C under autogenous pressure for 24 h. After the autoclave was cooled and depressurized, colorless slab-shaped crystals were deposited at the bottom of the Teflon vessel. After filtering and washing with aqueous acetonitrile solution for three times, they were dried under CaCl_2 (yield 66 %). Elemental analysis: found – C, 29.38 %; H, 3.81 %; N, 17.12 %; calc. for $\text{C}_8\text{H}_{12}\text{N}_4\text{O}_4\text{SZn}$ – C, 29.50 %; H, 3.71 %; N, 17.20 %.

Discussion

The asymmetric unit of the title structure being isotypic to [1–4] consists of three mononuclear tetraacetonitrile cations and three sulfate anions. In each cation, the central zinc(II) atom is four-coordinated by nitrogen atoms from four acetonitrile ligands. The average Zn–N bond lengths are 1.999(8) Å for Zn1, 2.033(7) Å for Zn2, and 1.996(8) Å for Zn3, respectively. The angles around each metal vary from 106.2(3)° to 113.0(3)° for Zn1, from 105.4(2)° to 111.5(3)° for Zn2, or from 107.3(3)° to 111.9(3)° for

Zn3, indicating that the polyhedra around the metal centers are slightly distorted tetrahedra. The Flack x parameter of 0.10(2) confirms the absolute structure.

Table 1. Data collection and handling.

Crystal:	colorless slab, size 0.30 × 0.35 × 0.45 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	18.90 cm ^{−1}
Diffractometer, scan mode:	Siemens SMART CCD, ϕ/ω
$2\theta_{\text{max}}$:	50.06°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	20950, 7197
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3964
$N(\text{param})_{\text{refined}}$:	499
Programs:	SADABS [1], SHELXTL [2]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
H(2A)	4a	1.1463	1.0489	0.3707	0.122
H(2B)	4a	1.1327	1.1023	0.3001	0.122
H(2C)	4a	1.1610	0.9384	0.3125	0.122
H(4A)	4a	0.8866	1.0906	0.5409	0.103
H(4B)	4a	0.8632	0.9218	0.5560	0.103
H(4C)	4a	0.8317	1.0338	0.5084	0.103
H(6A)	4a	0.8553	1.1037	0.1871	0.136
H(6B)	4a	0.8485	0.9376	0.1544	0.136
H(6C)	4a	0.9017	1.0383	0.1418	0.136
H(8A)	4a	0.9713	0.2219	0.2994	0.099
H(8B)	4a	0.9209	0.2237	0.3467	0.099
H(8C)	4a	0.9811	0.2159	0.3741	0.099
H(10A)	4a	0.0416	−0.2953	0.4679	0.115
H(10B)	4a	0.0116	−0.2845	0.5347	0.115
H(10C)	4a	0.0762	−0.2888	0.5317	0.115
H(12A)	4a	0.1754	0.5418	0.6598	0.134
H(12B)	4a	0.1501	0.4163	0.7069	0.134
H(12C)	4a	0.1203	0.5788	0.6964	0.134
H(14A)	4a	−0.1282	0.6100	0.5083	0.122
H(14B)	4a	−0.1489	0.4672	0.5500	0.122
H(14C)	4a	−0.1530	0.4599	0.4747	0.122
H(16A)	4a	0.1470	0.6193	0.3550	0.129
H(16B)	4a	0.1169	0.5244	0.3005	0.129
H(16C)	4a	0.1707	0.4565	0.3318	0.129
H(18A)	4a	0.4900	0.2891	0.7032	0.110
H(18B)	4a	0.4901	0.1959	0.6378	0.110
H(18C)	4a	0.4832	0.1047	0.7031	0.110
H(20A)	4a	0.2221	0.2268	0.4513	0.108
H(20B)	4a	0.1667	0.2332	0.4884	0.108
H(20C)	4a	0.1967	0.0717	0.4802	0.108
H(22A)	4a	0.2777	0.8846	0.6308	0.096
H(22B)	4a	0.3256	0.8846	0.6816	0.096
H(22C)	4a	0.2640	0.8796	0.7047	0.096
H(24A)	4a	0.1898	0.3122	0.8726	0.126
H(24B)	4a	0.2251	0.1620	0.8886	0.126
H(24C)	4a	0.1689	0.1442	0.8520	0.126

