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A dinuclear Eu(III) complex in the crystal structure of dodecaqua-bis(μ_2 -4-(1H-tetrazol-5-yl)benzoato- $\kappa^2 O:O'$) bis(5-(4-carboxylatophenyl)tetrazol-1-ide) tetrahydrate, $C_{32}H_{50}Eu_2N_{16}O_{24}$

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Abstract

$C_{32}H_{50}Eu_2N_{16}O_{24}$, monoclinic, $P2_1/c$ (no. 14), $a = 7.685(5)$ Å, $b = 13.482(5)$ Å, $c = 23.240(5)$ Å, $\beta = 93.578(5)^\circ$, $V = 2403.2(19)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0235$, $wR_{ref}(F^2) = 0.0577$, $T = 293$ K.

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A representative part of the title crystal structure is shown in the figure (uncoordinated water molecules are omitted for clarity.). Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	$0.05 \times 0.03 \times 0.02$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	2.69 mm^{-1}
Diffraction, scan mode:	Bruker APEX-II, ϕ and ω
$\theta_{\max}$, completeness:	26.1° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	14792, 4795, 0.030
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4062
$N(\text{param})_{\text{refined}}$:	410
Programs:	Bruker [1], SHELX [2, 3], Diamond [4]

Source of material

The title complex was synthesized from a mixture of $Eu(NO_3)_3 \cdot 6H_2O$ (0.446 g, 1 mmol), 4-(1H-tetrazol-5-yl) benzoic acid (4-Htzba) (0.190 g, 1 mmol) and H_2O (6.0 mL) sealed in a Teflon-lined reactor and heated at 120°C for 72 h. After the reactor was slowly cooled to room temperature over a period of 10°C/h , colorless block-like crystals were obtained as a single phase and washed with water, and dried at room temperature.

Experimental details

All the H atoms on the benzene rings were placed geometrically and refined without any constraints or restraints. The H

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Eu1	−0.022165(19)	−0.111096(10)	0.590380(6)	0.02402(6)
N1	0.4740(4)	0.5693(2)	0.73787(13)	0.0425(7)
O1	−0.4506(3)	0.25474(17)	0.46186(9)	0.0405(6)
OW1	0.5011(6)	0.3307(2)	0.80074(15)	0.0828(11)
H1B	0.594(5)	0.327(4)	0.782(2)	0.099*
H1A	0.470(6)	0.273(2)	0.807(2)	0.099*
C1	−0.4442(4)	0.2322(2)	0.51424(14)	0.0324(7)
C2	0.1640(4)	0.2226(2)	0.64432(13)	0.0297(7)
H9	0.153(4)	0.166(2)	0.6635(13)	0.036*
N2	−0.0361(4)	0.64605(19)	0.71510(11)	0.0353(6)
O2	−0.4988(3)	0.15159(18)	0.53301(10)	0.0471(6)
OW2	0.4810(3)	0.0576(2)	0.63335(12)	0.0431(6)
H2B	0.485(5)	0.101(3)	0.6024(17)	0.052*
H2A	0.448(6)	0.074(3)	0.6591(18)	0.052*
C3	−0.3123(5)	0.2777(2)	0.61223(14)	0.0348(8)
H3	−0.314(4)	0.216(3)	0.6250(14)	0.042*
O3	0.0225(3)	−0.14541(17)	0.49514(9)	0.0405(6)
OW3	0.2870(4)	−0.0917(2)	0.58926(16)	0.0589(9)
H3A	0.342(6)	−0.132(3)	0.583(2)	0.071*
N3	−0.1252(4)	0.61151(18)	0.66793(11)	0.0333(6)
H3B	0.336(5)	−0.047(3)	0.6095(15)	0.040*
C4	0.1131(4)	0.2271(2)	0.58636(12)	0.0253(6)
OW4	−0.2453(3)	−0.23176(17)	0.60090(11)	0.0404(6)
H4B	−0.338(3)	−0.240(2)	0.5793(13)	0.048*
H4A	−0.218(4)	−0.2854(18)	0.6169(14)	0.048*
O4	0.0446(3)	0.05706(16)	0.58321(9)	0.0377(5)
N4	−0.0004(4)	0.57332(19)	0.75104(11)	0.0343(6)
C5	0.2329(4)	0.3036(2)	0.67274(13)	0.0314(7)
H5	0.263(4)	0.301(2)	0.7127(14)	0.038*
OW5	−0.1960(3)	−0.0229(2)	0.65817(11)	0.0425(7)
H5B	−0.150(5)	0.017(3)	0.6768(17)	0.051*
H5A	−0.275(5)	−0.003(3)	0.6495(18)	0.051*
N5	0.3224(4)	0.5715(2)	0.65531(12)	0.0435(7)
C6	0.1992(5)	0.3980(2)	0.58570(14)	0.0336(7)
H7	0.216(4)	0.455(3)	0.5671(14)	0.040*
OW6	0.0662(4)	−0.16067(18)	0.68880(10)	0.0409(6)
H6B	0.062(5)	−0.120(3)	0.7172(17)	0.049*
H6A	0.042(5)	−0.214(3)	0.7039(16)	0.049*
N6	−0.0664(4)	0.48868(18)	0.72789(10)	0.0309(6)
C7	−0.3667(4)	0.3058(2)	0.55679(13)	0.0283(7)
OW7	0.1168(4)	−0.27953(18)	0.58445(11)	0.0402(6)
H7B	0.208(5)	−0.282(3)	0.5721(16)	0.048*
H7A	0.119(5)	−0.324(3)	0.6054(16)	0.048*
N7	0.4218(4)	0.4774(2)	0.72384(12)	0.0343(6)
C8	0.0399(4)	0.1366(2)	0.55599(13)	0.0270(7)
OW8	−0.2823(3)	−0.04661(16)	0.53760(10)	0.0379(5)
H8B	−0.354(4)	−0.080(2)	0.5167(13)	0.045*
H8A	−0.273(5)	0.0097(14)	0.5261(14)	0.045*
N8	0.4145(4)	0.6250(2)	0.69676(14)	0.0468(8)
C9	0.1290(5)	0.3163(2)	0.55712(13)	0.0330(7)
H6	0.098(4)	0.321(2)	0.5188(14)	0.040*
C10	0.3300(4)	0.4791(2)	0.67350(13)	0.0295(7)
C11	−0.1407(4)	0.5145(2)	0.67680(13)	0.0277(7)
C12	−0.2409(4)	0.3456(2)	0.65106(14)	0.0339(7)
H8	−0.205(4)	0.328(2)	0.6861(15)	0.041*

