Crystal Structure of the Bis[zinc(II)-hydroxide-(μ-perchlorate)-triaqua] Complex

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Abstract. Colorless single crystals of the title compound were accidentally obtained by a reaction of p-sulfophenylalanine with zinc perchlorate. The crystal structure (monoclinic, $P2_1/c$, Z = 4, a = 5.9031(7), b = 13.5404(16), c = 9.7932(8) Å, β = 126.438(5)°, V = 629.74(12) Å^3, $R_1[I>2\sigma(I)] = 0.0276$, $wR_2(all) = 0.0844$) reveals a discrete dinuclear $[Zn(OH)(\mu\text{-}ClO_4)(H_2O)_3]_2$ in which each perchlorate anion acts as a bidentate bridging linker to bind two Zn atoms whereas the hydroxy group is a terminal group. Thus, the local surrounding around the zinc atom can be best described as a slightly distorted octahedron.

Keywords: Crystal structure; Zinc; Hydrogen bonding; Perchlorate

The structural diversity in the inorganozinc perchlorates is well documented [1, 2]. Amongst these, the structures in which perchlorate anion acting as bridging ligand are rather rare. To the best of our knowledge, inorganozinc perchlorate compound containing two bridging perchlorate anions has not been reported. Here we report on the molecular and crystal structure of the title compound $[Zn(OH)(\mu\text{-}ClO_4)(H_2O)_3]_2$. This title compound is an example of the broader class of inorganozinc perchlorates.

Caution. Single crystals of $[Zn(OH)(\mu\text{-}ClO_4)(H_2O)_3]_2$ decompose upon heating and applied pressure. Dry powder samples, especially in larger quantities, should be handled with great care.

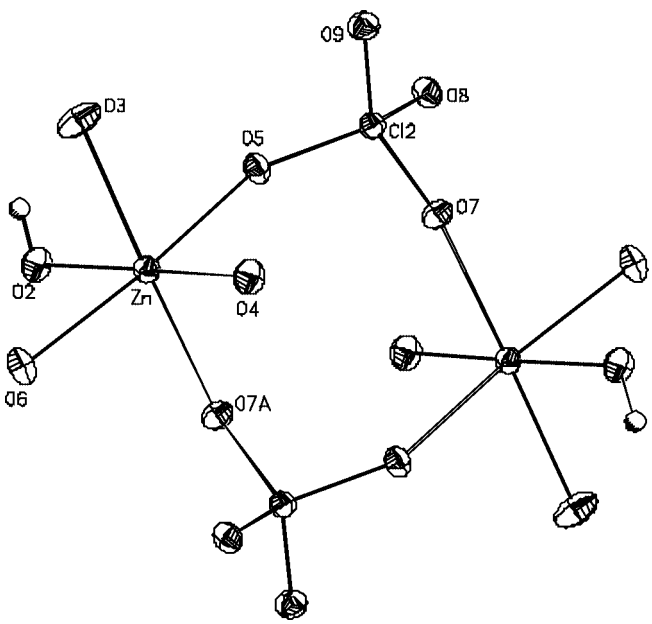

Figure 1 Molecular structure of $[Zn(OH)(\mu\text{-}ClO_4)(H_2O)_3]_2$ with hydrogen atoms of water omitted.

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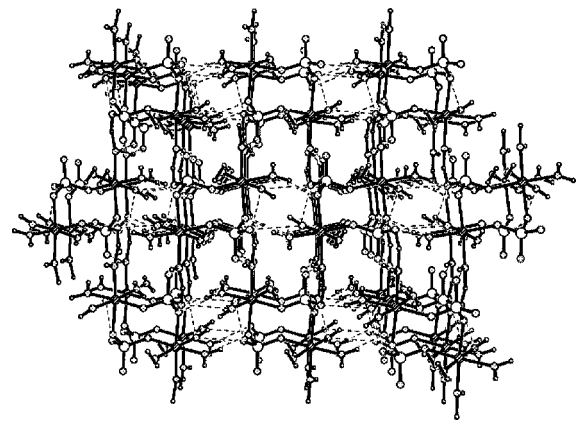

Figure 2 The packing perspective view of $[Zn(OH)(\mu\text{-}ClO_4)(H_2O)_3]_2$ along [100] direction.

Crystal Structure of $[Zn(OH)(\mu\text{-}ClO_4)(H_2O)_3]_2$

The reaction of $Zn(ClO_4)_2{\cdot}6H_2O$ with 4-sulfophenylalanine offers a precipitate which may be mono(4-sulfo-phenylalanine)(diaqua)-zinc(II) [3]. The evaporation of this mother liquid gives the title compound. X-ray crystallographic analysis indicates that the centrosymmetric dinuclear structure of $[Zn(OH)(\mu\text{-}ClO_4)(H_2O)_3]_2$, crystallizes with the monoclinic space group $P2_1/c$ with four formula units in the unit cell [4]. The molecular structure of the title compound (Fig. 1) features two bidentate perchlorate ligands that μ_2-bridge via two oxygen atoms each to two zinc atoms leading to the formation of an eight-membered ring. Other coordination sites were occupied by three water molecules and one hydroxy anion. This arrangement leads to six-coordinate zinc atoms that are best described as existing in square bipyramidal coordination. The Zn-O (perchlorate group and water molecule) bond distances (2.085-2.109 Å) are quite similar to normal Zn-O bond distances (2.050-2.132 Å) [1]. Zn-OH bond length (2.071 Å) also has a typical bond distance (2.020 Å) [5], the intramolecular Zn-Zn bond distance is 4.502 Å and Cl-O distances range from 1.459 to 1.479 Å. The extensive intermolecular hydrogen bonding interactions give rise to a three-dimensional network structure (Fig. 2).