* Correspondence author (e-mail: hailiang_zhu@fync.edu.cn)

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Zn(1)	4a	0.96036(4)	0.7985(2)	0.34889(4)	0.0605(7)	0.0633(8)	0.0540(8)	0.0037(6)	0.0008(5)	0.0032(9)
Zn(2)	4a	0.04329(4)	0.2871(1)	0.50597(5)	0.0609(7)	0.0596(7)	0.0632(8)	0.0011(6)	−0.0013(6)	−0.0004(9)
Zn(3)	4a	0.29149(4)	0.3044(1)	0.67127(6)	0.0589(5)	0.0673(6)	0.0591(6)	0.0000(5)	0.0009(5)	0.000(1)
N(1)	4a	1.0375(3)	0.8824(8)	0.3418(3)	0.061(4)	0.057(4)	0.048(4)	−0.003(4)	−0.002(3)	−0.004(4)
N(2)	4a	0.9232(3)	0.8855(8)	0.4274(3)	0.057(4)	0.060(5)	0.049(4)	−0.003(4)	−0.003(3)	0.002(4)
N(3)	4a	0.9191(3)	0.8822(8)	0.2713(3)	0.063(4)	0.058(5)	0.049(4)	0.011(4)	0.001(3)	0.006(4)
N(4)	4a	0.9595(3)	0.566(1)	0.3457(4)	0.063(5)	0.065(6)	0.054(5)	−0.001(4)	−0.006(3)	0.005(5)
N(5)	4a	0.0441(3)	0.0517(8)	0.5071(4)	0.070(5)	0.052(5)	0.064(5)	−0.005(4)	−0.013(4)	0.001(6)
N(6)	4a	0.0868(2)	0.3740(8)	0.5817(3)	0.051(4)	0.054(5)	0.054(4)	−0.003(3)	0.002(3)	0.009(4)
N(7)	4a	−0.0357(2)	0.3706(8)	0.5086(3)	0.049(4)	0.063(4)	0.055(4)	−0.008(3)	−0.001(4)	−0.008(4)
N(8)	4a	0.0816(3)	0.3754(8)	0.4247(3)	0.052(4)	0.060(5)	0.054(4)	0.005(4)	−0.004(3)	0.000(4)
N(9)	4a	0.3696(2)	0.2350(7)	0.6722(4)	0.041(3)	0.073(4)	0.064(4)	0.005(3)	−0.004(5)	−0.003(4)
N(10)	4a	0.2524(3)	0.2318(9)	0.5928(4)	0.059(5)	0.059(6)	0.060(5)	0.004(3)	−0.004(4)	−0.006(4)
N(11)	4a	0.2913(2)	0.5440(7)	0.6699(4)	0.056(3)	0.051(4)	0.051(3)	−0.002(4)	−0.005(4)	0.009(6)
N(12)	4a	0.2518(3)	0.2372(8)	0.7508(4)	0.064(5)	0.068(6)	0.051(4)	0.005(4)	0.013(4)	0.003(4)
O(1)	4a	0.9313(4)	0.715(1)	0.7311(4)	0.111(7)	0.27(1)	0.073(6)	0.002(7)	0.045(5)	0.031(7)
O(2)	4a	1.0127(2)	0.7089(9)	0.6752(5)	0.088(5)	0.184(8)	0.097(5)	0.022(5)	−0.007(6)	−0.019(7)
O(3)	4a	0.9547(4)	0.908(1)	0.6736(8)	0.23(1)	0.101(7)	0.36(2)	−0.003(7)	−0.07(2)	−0.03(1)
O(4)	4a	0.9320(4)	0.698(1)	0.6229(5)	0.107(7)	0.175(9)	0.124(7)	−0.011(6)	−0.019(6)	−0.047(7)
O(5)	4a	0.6824(5)	0.701(2)	0.7871(5)	0.17(1)	0.23(1)	0.131(9)	−0.080(9)	0.019(7)	−0.012(9)
