Crystal structure of sulfatobis{2-[*N*-(2-hydroxyethylaminoethyl)imino-methyl]phenolato}zinc(II)}, [(ZnC₁₁H₁₅N₂O₂)₂SO₄]

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Abstract

C₂₂H₃₀N₄O₈SZn₂, monoclinic, *P*12₁/*c*1 (no. 14), *a* = 8.2666(6) Å, *b* = 23.229(2) Å, *c* = 13.7531(9) Å, *β* = 102.329(1)°, *V* = 2580.1 Å³, *Z* = 4, *R*_{gt}(*F*) = 0.050, *wR*_{ref}(*F*²) = 0.114, *T* = 293 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.

Equimolar amounts of salicylaldehyde (1 mmol, 122 mg) and *N*-2-hydroxyethylaminoethylamine (1 mmol, 104 mg) were dissolved in anhydrous alcohol (5 ml) with stirring. To the above solution was added ZnSO₄ · 6H₂O (1 mmol, 270 mg) in water solution (5 ml). The resulted solution was kept under air-feed to evaporate. After about half of the solvents had escaped, colorless block crystals of the title compound were deposited. They were collected by filtration, washed with water and alcohol in turn, and dried in a vacuum desiccator using silica gel (yield 26 %). Elemental analysis: found – C, 41.00 %; H, 4.82 %; N, 8.62 %; calc. for C₂₂H₃₀N₄O₈SZn₂ – C, 41.20 %; H, 4.71 %; N, 8.74 %.

Experimental details

The following atoms are found to be disordered: C9A, C9B, C10A, C10B, C11A, C11B, C22A, C22B. Their site occupancy factors were refined to 0.56(2)/0.44, but 0.77(3)/0.23 for C22A/

C22B. The H atoms attached to all C atoms were fixed geometrically and constrained to ride on their parent atoms with *U*_{iso}(H) = 1.2 *U*_{eq}(C). The H atoms attached to N and O atoms were refined isotropically.

Discussion

Zinc-containing enzymes are well known in biology and constitute an essential class of metallo-proteins [1]. The study on the structure and property of metal in zinc enzymes has been a hot spot in the field of bioinorganic chemistry recently. In zinc-catalyzing systems the zinc ion is usually coordinated to three or four protein residues and a water ligand. A couple of chemical systems have been developed to reproduce the zinc coordination core. Previously, we reported two dinuclear zinc complexes, one is imidazolate-bridged [2] and the other [3] is hydroxyl-bridged. Recently we reported a mononuclear zinc complex with a new Schiff base [4]. Only few crystal structures with this 1-[(2-hydroxyethyl)amino]-2-(salicylideneamino)ethane as ligand have been reported [5,6]. As a subsequent research we report here an air- and water-stable dinuclear zinc complex with the same Schiff base ligand as used in [4–6].

The title complex is a discrete *μ*₂-sulfato dianion-bridged dinuclear zinc complex, in which the two ZnO₂N₂ subunits are bridged by a *μ*₂-sulfate. There are two Schiff base ligands, two zinc atoms and one sulfate bridge in each complex. Each Schiff base coordinates to one zinc atom by two nitrogen atoms and two oxygen atoms, and acts as a tetradentate ligand. The sulfate anion acts as a bidentate bridge and bridges the two monomeric zinc subunits by its two oxygen atoms to finish five coordination environments of the zinc atoms. The Zn—N_{imine} bond lengths (2.032(4) Å for Zn(1) and 2.014(3) Å for Zn(2)) are obviously shorter than the Zn—N_{amine} bond lengths (2.143(4) Å for Zn(1) and 2.133(4) Å for Zn(2)), and the Zn—O_{phenolate} distances (1.997(3) Å for Zn(1) and 1.988(3) Å for Zn(2)) are much shorter than the Zn—O_{alcohol} contacts (2.125(3) Å for Zn(1) and 2.121(3) Å for Zn(2)).

Both zinc atoms in the complex are in a trigonal bipyramidal coordination, with an oxygen atom from sulfate anion, an alcohol oxygen atom and an imine nitrogen atom constituting the equatorial plane and the left two donor atoms occupying the apical positions. The central metal atom is located 0.10(1) Å for Zn(1) atom (or 0.08(1) Å for Zn(2) atom) above the equatorial plane towards the phenolate atom. The diagonal angle of the ZnO₂N₂ polyhedron is 164.63(16)° for Zn(1) (or 161.68(17)° for Zn(2) atom), indicating a strongly distorted trigonal-bipyramid around the zinc atoms. The separation between the two zinc atoms in the dimer is 3.969(2) Å. The dihedral angle between the two equatorial planes of the two zinc polyhedra is 79.2(1)°.

