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Crystal structure of bis[triaqua-(μ_2 -1,2-di(4-pyridyl)ethylene- $\kappa^2 N:N'$)-(4-sulfonatobenzoato- $\kappa^2 O,O'$)zinc(II)], $C_{13}H_{15}NO_8SZn$

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Abstract

$C_{13}H_{15}NO_8SZn$, monoclinic, $C2/c$ (no. 15), $a = 12.3456(3)$ Å, $b = 13.7680(4)$ Å, $c = 19.9125(5)$ Å, $\beta = 107.051(2)^\circ$, $V = 3235.85(14)$ Å³, $Z = 8$, $R_{gt}(F) = 0.0325$, $wR_{ref}(F^2) = 0.0819$, $T = 293(2)$ K.

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The asymmetric unit of the dinuclear title structure is shown using ellipsoids in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

All chemicals were used as obtained without further purification. The mixtures of potassium 4-carboxybenzenesulfonate (4-khsb) (0.1 mmol, 24.03 mg), 1,2-di(4-pyridyl)ethylene (bpe) (0.05 mmol, 9.18 mg), $Zn(Ac)_2 \cdot 2 H_2O$ (0.1 mmol, 21.9 mg), ethanol (3.0 mL), and H_2O (3.0 mL) were sealed in a 23 mL Teflon-lined autoclave, heated to 393 K for 4 days, then cooled at 5 °C h⁻¹ to room temperature. Colorless block crystals were obtained.

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.38 × 0.34 × 0.31 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.69 mm ⁻¹
Diffractometer, scan mode:	SuperNova, ω
θ_{max} , completeness:	28.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	11762, 3481, 0.027
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 3031
$N(param)_{refined}$:	217
Programs:	CrysAlis ^{PRO} [1], SHELX [2], Olex2 [3]

Experimental details

The structure was solved and refined using the SHELX and OLEX2-system [1, 2]. Hydrogen atoms bonded to the carbon atoms were placed in calculated positions and refined with a riding mode. The water hydrogen atoms were initially located in the difference Fourier maps.

Comment

The design and construction of diverse metal complexes has attracted great attention in recent years because of the enormous variety of intriguing structure as well as their potential applications in many fields [4–6]. To the best of our knowledge, 4-khsb is a good candidate for the construction of complexes that display rich structural diversity, due to their extension ability both in covalent bonding and in supramolecular interactions (H-bonding and aromatic stacking) [7–10]. Furthermore, N-donor ancillary ligand can modify the structures and properties of the resulting materials. So far very interesting and promising results are constructed by mixed likers. With these considerations in mind, we report herein a dinuclear Zn(II) complex.

The asymmetric unit of the title complex contains one crystallographically independent Zn(II) center, one 4-sb²⁻ anion, a half bpe ligand and three coordination water molecules (see the figure). The Zn1 atom resides in a distorted octahedral environment [ZnO₅N] with the basal plane defined by O1 and O2 atoms from the carboxyl group of one 4-sb²⁻ anion and O3W from one coordination water molecule as well as N3 from one bpe molecule. Two O atoms (O1W and O2W)

