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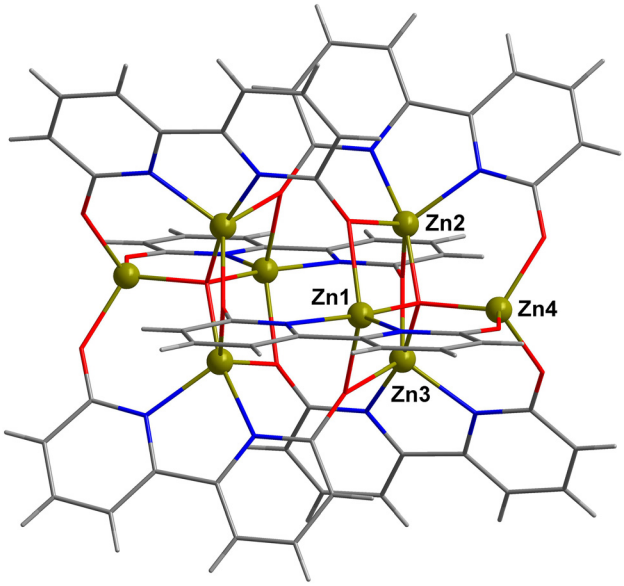
The crystal structure of (μ_4-oxo)-tri(μ_4-2,2′-bipyridine-6,6′-bis(olato)-$\kappa^5O,O':N:N':O''$) tetrazinc(II) – methylformamide (1/1), $C_{33}H_{25}N_7O_8Zn_4$



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Abstract

$C_{33}H_{25}N_7O_8Zn_4$, triclinic, $P\bar{1}$ (no. 2), a = 12.1524(7) Å, b = 12.2035(7) Å, c = 14.2730(7) Å, α = 78.669(4)°, β = 66.615(5)°, γ = 62.482(6)°, V = 1722.83(19) Å^3, Z = 2, $R_{gt}(F)$ = 0.0405, $wR_{ref}(F^2)$ = 0.1128, T = 293(2) K.

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Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.18 × 0.10 × 0.07 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	2.81 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω
θ_{max}, completeness:	26.4°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	14,593, 7023, 0.023
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 5148
$N(param)_{refined}$:	473
Programs:	Bruker,[1] SHELX,[2–4] Diamond[5]

CCDC no.: 2372259

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

1 Source of material

All reagents used were purchased and used without further purification. A mixture of 6,6′-dihydroxy-2,2′-bipyridine(H_2dhbp, 24.4 mg, 0.1 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (22.0 mg, 0.1 mmol) was dissolved in 2 mL H_2O and 2 mL dimethylformamide (DMF). The resulting solution was placed in a 25 mL Teflon-lined stainless steel reactor, which was sealed and heated to 413 K for 72 h. After the mixture was cooled to room temperature over 24 h, yellow crystals of the title complex were obtained.

2 Experimental details

Absorption corrections were applied by using multi-scan program.[1] The structure was refined with the SHELXL software package.[2–4] The figure of the title crystal structure was drawn by the DIAMOND software.[5] Hydrogen atoms attached to C were treated as riding atoms. The U_{iso} values of the hydrogen atoms of water molecules were set to 1.5 U_{eq}