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Table 1. Data collection and handling.

Crystal:	colorless block, size 0.18 × 0.24 × 0.26 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	19.94 cm ⁻¹
Diffractometer, scan mode:	Siemens SMART CCD, φ/ω
$2\theta_{\max}$:	56.56°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	16256, 6307
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 3550
$N(\text{param})_{\text{refined}}$:	389
Programs:	SADABS [7], SHELXTL [8]

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(2A)	4e		0.6573	0.8413	0.5382	0.067
H(3A)	4e		0.6934	0.9379	0.5472	0.082
H(4A)	4e		0.5084	0.9961	0.6051	0.084
H(5A)	4e		0.2829	0.9557	0.6501	0.072
H(7A)	4e		0.1190	0.8804	0.6755	0.063
H(8A)	4e	0.56	-0.1061	0.7825	0.6395	0.119
H(8B)	4e	0.56	-0.0318	0.8154	0.7372	0.119
H(8C)	4e	0.44	-0.1048	0.8053	0.6541	0.119
H(8D)	4e	0.44	0.0056	0.8004	0.7597	0.119
H(9AA)	4e	0.56	-0.0908	0.7196	0.7541	0.079
H(9AB)	4e	0.56	0.0845	0.7406	0.8093	0.079
H(10A)	4e	0.56	0.1359	0.6364	0.8112	0.092
H(10B)	4e	0.56	0.1813	0.6101	0.7161	0.092

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(9BA)	4e	0.44	-0.1374	0.7183	0.6372	0.098
H(9BB)	4e	0.44	-0.0952	0.7195	0.7538	0.098
H(10C)	4e	0.44	0.1930	0.7080	0.8426	0.071
H(10D)	4e	0.44	0.1272	0.6443	0.8295	0.071
H(11A)	4e	0.56	0.3388	0.6937	0.8516	0.084
H(11B)	4e	0.56	0.4136	0.6333	0.8357	0.084
H(11C)	4e	0.44	0.4163	0.6277	0.8449	0.072
H(11D)	4e	0.44	0.3175	0.6080	0.7385	0.072
H(13A)	4e		0.7486	0.6290	0.8650	0.061
H(14A)	4e		0.9546	0.5778	0.9684	0.074
H(15A)	4e		1.0973	0.5070	0.9047	0.085
H(16A)	4e		1.0233	0.4839	0.7395	0.072
H(18A)	4e		0.8755	0.4972	0.5769	0.054
H(19A)	4e		0.5868	0.5082	0.3978	0.069
H(19B)	4e		0.7811	0.5060	0.4144	0.069
H(20A)	4e		0.7926	0.6020	0.3736	0.077
H(20B)	4e		0.6619	0.5730	0.2877	0.077
H(21A)	4e	0.77	0.4648	0.6999	0.3298	0.115
H(21B)	4e	0.77	0.6222	0.6838	0.2912	0.115
H(21C)	4e	0.23	0.4870	0.6901	0.2907	0.115
H(21D)	4e	0.23	0.6762	0.6859	0.3276	0.115
H(22A)	4e	0.77	0.7879	0.7066	0.4324	0.071
H(22B)	4e	0.77	0.6590	0.7570	0.4094	0.071
H(22C)	4e	0.23	0.4566	0.7373	0.3976	0.068
H(22D)	4e	0.23	0.6384	0.7539	0.3935	0.068
H(1N2)	4e		0.031(7)	0.665(2)	0.657(4)	0.08(2)
H(1N4)	4e		0.469(6)	0.607(2)	0.354(4)	0.07(2)
H(108)	4e		0.501(6)	0.669(2)	0.719(3)	0.04(1)
H(107)	4e		0.561(7)	0.734(2)	0.537(4)	0.08(2)

