Crystal structure of μ_2 -hydroxyl-bis(5-methyl-1,4,9-triazanonanezinc(II)) triperchlorate, $C_{14}H_{39}Cl_3N_6O_{13}Zn_2$

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Abstract

$C_{14}H_{39}Cl_3N_6O_{13}Zn_2$, monoclinic, $P12_1/m1$ (No. 11), $a = 7.802(2)$ Å, $b = 12.121(3)$ Å, $c = 15.662(3)$ Å, $\beta = 104.29(2)^\circ$, $V = 1435.3$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.055$, $wR_{\text{ref}}(F^2) = 0.152$, $T = 293$ K.

Source of material

All reagents and solvents were used as obtained without further purification. A solution of 5-methyl-1,4,9-triazanonane (mdipt) (1 mmol, 145 mg) in acetonitrile (5 ml) was added to a stirred solution of zinc(II) perchlorate (1 mmol, 370 mg) in water (5 ml). A few drops of 0.1 M solution of $HClO_4$ in water was added to the above solution to adjust the pH = 4–6. Slow evaporation of the resulting solution in air for about a week, a large stack of colorless micro-crystals of 1, $[(\text{mtan})Zn(\text{OH}_2)](\text{ClO}_4)_2$, were deposited and collected by filtration, washed with aqueous acetonitrile and dried in a vacuum desiccator over silica gel (yield 39%). When the pH value of 1 was adjusted to about pH 7–11 and was stood for two days, X-ray suitable colorless prism crystals of the title complex, $[(\text{mtan})Zn(\mu_2\text{-OH})Zn(\text{mtan})](\text{ClO}_4)_3$, were deposited and collected by filtration, washed with aqueous acetonitrile and dried in a vacuum desiccator over silica gel (yield 88%). Elemental analysis: found – C, 22.8%; H, 5.4%; N, 11.2%; Cl, 14.6%; Zn, 17.6%; calc. for $C_{14}H_{39}N_6Cl_3O_{13}Zn_2$ – C, 22.8%; H, 5.3%; N, 11.4%; Cl, 14.4%; Zn, 17.8%.

Experimental details

Several oxygen atoms of two perchlorate anions were disordered (s.o.f. = 0.5 for O7, O8 attached to Cl2, and also s.o.f. = 0.5 for O10, O11, O10', O11' attached to Cl3). One of the ordering arrangements is shown in the figure.

Discussion

Zinc-containing enzymes are ubiquitous in biology and constitute an essential class of metallo-proteins [1]. The study on the structure and property of zinc-site in zinc enzymes has been hot spots in the field of bioinorganic chemistry recently. Surprisingly, zinc-aqua model complexes have proven extremely difficult to stabilize, and all classical models have failed to stabilize a tetrahedral dicationic Zn-aqua species [2,3]. Previously [4], we reported an imidazolated-bridged dinuclear zinc complex, $[Zn(2,3,2\text{-tet})_2(\mu_2\text{-Im})Zn(2,3,2\text{-tet})](\text{ClO}_4)_3$ (2,3,2-tet is 1,4,8,11-tetraazaundecane and Im is imidazolate anion), which is structurally similar to copper/zinc superoxide dismutase ($\text{Cu}_2\text{Zn}_2\text{-SOD}$), however, as expected, has no any activity in catalyzing the dismutation of the superoxide ion (O_2^-) to hydrogen peroxide and molecular oxygen.

The title complex is a discrete OH^- bridged dinuclear zinc complex. The four-coordinate zinc ions in the complex exhibit a slightly distorted tetrahedral geometry. The average Zn–N bond length (2.024(2) Å) is significantly shorter than that (2.140 Å) in $[Zn_2L(\text{OH})(\text{NO}_3)_2]$ [5,6]. The Zn–O bond length (1.924(2) Å) is shorter than those in zinc water complexes (~1.97 Å), but significantly longer than those (1.85 Å, 1.86 Å) for the zinc hydroxide complexes in [3]. The Zn–Zn distance (3.554(3) Å) is close to those (3.4 Å – 3.5 Å) in several native enzymes. The Zn–O–Zn angle (135.3(1)°) is also comparable to those in literature for the enzymes *Stenotrophomonas maltophilia* and *Bacteroides fragilis*. One oxygen atom from a perchlorate and N(1) atom contributes to the formation of the hydrogen bond, with the hydrogen contact $d(\text{N1}\cdots\text{H-O2}) = 2.928(2)$ Å and the angle 173.1°.

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.30 × 0.40 × 0.50 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	20.18 cm ⁻¹
Diffractionmeter, scan mode:	Siemens R3m, ω
$2\theta_{\text{max}}$:	55°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	3704, 3458
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 2387
$N(\text{param})_{\text{refined}}$:	211
Programs:	SHELXTL [7], SHELXTL-plus [8]

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

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(1H)	2e	0.4596	1/4	0.1971	0.08
H(1)	4f	−0.0258	0.1112	0.2732	0.08
H(2)	4f	0.1637	0.1334	0.3606	0.08
H(3)	4f	0.1230	−0.0117	0.1075	0.08
H(4)	4f	0.1464	0.0902	0.0673	0.08
H(1A)	4f	0.0439	−0.0788	0.2869	0.08
H(1B)	4f	0.0118	−0.0333	0.3745	0.08
H(2A)	4f	0.2587	−0.1349	0.4177	0.08
H(2B)	4f	0.3245	−0.0140	0.4245	0.08
H(3A)	4f	0.4960	−0.1398	0.3597	0.08