O(6)	4a	0.6817(4)	0.718(1)	0.8943(4)	0.118(8)	0.178(9)	0.076(5)	−0.020(6)	0.004(5)	0.023(6)
O(7)	4a	0.7565(4)	0.751(2)	0.8340(4)	0.082(7)	0.39(2)	0.096(7)	0.006(8)	0.002(5)	−0.001(8)
O(8)	4a	0.6966(7)	0.908(2)	0.8316(8)	0.39(2)	0.15(1)	0.26(2)	−0.00(1)	0.08(2)	−0.00(1)
O(9)	4a	0.1755(3)	0.783(1)	0.5641(3)	0.074(5)	0.207(9)	0.056(4)	0.010(5)	0.024(4)	−0.038(5)
O(10)	4a	0.1794(3)	0.781(1)	0.4541(4)	0.102(6)	0.139(7)	0.071(5)	−0.004(5)	−0.025(4)	0.003(5)
O(11)	4a	0.2079(4)	0.573(1)	0.5062(6)	0.22(1)	0.068(6)	0.20(1)	0.003(6)	−0.027(9)	0.007(7)
O(12)	4a	0.2593(3)	0.7995(9)	0.5112(4)	0.080(5)	0.135(6)	0.089(5)	−0.045(4)	0.017(4)	−0.019(5)
S(1)	4a	0.95839(8)	0.7623(5)	0.6742(2)	0.058(1)	0.056(2)	0.064(1)	0.0024(9)	−0.006(2)	−0.013(1)
S(2)	4a	0.7037(1)	0.7692(4)	0.8376(2)	0.055(2)	0.053(2)	0.050(2)	−0.005(1)	−0.002(1)	−0.004(1)
S(3)	4a	0.2058(1)	0.7330(4)	0.5098(2)	0.055(2)	0.056(2)	0.045(2)	−0.004(1)	0.004(1)	−0.004(1)
C(1)	4a	1.0806(3)	0.9387(9)	0.3337(3)	0.060(5)	0.047(5)	0.042(5)	0.011(4)	−0.007(4)	−0.003(4)
C(2)	4a	1.1348(4)	1.014(1)	0.3288(6)	0.058(6)	0.083(8)	0.103(9)	−0.025(6)	0.004(6)	0.005(6)
C(3)	4a	0.8996(3)	0.935(1)	0.4684(4)	0.054(5)	0.055(5)	0.052(5)	−0.001(4)	0.013(4)	−0.011(4)
C(4)	4a	0.8674(4)	1.001(1)	0.5233(5)	0.083(7)	0.067(6)	0.057(7)	0.017(5)	0.020(5)	−0.029(5)
C(5)	4a	0.9005(3)	0.9373(9)	0.2274(4)	0.049(5)	0.045(5)	0.049(5)	0.008(4)	0.004(4)	−0.004(4)
C(6)	4a	0.8744(3)	1.010(1)	0.1733(7)	0.124(8)	0.073(6)	0.075(6)	0.000(6)	−0.014(8)	0.019(8)
C(7)	4a	0.9603(3)	0.433(1)	0.3425(4)	0.055(5)	0.053(6)	0.043(5)	−0.001(5)	0.000(4)	−0.010(6)
C(8)	4a	0.9582(4)	0.2583(9)	0.3405(6)	0.087(8)	0.043(7)	0.068(8)	0.006(5)	−0.010(7)	−0.013(6)
C(9)	4a	0.0446(3)	−0.081(1)	0.5068(5)	0.048(5)	0.055(6)	0.056(5)	0.006(5)	−0.009(4)	−0.016(7)
C(10)	4a	0.0434(4)	−0.2518(9)	0.5106(7)	0.074(8)	0.069(8)	0.087(9)	0.008(5)	0.022(8)	0.002(8)
C(11)	4a	0.1101(3)	0.429(1)	0.6224(4)	0.052(5)	0.049(5)	0.051(5)	0.002(4)	−0.005(4)	0.001(4)
C(12)	4a	0.1417(3)	0.497(1)	0.6760(7)	0.112(7)	0.080(6)	0.076(6)	−0.017(5)	−0.031(8)	−0.016(7)