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

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn(1)	4e		0.25781(6)	0.73031(2)	0.61881(4)	0.0413(3)	0.0432(3)	0.0501(3)	-0.0029(2)	0.0105(2)	-0.0067(2)
Zn(2)	4e		0.56447(6)	0.61912(2)	0.53337(3)	0.0437(3)	0.0460(3)	0.0345(3)	0.0084(2)	0.0059(2)	0.0025(2)
S(1)	4e		0.1786(2)	0.63330(5)	0.47290(8)	0.0416(7)	0.0483(7)	0.0478(7)	-0.0052(5)	0.0030(5)	-0.0126(5)
O(1)	4e		0.3313(4)	0.6104(2)	0.5399(2)	0.046(2)	0.098(3)	0.059(2)	0.004(2)	0.009(2)	0.014(2)
O(2)	4e		0.1871(5)	0.6965(1)	0.4850(2)	0.105(3)	0.046(2)	0.054(2)	-0.004(2)	0.013(2)	-0.008(2)
O(3)	4e		0.0418(4)	0.6098(2)	0.5082(3)	0.049(2)	0.094(3)	0.098(3)	-0.035(2)	0.016(2)	-0.009(2)
O(4)	4e		0.1792(5)	0.6192(1)	0.3711(2)	0.087(3)	0.076(2)	0.044(2)	-0.001(2)	-0.001(2)	-0.020(2)
O(5)	4e		0.4316(4)	0.7804(1)	0.5817(2)	0.054(2)	0.040(2)	0.078(2)	-0.004(2)	0.033(2)	-0.007(2)
O(6)	4e		0.6467(4)	0.6217(1)	0.6801(2)	0.067(2)	0.066(2)	0.035(2)	0.031(2)	0.003(2)	0.000(2)
O(7)	4e		0.6267(4)	0.7069(1)	0.5194(2)	0.058(2)	0.048(2)	0.049(2)	0.005(2)	0.022(2)	0.002(2)
O(8)	4e		0.4299(4)	0.6887(1)	0.7343(2)	0.045(2)	0.063(2)	0.044(2)	0.007(2)	0.014(2)	-0.004(2)
N(1)	4e		0.1358(5)	0.8007(2)	0.6538(3)	0.045(3)	0.052(2)	0.080(3)	0.001(2)	0.019(2)	-0.013(2)
N(2)	4e		0.0914(6)	0.6883(2)	0.6960(4)	0.047(3)	0.058(3)	0.071(3)	-0.014(2)	0.010(2)	-0.006(2)
N(3)	4e		0.7024(4)	0.5486(1)	0.5248(3)	0.041(2)	0.043(2)	0.046(2)	0.005(2)	0.015(2)	0.003(2)
N(4)	4e		0.5568(6)	0.6230(2)	0.3775(3)	0.069(3)	0.062(3)	0.036(2)	0.001(3)	0.002(2)	-0.001(2)
C(1)	4e		0.4442(6)	0.8365(2)	0.5878(3)	0.051(3)	0.046(3)	0.031(2)	-0.001(2)	0.002(2)	0.001(2)
C(2)	4e		0.5798(6)	0.8638(2)	0.5608(3)	0.066(4)	0.060(3)	0.043(3)	-0.011(3)	0.017(2)	-0.006(2)
C(3)	4e		0.6023(7)	0.9217(2)	0.5665(4)	0.093(5)	0.066(4)	0.049(3)	-0.019(3)	0.020(3)	0.004(3)
C(4)	4e		0.4919(8)	0.9565(2)	0.6004(4)	0.114(5)	0.041(3)	0.055(3)	-0.011(3)	0.018(3)	0.007(2)
C(5)	4e		0.3577(7)	0.9321(2)	0.6272(3)	0.081(4)	0.047(3)	0.047(3)	0.015(3)	0.007(3)	0.009(2)
C(6)	4e		0.3292(6)	0.8727(2)	0.6213(3)	0.053(3)	0.041(2)	0.034(2)	0.008(2)	0.003(2)	0.003(2)
C(7)	4e		0.1838(6)	0.8526(2)	0.6532(3)	0.051(3)	0.053(3)	0.051(3)	0.017(2)	0.008(2)	-0.004(2)
C(8)	4e		-0.0109(8)	0.7856(3)	0.6931(6)	0.061(4)	0.081(4)	0.170(7)	0.000(3)	0.056(4)	-0.009(5)
C(9A)	4e	0.56(2)	0.015(2)	0.7335(7)	0.744(1)	0.05(1)	0.083(9)	0.07(1)	-0.016(7)	0.037(7)	-0.005(8)
C(10A)	4e	0.56	0.189(2)	0.6448(7)	0.756(1)	0.09(1)	0.060(8)	0.09(1)	-0.018(7)	0.038(8)	0.011(7)
C(9B)	4e	0.44	-0.051(3)	0.727(1)	0.695(2)	0.05(1)	0.09(1)	0.11(2)	-0.03(1)	0.03(1)	-0.02(1)
C(10B)	4e	0.44	0.185(2)	0.6741(9)	0.801(1)	0.055(9)	0.08(1)	0.054(9)	-0.009(7)	0.035(7)	-0.004(7)
C(11A)	4e	0.56	0.349(3)	0.6650(8)	0.802(2)	0.09(1)	0.07(1)	0.06(1)	0.03(1)	0.022(8)	0.013(8)
C(11B)	4e	0.44	0.347(4)	0.641(1)	0.783(2)	0.07(1)	0.06(1)	0.06(1)	0.02(1)	0.037(9)	0.01(1)
C(12)	4e		0.7613(5)	0.5889(2)	0.7362(3)	0.037(3)	0.053(3)	0.039(3)	0.003(2)	0.009(2)	0.012(2)
C(13)	4e		0.8043(6)	0.6003(2)	0.8384(3)	0.050(3)	0.064(3)	0.039(3)	0.002(2)	0.009(2)	0.014(2)
C(14)	4e		0.9281(6)	0.5695(2)	0.9007(4)	0.054(3)	0.088(4)	0.039(3)	-0.011(3)	0.000(2)	0.030(3)
C(15)	4e		1.0118(7)	0.5268(2)	0.8631(4)	0.053(3)	0.082(4)	0.074(4)	0.010(3)	0.005(3)	0.042(3)
C(16)	4e		0.9685(6)	0.5137(2)	0.7641(4)	0.047(3)	0.059(3)	0.075(4)	0.013(2)	0.016(3)	0.030(3)