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

Atom	x	y	z	U_{iso}*/U_{eq}
Zn1	0.21165(4)	0.01652(4)	−0.12247(3)	0.04315(14)
Zn2	−0.03881(4)	0.07655(4)	−0.17134(3)	0.04346(14)
Zn3	0.12496(4)	−0.19123(4)	−0.11148(3)	0.04318(14)
Zn4	0.24211(5)	−0.08058(5)	−0.32739(3)	0.05190(15)
C1	0.4320(4)	0.0788(3)	−0.1836(3)	0.0394(9)
C2	0.5420(4)	0.0997(4)	−0.2407(4)	0.0550(11)
H2	0.576496	0.131591	−0.210946	0.066*
C3	0.6007(5)	0.0722(5)	−0.3437(4)	0.0669(14)
H3	0.674768	0.086468	−0.383785	0.080*
C4	0.5502(5)	0.0244(5)	−0.3861(4)	0.0668(14)
H4	0.589573	0.005908	−0.455150	0.080*
C5	0.4375(4)	0.0031(5)	−0.3249(3)	0.0586(12)
C6	0.3624(4)	0.1051(3)	−0.0728(3)	0.0392(9)
C7	0.4044(4)	0.1457(3)	−0.0165(3)	0.0474(10)
H7	0.480371	0.159375	−0.047344	0.057*
C8	0.3331(4)	0.1664(4)	0.0866(3)	0.0504(10)
H8	0.360838	0.194131	0.125564	0.061*
C9	0.2215(4)	0.1459(3)	0.1311(3)	0.0464(10)
H9	0.173331	0.159276	0.200438	0.056*
C10	0.1802(4)	0.1047(3)	0.0716(3)	0.0365(8)
C11	0.1905(4)	−0.2250(4)	0.2986(3)	0.0502(10)
C12	0.2307(6)	−0.2718(5)	0.3805(4)	0.0724(15)
H12	0.316882	−0.330572	0.371730	0.087*
C13	0.1399(6)	−0.2297(5)	0.4773(4)	0.0823(17)
H13	0.165535	−0.260447	0.534010	0.099*
C14	0.0152(6)	−0.1447(5)	0.4893(4)	0.0723(15)
H14	−0.045307	−0.117030	0.554160	0.087*
C15	−0.0237(5)	−0.0972(5)	0.4024(3)	0.0571(12)
C16	0.2809(4)	−0.2635(4)	0.1920(3)	0.0476(10)
C17	0.4069(5)	−0.3558(4)	0.1660(4)	0.0601(12)
H17	0.441872	−0.400717	0.216080	0.072*
C18	0.4816(5)	−0.3813(4)	0.0634(4)	0.0621(13)
H18	0.567881	−0.443105	0.044718	0.074*
C19	0.4300(4)	−0.3168(4)	−0.0105(4)	0.0520(11)
H19	0.480423	−0.333895	−0.079161	0.062*
C20	0.3004(4)	−0.2249(3)	0.0188(3)	0.0409(9)
C21	−0.1492(4)	0.4339(4)	0.0403(3)	0.0508(11)
C22	−0.1403(5)	0.5302(4)	−0.0268(4)	0.0700(14)
H22	−0.179716	0.610085	−0.003121	0.084*
C23	−0.0723(6)	0.5063(5)	−0.1294(4)	0.0830(17)
H23	−0.067100	0.570936	−0.175308	0.100*
C24	−0.0127(5)	0.3891(4)	−0.1644(4)	0.0686(14)
H24	0.033377	0.373053	−0.233670	0.082*
C25	−0.0222(4)	0.2924(4)	−0.0934(3)	0.0426(9)
C26	−0.2227(4)	0.4481(4)	0.1515(4)	0.0518(11)
C27	−0.2806(5)	0.5588(4)	0.1994(4)	0.0672(13)
H27	−0.274346	0.628782	0.162463	0.081*
C28	−0.3484(5)	0.5639(5)	0.3034(5)	0.0783(16)
H28	−0.389225	0.638283	0.336921	0.094*
C29	−0.3557(5)	0.4617(5)	0.3567(4)	0.0716(14)
H29	−0.399857	0.465443	0.426951	0.086*
C30	−0.2961(4)	0.3485(4)	0.3058(4)	0.0586(12)
N1	0.3806(3)	0.0315(3)	−0.2251(2)	0.0466(8)
N2	0.2517(3)	0.0848(3)	−0.0282(2)	0.0359(7)
N3	0.0655(3)	−0.1380(3)	0.3092(2)	0.0463(8)
N4	0.2294(3)	−0.2000(3)	0.1190(2)	0.0415(8)
N5	−0.0906(3)	0.3176(3)	0.0056(2)	0.0410(8)
N6	−0.2297(3)	0.3442(3)	0.2038(3)	0.0477(8)
O1	0.3929(3)	−0.0443(4)	−0.3655(2)	0.0805(11)
O2	0.0747(2)	0.0845(2)	0.10920(19)	0.0418(6)
O3	0.2434(3)	−0.1608(2)	−0.0464(2)	0.0451(6)
O4	−0.1431(3)	−0.0171(3)	0.4156(2)	0.0700(9)
O5	0.0327(3)	0.1786(2)	−0.1216(2)	0.0451(6)
O6	−0.3047(3)	0.2524(3)	0.3571(2)	0.0694(9)
O7	0.1391(2)	−0.0464(2)	−0.18649(18)	0.0390(6)
N7	0.7194(14)	0.6645(12)	0.5877(11)	0.215(4)
C33	0.796(2)	0.6898(19)	0.5925(16)	0.283(6)
H33	0.851670	0.708564	0.531457	0.339*
O8	0.8148(16)	0.6954(13)	0.6824(11)	0.352(6)
C31	0.7105(17)	0.6912(14)	0.4946(10)	0.294(7)
H31A	0.697628	0.775195	0.476448	0.441*
H31B	0.636722	0.680830	0.494824	0.441*
H31C	0.790659	0.636744	0.445733	0.441*
C32	0.6373(16)	0.6502(14)	0.7081(14)	0.342(10)
H32A	0.608758	0.723324	0.743427	0.513*
H32B	0.693547	0.579815	0.737296	0.513*
H32C	0.561423	0.639207	0.714427	0.513*