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C13	0.2535(4)	0.3926(2)	0.64355(13)	0.0286(7)
C14	−0.2234(4)	0.4439(2)	0.63553(12)	0.0270(6)
C15	−0.2785(5)	0.4729(2)	0.58014(14)	0.0373(8)
H2	−0.271(5)	0.539(3)	0.5693(14)	0.045*
C16	−0.3486(5)	0.4039(2)	0.54124(15)	0.0373(8)
H4	−0.384(5)	0.419(3)	0.5030(15)	0.045*
H1	0.448(6)	0.428(3)	0.7435(19)	0.070(14)*

atoms on the water molecules and the tetrazolium ring were identified by the Dif-fourier map. Their *U*_{iso} values were set to 1.2 *U*_{eq} of the parent atoms. The H atoms around OW1, OW4 and OW8 were restrained using a DFIX command [3].

Comment

4-(1*H*-Tetrazol-5-yl) benzoic acid (4-Htzba) is a multidentate ligand containing both a carboxyl group and up to four *N*-coordination sites if deprotonated, which can exhibit various coordination modes. Many transition-metal coordination polymers based on 4-Htzba have been reported, such as [Co(4-TZBA^{2−})(H₂O)₂] [5], [Cd(4-tzba)(H₂O)]_n [6], [Mn(4-TZBA^{2−})(H₂O)₂] [7], [Zn₂(4-tzba)₂(H₂O)]_n [8]. In comparison, the Htzba-based Eu complexes are relatively less reported [9, 10]. As is documented, such ligand anions could exhibit different forms in the Eu complexes, examples including [Ln₂(3-Htzba)₂(3-tzba)₂(H₂O)₈]·4 H₂O (3-Htzba = 3-(1*H*-tetrazol-5-yl) benzoic acid) [9] and [LnL(HL)(H₂O)₅] (Ln = Eu and Tb) (L = 4-Htzba) [10]. Due to the variety of coordination modes of the ligands, and the influence of the synthesis conditions, different kinds of Eu(III) complexes will be formed.

The asymmetric unit of the title structure contains one [Eu(C₈H₅N₄O₂)(H₂O)₆]²⁺ unit and one discrete (C₈H₄N₄O₂)^{2−} (4-tzba^{2−}) unit and two H₂O molecules (*cf.* the figure). The crystallographically unique Eu(III) is eight-coordinated by two oxygen atoms of the carboxylate group of the ligand anions and six oxygen atoms from six different water molecules (the average d(Eu—OW) = 2.446(6) Å), completing a dodecahedron environment of Eu(III). Two ligand anions bridge adjacent Eu(III) ions forming a Eu₂ unit, named [Eu(C₈H₅N₄O₂)(H₂O)₆]₂⁴⁺. The bond lengths of coordinated Eu—O (d(Eu1—O3) = 2.308(1) Å and d(Eu1—O4) = 2.331(7) Å) is comparable to the previously reported Eu—O bond lengths [9, 10]. The uncoordinated counter anion 4-tzba^{2−} is almost parallel to a ligand anion coordinated to Eu(III). The weak π···π interactions exist between them and the distance between the two benzene rings is about 3.777(8) Å.

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