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U_{iso}^*/U_{eq}
Zn1	0.54265(2)	0.67311(2)	0.45790(2)	0.02716(10)
S1	0.83898(5)	0.50448(5)	0.88844(3)	0.02908(14)
O1	0.71180(15)	0.65672(13)	0.55134(9)	0.0383(4)
O1W	0.53705(16)	0.81464(13)	0.49183(10)	0.0445(5)
H1WA	0.5736	0.8185	0.5352	0.067*
H1WB	0.4980	0.8661	0.4890	0.067*
O2	0.54207(14)	0.62057(13)	0.55678(8)	0.0369(4)
O2W	0.57738(15)	0.53409(13)	0.42577(10)	0.0411(4)
H2WA	0.6296	0.4926	0.4290	0.062*
H2WB	0.5251	0.4949	0.4276	0.062*
O3	0.81569(15)	0.40008(13)	0.88624(9)	0.0394(4)
O3W	0.62555(14)	0.71734(13)	0.38827(8)	0.0345(4)
H3WA	0.6633	0.6688	0.3811	0.052*
H3WB	0.6717	0.7630	0.4056	0.052*
O4	0.77728(16)	0.55695(15)	0.92854(9)	0.0438(5)
O5	0.95914(14)	0.52554(14)	0.90855(9)	0.0393(4)
N1	0.37271(16)	0.67166(14)	0.40144(10)	0.0287(4)
C1	0.6484(2)	0.62631(17)	0.58547(12)	0.0303(5)
C2	0.69611(19)	0.59643(17)	0.66059(11)	0.0272(5)
C3	0.6251(2)	0.5854(2)	0.70241(13)	0.0383(6)
H3	0.5477	0.5960	0.6836	0.046*
C4	0.6686(2)	0.5585(2)	0.77216(12)	0.0390(6)
H4	0.6207	0.5508	0.8002	0.047*
C5	0.78323(18)	0.54346(17)	0.79971(11)	0.0258(5)
C6	0.8548(2)	0.55506(19)	0.75893(12)	0.0340(6)
H6	0.9323	0.5455	0.7782	0.041*
C7	0.8113(2)	0.58107(19)	0.68903(12)	0.0347(6)
H7	0.8595	0.5882	0.6612	0.042*
C8	0.2911(2)	0.6638(2)	0.43257(13)	0.0382(6)
H8	0.3120	0.6570	0.4811	0.046*
C9	0.1773(2)	0.6653(2)	0.39625(13)	0.0402(6)
H9	0.1234	0.6594	0.4203	0.048*
C10	0.14351(19)	0.67578(17)	0.32361(12)	0.0310(5)
C11	0.2290(2)	0.68347(19)	0.29133(13)	0.0348(6)
H11	0.2107	0.6901	0.2428	0.042*
C12	0.3403(2)	0.68119(19)	0.33127(13)	0.0347(6)
H12	0.3961	0.6865	0.3086	0.042*
C13	0.0216(2)	0.67632(18)	0.28455(13)	0.0349(6)
H13	−0.0293	0.6767	0.3109	0.042*

from two coordination water molecules are positioned at the axial positions. All the Zn—O bond lengths are in the range of 2.0429(16)–2.3653(17) Å and the Zn—N bond is 2.0695(19) Å. The sulfonate group remains uncoordinated. The adjacent Zn···Zn atoms are separated by one bpe connector 13.528 Å.

There are hydrogen bonds between coordinated water oxygen atoms and coordinated oxygen atoms of carboxylate (O2W—H2WB···O2⁴ with the donor-acceptor distance of 2.670(2) Å and a bond angle of 158.6° as well as O3W—H3WB···O1⁵ with the donor-acceptor distance of 2.659(2) Å

and a bond angle of 169.8°). Several kinds of hydrogen bonding between coordinated water oxygen atoms and uncoordinated oxygen atoms of the sulfonate group are observed [(1) O1W—H1WA···O3¹ with the donor-acceptor distance of 2.828(2) Å and a bond angle of 146.5°; (2) O1W—H1WB···O5² with the donor-acceptor distance of 2.753(3) Å and a bond angle of 129.0°; (3) O2W—H2WA···O4³ with the donor-acceptor distance of 2.754(3) Å and bond angle of 157.7°; (4) O3W—H3WA···O3³ with the bond distance of 2.860(2) Å and a bond angle of 151.8°]. (symmetric code: $\frac{1}{3}2-x$, $\frac{1}{2}+y$, $\frac{3}{2}-z$; $\frac{2}{3}-\frac{1}{2}+x$, $\frac{3}{2}-y$, $-\frac{1}{2}-z$; $\frac{3}{3}+x$, $1-y$, $-\frac{1}{2}+z$; $\frac{4}{4}1-x$, $1-y$, $1-z$; $\frac{5}{5}3/2-x$, $3/2-y$, $1-z$) The weaker face to face π - π stacking interactions occur between bpe (the ring of N1/C8—C12) and 4-sb²⁻ (the ring of C2—C7) with a centroid-centroid distance is 3.8344(1) Å.

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