(O) and the U_{iso} values of all other hydrogen atoms were set to 1.2 U_{eq} (C).

3 Comment

The modification of commonly used diimine ligands, such as bipyridine, is a convenient method to design and synthesize various metal complexes suitable for different applications.[6–9] According to literature, the incorporation of different substituents (such as –OH, –CN, –OCH_3, –COOH and so on) on the different positions of the 2,2′-bipyridine ligands into various metal complexes could efficiently modify their properties and applications.[10–15]

The molecular structure of the title complex contains two connected asymmetrical units-[Zn^{II}_4], each of which composes of four Zn(II) ions, one μ_4–O, three deprotonated $dhbp^{2-}$ ligands, and one free DMF solvent molecule (see the Figure). All Zn(1), Zn(2), and Zn(3) ions are five-coordinate to display distorted triangular bipyramidal geometries. The equatorial plane is occupied by two hydroxyl O and one N atom from three different $dhbp^{2-}$, whereas the axial places are one μ_4–O and one N atoms from one $dhbp^{2-}$. Among them, μ_4–O is located at the vertex position of these triangular bipyramidal axes, and the bond angles of O(7)–Zn(1)–N(2), O(7)–Zn(2)–N(4)#1, O(7)–Zn(3)–N(5)#1 (symmetry codes: #1 −*x*, −*y*, −*z*) are 167.28, 165.86, and 166.92°,

respectively, all close to linear. Each Zn(4) shows a tetrahedral geometry and coordinates with a μ_4–O and three hydroxyl O atoms from three different $dhbp^{2-}$ ligands. The Zn–O bond lengths range from 1.921 to 2.182 Å, while the Zn–N bond lengths range from 2.004 to 2.069 Å.

The whole molecular structure of the title complex consists of two of the aforementioned asymmetrical [Zn^{II}_4] pyramids bridged by a μ_4–O bridge, resulting an octanuclear {Zn^{II}_8} cluster. The {Zn^{II}_8}-core can be viewed in a bicapped anti-trigonal-prism, in which six Zn(II) construct the anti-trigonal-prism and other two Zn(II) are located at the cap sites. All Zn⋯Zn distances range from 3.100 to 4.106 Å. The periphery of {Zn^{II}_8 } is surrounded by six $dhpb^{2-}$ ligands, forming a zero dimensional molecular structure, which is very similar to that of the reported two novel 3d-4f clusters with {Co^{II}_6 Ln^{III}_2} (Ln = Dy, Ho) cores.[7] These {Zn^{II}_8} clusters are further linked together by intermolecular interactions (C–H⋯O hydrogen bonds) to form a three-dimensional supramolecular structure, and the solvents (DMF) are placed at the void of the structure.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Competing interests: The authors declare no conflicts of interest regarding this article.

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