Experimental Details

A solution of $Zn(ClO_4)_2{\cdot}6H_2O$(0.5 mmol) in methanol(5 mL) was added to a solution of 4-sulfophenylalanine(0.5 mmol) prepared by

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Table 1 Atomic coordinates, equivalent temperature factors, distances (in Å) and angles (in deg) for $[Zn(OH)(\mu\text{-}ClO_4)(H_2O)_3]_2$.

Atom	x/a	y/b	z/c	U_{eq}
Zn	0.15(1)	0.1035(1)	0.2818(1)	0.016(1)
Cl(2)	0.3705(2)	0.1074(1)	0.3243(1)	0.017(1)
O(2)	0.0085(5)	0.0758(2)	0.1453(3)	0.023(1)
O(3)	0.5537(6)	0.1265(2)	0.0599(3)	0.031(1)
O(4)	0.3143(5)	0.1409(2)	0.4148(3)	0.025(1)
O(5)	0.2462(5)	0.0485(2)	0.2569(3)	0.020(1)
O(6)	0.0374(5)	0.2486(2)	0.2841(3)	0.024(1)
O(7)	0.2532(4)	0.0737(2)	0.4983(3)	0.021(1)
O(8)	0.3099(5)	0.2115(2)	0.3213(3)	0.021(1)
O(9)	0.6788(5)	0.0917(2)	0.2169(3)	0.022(1)

Zn-O(2)	2.071(2)	Zn-O(6)	2.074(2)
Zn-O(4)	2.096(2)	Zn-O(7)A	2.092(2)
Zn-O(5)	2.109(2)	Cl(2)-O(7)	1.479(2)
Cl(2)-O(8)	1.459(2)	Cl(2)-O(5)	1.479(2)
O(2)-Zn-O(6)	85.16(10)	O(2)-Zn-O(7)A	87.50(9)
O(9)-Cl(2)-O(7)	108.14(13)	O(5)-Cl(2)-O(7)	109.25(13)

Symmetry transformations used to generate equivalent atoms: A, −x, −y, −z+1

standard methods in methanol/water (5 mL/5 mL). This mixture was stirred at 60 °C for 2 h and the precipitated compound (may be mono(4-sulfo-phenylalanine)(diaqua)zinc(II)) [3] was filtered off. Colorless crystals were obtained from the slow evaporation of the mother liquid. Some of these were selected and sealed in thin-walled glass capillaries of 0.1-0.2 mm outer diameter and were tested for their quality on a single-crystal X-ray diffractometer (Bruker P4). The best specimen was used to collect a complete intensity data set with the aid of the same diffractometer at 293 K. For structure solution and refinement see ref. [4] and for crystal data Table 1.

[1] S. Ghosh, M. Mukherjee, A. Seal, S. Ray, *Acta Cryst*allogr. **1997**, *B53*, 639.

[2] M. Ghosh, S. Ray, *Z. Kristallogr.* **1977**, *145*, 146.

[3] Y.-R. Xie, R.-G. Xiong, X. Xue, X.-T. Chen, Z. Xue, X.-Z. You, *Inorg. Chem.* **2002**, *41*, 3323.

[4] $[Zn(OH)(\mu\text{-}ClO_4)(H_2O)_3]_2$: Colourless single crystal; diffractometer Bruker P4; Mo-Kα radiation, graphite monochromator, λ = 0.71073 Å; T = 293(2) K; monoclinic, $P2_1/c$, Z = 4, a = 5.9031(7), b = 13.5404(16), c = 9.7932(8) Å, β = 126.438(5)°, V = 629.74(12) $Å^3$; F(000) = 472, μ = 4.321 cm^{-1}; θmin = 2.99°, θmax = 26°, −7<h<7, −16<k<13, −12<l<12; 3700 reflection intensities measured of which 1238 were symmetrically independent, Rint = 0.0307, 117 parameters. Largest diffraction peak and hole 0.64 and −0.76 $eÅ^{-3}$. Structure solution and refinement with the programs SHELXS-97 and SHELXL-97 (G. M. Sheldrick, Göttingen), scattering factors from *Int. Tables for X-ray Crystallogr.*, Vol C. R values: R1/wR2 for 1121 reflections with $I_0 > 2\sigma(I_0)$: 0.0276/0.0826 and for all data: 0.0312/0.0844; Goof: 1.084. Further details may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, crysdata@FIZ-Karlsruhe.de, referring to CSD No. 413949, the authors and the journal citation.

[5] V. W. Nowachi, J. N. Silverman, *Z. Kristallogr.* **1961**, *115*, 21.