Table 3. Continued.

Atom	Site	Occ.	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
C(17)	4e		0.8434(5)	0.5439(2)	0.6982(3)	0.040(3)	0.041(2)	0.052(3)	0.003(2)	0.019(2)	0.014(2)
C(18)	4e		0.8110(5)	0.5267(2)	0.5941(3)	0.040(3)	0.037(2)	0.061(3)	0.003(2)	0.020(2)	0.005(2)
C(19)	4e		0.6879(6)	0.5301(2)	0.4201(3)	0.064(3)	0.056(3)	0.057(3)	0.002(2)	0.023(3)	−0.019(2)
C(20)	4e		0.6852(7)	0.5833(2)	0.3577(3)	0.069(4)	0.086(4)	0.038(3)	−0.016(3)	0.008(2)	−0.010(3)
C(21)	4e		0.573(1)	0.6829(3)	0.3484(4)	0.163(7)	0.078(4)	0.042(3)	−0.024(4)	0.009(4)	0.015(3)
C(22A)	4e	0.77(3)	0.672(2)	0.7165(4)	0.4264(7)	0.079(9)	0.045(4)	0.062(5)	−0.006(5)	0.031(6)	0.005(4)
C(22B)	4e	0.23	0.569(7)	0.723(1)	0.408(2)	0.06(2)	0.06(2)	0.05(2)	0.01(2)	0.02(2)	−0.00(1)

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References

1. Lipscomb, W. N.; Strater, N.: Recent Advances in Zinc Enzymology. *Chem. Rev.* **96** (1996) 2375–2433.
2. Zhu, H.-L.; Tong, Y.-X.; Zhao, J.; Duan, C.-Y.; Chen, X.-M.; Tang, W.-X.: Synthesis, Crystal Structure and Characterization of [Bis(*N,N'*-bis(2-aminoethyl)propane-1,3-diamine)(μ -imidazolato-*N,N'*)dizinc(II)] Triperchlorate. *Aust. J. Chem.* **52** (1999) 709–711.
3. Zhu, H.-L.; Meng, F.-J.; Wang, Z.-D.; Yang, F.: Crystal structure of 2-hydroxyl-bis(5-methyl-1,4,9-triazanonezinc(II)) triperchlorate, C₁₄H₃₉Cl₃N₆O₁₃Zn₂. *Z. Kristallogr. NCS* **219** (2003) 321–322.
4. Usman, A.; Fun, H.-K.; Chantrapromma, S.; Zhu, H.-L.; Liu, Q.-X.: Dichloro{2-[*N*-(2-hydroxyethylammonio-ethyl)iminomethyl]-phenolate}zinc(II). *Acta Crystallogr. E* **59** (2003) o215–o217.
5. Mikuriya, M.; Takebayashi, H.; Matsunami, K.: A manganese(III) complex with 1-[(2-hydroxyethyl)amino]-2-(salicylideneamino)ethane. *Bull. Chem. Soc. Jpn.* **67** (1994) 3128–3130.
6. Swamy, G. Y. S. K.; Ravikumar, K.; Chandramohan, K.; Lakshmi, N. V.: The Crystal and Molecular Structure of (μ -terephthalato)bis[(*N*-salicylidene-*N'*-(2-hydroxyethyl)ethylenediamine)copper(II)]. *Cryst. Res. Technol.* **36** (2001) 1273–1279.
7. Sheldrick, G. M.: SADABS. Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Germany 1996.
8. Sheldrick, G. M.: SHELXTL V5.1 Software Reference Manual, Bruker AXS, Inc., Madison, Wisconsin, USA 1997.