Table 2. Continued.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(3B)	4f	0.3365	−0.1432	0.2780	0.08
H(4A)	4f	0.6890	0.0122	0.3885	0.08
H(4B)	4f	0.6446	0.1235	0.3369	0.08
H(4C)	4f	0.5340	0.0864	0.4029	0.08
H(5A)	4f	0.6525	−0.0955	0.2538	0.08
H(5B)	4f	0.6408	0.0211	0.2123	0.08
H(6A)	4f	0.3835	−0.1376	0.1511	0.08
H(6B)	4f	0.5415	−0.1218	0.1087	0.08
H(7A)	4f	0.4317	0.0626	0.0722	0.08
H(7B)	4f	0.3194	−0.0306	0.0173	0.08

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

Atom	Site	Occ.	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Zn(1)	4f		0.26729(6)	0.10338(4)	0.22612(3)	0.0394(2)	0.0233(2)	0.0344(2)	0.0018(2)	0.0117(2)	0.0005(2)
O(1)	2e		0.3595(6)	1/4	0.2236(3)	0.047(2)	0.021(2)	0.080(3)	0	0.031(2)	0
N(1)	4f		0.0970(5)	0.0845(3)	0.3021(2)	0.049(2)	0.055(2)	0.047(2)	0.012(2)	0.022(2)	0.010(2)
N(2)	4f		0.4698(4)	0.0006(3)	0.2885(2)	0.038(2)	0.030(2)	0.043(2)	0.002(1)	0.006(1)	0.003(2)
N(3)	4f		0.2024(5)	0.0395(3)	0.1041(2)	0.048(2)	0.046(2)	0.036(2)	−0.000(2)	0.010(2)	−0.005(2)
C(1)	4f		0.0900(6)	−0.0306(4)	0.3358(3)	0.057(3)	0.053(3)	0.056(3)	−0.007(2)	0.026(2)	−0.001(2)
C(2)	4f		0.2710(7)	−0.0707(4)	0.3839(3)	0.072(3)	0.051(3)	0.050(3)	0.000(3)	0.018(2)	0.018(2)
C(3)	4f		0.3984(6)	−0.0977(4)	0.3259(3)	0.054(3)	0.037(2)	0.069(3)	0.007(2)	0.016(2)	0.016(2)
C(4)	4f		0.5955(6)	0.0613(5)	0.3605(3)	0.051(3)	0.068(3)	0.047(3)	−0.006(3)	−0.003(2)	0.003(3)
C(5)	4f		0.5717(6)	−0.0394(4)	0.2252(3)	0.040(2)	0.047(3)	0.067(3)	0.011(2)	0.018(2)	0.006(2)
C(6)	4f		0.4643(6)	−0.0841(4)	0.1382(3)	0.059(3)	0.046(3)	0.067(3)	0.012(2)	0.032(2)	−0.009(2)
C(7)	4f		0.3570(6)	0.0005(4)	0.0752(3)	0.052(2)	0.055(3)	0.043(2)	0.001(2)	0.020(2)	−0.009(2)
Cl(1)	2e		0.7837(2)	1/4	0.1290(1)	0.0399(8)	0.0500(9)	0.0555(9)	0	0.0118(7)	0
O(2)	2e		0.7667(9)	1/4	0.2189(4)	0.129(5)	0.074(4)	0.085(4)	0	0.065(4)	0
O(3)	2e		0.6159(9)	1/4	0.0728(6)	0.071(4)	0.079(5)	0.184(8)	0	−0.052(5)	0
O(4)	4f		0.8720(7)	0.1536(5)	0.1169(3)	0.142(4)	0.154(4)	0.087(3)	0.101(3)	0.017(3)	−0.012(3)
Cl(2)	2e		0.1198(2)	1/4	0.5078(1)	0.069(1)	0.0487(9)	0.0429(8)	0	0.0168(8)	0
O(5)	2e		0.170(1)	1/4	0.6008(3)	0.161(7)	0.151(7)	0.059(4)	0	0.018(4)	0
O(6)	2e		0.2641(7)	1/4	0.4684(4)	0.097(5)	0.23(1)	0.118(6)	0	0.056(4)	0
O(7)	4f	0.50	0.059(1)	0.3700(5)	0.4903(6)	0.36(2)	0.063(7)	0.135(9)	0.02(1)	0.13(1)	0.011(7)
O(8)	4f	0.50	−0.0213(9)	0.1873(7)	0.4675(6)	0.120(7)	0.150(9)	0.150(9)	−0.088(6)	0.044(7)	−0.082(7)
Cl(3)	2e		−0.0722(2)	3/4	0.1096(1)	0.0422(8)	0.0407(8)	0.0557(9)	0	0.0117(7)	0
O(9)	2e		−0.1572(8)	3/4	0.1820(4)	0.144(6)	0.170(8)	0.119(6)	0	0.074(5)	0
O(10)	2e	0.50	−0.206(1)	3/4	0.0284(5)	0.15(1)	0.08(1)	0.076(9)	0	−0.032(9)	0
O(10')	2e	0.50	0.1148(8)	3/4	0.1488(8)	0.045(6)	0.10(1)	0.23(2)	0	0.034(9)	0
O(11)	4f	0.50	0.042(1)	−0.3360(9)	0.1142(8)	0.34(2)	0.18(1)	0.31(2)	0.21(1)	0.03(2)	−0.03(1)
O(11')	4f	0.50	−0.114(1)	−0.3524(7)	0.0665(7)	0.18(1)	0.152(8)	0.22(1)	−0.094(8)	0.104(8)	−0.142(8)

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