C(13)	4a	−0.0768(3)	0.4269(8)	0.5074(4)	0.051(5)	0.046(5)	0.047(4)	0.007(4)	0.009(4)	0.001(4)
C(14)	4a	−0.1313(3)	0.497(1)	0.5104(7)	0.052(5)	0.087(7)	0.105(7)	0.005(5)	−0.004(6)	0.023(7)
C(15)	4a	0.1056(3)	0.4369(9)	0.3867(4)	0.049(5)	0.045(5)	0.049(5)	0.000(4)	0.004(4)	−0.001(4)
C(16)	4a	0.1376(4)	0.516(1)	0.3398(6)	0.116(9)	0.074(8)	0.068(7)	0.009(7)	0.010(7)	−0.003(6)
C(17)	4a	0.4141(3)	0.2189(8)	0.6759(5)	0.057(5)	0.051(5)	0.050(4)	−0.004(4)	0.001(5)	−0.009(5)
C(18)	4a	0.4747(3)	0.2005(9)	0.6804(6)	0.059(5)	0.075(7)	0.086(7)	0.015(4)	0.000(6)	−0.005(7)
C(19)	4a	0.2305(3)	0.211(1)	0.5464(4)	0.044(5)	0.059(5)	0.051(6)	0.007(5)	0.003(4)	−0.012(5)
C(20)	4a	0.2013(3)	0.183(1)	0.4865(4)	0.057(6)	0.093(8)	0.065(6)	0.002(6)	−0.013(4)	−0.005(6)
C(21)	4a	0.2906(3)	0.6755(8)	0.6704(5)	0.046(4)	0.048(5)	0.043(4)	−0.006(4)	0.004(4)	0.016(7)
C(22)	4a	0.2894(3)	0.8451(7)	0.6720(6)	0.084(5)	0.042(4)	0.065(5)	0.002(5)	0.008(6)	0.005(8)
C(23)	4a	0.2296(4)	0.226(1)	0.7959(4)	0.048(5)	0.071(6)	0.040(5)	−0.007(4)	−0.001(4)	−0.006(5)
C(24)	4a	0.2009(4)	0.210(1)	0.8576(5)	0.073(7)	0.13(1)	0.052(6)	−0.017(7)	0.007(5)	0.000(7)

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References

1. Csoregh, I.; Kierkegaard, P.; Norrestam, R.: Copper(I) tetraacetonitrile perchlorate. *Acta Crystallogr. B* **31** (1975) 314–317.
2. Jones, P. G.; Bembek, E.: Redetermination of the structure of tetrakis(acetonitrile-*N*)silver(I) perchlorate at 173 K. *Z. Kristallogr.* **208** (1993) 213–218.
3. Jones, P. G.; Crespo, O.: Tetrakis(acetonitrile-*N*)copper(I) tetrafluoroborate. *Acta Crystallogr. C* **54** (1998) 18–20.
4. Yokota, Y.; Young Jr., V. G.; Verkade, J. G.: The homoleptic lithium complex. *Acta Crystallogr. C* **55** (1999) 196–198.
5. Sheldrick, G. M.: SADABS. Program for Empirical Absorption Correction of Area Detector Data. University of Göttingen, Germany 1996.
6. Sheldrick, G. M.: SHELXTL V. 5.1. Software Reference Manual, Bruker AXS, Inc., Madison, Wisconsin, USA 1997.